

**RIGA TECHNICAL UNIVERSITY**  
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**HETEROGENEOUS COMPOSITES  
OF POLYVINYL ALCOHOL AND POLYVINYL  
ACETATE**

**Summary of Doctoral Thesis**

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**ENGINEERING SCIENCES**

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I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Engineering Sciences is my own and does not contain any unacknowledged material from any source. I confirm that this Thesis has not been submitted to any other university for the promotion to other scientific degree.

Natalja Geisari .....

Date: .....

The Doctoral Thesis has been written in the Latvian language; it contains an introduction, 3 chapters, conclusions, a list of references with 249 information sources. It has been illustrated by 131 figures. The volume of the present Doctoral Thesis is 177 pages.

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## CONTENTS

LIST OF THE MOST IMPORTANT ABBREVIATIONS .....	7
GENERAL CHARACTERISTICS OF THE DOCTORAL THESIS .....	9
Topicality of the Research .....	9
The Aim of the Doctoral Thesis .....	10
The Tasks of the Doctoral Thesis .....	10
Scientific Novelty of the Doctoral Thesis .....	10
Practical Value of the Doctoral Thesis .....	11
Thesis Statements to Be Defended .....	11
The Structure and Volume of the Thesis .....	11
BRIEF CONTENTS OF THE DOCTORAL THESIS .....	12
SUMMARY OF THE EXPERIMENTAL RESULTS AND THEIR ESTIMATION.....	12
1. The Choice of the System to Be Investigated .....	12
2. Rheological Properties of the Water Systems of Components (PVA, PVAc) and Mixtures (PVA/PVAc) .....	12
3. Film Formation of the PVA/PVAc Composite from the Water Systems. Morphology of the Films .....	14
4. The PVA Crystallinity in the PVA/PVAc System.....	16
4.1. The PVA Crystallinity in the Films without PVAc .....	16
4.2. The PVA Crystallinity in the PVA/PVAc System.....	17
5. The Strength-Deformation Properties of the Films of the PVA/PVAc Systems. Estimation of the PVA and PVAc Adhesive Interaction .....	18
5.1. The strength-Deformation Properties of the Films of the PVA/PVAc Systems .....	18
5.2. Estimation of the PVA and PVAc Adhesion Interaction .....	20
6. Modulus of Bending Elasticity of the Films of the PVA/PVAc Systems .....	21
6.1. Determination Method of the Elasticity Modulus of a Thin Wall Cylindrical Sample.....	21
6.2. Dependence of the Bending Elasticity Modulus of the PVA Film on the Moisture Content .....	23
7. Filled PVA/PVAc Composites .....	24
7.1. Influence of Fillers upon the Crystallinity of Pure PVA.....	24
7.2. The Bending Elasticity Modulus E of the PVA, PVAc and PVA/PVAc Films Containing a Filler .....	24
7.3. Dependence of the Water Adsorption Capacity and Bending Elasticity Modulus of the Films of Filled PVA/PVAc Composite Materials on the Moisture Content.....	25
7.4. Projection of the Values of the Elasticity Modulus Using the Response Surface Methodology and Optimisation of the Composition of the Films from Composites PVA/PVAc/Filler .....	25
8. Biodestruction of the PVA/PVAc Composites.....	27

9. Principal Technological Scheme for Producing a Film from the Water System PVA/PVAc/Filler by a Casting Method .....	28
CONCLUSIONS .....	30
REFERENCES .....	31
APPROBATION OF THE RESEARCH RESULTS .....	32

## LIST OF THE MOST IMPORTANT ABBREVIATIONS

$A$  — specific work of peeling;  
 $AC$  — adhesive compound;  
 $C_{\text{plast}}$  — plasticiser content;  
 $DEG$  — diethylene glycol;  
 $DH$  — degree of hydrolysis;  
 $DSC$  — differential scanning calorimetry;  
 $E$  — modulus of elasticity;  
 $\bar{E}$  — average modulus of elasticity;  
 $E^*$  — estimated modulus of elasticity;  
 $E_{AD}$  — additive modulus;  
 $FFD$  — full factorial design;  
 $G$  — shear modulus,  
 $K$  — volume modulus;  
 $K^*$  — measure of environmental consistency;  
 $K_{KR}$  — degree of crystallinity;  
 $L$  — length;  
 $L_F$  — thickness of the PVA<sup>a</sup> molecule layer;  
 $L_M$  — length of macromolecular conformation;  
 $MCC$  — microcrystalline cellulose;  
 $MMT$  — montmorillonite clay;  
 $m_0$  — sample mass before biodestruction;  
 $m_t$  — sample mass in time  $t$ ;  
 $n_{\text{tec}}$  — flow index;  
 $P$  — force;  
 $PVA$  — polyvinyl alcohol;  
 $PVAc$  — polyvinyl acetate;  
 $PVA^a$  — polyvinyl alcohol which forms a PVAc protective layer;  
 $PVA/PVAc$  — polyvinyl alcohol and polyvinyl acetate composite;  
 $R$  — radius;  
 $RSM$  — Response surface methodology;  
 $SEM$  — scanning electron microscopy;  
 $T$  — temperature;  
 $T_{mS}$  — initial melting temperature;  
 $T_{m\text{max}}$  — maximal melting temperature;  
 $T_{mB}$  — final melting temperature;  
 $t$  — time;  
 $t_D$  — drying time;  
 $VA$  — vinyl acetate;  
 $V_D$  — drying speed;  
 $v_{m\text{PVA}}$  — the measure of the PVA destruction speed;  
 $\alpha$  — displacement;  
 $\beta$  — load;  
 $\dot{\gamma}$  — shear rate;  
 $\Delta$  — displacement;

$\Delta H$  — specific heat of melting;  
 $\Delta m$  — relative value of the mass loss rate;  
 $\Delta m^*$  — relative value of the mass decrease;  
 $\varepsilon$  — relative elongation;  
 $\varepsilon_B$  — elongation at break;  
 $\mu$  — viscosity;  
 $\mu_{\text{COMP}}$  — viscosity of the mixture;  
 $\mu_{\text{PVA}}$  — viscosity of the polyvinyl alcohol solution;  
 $\sigma$  — tensile strength;  
 $\sigma_B$  — tensile strength at break;  
 $\sigma_{\text{COMP}}$  — tensile strength of the composite;  
 $\sigma_{\text{MAX}}$  — maximal tensile strength;  
 $\rho$  — density of the polymer;  
 $\rho^*$  — estimated values of density;  
 $\varphi_f$  — volume fraction of the filler;  
 $\varphi_{\text{POL}}$  — volume fraction of the polymer;  
 $\varphi_{\text{PVAc}}$  — volume fraction of PVAc;  
 $\Psi_{\text{H}_2\text{O}}$  — water content.

# GENERAL CHARACTERISTICS OF THE DOCTORAL THESIS

## Topicality of the Research

Longevity of polymer materials — the aim the creators of these materials so aspired to achieve and which was considered one of their most valuable properties — has turned into one of their essential shortcomings. The conventional products, predominately made from such polymer materials as polyethylene, polystyrene, polyethylene terephthalate, etc., practically do not decompose in natural environment. Decomposition, which takes place during the photooxidative process, is extremely slow.

The application rate of polymer materials is increasing, and hence the amount of the undegraded waste is also increasing, polluting the environment.

According to the data of the International Solid Waste Association (ISWA), in 2013 1.84 billion tonnes of solid waste were produced all over the world. Scientists have calculated that till 2025 the amount of waste will grow to 6 million tonnes of waste a day, reaching 2.2 billion tonnes.

Under contemporary conditions it is becoming an acute necessity to make certain widely used kinds of polymer products (wrapping, disposable or short-time products, etc.) from materials which are capable of efficient biological decomposing.

The biodegradable polymer composites are an alternative solution to the conventional polymer materials based on the petroleum products. The applied purpose of the investigation is to develop polymer composites to be used for making biologically degradable wrapping materials.

The study of a range of the most important operational properties of individual synthetic polymers showed that polyvinyl alcohol (PVA) was suitable for the development of such biocomposite materials.

PVA is characterised by a great content of hydroxyl groups, which ensures solubility of the polymer in water.

The hydroxyl groups of the PVA macromolecules form a dense lattice of intermolecular hydrogen bonds, ensuring sufficiently high strength-deformation indicators of the polymer (comparatively high values of the elasticity modulus and the marginal stress of strength, yet a small breaking elongation [1]), low oxygen permeability, good stability in various environments.

This makes PVA a perspective basic component to produce film-type composites to be used as wrapping materials.

