

RIGA TECHNICAL UNIVERSITY

Faculty of Material Science and Applied Chemistry

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Doctoral study programme „Materials Science”

**STRUCTURE AND PROPERTIES OF
POLYOXYMETHYLENES, ETHYLENE-OCTENE COPOLYMERS
AND NANO ZINC OXIDE COMPOSITES**

Summary of Doctoral thesis

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„Nanostrukturēto elektropasīvo polimēru kompozītmateriālu ekspluatācijas īpašību izpēte,,



IEGULDĪJUMS TAVĀ NĀKOTNĒ

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**THE DOCTORAL DISSERTATION IS PROMOTED TO BE DEFENDED FOR THE
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APPROVAL

With the following I approve that I have elaborated present doctoral dissertation, which is submitted to be reviewed in Riga Technical University to qualify for the doctoral degree in Materials Science. The doctoral dissertation is not submitted anywhere else to qualify for a scientific degree.

Agnese Grigaloviča

Date.....

The thesis is written in Latvian language and volume of the dissertation is 193 pages, including 134 pictures, 25 tables, 17 equations, a list with 102 references and the annex.

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ABBREVIATIONS

E17	- ethylene α -octene copolymer „Engage 8540”
E38	- ethylene α -octene copolymer „Engage 8200”
EOC	- ethylene α -octene copolymer
P3	- polyoxymethylene „Kocetal 300”
P9	- polyoxymethylene „Kocetal 900”
POM	- polyoxymethylene
UV	- ultraviolet light
ZnO	- zinc oxide
η	- viscosity
A	- impact strength
D	- coefficient of diffusion
E	- elastic modulus
E''	- flexural loss modulus
F	- impact load
G'	- melt storage modulus
G''	- melt loss modulus
I	- deformation
KI	- melt flow rate
Δm	- mass change
n_{tec}	- flow behavior index
P	- permeability
S	- solubility
$\tan\delta$	- loss factor
$\dot{\gamma}$	- shear rate
τ	- shear stress
χ	- crystallinity degree
ε_B	- strain at break
ε_Y	- strain at yield
σ_B	- stress at break
σ_Y	- stress at yield

OVERALL REVIEW OF THE THESIS

Introduction

Nowadays in different sectors of national economy polymer materials with broad range of technological and exploitation properties are increasingly exploited. Among the perspective materials are compositions of thermoplastic polymers, because in this way different chemical and physical properties of two or more polymeric components can be combined in a single material. In result new multifunctional systems with specific properties, higher than those of neat polymers, can be obtained.

Polyoxymethylene (POM) is known as a high performance engineering polymer with good mechanical strength, low friction and wear, excellent dimensional stability, as well as high resistance to chemicals. These properties make POM attractive as a potential matrix for compositions. By purposeful modification of POM with elastomers it is possible to obtain polymer systems with interesting stress-strain properties, improved thermal stability, specific barrier properties etc. Addition of nanosize particles can increase some of exploitation properties of the compositions at considerably smaller filler content than in the case of microcomposites.

Taking into account that POM compositions with elastomers till now have been studied in a limited content range and a relatively narrow set of properties of the compositions have been analyzed, in this research POM blends with ethylene-octene copolymers (EOC) at wide range of weight-to-weight ratios are investigated. Relationships between characteristic structural parameters with quasistatic and dynamic mechanical properties, gas permeability and solvent vapor sorption behavior, thermal and rheological properties of the investigated compositions have been revealed. Considering the properties of the new multifunctional systems, POM/EOC blends were modified with nanosize zinc oxide to decrease coefficient of friction and increase stability under ultraviolet light.

The state of the art

Polyoxymethylene (POM) is used for development of thermoplastic composites due to its high tensile strength, low wear and friction. POM compositions with other thermoplastic polymers (polyurethane, polyethylene etc.) and inorganic fillers (carbon nanotubes, zinc oxide, titanium dioxide, clay etc.) are formed. In result composites with higher superelasticity, thermal and ultraviolet stability are obtained.

Up to date there are limited investigations on POM matrix blends: only few thermoplastic co-components are used and the range of the studied compositions is limited/does not cover the whole wt.-to-wt. ratio spectrum. Only few investigations are

devoted to three component systems. There is lack of investigations about 1) rheological and 2) gas and solvent vapor sorption properties, as well as 3) influences of nanofillers on the technological and exploitation characteristics of POM/elastomer blends.

Aim

The aim of the work is development of thermoplastics blends from distinct polyoxymethylenes (POM) and ethylene octene copolymers (EOC), as well as their composites with nanostructured ZnO particles; investigate structure-properties relationships of these systems.

Tasks

Solutions of the following tasks are envisaged:

1. To develop technological approaches for development and processing of POM-EOC-ZnO compositions in a broad range of weight-to-weight ratios of the components.
2. To investigate the influences of the components weight-to-weight ratios and technological parameters on the structure, stress-strain, rheological, thermal, barrier and other properties, as well as durability.
3. To assess the effects of ZnO on the tribological properties and UV stability of the selected compositions.

Scientific novelty

1. Complex studies of structural parameters and performance properties (stress-strain, tribological, rheological, thermal and barrier characteristics) of binary composites built from the polymers (polyoxymethylenes (POM) and ethylene-octene copolymers (EOC)) with various stress-strain and rheological behavior, are performed in a full range of weight-to-weight ratios of the components by using modern research methods.
2. POM/EOC composites have heterogeneous structure with clearly expressed interface. Development of compatible boundary layer between both polymers is not observed in a molecular level.
3. Properties of the investigated composites as a function of volumetric content depend on morphology. At similar morphology strength-deformation and barrier properties of the composites are highly dependent on the crystallinity degree. Components hinder each other's crystallization during formation of the composites.
4. In general addition of ZnO to POM/EOC composites does not significantly affect its structure and stress-strain parameters. Presence of ZnO in the investigated composites

provide lower friction to steel, higher thermal stability and improved resistance to ultraviolet irradiation.

The practical meaning

1. Manufacturing technologies for development and processing of various blends of polyoxymethylenes (POM) and ethylene octene copolymers (EOC), as well as POM and POM/EOC systems with nanostructured ZnO nanoparticles have been developed.
2. Structural characteristics and their influence on the important exploitation properties of the investigated composites have been evaluated.
3. Investigated POM/EOC and POM/EOC/ZnO compositions depending on the ratio of the constituents, form a group of thermoplastic materials possessing broad range of properties.

Defendable thesis

1. Using various thermoplastic polymers (possessing different chemical structure, polarity and stress-strain parameters) as a components of the investigated compositions, allows purposefully control formation of the composites structure and obtain the materials with preferable set of stress-strain, tribological, barrier and thermal properties and improved ultraviolet radiation resistance.
2. Morphology, as well as actual degree of crystallinity, formed at equal manufacturing prehistory, both determine quasi-static and dynamic stress-strain characteristics, barrier properties, thermal stability and durability (under the exposure of aggressive media) of the investigated systems.

Composition and volume of the thesis

The thesis is written in Latvian language and contains introduction, literature review, methodology, experimental results and discussion, and overall conclusions. Volume of the dissertation is 193 pages, including 134 pictures, 25 tables, 17 equations, a list with 102 references and the annex.

Approbation of the thesis

Results presented in the dissertation are published in 7 scientific journal articles (6 SCI journal articles). Results of the work are presented in 26 international conferences in the form of either oral or poster presentations.

GENERAL CHARACTERISTICS OF THE STUDY

Literature review

In the literature part of the thesis polyoxymethylene (POM) and ethylene octene-copolymers (EOC) as potential polymers for obtaining multiphase compositions, as well as zinc oxide (ZnO) as inorganic filler for developing nanocomposites have been particularly described. At the same time possibilities of forming POM compositions with other thermoplastic polymers and inorganic fillers have been summarized. Influences of the components nature and volumetric content on the structure, stress-strain characteristics, impact resistance and other significant exploitation properties of the investigated systems have been discussed. According to analysis of the reviewed scientific literature, it has been concluded that investigations generally are related to evaluation of the mechanical properties of two components systems in the limited content range of the compositions. Consequently the aim and the tasks of the experimental studies have been formulated at the end of the literature review.

Methodology

The basic content of the methodology part is devoted to the description of the used testing methods and determinable parameters. All experiments were performed by using equipment accessible in RTU Institute of Polymer Materials. Separate experiments were performed in collaboration with RTU Institute of General Chemical Engineering, LU Institute of Solid State Physics, Kassel University and Institute of Mechanics, Bulgarian Academy of Science.

As polymer components of binary compositions we used two types of polyoxymethylenes (POM *Kocetal 300* (P3) and *Kocetal 900* (P9) with different average molecular weights: P3- 84 Da, P9- 55 Da) and ethylene α -octene copolymers (EOC, *DuPont Dow Elastomers, Engage 8200* (E38) and *Engage 8540* (E17) with various α -octene contents: E38- 38 %, E17- 17%). As nanofiller we used zinc oxide (ZnO), which was synthesized in the RTU Institute of Inorganic Chemistry (Salaspils, Latvia).

POM/EOC composites were prepared by using twin screw extruder *Thermo ELECTRON CORPORATION PRISM TSE 16 TC* at broad component wt.-to-wt. ratios (0/1, 0,95/0,05, 0,9/0,1, 0,8/0,2, 0,7/0,3, 0,5/0,5, 0,3/0,7, 0,1/0,9, 1/0). Temperatures in the extruder zones were varied between 170 °C-180 °C, screw rotation speed was 70 rpm.

Nanocomposites with various ZnO (0,02 and 0,05 wt.p.) contents were prepared by using two-roll mills at 170 °C (POM matrix compositions); 110 °C (E17 matrix compositions) and 80 °C (E38 matrix compositions).

Specimens for tensile, flexural and impact strength investigations were injection molded by using vertical injection molding machine *Minijector 55*. Melt temperatures in the heater zones were varied according to the material processed: in case of POM and POM/EOC blends 180 °C - 185 °C -190 °C; in case of EOC and EOC nanocomposites 130 °C – 185 °C - 190 °C.

Specimens (sheets with planar dimensions $10 \times 6 \text{ mm}^2$ and various thicknesses of 0,2, 0,3, 1 and 2 mm) were compression molded by using hydraulic press *Carver CH 4386* at 190 °C and pressure of 30 MPa.

Structural investigations

Scanning electron microscopes *Tescan Mira/LMU*, *SEM-FIB TESCAN LYRA* and *CAMSCAN MV2300* were used to investigate fracture morphology.

Surfaces morphologies before and after tribological test were investigated on confocal laser scanning microscope *LEXT-OLS Series*.

Density ρ (g/cm^3) was determined by use of *Sartorius KB BA 100 electronic* scales equipped with *YDK 01 01* density measurement kit.

Calorimetric properties (glass transition temperature T_g , melting onset temperature $T_{on m}$, maximal melting temperature T_m , melting offset temperature $T_{off m}$, melting enthalpy, crystallization enthalpy) were measured by using differential scanning calorimeter *DSC1/200W (Mettler Toledo)*. Test cycles: heating-cooling-heating; interval of the first heating -100 °C - +200 °C; colling interval 200 °C - -100 °C; interval of the second heating - 100 °C - +200 °C; heating /cooling rate 10 °C/min ; test media - N₂ flow.

Infra-red spectra were recorded by using Fourier transforms infrared spectroscopy *Thermo Fisher Scientific, Nicolet 6700* in the range of wave numbers from 4000 cm^{-1} to 650 cm^{-1} .

Determination of the structure-deformation parametrs

Dynamical mechanical thermal properties in bending (flexural storage modulus E' , flexural loss modulus E'' , loss factor $\tan\delta$, glass transitions T_g) were determined by use of *Mettler Toledo DMA/SDTA861^e* equipment. Test regime: heating from -100 °C to +100 °C with heating rate of 3 °C/min and frequency of 1 Hz.

Determination of stress- strain characteristics

Tensile and flexural properties (modulus of elasticity E , stress at yield σ_y , strain at yield ε_y , stress at break σ_b and strain at break ε_b , maximal flexural stress σ_M) were measured by use of universal testing machine *Zwick Roell BDO-FB020TN*.

Charpy impact strength was determined by use of instrumented *Zwick 5102* equipment at 25 °C \pm 2 °C and -160 °C; impact energy of the pendulum - 4 J.

Falling weight impact strength was measured by *CEAST DAS FRACTOVIS/ DAS 16000* testing equipment at $25\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$, impact energy of the falling weight - 133 J.

Determination of rheological characteristics

Melt viscosity η , storage modulus G' , loss modulus G'' , shear strength τ and shear rate $\dot{\gamma}$ were determined by use of *REOLOGICA StressTech NOVA* rotational viscometer. Experiments were performed at various temperatures - 180 $^{\circ}\text{C}$, 190 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$ at oscillation stress sweep, oscillation and viscometry modes.

Melt flow rate was determined by use of *IIIPT - AM* plastometer at 190 $^{\circ}\text{C}$ and load 2,16 kg.

Determination of tribological properties

Coefficient of friction was measured by use of *CETR Universal Material Tester UMT*, pin on plate mode. Measurements were made for 1200 s by using stainless steel metallic pin (diameter 6,35 mm, length 25,4 mm) contacted with the flat surface of polymer sample under the pre-load of 20 N. The polymer sample was attached to the stainless steel base, which reciprocally moved with speed of 10 mm/s.

Determination of barrier properties

Barrier properties (coefficient of diffusion D , permeability P , solubility S) were determined by use of *IGA002* sorption equipment. Experiments were realized at 25 $^{\circ}\text{C}$ in a full partial pressure range 0 to 0,9 by using rectangular samples with thickness $\sim 0,20$ mm.

Permeability characteristics (coefficient of diffusion D , permeability P , solubility S) were analyzed by use of specially designed test equipment consisting from diffusion cell, pressure applying system and gas chromatograph *ACM 6100 GC*. Samples with thickness $\sim 0,30$ mm and cross-sectional area $14,82\text{ cm}^2$ were used to measure permeability characteristics to nitrogen gas (N_2) at 30 $^{\circ}\text{C}$. Helium (He) was used as carrier gas.

Determination of thermal stability

Mettler/Toledo TGI/SF thermogravimetric analyzer coupled with *ThermoFischer Nicolet 6700 FTIR* spectrometer was used for determination of thermal stability and registration of the evolved gaseous species. About 10 mg test samples were heated under N_2 flow from 25 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. FTIR spectrums were recorded every 6 s.