In order to reduce the value of the elasticity modulus of individual stiff polymers, good results have been achieved by forming these polymer composites with low elasticity modulus polymers. The same principle could also be applied to modify a comparatively stiff PVA.

Polyvinyl acetate (PVAc) — a synthetic, thermoplastic linear, water insoluble polymer of an amorphous structure — could be used as a potential component for this purpose. The indicators of its deformation properties characterise PVAc as submissive. PVAc is capable of biological decomposition. There is a reason to believe that by forming PVA/PVAc composites one will succeed in producing materials with a higher water resistance, lower stiffness and greater breaking elongation.

Using the good solubility of PVA, it is intended in this Doctoral Thesis to form PVA composites by mixing low-viscosity water systems, and to obtain a film-type composite material applying the casting method with subsequent water evaporation (drying) at the room temperature. The PVAc water suspension (a product of the vinyl acetate emulsion polymerisation) would be conveniently used in order to produce PVA/PVAc composites from the water systems.

### **The Aim of the Doctoral Thesis**

To form from the PVA/PVAc water system biologically degradable composites that could be used to produce a wide range of wrapping materials.

To find out the range of the components and the conditions for the composite formation that would make it possible to achieve sufficient integrity of the composites with simultaneous formation of such structures which would enhance efficient disintegration of the composites during the biological decomposition process.

### **The Tasks of the Doctoral Thesis**

To develop a PVA/PVAc composite film production methodology from the PVA and the PVAc water systems in a full range of the component proportions, applying the casting method.

To identify the rheological properties of the PVA, PVAc and PVA/PVAc water systems.

To investigate the formation process of the PVA/PVAc films, the morphology of the produced composites and the parameters that characterise their structure and correlation with the strength-deformation properties of the composites, as well as their ability to biologically decompose.

To develop a principal technological scheme for the production of the PVA/PVAc composite films.

### **Scientific Novelty of the Doctoral Thesis**

Correlation of the indicators characterising the PVA/PVAc morphology of the composites and the PVA matrix has been established with the indicators of the strength-deformation of the composites, as well as their ability to biologically decompose.

It has been found that the decisive role in the biological decomposition of composites belongs to the disordered diffuse layer formed by the protective layer of the polyvinyl alcohol macromolecules around the PVAc particles, and the PVA matrix macromolecules diffused in it.

A method has been developed for the identification of the stress-deformation indicators of thin films which allows for repeated and frequent measurements using one and the same sample.

It has been proven that by means of the mathematical method of the response surface it is possible to optimise the composition of the composite, choosing the value of the modulus of tensile elasticity of the composites as an object of optimisation.

## **Practical Value of the Doctoral Thesis**

Film-type PVA/PVAc composite materials have been developed that are produced from the mixture of the PVA water solution and the PVAc water dispersion applying the casting method. There are materials obtained with a wide complex of the strength-deformation indicators (the modulus of tensile elasticity: 0.3–2.3 GPa, ultimate stress of strength: 10–40 MPa, breaking elongation: 0.3–3.5) and the biological decomposition ability (the decomposition period: 1500–6000 days), used for the production of a wide range of wrapping materials.

A technological scheme has been developed for the production of film-type composite materials.

## **Thesis Statements to Be Defended**

The system which is formed as a result of drying of the mixture of the PVA water solution and the PVAc water suspension is a *heterogeneous composite* at all the PVA/PVAc content proportions.

*Morphologically*, the PVA/PVAc composite is formed as continuous PVA matrix in which spherical PVAc particles are arranged. When the content of the PVAc particles is increased in the system, the distances between the particles decrease. As a result of the interphase forces, the particles get deformed, obtaining a shape which is close to polyhedra.

*In a structural aspect*, the matrix of the PVA/PVAc composite is a partially crystalline polymer (PVA), the amorphous part of which is glassy at the room temperature. The PVAc particles dissipated in the matrix are amorphous, and at the room temperature they are superelastic. During the formation of the composite structure the presence of the PVAc particles influences the PVA crystallinity.

From the viewpoint of the *strength-deformation properties*, the system PVA/PVAc is a composite formed by a stiff matrix (PVA) and compliant particles (PVAc). The elastic properties of the components PVA and PVAc can be adjusted by changing the content (proportion) of the plasticising additives.

*The ability* of a composite to *biologically decompose* and disintegrate is determined by the decomposition rate of the PVA component. Enhanced biological decomposition of PVA occurs in the disordered diffuse layer around the PVAc particles.

## **The Structure and Volume of the Thesis**

The Doctoral Thesis has been written in the Latvian language; it contains the introduction and main chapters: a review of literary sources, the methodological part, a summary of the experimental results and its estimation, conclusions, a list of references with 249 sources of information. It has been illustrated by 131 figures and 48 tables. The volume of the Doctoral Thesis is 177 pages.

## **Approbation of the Research Results**

The results of the Doctoral Thesis have been presented at 13 international conferences and published in 10 articles.

## BRIEF CONTENTS OF THE DOCTORAL THESIS

**Introduction** comprises substantiation of the topicality of the Doctoral Thesis, formulates the aim and the main tasks of the research; it lays out the basic approaches to the research.

**Chapter One** is a literature review of the application of polymers in the production of wrapping materials. It contains characteristics of the most important properties and structure of PVA and PVAc, as well as the fields of their application. There is a description of the fillers of natural origin used in the research — montmorillonite clay (*MMT*) and microcrystalline cellulose (*MCC*).

**Chapter Two** presents detailed characteristics of the materials used in the research. The chapter describes the production procedure of composite materials.

It is devoted to research methods of the films produced from the composite materials and the characteristics of the parameters to be identified: rheological studies of the water systems, determination of the tensile and bending strength-deformation indicators of the films, studies of adhesion, *DSC* and *TG* methods, *FTIR* spectroscopy, *UV-VIS* spectrometry, *XR* diffraction method, *SEM* studies, density determination technology, water mass exchange research technology, and biodestruction studies.

## SUMMARY OF THE EXPERIMENTAL RESULTS AND THEIR ESTIMATION

### 1. The Choice of the System to Be Investigated

From several (9) types of PVA at our disposal, on the basis of the experimentally determined data about the water absorption capacity, the impact of the amount of the absorbed water upon the tensile strength-deformation indicators of the polymer film and the capacity of the polymers to biologically decompose in the earth, PVA was selected for research with a molecular weight (130 000 g/mol and a degree of hydrolysis *DH*-98 %).

Having assessed a wide range of plasticisers, diethylene glycol (*DEG*) [1] was chosen as a plasticiser, which was a common plasticiser for the two polymers efficiently plastifying both PVA [2], [3] and PVAc [4]; besides it dissolved well in water.

In order to find the necessary *DEG* amount (proportion) for the plastification of the PVA/PVAc composite materials, the influence of the *DEG* content was studied upon the tensile strength-deformation indicators of both the polymer films.

Having evaluated the obtained data, the optimal *DEG* amount (proportion) was selected for the plastification of the PVA/PVAc composites: 10 %, and the temperature of the *DEG* introduction into the composite was 20 °C.

### 2. Rheological Properties of the Water Systems of Components (PVA, PVAc) and Mixtures (PVA/PVAc)

The rheological indicators of the components and the water systems of the mixtures (dependence of viscosity on the polymer concentration, shear rate,

temperature, etc.) are important both for the formation of mixtures and for the production of the films by casting.

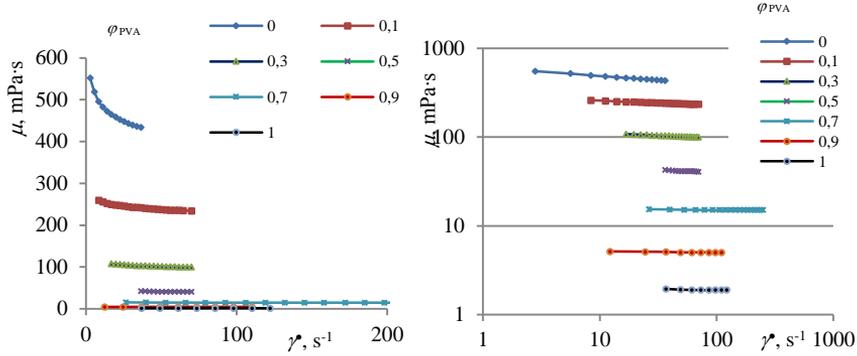


Fig. 1. Correlations of the investigated PVA/PVAc systems  $(\mu)/(\dot{\gamma}^{\bullet})$  and  $(\mu)/(\dot{\gamma}^{\bullet})$  correlations in lg coordinates.

Viscosity  $\mu$  of the components and the water systems of the mixtures were determined depending on shear rate in a relatively narrow range of the  $\dot{\gamma}^{\bullet}$  values: 10–120  $\text{s}^{-1}$  (See Fig. 1). Such shear rate values correspond to most mixing modes.

The viscosity of the water systems of the output components sharply differ. At an equal shear rate ( $\dot{\gamma}^{\bullet} = 36 \text{ s}^{-1}$ ) the viscosity value of the PVA solution surpasses more than 200 times the viscosity value of the PVAc dispersion (See Fig. 2).

The viscosity of the PVA/PVAc mixture decreases increasing the content (proportion) of the less viscous component (PVAc). Already a small amount (proportion) of the PVAc component rapidly reduces the viscosity of the mixture. This can be considered as positive because it facilitates the mixing and the subsequent casting operations.

Treating the correlations  $\mu(\dot{\gamma}^{\bullet})$  in logarithmic coordinates (See Fig. 2), it is evident that the linear decrease in the viscosity of the PVA solution and its mixtures with a small PVAc content, with shear rate increasing, is witness of pseudoplasticism. The correlations are linear and can be described with the traditional equation typical of pseudoplastic environments [5]:

$$\lg \mu = \lg K - (n_{\text{tec}} - 1) \lg \dot{\gamma}^{\bullet} \quad \text{or} \quad \mu = K \dot{\gamma}^{\bullet(n_{\text{tec}} - 1)} \quad (1)$$

where:  $n_{\text{tec}}$  — flow index which shows to what degree the investigated environment differs from the Newtonian liquid;

$K$  — the environmental consistency measure — viscosity of the system under normalised conditions ( $\dot{\gamma}^{\bullet} = 1$ ).

In Fig. 2 the continuous line corresponds to equation:  $\mu_{\text{COMP}} = \mu_{\text{PVA}} \exp(-0.05 \varphi_{\text{PVAc}})$ ; the dashed line corresponds to the additive change of viscosity:  $\mu_{\text{COMP}}^{\text{ad}} = \mu_{\text{PVA}} - 440 \varphi_{\text{PVAc}}$  (where  $\mu_{\text{COMP}}$  — viscosity of the mixture,  $\mu_{\text{PVA}}$  — viscosity of the PVA water systems).

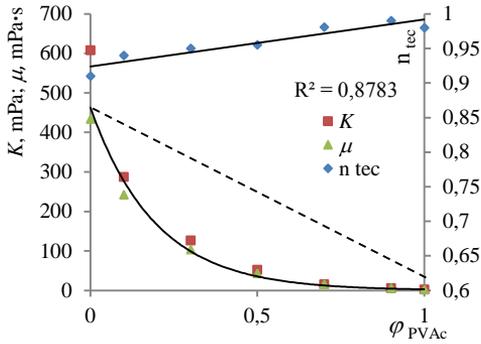


Fig. 2. Dependence of the viscosity of the PVA/PVAc water systems  $\mu$  (at  $\dot{\gamma}^* = 36 \text{ s}^{-1}$ ), the viscosity measure  $K$  and the flow index  $n_{tec}$  on the PVAc content in the water system.

pseudoplastic character of the environment, when the content (proportion) of the PVAc water dispersion is increased, are a result of the influence not only of the PVA decreased concentration but also of the PVAc particles themselves.

The experimental points of the viscosity measurements are clearly below the additive correlation. It means that the PVAc dispersion causes sharp destruction of the structure of the PVA solution.

### 3. Film Formation of the PVA/PVAc Composite from the Water Systems. Morphology of the Films

Individual indications that could characterise the formation of the film structure during the drying period of the mixtures of the PVA and PVAc water systems seemed already predictable.

First of all, this applies to the PVAc component. Swelling of the PVAc particles, as well as their dissolution in the PVA water solution is out of the question. This means that in the film formation process the PVAc particles should preserve their initial shape.

However, when the water concentration in the PVA/PVAc system decreases, there are no formal obstacles to mutual approaching of the PVAc particles and, further, to their possible coalescence [8]. Thus, a separate PVAc phase may develop both as inclusions of the PVAc phase into the PVA environment (when the PVAc content is small), and as an uninterrupted PVAc phase (when the PVAc component prevails). It would be interesting to find out if this is so.

By studying the brittle fracture of the samples in the SEM microphotographs (separate samples — Fig. 3), information about the morphology of the composites PVA/PVAc was obtained.

Under the PVAc content is  $\phi_{PVAc} < 0.5 - 0.7$ , the plastified PVAc particles retain their initial form, and the final structure of the system is the initial spherical PVAc particles which are dissipated in the PVA matrix (See Fig. 3a).

The situation changes if value  $\phi_{PVAc}$  is greater. The PVAc particles approach the maximum degree. The same complex of interphase forces starts playing the decisive role, which determines the formation of the PVAc film from the PVAc water

Comparatively great value of the PVA water solution viscosity, and its pseudoplastic character are typical of the polymer systems with powerful intermolecular impact. In the case of the PVA water systems a stable lattice of hydrogen bonds arises among the hydroxyl groups of the PVA macromolecules in which the water molecules also take part [6], [7].

There is no doubt that the viscosity of the PVA/PVAc system is determined by the concentration of the PVA solution. Sharp decrease in the viscosity of the system and disappearance of the

suspension. The difference is that instead of water there is the PVA solution, the viscosity and surface tension of which change during the drying process.

As in the case of pure PVAc suspension, also in the PVA/PVAc system at  $\varphi_{PVAc} > 0.7$ , when the film is formed under the influence of the interphase and capillary forces, the PVAc particles, mutually approaching, are gradually deforming, obtaining a shape which is close to a polyhedron [9], [10], [11]. The thickness of the PVA intermediate layer decreases (See Fig. 3b).

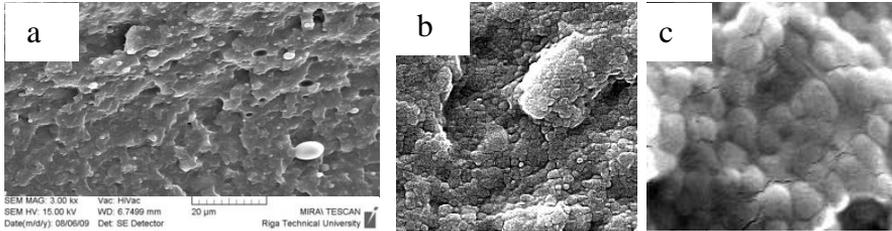


Fig. 3. SEM microphotographs of the PVA/PVAc composite fractures.

From Fig. 3 c it is evident that direct contact and coalescence of the PVAc particles do not occur even at  $\varphi_{PVAc} = 0.9$ . The PVA intermediate layer between the PVAc particles is retained.

Consequently, from the viewpoint of the composite structure, the system PVA/PVAc is a composite in which PVA plays the role of a matrix but PVAc — the role of peculiar filler. In the PVA/PVAc system, the PVAc particles do not form a separate phase within the entire range of the PVA/PVAc content relations.

A visually clean PVA film is transparent and lucid. The light permeability of the PVA film within the range of the visible light (the wavelength 400 and 700 nm) is more than 90 % (See Fig. 4). This indicates the formation of a homogeneous structure.

With the PVAc content increasing in the composite, the obtained films become visually more and more opalescent. The light permeability of the samples rapidly decreases (Fig. 4.), reaching its minimal value  $\approx 20$  % if  $\varphi_{PVAc} = 0.7 - 0.9$ . This means that a direct optic contact between the PVAc particles and the PVA matrix is not achieved, and the PVAc particles are the light diffusion centres. Judging by the light permeability, this is not achieved also in the case of pure PVAc.

Let us find out what a possible role in the formation of the PVA/PVAc composite morphology the protective layer has on the surface of the PVAc particles. It is already formed in the polymerisation process of the monomer — vinyl acetate for the stabilisation of the emulsion [12].

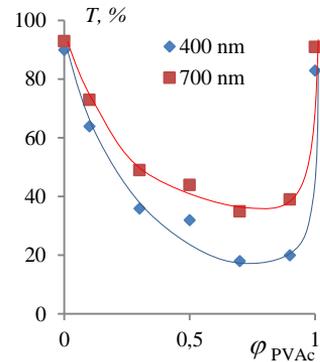


Fig. 4. The light permeability of the PVAc/PVA films depending on the PVAc content in the composite.