Determination of durability to ageing

Weathering test was carried out by using *Q-Lab QUV* accelerated weathering tester. Samples were exposed to the sequence of the following cycles: UV light for 8 h at 60 $^{\circ}\text{C}$ (irradiance $0,76\text{ W}\cdot\text{m}^{-2}\cdot\text{nm}^{-1}$ measured at 340 nm), condensation without UV irradiation for 4 h at $50\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$. The whole experiment duration was 366, 672 and 1344 hours. The effects

of weathering on the sample stress-strain characteristics, crystallinity and hydroxyl and carbonyl absorption peaks were investigated.

Ageing tests in the submerged state were realized in water and hydraulic oil at $20\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$. Test specimen dimensions, mass changes, tensile properties and impact strength were measured at various exposure times (Days 7th, 14th, 21th, 28th).

Results and discussion

In the experimental part of the work structural characteristics and their influence on the stress-strain parameters, impact strength, tribological, barrier, rheological, thermal and durability properties of the investigated binary composites (POM/EOC) and three component (POM/EOC/ZnO) systems are summarized and discussed.

1. Manufacturing technologies

POM/EOC composites were prepared by using twin screw extruder, while POM/EOC/ZnO nanocomposites were obtained by using two-roll mills. Suitability of the technological approach was evaluated by the analysis of the stress-strain, density and melt index parameters. It was determined that:

- extrusion zone temperatures must be between $170\text{ }^{\circ}\text{C}$ - $180\text{ }^{\circ}\text{C}$ and screw rotation speed - 70 rpm;
- two extrusion cycles per composition should be realized; by increasing the number of the mixing cycles up to 3, no further changes in the properties of the compositions were observed;
- processing by using two-roll mills should be approximately 8 min at $170\text{ }^{\circ}\text{C}$, $110\text{ }^{\circ}\text{C}$ and $80\text{ }^{\circ}\text{C}$ for POM, EOC17 and EOC38 matrix compositions respectively.

2. Morphology

At the temperatures, considerably lower than glass transition temperatures of the components, all the investigated compositions are broken in a brittle failure mode at negligible elastic deformations. Consequently one can assume that surface morphology of the investigated compositions corresponds to the morphology in bulk. Components (POM and EOC) of the investigated compositions are characterized with different fracture surface morphologies. POM as a more crystalline component has rougher morphology than EOC.

Dependence of the fracture morphology of the investigated compositions on the volumetric content of the components is schematically shown in Fig.1. Size and distribution of the dispersed phase particles within the matrix depends on the components ratios in the

composition. By approaching the phase transition region, size of the dispersed phase particles increases. At phase transition region it is practically not possible to distinguish dominant phase and interpenetrating network structure is observed.

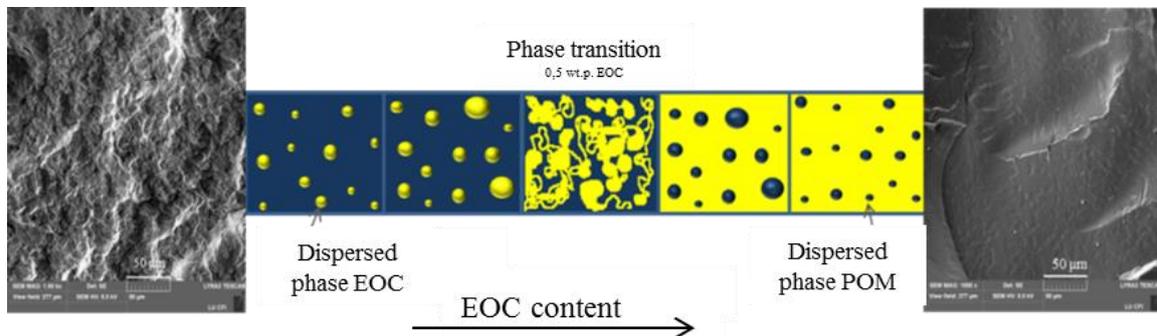


Fig. 1. Schematic representation of one polymer dispersion in second polymer matrix

Using SEM image processing program „Image – Pro Plus” areas of each disperse phase particles have been determined. Calculated average particle sizes are shown in Table 1. As one can see, average size of EOC particles in the POM matrix (especially P9) composites is considerably greater than average size of POM particles in the EOC matrix. Besides it size distribution of EOC particles is broader.

Table 1.

Average particle size of the dispersed phase in POM/EOC composites				
EOC, wt.p.	d, µm			
	P3 E17	P9 E17	P3 E38	P9 E38
0,95/0,05	2,6	3,6	1,3	2
0,9/0,1	2,7	5,7	2,2	2,8
0,1/0,9	1,4	1,2	1,2	1,1

From SEM micrographs one can see that the composites have been broken along the interface between POM and EOC, because of smooth fracture surfaces of the dispersed phase particles and clearly observable gap between the particle and the matrix (see Fig.2). These gaps probably are formed because of both, small plastic deformations during loading and during manufacturing of the compositions (technological voids), about which deviations of experimental densities from theoretical ones testifies (especially at EOC content of 0,3 to 0,7 wt.p.).

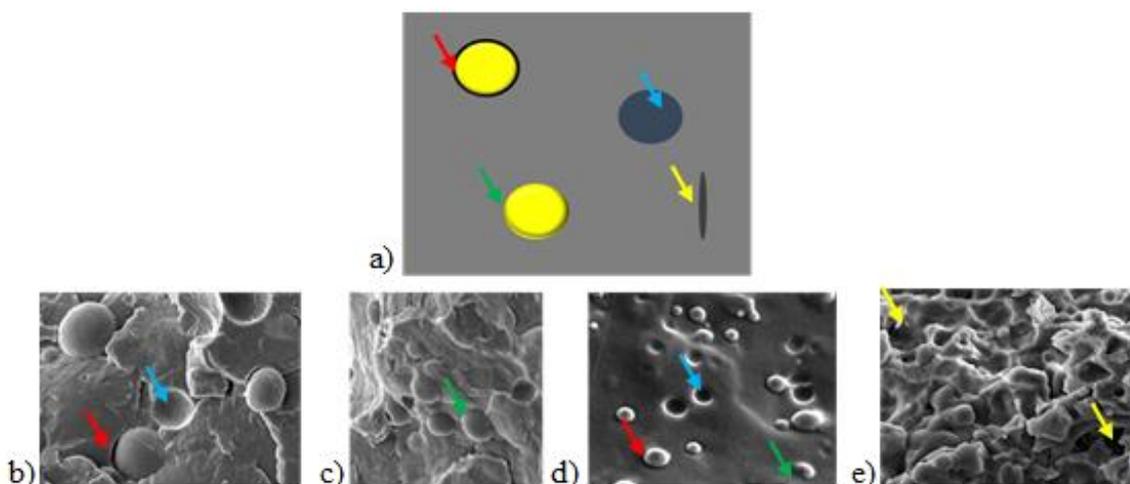


Fig. 2. Interaction between the dispersed phase and the matrix: schematic representation (a) and respective SEM micrographs (b-e) showing EOC particle without adhesion in 0,9/0,1 blend (b), EOC particle with small level of adhesion in 0,9/0,1 (c), POM particle with adhesion with matrix 0,1/0,9 blend (d) and technological voids in 0,5/0,5 blend (e) (red arrow- interparticle gap, green arrow – insignificant gap between matrix and dispersed phase particle, blue – particle fallen out, yellow arrow – void)

3. Differential scanning calorimetry and dynamical mechanical thermal analysis

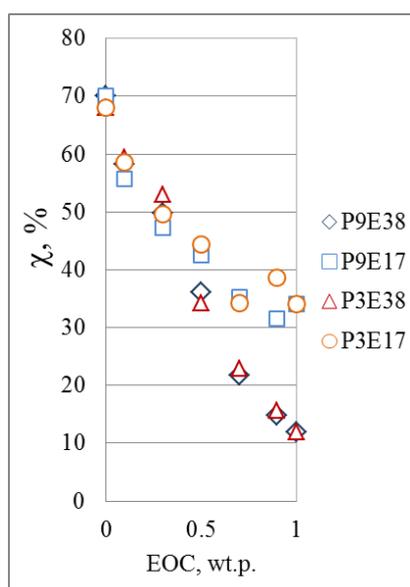


Fig. 3. Actual crystallinity of POM/EOC composites as a function of EOC content

DSC and DMTA have been performed to determine influence of the content of the compositions on the crystalline and amorphous phases of each component in the investigated systems. By thermoplastic compounding, POM and EOC form separated/ individual phases. By increasing EOC content in the compositions, melting temperature of POM phase is significantly affected (8 °C); maximal melting temperature of EOC phase, in its turn, changes no more than within borders of 2 °C. Both components, however, hinder each other's crystallization, in result, crystallinity degrees of the component phases in the compositions are smaller in comparison to neat POM and EOC (see Fig. 3).

Deviations between glass transition temperatures of both components increases with raising the content of minor phase component (as it is shown in Fig.4), which is clear indication of incompatible heterogeneous multiphase systems. The content of the investigated compositions has a considerable influence also on the intensities of relaxation transitions: by increasing the content of EOC, intensities of relaxation transitions of EOC phase increases, while those of POM decreases. At the same time it should be taken into account, that certain relaxations of polymeric

constituents of the investigated compositions occur in the same temperature range, resulting in overlapping of the corresponding $\tan\delta$ and E'' peaks.

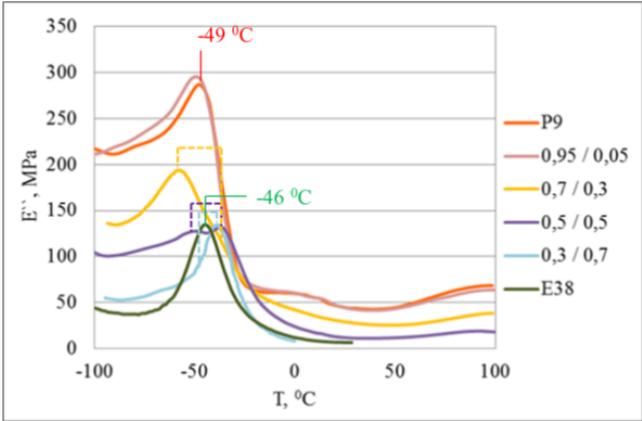


Fig. 4. Loss modulus of P3E38 composites

4. Mechanical properties

Results of mechanical properties investigations of the composites are revealed in this chapter.

As one can see in Fig.5, tensile modulus of elasticity and yield strength of EOC/POM blends decrease, while ultimate deformation increases along with rising the content of the elastomer.

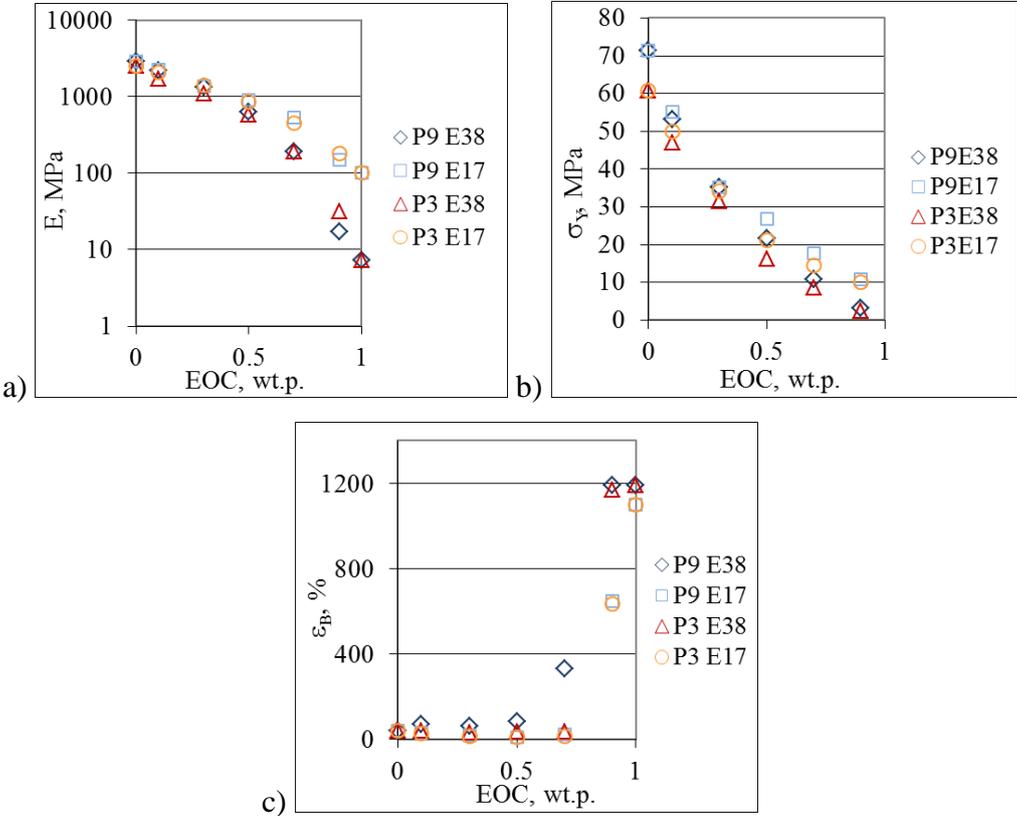


Fig. 5. Modulus of elasticity (a), yield strength (b) and strain at break (c) values of POM/EOC composites as a function of EOC content

Stress-strain characteristics of the investigated compositions are considerably affected by structural features (int. al. crystallinity degree) of the components. Consequently more crystalline POM (P9) and more crystalline EOC (E17) form composites with higher stress-strain characteristics (modulus of elasticity, yield strength and stress at break), but P3E38 blends have higher values of strain at yield and strain at break. Somewhat lower values of tensile deformations for compositions of phase transition range (0,3 to 0,7 wt.p.) are most probably because of decreased interfacial adhesion, i.e., reduced contact area between both incompatible polymer phases due to presence of voids.