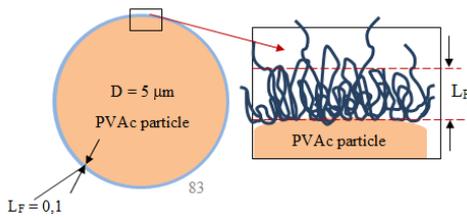


Fig. 5. A diagrammatic view of a PVAc particle with a PVA<sup>a</sup> protective layer and a scheme of the PVAc protective layer.

recommended PVA<sup>a</sup> molecular weight is  $\approx 10^5$  g/mol [14]. The conformation length of a corresponding, completely outstretched macromolecule is  $L_M \approx 10^4$  nm = 10  $\mu$ m. The most possible length of the macromolecule fragments attached to the surface PVAc may be within the limits of 0.01 – 0.1  $L_M$ ; consequently,  $10^2$  –  $10^3$  nm (0.1 – 1  $\mu$ m). The thickness  $L_F$  of the layer of the PVA<sup>a</sup> macromolecules attached to a PVAc particle may be similar (Fig. 5). The PVAc particle depicted in Fig. 6 with the diameter of 5  $\mu$ m and the thickness of the attached PVA<sup>a</sup> of 0.1  $\mu$ m seems more realistic.

When the PVAc particles are in the PVA water solution, diffusion of the PVA macromolecules occurs in the protective layer of each particle. After water disappears, a diffuse layer of PVA<sup>a</sup> / PVA arises. At a low content of the PVAc particles ( $\phi_{PVAc} < 0.5$ ) the space between the particles is filled by the PVA phase and the diffuse layer PVA<sup>a</sup> / PVA. If the particle content is great, it is not ruled out that the space between the particles is filled only by the diffuse layer PVA<sup>a</sup> / PVA. A direct contact arising between the PVAc particles of pure PVAc water suspension and mutual diffusion of the protecting layer of the PVA<sup>a</sup> macromolecules takes place. A diffuse layer appears: PVA<sup>a</sup> / PVA<sup>a</sup>.

A pure PVAc film is not completely light permeable (the light permeability is 84–90 %) because the diffuse layer PVA<sup>a</sup> / PVA<sup>a</sup> existing between the PVAc particles is the reason for the light diffusion.

## 4. The PVA Crystallinity in the PVA/PVAc System

### 4.1. The PVA Crystallinity in the Films without PVAc

PVA is a polymer, capable of crystallisation, which in this process reaches a sufficiently high degree of crystallisation  $K_{KR}$ . Polymer films are used in the research, which are formed from a water system gradually decreasing the water content.

It has been established that the crystalline phase appears only at sufficiently low water content (< 15 %).

For stabilisation PVA<sup>a</sup> is used with a great (< 25 %) content of the vinylacetate groups (VA) and a comparatively great molecular weight ( $\leq 10^5$ ), forming mobile “fringes” (“loops” and “tails”) [13].

It is important to estimate the possible “thickness” of the layer of the PVA<sup>a</sup> macromolecules attached to a PVAc particle (we failed to find such information in the literature). The

Table 1

Comparison of the Values of the PVA Degrees of Crystallinity Determined by Various Methods

Method	$K_{KR}$ , %	Thermal pre-history
<i>DSC</i>	45	The sample is kept 17 min in a temperature interval 20–190 °C
IR spectroscopy	49	The sample is kept at 20 °C
X-ray diffractometry	38	
Density measurements	32	

In order to determine  $K_{KR}$ , several different methods were applied: X-ray diffractometry, IR spectroscopy, density measurements, and differential scanning calorimetry (*DSC*). The values of the PVA degree of crystallinity are summed up in Table 1.

The degree of crystallinity of PVA, when it crystallises from the water solution, with water evaporating at the room temperature, differs but little from the degree of crystallinity reached when the polymer crystallises from the fusion.

#### 4.2. The PVA Crystallinity in the PVA/PVAc System

In order to determine the PVA crystallinity in the PVA/PVAc system, *DSC* and the density method were applied.

Table 2

Melting Characteristics of PVA in the PVA/PVAc Mixtures

$\varphi_{PVAc}$	Melting temperature, °C			Melting heat, $\Delta H$ J/g	$K_{KR}$ , %
	$T_{mS}$	$T_{m\max}$	$T_{mB}$		
0	191	224	234	62	45
0.1	180	222	232	46	33
0.3	172	209	220	39	28
0.5	160	187	248	30	22

The presence of the PVAc particles influences the PVA crystallinity. When the PVAc content increases in the mixture, the initial PVA melting temperature  $T_{kuš\ S}$ , the maximum melting temperature  $T_{kuš\ \max}$  and the crystallinity degree  $K_{KR}$  essentially decrease (See Table 2).

The experimentally determined density values  $\rho$ , depending on the content of the system ( $\varphi_{PVAc}$ ), are shown in Fig. 6.

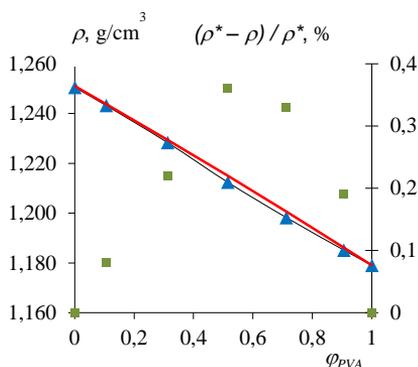


Fig. 6. The experimentally determined values of density  $\rho$  (points), the calculated values of density  $\rho^*$  (red line) of the systems PVA/PVAc and the relative deviation of these values  $(\rho^* - \rho) / \rho^*$ .

crystallinity of PVA in the composite is influenced by the disordered protective layer of the PVA<sup>a</sup> macromolecules on the surface of the PVAc particles. That part of the PVA macromolecules which forms the diffuse layer of PVA<sup>a</sup>/PVA does not crystallise. If value  $\phi_{PVAc}$  increases, the volume fraction of the diffuse layer also increases, and, as a result, the remaining part of PVA, which is capable of crystallisation, decreases (See Fig. 7).

## 5. The Strength-Deformation

### Properties of the Films of the PVA/PVAc Systems. Estimation of the PVA and PVAc Adhesive Interaction

#### 5.1. The strength-Deformation Properties of the Films of the PVA/PVAc Systems

The characteristic tensile strength-deformation ( $\sigma(\varepsilon)$ ) curves of the film-type components (PVA and PVAc), as well as of the mixtures are presented in Fig. 8.

The PVA films, when stretched at the temperature of the experiment (25 °C), get deformed as a typical partially crystalline glassy polymer. A plastified PVAc film is deformed as a superelastic polymer.

The experimentally determined values  $\rho$  are little lower than the corresponding values of density estimated on the basis of the additivity correlation. Most probably, the reason of the inequality  $\rho < \rho^*$  is that, under the impact of the surface of the PVAc particles, the PVA crystallinity degree decreases.

On the basis of the experimentally obtained density values the PVA crystallinity degree in the composite was determined.

Both the density measurements and the DSC data witness a decrease in the PVA degree of crystallinity, increasing the PVAc content in the PVA/PVAc composites.

Most probably, the degree of

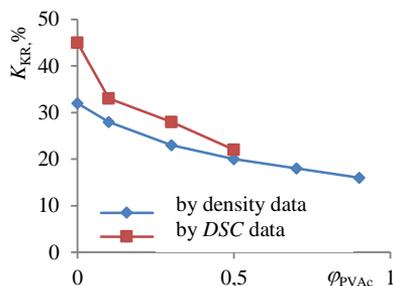


Fig. 7.  $K_{KR}$  ( $\phi_{PVAc}$ ) dependence.

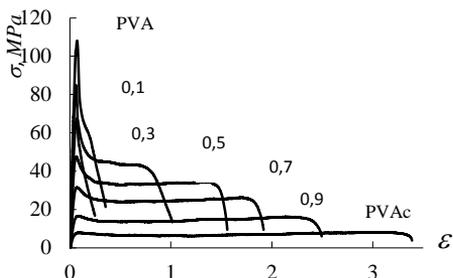


Fig. 8. Characteristic curves  $\sigma(\varepsilon)$  of PVA, PVAc and their mixtures in a tensile mode (numbers at the curves – the PVAc volume content in the mixture).

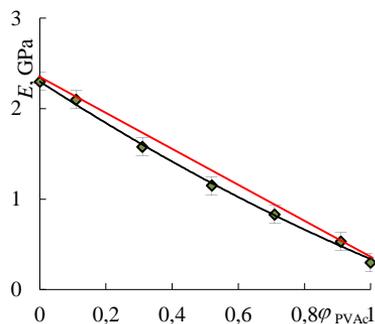


Fig. 9. Dependence of the initial modulus  $E$  of the PVA/PVAc composites on the PVAc volume fraction in the composite  $\varphi_{PVAc}$ .