Elastic properties of composite materials can be predicted by using a range of mathematical models. By considering the morphology of the investigated compositions (almost spherical particles in the continuous matrix) Kerner ^[1] approach have been chosen. It is possible to calculate (Eq. 1) upper (it is assumed that more rigid component (POM) is matrix) and lower (it is assumed that less rigid component (EOC) forms a matrix) boundaries of the elastic modulus E , where K_m - bulk modulus of matrix, G_m - shear modulus of matrix, calculated according to Eqs. 2. and 3.

$$E = \frac{9K_m G_m}{3K_m + G_m} \quad (1.)$$

$$K = K_m + \frac{(K_f - K_m)\phi_f}{1 + (1 - \phi_f) \times \frac{K_f - K_m}{K_m + \frac{4}{3} * G_m}} \quad (2.)$$

$$G = G_m + \frac{(G_f - G_m)\phi_f}{1 + (1 - \phi_f) \times (G_f - G_m) \frac{6(K_m + 2G_m)}{5G_m(3K_m + 4G_m)}} \quad (3.)$$

where m- matrix, f- dispersed phase, ϕ - volumetric content of components, $K_m = \frac{E_m}{3(1 - 2\nu_m)}$;

$K_f = \frac{E_f}{3(1 - 2\nu_f)}$; $G_m = \frac{E_m}{2(1 + \nu_m)}$; $G_f = \frac{E_f}{2(1 + \nu_f)}$; ν - Poisson's ratio (assumed to be

0,35 for P3 and P9 and 0,49 for E17 and E38).

Experimental and theoretically calculated values of elastic modulus of the investigated compositions are shown in Fig.6. As one can see phase transition region of the compositions with E17 is shifted to somewhat higher EOC volumetric contents in comparison to the compositions with E38.

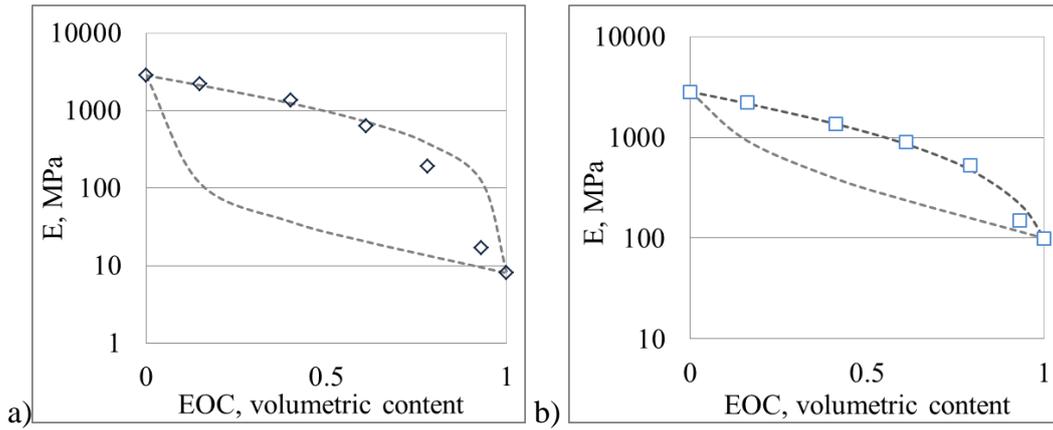


Fig. 6. Modulus of elasticity of P9E38 (a), P9E17 (b) composites as a function of volumetric content of EOC, where \diamond \square - experimental values, --- theoretical values calculated according to the Kerner

Simultaneously it has been observed that as soon as small amount (0,05 wt.p.) of elastomer is added to POM matrix, impact strength of the investigated blends is considerably increased (up to 39 % for the blends containing components with lower crystallinity degrees - P3E38). In general, by increasing elastomer content, fracture propagation path I of the investigated compositions increases, but impact load F decreases (see Fig.7). If decrement of F values of the investigated compositions along with increasing elastomer content is practically independent from the elastomer used (up to 39 % decrement if to compare with neat POM), than increment of I is highly dependent on the elastomer used (up to 77 % increment at E38 content of 0,3 wt.p. in comparison to 19 % increment at the same content of E17).

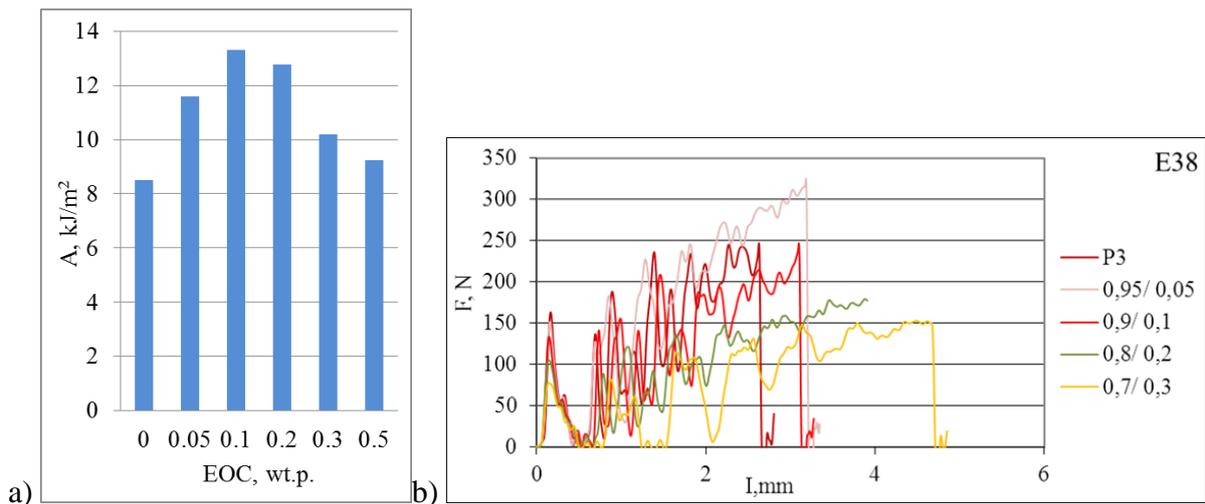


Fig.7. Impact strength (a) and load-deformation curves (b) of P3E38 blends at room temperature

Falling weight impact strength of the investigated compositions also increases along with addition of elastomer, especially E17, in P9 matrix systems. As shown in Fig.8, P9E17 composites are characterized with complicated deformation behavior.

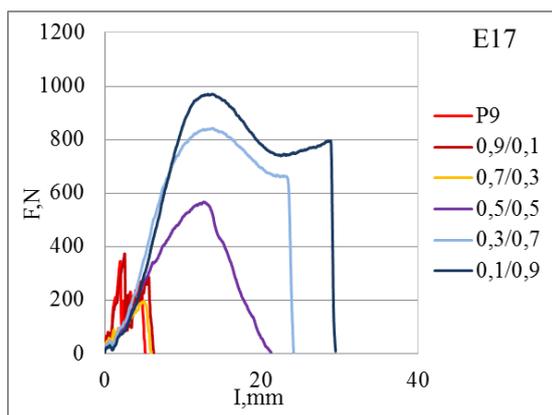


Fig.8. Falling weight impact load- deformation curves of P9E17 blends

For POM, P9/E17 0,9/0,1 two local maxima can be clearly distinguished, the first one describing formation of first significant defects in the test specimen, but the second describing formation of the stable crack network, followed by crack propagation and final rupture, mostly of explosive type. By increasing EOC content up to 0,3 wt.p., intensity of vibrations is significantly decreased, while at EOC content of 0,5 wt.p initial vibrations are practically absent, testifying about considerable change of the rupture character.

Photographs, characterizing ruptured test specimens of P9E17 compositions, are shown in Fig. 9. At EOC content of 0.1 wt.p., brittle rupture is generally observed, however, with less expressed cracking tendency in comparison to POM. At higher EOC content change of rupture character occurs, i. e., yielding of the material becomes increasingly expressed, as demonstrated by the development of deformation cone and increment of its height along with rising elastomer content.