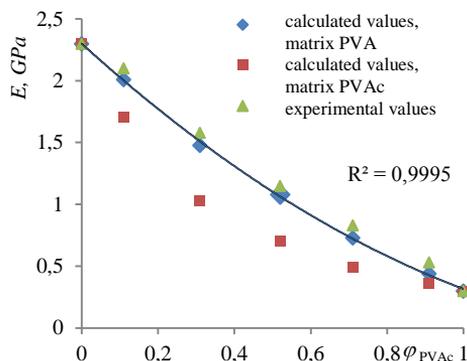


Fig. 10. The estimated (*Kerner's model*) values of the tensile elasticity modulus  $E^*$  of the composite in comparison with the experimentally determined values of the elasticity modulus  $E$  at various PVAc contents in the composite ( $\varphi_{PVAc}$ )

The value of the PVA modulus of elasticity  $E$  exceeds almost 7 times the elasticity modulus of the plastified completely amorphous PVAc used in the research. There is every reason to consider that PVA is rigid but the plastified PVAc — is clearly compliant.

As one could expect, value  $E$  of the composite is between the rigid (PVA) and the compliant (PVAc) values  $E$ . Value  $E$  decreases increasing the PVAc content in the composite: the volume fraction of more compliant component increases in the stiffer matrix, the volume fraction of the stiff matrix decreases (See Fig. 9).

The experimental values  $E$  are lower than the additive ones, yet they are close (the curve in Fig. 9). The reason of the increased  $E_{AD} - E$  value most likely is the disordered diffuse layers around the PVAc particles, the stiffness of which is lower than that of PVA matrix, and it is hard to consider  $E_{AD}$  in the estimate.

It was interesting to describe analytically the dependence of the experimentally obtained value of the tensile elasticity modulus  $E$  upon the composition of the composite.

In order to determine the deformative elastic constants of isotropic two-component polymer composites, the morphology of which corresponds to the dispersion of isolated

particles in a continuous matrix, we used the generally acknowledged and widely applied *Kerner's* approach [15].

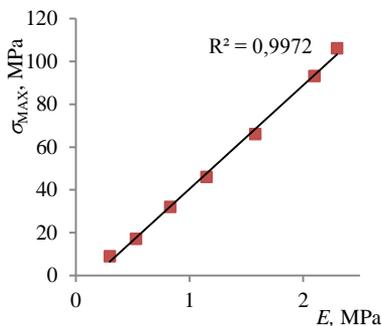


Fig. 11. Correlation of values  $\sigma_{MAX}$  and  $E$ .

tensile elasticity modulus  $E$  (See Fig. 11).

The composite loses integrity and fractures in two ways (See Fig. 12.):

- the PVAc particle is deformed and bursts without losing the link with the PVA matrix (Type A);
- the PVAc particle tears off the PVA matrix (Type B).

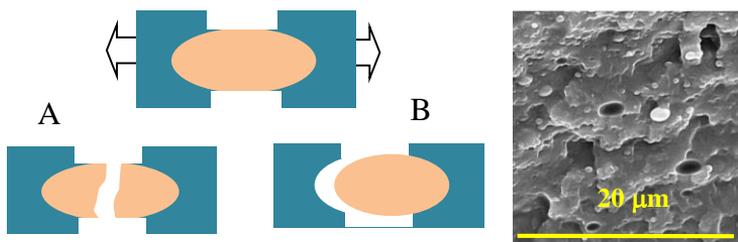


Fig. 12. The decomposition scheme of the composite PVA/PVAc and a SEM microphotograph of the fractures of the composite PVA/PVAc ( $\phi_{PVAc} = 0.3$ ).

In the SEM microphotograph of the fracture (See Fig. 12.) one can clearly see the traces of the fracture, type B. We failed to detect with sufficient certainty the fracture of type A. It seems that the fracture type B is dominant. In this case adhesive interaction between the PVAc and the PVA matrix may have an important role. It seemed expedient to try estimating the adhesive interaction of the system PVAc/PVA in a quantitative way.

## 5.2. Estimation of the PVA and PVAc Adhesion Interaction

Departing from the considerations mentioned in Chapter 5.1., it was important to have an idea about the mutual adhesive correlation of the PVA matrix and the PVAc particles. It may influence the loss of the strength-deformation of the composite and the integrity of the system in the deformation and also the biological decomposition process of the composite.

The layers of PVA and PVAc (I), which were prepared beforehand and partly dried out, are brought nearer, pressed (II) and kept for certain time (48 hours) under pressure.

The layers contain a definite amount of water (PVA — 8 %, PVAc — 3 %), which ensures their plasticity. As a result, an adhesive compound arises (III) with a definite direct contact surface PVA/PVAc.

By keeping the obtained adhesive compound AC under weight until its decomposition, it is possible to clear up its decomposition force (or work). If the AC decomposes along the contact surface, information is obtained about the strength of the adhesion links PVA/PVAc. If the AC decomposes in a cohesive way along the PVA or the PVAc, it demonstrates that the strength of the adhesion links exceeds the cohesive strength of the layers.

To estimate the AC strength, we selected the peeling method [16], [17] which provides for gradual decomposition of the adhesive compound. In order to implement the method, it is necessary to form two thin, flexible and sufficiently durable polymer layers creating an adhesive link between them. To raise the mechanical strength of the polymer layers, they are reinforced with fabric.

The developed methodology ensures production of adhesive compounds under conditions that are close to the interaction of the components during the formation process of the composite.

During the peeling process of a sample of the adhesive compound adhesiogrammes were fixed: the change of the peeling force  $P$  on the peeling way  $L$ .

By analysing the fractured surfaces of the adhesive compounds (by microscope, magnification x50), it was established that most samples fracture along the boundary surface PVA/PVAc. This leads to a conclusion that the weakest link of the AC compound PVA/PVAc is the adhesion link between the PVA matrix and the PVAc particle.

Dependence of the value of the specific work of peeling  $A$  was obtained upon the moisture content in the environment, the drying temperature, the contact time (duration).

When peeling the samples, made under different conditions, the obtained value  $A$  is within the limits of 160–970 J/m<sup>2</sup>.

## **6. Modulus of Bending Elasticity of the Films of the PVA/PVAc Systems**

### **6.1. Determination Method of the Elasticity Modulus of a Thin Wall Cylindrical Sample**

A flat sample of the film to be tested is bent into the shape of a cylindrical ring and fixed in the testing device (Fig. 13). Testing is carried out by compressing or stretching the ring perpendicular to its geometric axis, determining mutual correlation of the deformation force  $P$  and displacement  $\Delta$ :  $P(\Delta)$  [18, 19]. After the test the sample is returned to its initial flat condition.

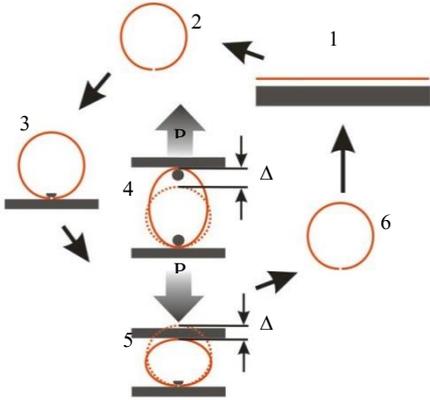


Fig. 13. A schematic diagram of testing of a flat sample of a film.  
 1 — a sample in a flat shape, 2 — curling of the sample, 3 — fixing of the sample in the holder, 4 — tensile testing, 5 — compression testing, 6 — removing of the sample from the holder and returning to a flat shape

Fig. 15).

In the beginning, several values  $P$  are determined in an experimental way and their respective values  $\Delta$  within the range  $\alpha = 0.2 - 0.8$  ( $\alpha = \Delta / 2R$ ). The entire cycle of measurements lasts 2 minutes, which is in correspondence with the quasistatic conditions. The obtained relationship  $P(\alpha)$  is recalculated into a relationship of nondimensional parameters  $\beta(\alpha)$ . Using the *Excel* calculation programme values of modulus  $E$  are determined corresponding to each experimentally determined value  $\alpha$ :  $E[\alpha]$ . The average  $E$  value is calculated  $\bar{E}$ .

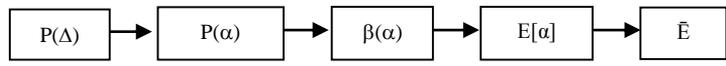


Fig. 15. The sequence of calculation.

The developed method is suitable for the identification of the indicators of strength-deformation of thin polymers and films from polymer materials (< 0.3 mm). The method allows for measurements within the range of small deformation values in which no tangible irreversible changes in the polymer structure have occurred.

By means of this method it is possible to conduct an experiment, applying the principle of a single sample. After measurement is finished, one and the same sample can be subject to the impact of certain conditions (temperature, environment) and, after

The testing device is shown in Fig. 14 where 1 — the base; 2 — the balance; 3 — the sample holder; 4 — the ring-shaped sample; 5 — the mobile platform; 6 — the digital calliper.

The measuring scheme:  $\Delta \rightarrow P$

Deformation of the sample is carried out by means of a micrometric screw, displacing the platform step after step, which compresses or stretches out the ring-shaped sample, thus increasing value  $\Delta$ . Value  $\Delta$  is measured by the digital calliper. After each displacement of the platform value  $P$  is read using the balance. Each current deformation  $\Delta$  is set for approximately 3 s, the measurement  $P$  is carried out after 1–2 s. The next value  $\Delta$  is set after 5 s.

The elasticity modulus is determined in an experimental way according to the following scheme (See

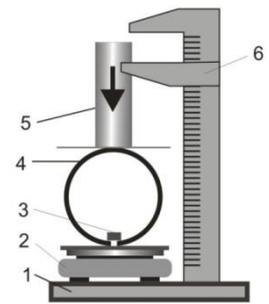


Fig. 14. The testing device.

that, it is possible to carry out repeated or multi-fold measurements. The sample is not damaged during its fixing and measuring.

## 6.2. Dependence of the Bending Elasticity Modulus of the PVA Film on the Moisture Content

Samples of PVA were used for the measurements with various plasticiser diethylene glycol (DEG) contents. The samples are dried in vacuum at 60 °C till they reach a constant weight, then weighed and tested.

As it is evident (Fig. 16), values  $E$  of the dry samples decrease, increasing the plasticiser content.

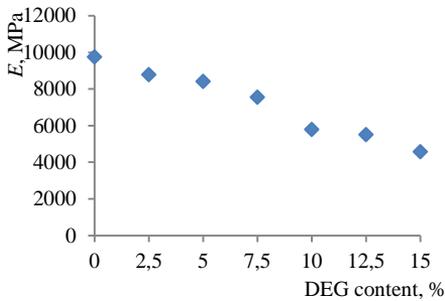


Fig. 16. Dependence of the values of the elasticity modulus of the PVA samples on the plasticizer content.

After testing, the samples in a flat shape are kept in the desiccator with the relative air moisture content  $\sim 55\%$  and tested after certain intervals of time. Before each test the samples are weighed in order to determine the moisture content in the sample. The experiment is continued until the samples reach moisture equilibrium. For the following compression tests only one parallel sample is used. During the last test all the samples are tested again, and the values of the moduli are compared for the samples with equal plasticiser content, which are tested

regularly and only in the beginning and in the end.

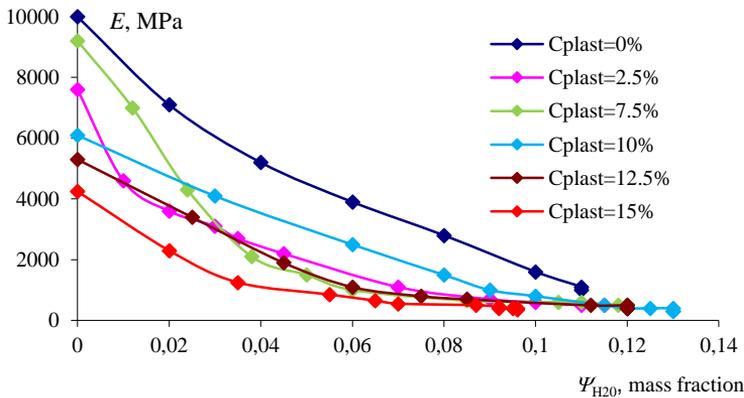


Fig. 17. Dependence of the value of the elasticity modulus  $E$  of the PVA samples on the moisture content  $\psi_{H_2O}$ .

If the measurements are made for one and the same sample, successively subject to the impact of definite factors which cause structural changes in the material and, as a result, corresponding changes in value  $E$ , interest arises in a possibility to execute relative changes of the modulus without carrying out labour intensive direct identification of values  $E$ .

In order to estimate the relative change of the value of the modulus of a polymer, determination of value  $E$  from experimental  $P(\alpha)$  relationships is not obligatory, and for this purpose the respective  $P_{\alpha=const}$  values can be used.

## 7. Filled PVA/PVAc Composites

### 7.1. Influence of Fillers upon the Crystallinity of Pure PVA

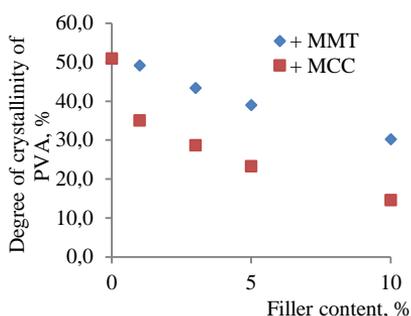


Fig. 18. Impact of *MMT* and *MCC* upon the degree of crystallinity of PVA.

The  $K_{KR}$  of PVA decreases when the contents of both the fillers increase (See Fig. 18).

Greater diminution in value  $K_{KR}$  is observed for the PVA/*MCC* systems. Most probably, when the structure of the system is forming, a part of the PVA macromolecules diffuse in the outer part of the particles of the swollen *MCC* gel and do not crystallise (a sharp boundary surface PVA-*MCC* is not visible). When the *MCC* content increases, the specific weight of this part also increases; as a result, the total degree of crystallinity PVA decreases (Fig. 19). At the presence of

the *MMT* particles the PVA crystallinity diminishes to a lesser extent.

### 7.2. The Bending Elasticity Modulus $E$ of the PVA, PVAc and PVA/PVAc Films Containing a Filler

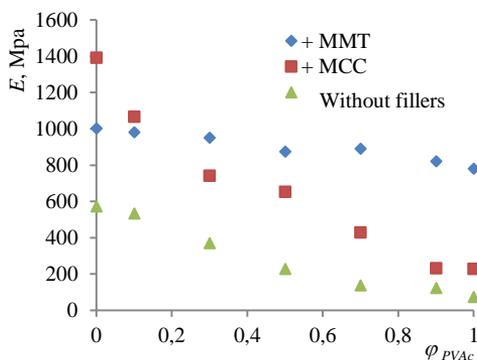


Fig. 19. Dependence of the values of the elasticity modulus  $E$  of the PVA/PVAc composites on the PVAc content.

The values of the elasticity modulus of filled PVA/PVAc systems are considerably higher in comparison with a PVA/PVAc system, which does not contain fillers at all the  $\varphi_{PVAc}$  values of the PVAc content (Fig. 19).

### 7.3. Dependence of the Water Adsorption Capacity and Bending Elasticity Modulus of the Films of Filled PVA/PVAc Composite Materials on the Moisture Content

First of all, the ability of the PVA/PVAc composite materials to absorb moisture was determined (Fig. 20).

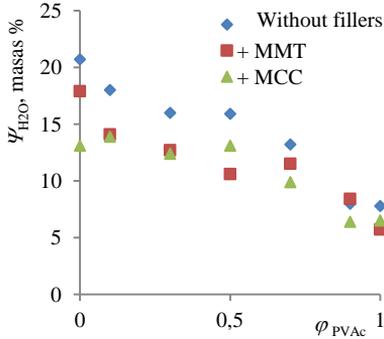


Fig. 20. The amount of water of the PVA/PVAc composite materials during 48 hours at the relative moisture content of 75% in the environment.

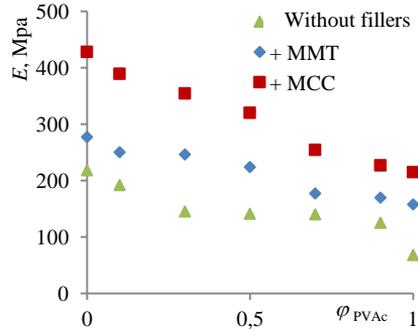


Fig. 21. Values of the elasticity modulus of the PVA/PVAc composite materials after 48 hours of keeping in the environment with a relative moisture content of 75%.

As it is evident (See Figs. 20 and 21), the composites containing fillers absorb a lesser amount of water and retain a greater value of the elasticity modulus.

### 7.4. Projection of the Values of the Elasticity Modulus Using the Response Surface Methodology and Optimisation of the Composition of the Films from Composites PVA/PVAc/Filler

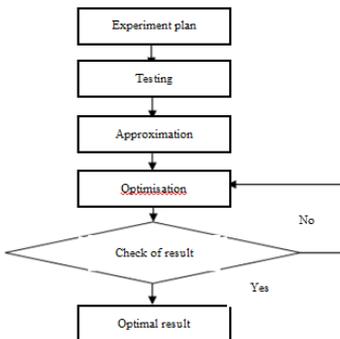


Fig.22. A block diagram of the optimisation procedure.