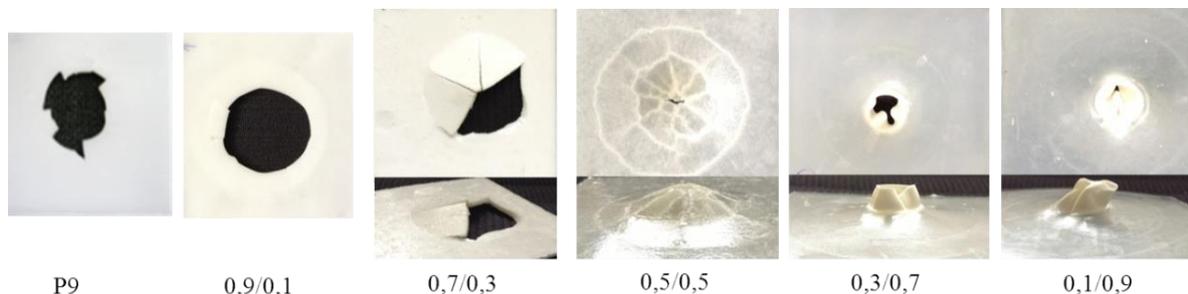


Fig. 9. Photographs of ruptured specimens of falling weight impact test of various compositions of P9E38 blend

5. Rheological properties

Structure and mechanical properties are strongly dependent on the melt rheological properties; rheological behavior determines also the ease of processing of polymer material. More detailed analysis of rheological properties of P3E38 has been carried out by considering their high impact properties.

As shown in Fig.10, experimental melt flow index (MFI) values of the investigated blends were higher than additive in the EOC content interval 0- 0,4 wt.p. The opposite situation was observed for composites containing more than 0,4 wt.p. of E38.

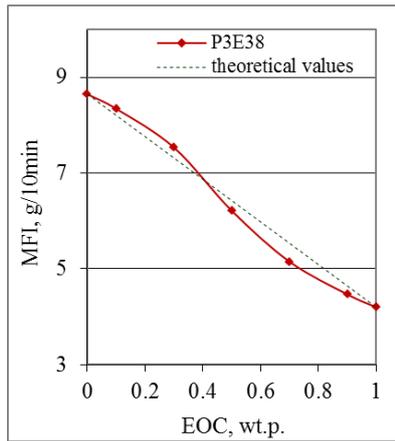


Fig.10. Melt flow index of P3E38 blends as a function of EOC content

By considering that MFI values are inversely proportional to viscosity values, as well as positive viscosity deviation testify about mutual interaction of the components and negative viscosity deviation, in its turn, testify about weak interaction between the components, one can conclude that in the compositions with higher EOC content (>0,4 wt.p.) interaction between the components is higher than in the compositions with lower elastomer content.

Viscosities η of the investigated compositions depend on the component wt.-to-wt. ratios (see Fig. 11.); for compositions, except of P3E38 0,9/0,1 decrease of η is more rapid in comparison to neat components, most probably due to decreased interfacial interaction.

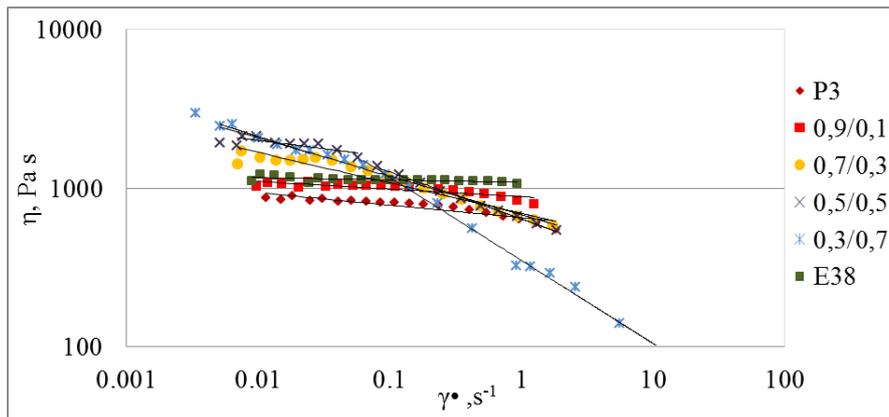


Fig. 11. Viscosity of P3E38 composites as a function of shear rate at 190 °C temperature

In the defined range of shear rates the slope of the linear relationship between shear stress (τ) and shear rate ($\dot{\gamma}$) (see Fig.12), depicted in log-log plot, allows to judge about pseudoplasticity of the melts. Relationship $\tau(\dot{\gamma})$ can be described by means of power law (Eq.4).

$$\tau = K \dot{\gamma}^{n_{tec}} \quad (4.)$$

Investigated compositions cannot be described by single linear relationship in logarithmic coordinates in the investigated range, so they are considered as more pseudoplastic if compared to neat components.

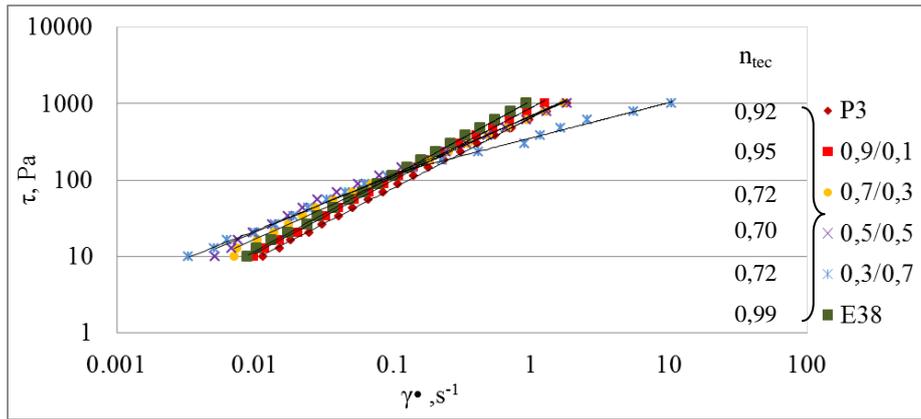


Fig. 12. Shear stress of P3E38 composites as function of shear rate at 190 °C temperature

6. Barrier properties

To evaluate the possibility of use of POM/EOC composites for packing, protective coating and membrane applications, barrier properties were investigated by using nitrogen and water vapor as permeants.

By raising the content of EOC, as more amorphous component, in the investigated polymer compositions, increased permeability P and diffusion D coefficients of nitrogen gas are expected. Mass transfer properties of the investigated compositions considerably depend on crystallinity; for an example, permeability of nitrogen gas through P9E17 0,9/0,1 (χ 56 %) is 20 times higher than permeability through P9E17 0,7/0,3 (χ 47 %).

Table 2.