The response surface methodology (RSM) provides a possibility to clarify the relationship between the content proportions of components of the composite and the properties of the material (for instance, the strength- deformation properties), considerably diminishing the number of experiments. The response surface methodology is a combination of mathematical and statistical methods used to simulate and analyse tasks, in which the response function depends on several variable values and which are presented in the form of a regression equation [10].

The value of the tensile elasticity modulus of the composite was chosen as an optimisation object.

A general block diagram of the optimisation procedure is shown in Fig. 22.

The plan of experiments is formulated for 3 intended variable values, namely, the content of the montmorillonite *MMT* nanoparticles, mas.%; the content of the microcrystalline cellulose *MCC* nanoparticles, mas.%; the PVA volume content in the

PVA/PVAc mixture, %; and 27 points of experiment. Performing tests at the points of the experimental design, numerical data were obtained that were used in order to build approximation functions. A view of the response surfaces is shown in Fig. 23. This figure demonstrates a possible response function for a various amount of fillers and various combinations of the PVA volume fraction.

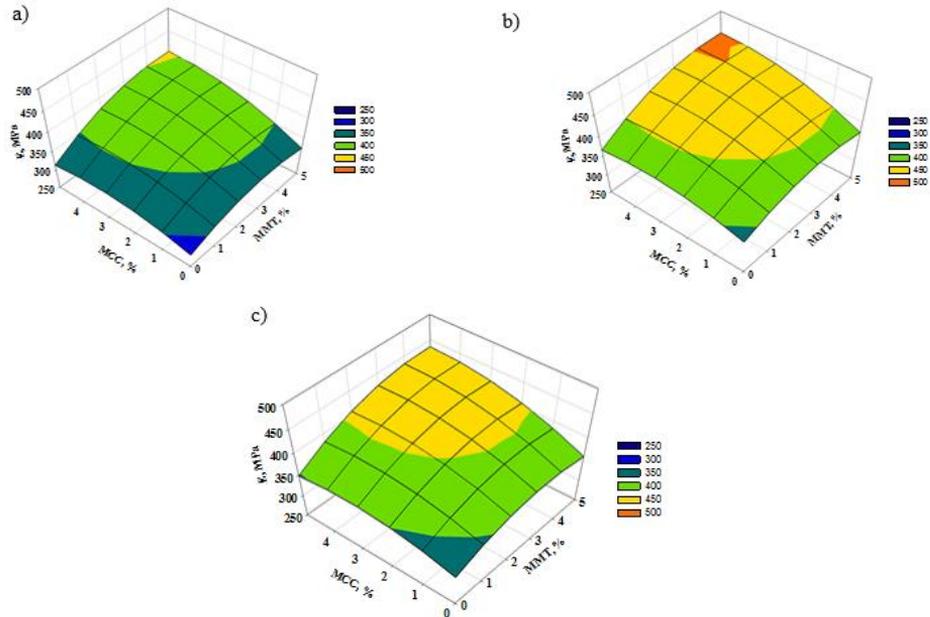


Fig. 23. Dependence of the elasticity modulus  $E$  on the filler content (the PVA volume fraction in the composite: a — 10 %, b — 50% and c — 90%)..

The values of the elasticity modulus increase in proportion to the growth of the number of nanoparticles. Depending on the individual properties of the intended variables, the most efficient factor of the impact upon the elasticity modulus is the montmorillonite clay nanoparticles. The maximum value of the elasticity modulus can be reached when the PVA and the PVAc contents are equal.

The optimisation result obtained for the films of the PVA/PVAc mixture is depicted in Fig. 3. The maximum elasticity modulus reaches 454 MPa when the montmorillonite clay content is 4.5 %, the microcrystalline cellulose content is 5.0 % and the PVA volume fraction in the PVA/PVAc mixture is 60 %. Differences between the optimal and the experimental result do not exceed 2.5 %, which shows a good correlation of the approximation functions.

Table 3

The Result of Optimisation

Name	Variable values			Objective function
	$MMT$	$MCC$	$\varphi_{PVAc}$	
Optimisation	4.5	5.0	0.4	454
Experimental testing	4.5	5.0	0.4	443

## 8. Biodestruction of the PVA/PVAc Composites

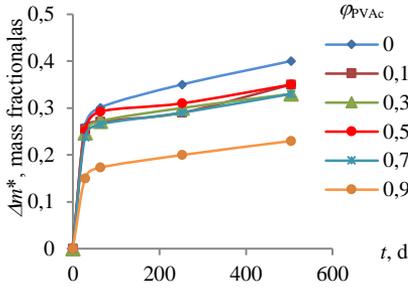


Fig. 24. Changing of the PVA/PVAc composite materials  $\Delta m^*$  in time  $t$ .

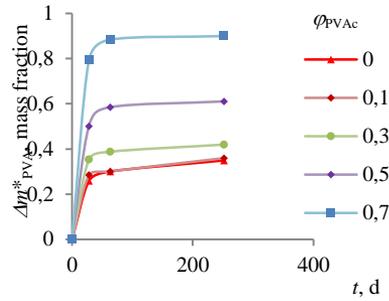


Fig. 25. Dependence of  $\Delta m^*_{PVA}$  on the biodestruction time  $t$ .

As a quantitative indicator of the biodecomposition process we used the value of the relative diminution of the mass of the samples  $\Delta m^*$  (2):

$$\Delta m^* = \frac{(m_0 - m_t)}{m_0} \quad (2)$$

where:  $m_0$  — the initial mass of the sample;

$m_t$  — the mass of the sample after the time  $t$ .

Dependence of value  $\Delta m^*$  of the composites PVA/PVAc on time is presented in Fig. 24.

As it is evident, curves  $\Delta m^*(t)$  for the composites of various content essentially differ.

The mass of the PVAc component in the investigated biodestruction time interval of the composite practically did not decrease. There are only destructions of the PVA component. Knowing the PVA content in the composition, from  $\Delta m^*(t)$  relationships the relative mass diminution was estimated, related to the mass —  $\Delta m^*_{PVA}$  of the PVA component. As it is evident from Fig. 25, the PVA biodestruction essentially accelerates in the composite, increasing the PVAc content in the composite.

There is a reason to believe that the PVA biodestruction is more intense in the

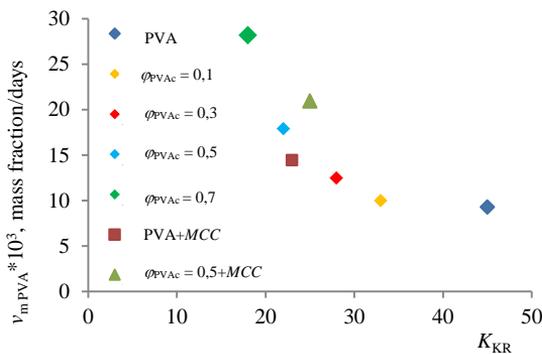


Fig. 26. The initial speed  $v_{mPVS}$  of the PVA (PVS) biodestruction depending on the PVA (PVS) crystallinity degree  $K_{KR}$  in various systems.

disordered diffuse layer in comparison with the rest of the ordered PVA matrix. When value  $\phi_{PVAc}$  increases, the volume fraction (proportion) of the diffuse layer increases, and the total crystallinity degree of the PVA matrix correspondingly decreases.

Apparently, there is a convincing correlation between the total crystallinity  $K_{KR}$  of the PVA polyvinyl alcohol component and the measure of the PVA

biodestruction speed —  $v_{mPVA}$ . (Fig. 26). Higher  $v_{mPVA}$  values correspond to lower  $K_{KR}$  values.

When *MCC* is added to the PVA or PVA/PVAc composite materials, the losses of the PVA mass increase during the biological decomposition. It can also be observed with the systems containing *MCC* that to lower degrees of the PVA crystallinity there correspond higher  $v_{mPVA}$  values (See Fig. 26).

## 9. Principal Technological Scheme for Producing a Film from the Water System PVA/PVAc/Filler by a Casting Method

The most time-intensive part of the film production process is drying of the layer of the PVA/PVAc/*MCC*/*MMT* water system.

There is a fixed initial drying speed  $v_D = \lim (d\psi_{H_2O}/dt)|_{t \rightarrow 0}$  and drying time  $t_D$  for the films of various contents and various initial thicknesses of the layers. It has been established that the PVAc content in the composite has little impact upon both the values  $v_D$  and  $t_D$ . Value  $v_D$  increases but value  $t_D$  decreases essentially, the thickness of the drying layer decreases.