Characteristic permeability parameters of N_2 gas through P9E17 composite samples

EOK, wt.p.	30 °C		
	$P,$ ($cm^2/s * cmHg$) $*10^7$	$D, cm^2/s$ $*10^5$	$S,$ $1/ cmHg$ $*10$
0	0,01	0,03	3,41
0,1	0,14	0,79	1,80
0,3	2,73	0,93	29,4
0,5	2,61	3,12	8,37
0,7	5,71	2,20	26,0
0,9	2,72	2,30	11,8
1	1,92	2,60	7,38

By evaluating mass transfer properties of water vapors through POM/EOC composites it was observed that addition of EOC considerably affected equilibrium quantity of the solvent absorbed (see Fig.13.). By rising the EOC content up to 0,1 wt.p. P and D both decrease approximately by 60 %. Mass transfer behavior is strongly influenced by both affinity between the components of investigated compositions and solvent vapor, and

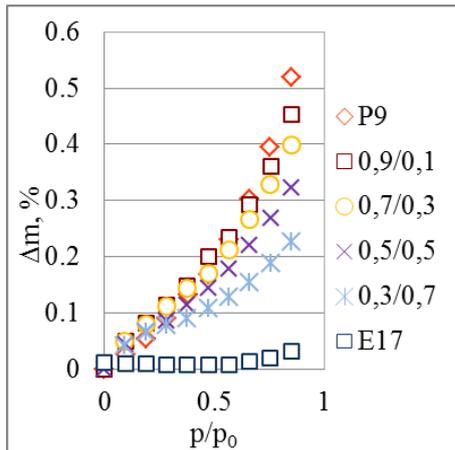


Fig.13. Isotherms of water vapor sorption through P9E17 composites

materials structure (int.al. crystallinity). POM is more polar than EOC (solubility parameter is about $5 \text{ MPa}^{1/2}$ higher) and has greater potential to interact with water vapor; consequently POM and POM matrix blends/compositions are characterized by significantly lower values of D , P and S . In addition it was observed that compositions containing more crystalline components had lower equilibrium mass change in comparison to the compositions containing more amorphous constituents.

Mass transfer properties of the investigated compositions are strongly affected also by morphology: especially the amount of microvoids. Due to the presence of structural defects, transfer of the penetrant into the polymer proceeds not only through the amorphous regions but also via interfacial defects and microvoids.

7. POM matrix systems: influence of ZnO addition

Plasma synthesized ZnO nanoparticles are characterized with tetrapod shape (Fig.14. a), with the arm length (l) of 70 –100 nm and diameter (d) of 10 nm (Fig.14. b). Distribution of ZnO nanoparticles in the polymer matrix is rather good (see Fig.15.).

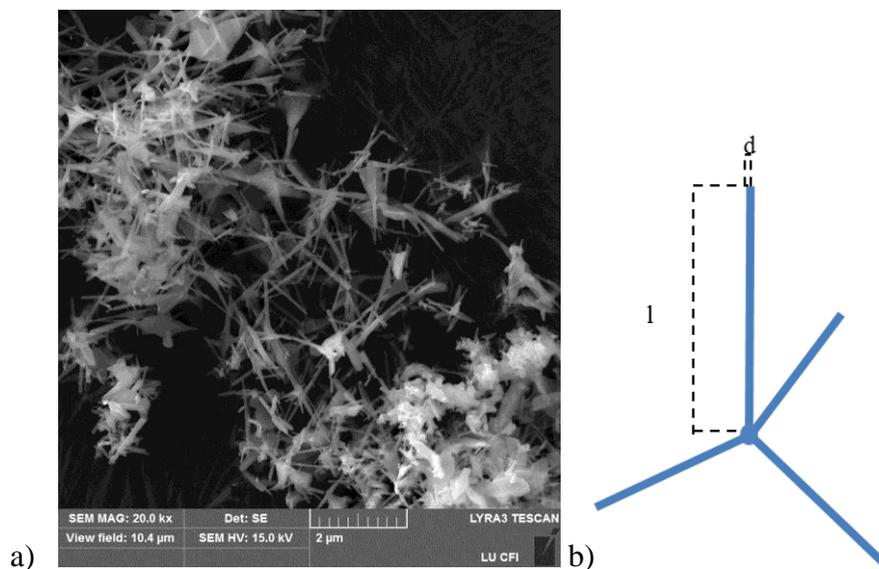


Fig.14. SEM micrograph of ZnO particles (a) and schematic interpretation of the particle (b)

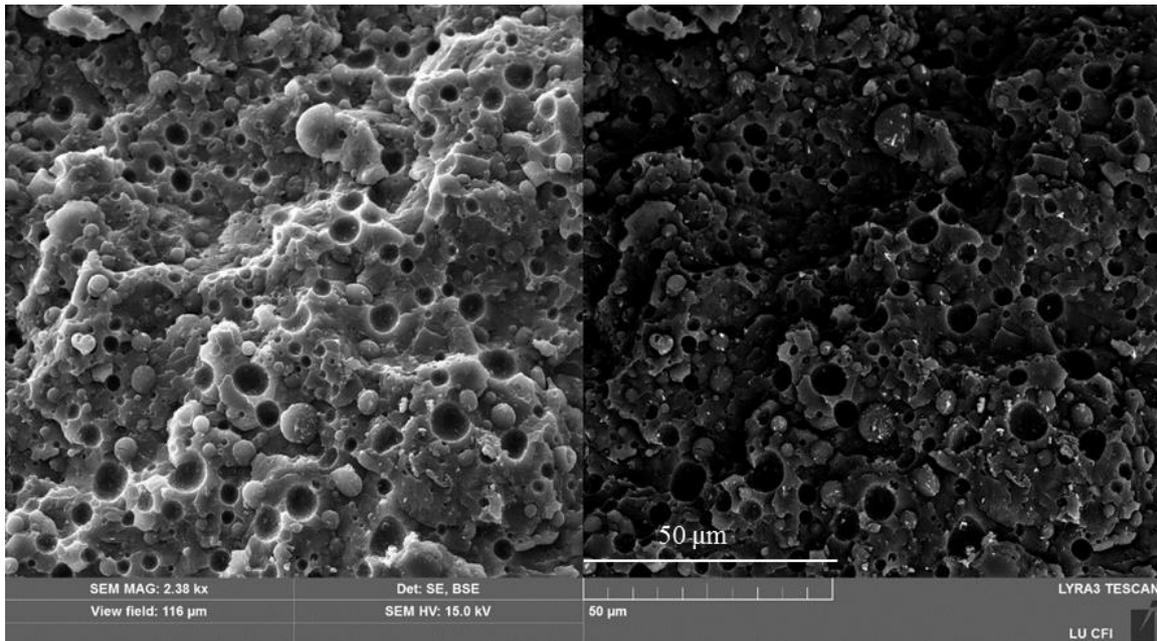


Fig.15. SEM micrographs of P9 nanocomposites with 0,1 wt.p. of E38 and 0,02 wt.p. of ZnO at magnification 2,38kx

It is known that addition of nanoparticles may affect both quantity and quality of the crystalline phases of polymer matrices. Consequently calorimetric investigations have been carried out. Although the effect of ZnO on the crystallinity degree and maximum melting temperatures of POM, EOC and their blends is insignificant, the nanocomposites are

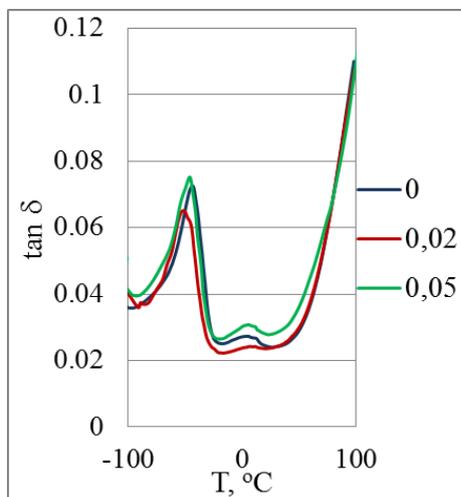


Fig.16. $\tan\delta(T)$ relationships of POM and its nanocomposites

characterized with narrower distribution of polymer crystallites. The nucleating effect of ZnO on the crystallization of POM based blends has been also observed. Besides it has been observed that, addition of ZnO decrease β - transition temperature of POM, (Fig.16).