All the above-mentioned experiments were carried out, drying under the conditions of a minimal flow of the heat carrier (convection in the drying chamber), and values  $t_D$  (in the range of 6–23 hours) were not technologically acceptable.

By conducting the drying experiment at 35 °C relationship  $\psi_{H_2O}(t)$  was obtained (See Fig. 27).

Under these drying conditions value  $v_D$  reached 4.7 %/min and  $t_D$  — 54 min at  $\psi_{H_2O} = 3\%$ .

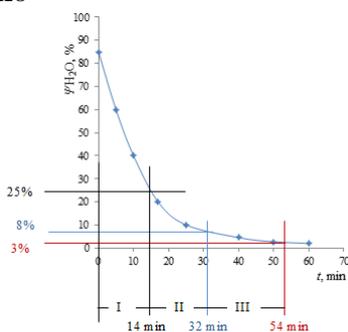


Fig. 27. The drying curve of the PVA/PVAc/*MCC*/*MMT* water system under the conditions of intense air flow at 35 °C (the initial water content in the system  $\psi_{H_2O} = 85\%$ , the initial thickness of the layer 1.8 mm), stage of the drying process I, II and III.

From relationship  $\psi_{H_2O}(t)$  it is possible to distinguish several stages important for the production of the film. For  $\psi_{H_2O} \leq 25\%$  the drying layer must be placed on a horizontal flat support surface (Stage I). After that a change of the position of the drying layer and the support surface is allowed without a tendency to flow down from the support surface (Stage II). When  $\psi_{H_2O} \leq 8\%$  is reached, separation of the produced film from the support surface is allowed and further drying until the final moisture content  $\psi_{H_2O} = 3\%$  is achieved (Stage III).

The scheme of the equipment is depicted in Fig. 28. Characteristics of the drying process of the layer and of the drying equipment are presented in Table 4.

Table 4

Characteristics of the Drying Process of the Layer of the PVA/PVAc/MCC/MMT (PVS/PVA/MCC/MMT) Water System and of the Drying System

Indicator	Drying stages of the layer of the PVA/PVAc/MCC/MMT water system		
	I	II	III
Moisture content, $\psi_{H_2O}$ , %	85–25	25–8	8–3
Duration of the stage, min	14	18	22
Length of the dried layer corresponding to the stage, m	70	90	110

By means of the feeder the water system of PVA/PVAc/MCC/MMT is continuously dispensed in a definite layer on a stainless steel conveyor belt. The conveyor belt is arranged in a tunnel in which the required air temperature and speed of flow are ensured. The layer freely lies on the mobile belt in a horizontal position (Stage I).

When the belt changes its position in space, the drying layer remains stuck to the surface of the steel belt (Stage II). At the end of Stage II the moisture content in the layer reaches 8 %.

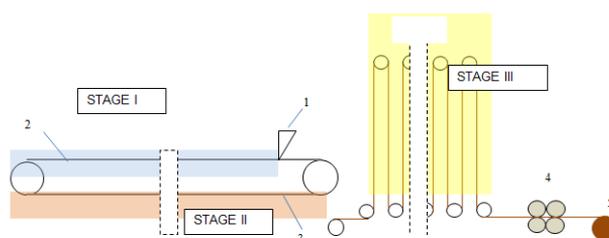


Fig. 28. Equipment for the production of a film from the PVA/PVAc/MCC/MMT water system: 1 — the feeder; 2 — the steel conveyor belt; 3 — the drying layer; 4 — the pulling mechanism; 5 — the ready roll of the film.

The mechanical strength of the layer becomes sufficient to separate it from the steel belt and to perform further drying (Stage III) to  $\psi_{H_2O} = 3\%$ . The movement of the film in Stage III is ensured by means of the pulling mechanism. Its running is synchronised with the movement of the steel conveyor belt. The ready film is wound onto a roll.

In this way it is planned to make film materials for different purposes, which will be able to substitute many materials that are currently in use, environmentally unfriendly and biologically non-degradable. These could be:

- Film type materials for packaging (bags, vacuum packaging);
- Multilayer films;
- Coating (film on fabric or paper);
- Protection of seed and plants — seed incrustation tape.

## CONCLUSIONS

1. A sharp decrease in the viscosity of the water system PVA/PVAc within the shear rate range  $\dot{\gamma} = 10 - 120 \text{ s}^{-1}$  and disappearance of the pseudoplastic character of the medium, when the PVAc water dispersion content is increased, is not only the result of diminished concentration of the PVA water solution but also the impact of the PVAc particles themselves.
2. Composite PVA/PVAc is made of a continuous PVA matrix, in which PVAc particles are dispersed. Below the PVAc content  $\phi_{\text{PVAc}} < 0.5-0.7$ , PVAc particles keep their initial spherical shape. At higher PVAc content, the particles get close to each other, gradually deform and obtain the shape that is close to polyhedrons. Interdiffusion of polyvinyl alcohol macromolecules creating the protective layer of PVAc and of PVA macromolecules takes place. A diffuse layer is created around each PVAc particle.
3. When pure PVA crystallises from an aqueous solution (when water evaporates at ambient temperature) and crystallises from the melt, it achieves practically equal crystallinity. The crystallinity of PVA in PVA/PVAc composites reduces with the increase of the PVAc content, because the share of PVA macromolecules forming a disorderly diffuse layer increases.
4. The value of the tensile elasticity modulus  $E$  of the composite is between  $E$  values of rigid (PVA) and compliant (PVAc) components. The  $E$  value reduces as the PVAc content increases in the composite.  
The load-bearing component of the composite is a PVA matrix, the volume part of which determines the nature of tensile strength-deformation relationships of the composite.  
The composite loses integrity and fractures in two ways: by deformation and fracture of PVAc particles (without losing cohesion with the PVA matrix), and by tearing off the PVAc particle from the PVA matrix.
5. A method for determination of stress-deformation parameters of thin films has been developed. The method provides the possibility to perform the experiment repeatedly and several times using one and the same sample.  
The dependence of the  $E$  value of the modulus of elasticity of polyvinyl alcohol containing different amount of plasticizers on the absorbed moisture content has been ascertained.
6. PVA crystallinity in PVA and PVA/PVAc composites containing nanofillers (microcrystalline cellulose, *MCC*, and montmorillonite, *MMT*) is smaller, but values of the bending modulus of elasticity are higher in comparison with systems without fillers at all values of PVAc content. Composites containing fillers absorb less water and retain higher value of the modulus of elasticity.  
The impact of the component proportion of the composites PVA/PVAc/filler on the modulus of elasticity using the response surface method has been ascertained. The composition of the composite, in which the modulus of elasticity has the highest value, has been determined and experimentally tested.
7. In case of all the studied PVA/PVAc systems, the disordered diffuse layer between PVAc particles and the PVA matrix is part of PVA/PVAc structure of the composite, in which accelerated biodegradability of the PVA component and disintegration of the composite take place.

It is possible to control the biodegradability, as well as some most important operational properties of composite PVA/PVAc within certain limits.

8. A principal technological scheme has been developed for the production of a film-type PVA/PVAc composite.

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## APPROBATION OF THE RESEARCH RESULTS

The main scientific achievements and results of the research have been presented at 14 international scientific conferences.

There are 10 full-text scientific articles and 14 conference theses published on the subject of the doctoral thesis.

### **The main research results are reflected in the following full-text articles:**

1. Geisari N., Kalnins, M. Poly(vinyl alcohol) – Poly(vinyl acetate) Composite Films from Water Systems: Formation, Strength-Deformation Characteristics, Fracture. *IOP Conf. Series: Materials Science and Engineering*, 2015, Vol. 111, No.1. **(SCOPUS)**
2. Jelinska, N., Kalnins, M., Kovalovs, A., Cate, A. Design of the Elastic Modulus of Nanoparticles-Containing PVA/PVAc Films by the Response Surface Method. *Mechanics of Composite Materials*, 2015, Vol.51, No.5, 669–676. **(SCOPUS)**
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**The main research results are reflected in the following conference theses:**

1. Kovalovs, A., Geisari, N., Cate, A., Kalnins, M. Effects of Nanoparticles on the Elastic Modulus in the Poly (Vinyl Alcohol)/Poly (Vinyl Acetate) Blends by the Response Surface Methodology. *Baltic Polymer Symposium 2015: Programme and Proceedings*, Latvia, Sigulda, 16–18 September, 2015. Riga: RTU Press, 2015, 104–104.
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