Addition of ZnO nanoparticles to the investigated polymer matrices contributes to the increment of modulus of elasticity and tensile strength, especially in the case of the systems based on more amorphous components, i.e., P3 and E38.

In general, as one can see in Fig.17, the investigated compositions form a group of thermoplastic materials possessing broad range of properties.

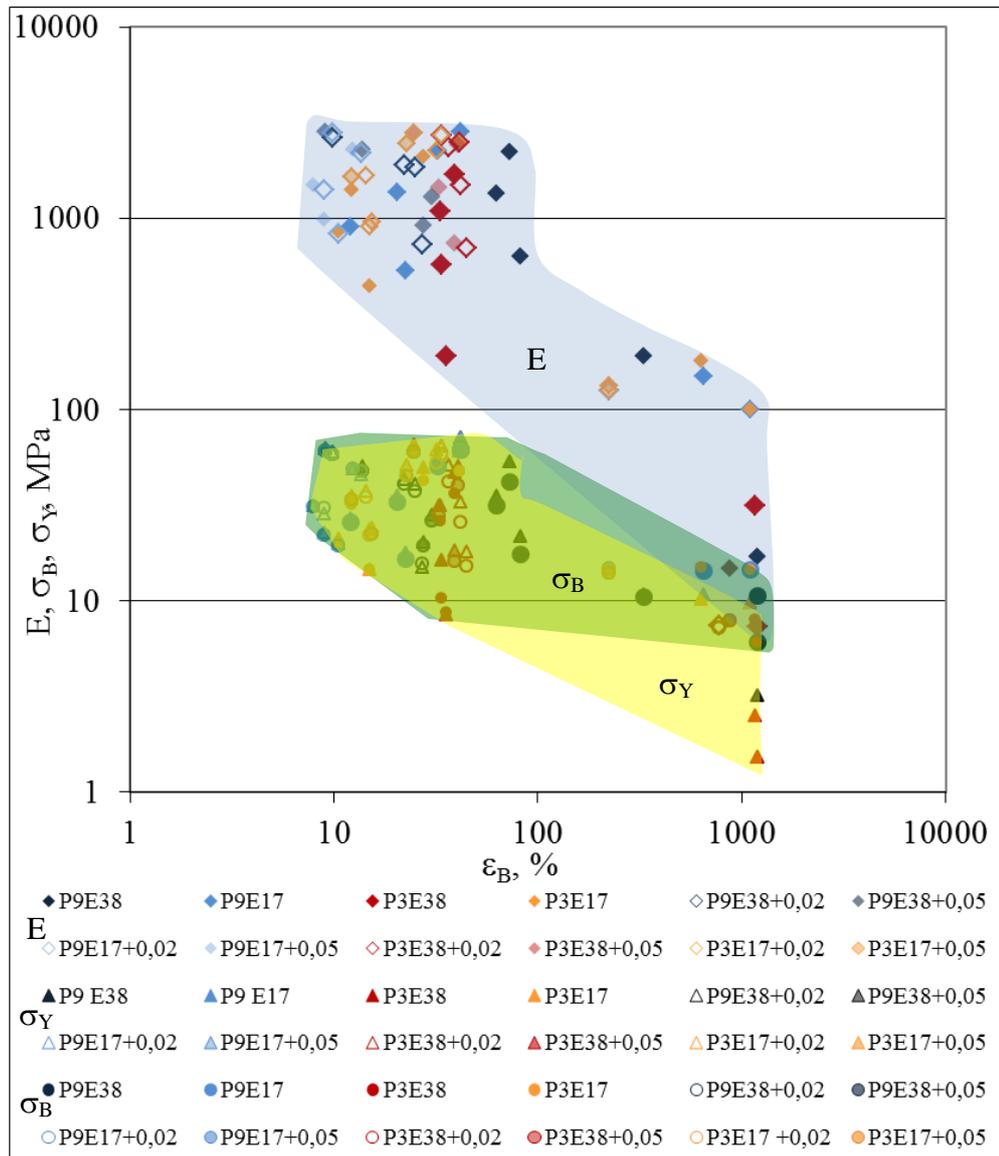


Fig.17. Stress-strain properties of POM/EOC blends and POM/EOC/ZnO nanocomposites

Apart from evaluating stress-strain characteristics of the investigated compositions, their frictional behavior has been also assessed. Coefficient of friction of POM/EOC blends increases along with elastomer addition. Addition of ZnO also allows successfully decrease coefficient of friction of the investigated POM, EOC and their blend POM/EOC compositions, which clearly reveals antifrictional capability of the nanofiller. Besides it has been observed that addition of ZnO considerably improves surface quality of the investigated compositions: roughness decreases two times if compared with binary systems (see Fig.18).

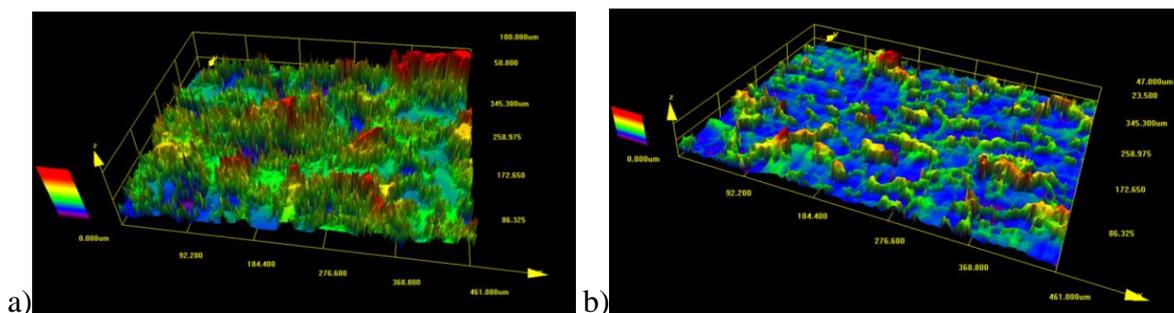


Fig.18. Confocal laser scanning micrographs after tribological experiments of E38 (a) and E38 nanocomposites with 0,02 wt.p. of ZnO (b)

ZnO contributes also to the increment of thermal stability of the investigated nanocomposites in comparison to POM, which thermal stability is low, because of the presence of thermally labile $-CH_2-O-$ linkages in the polymer backbone chain. POM/EOC based compositions are characterized with two step degradation. Such behavior is characteristic for heterogeneous blends. By addition of elastomer onset destruction temperature increases, but offset destruction temperature decreases. ZnO positively affects also percentage mass loss temperatures as it shown in the Table 3.

Table 3.

Characteristic degradation temperatures of ZnO modified P9E17 blends

	temperature at 5 % mass loss			temperature at 10 % mass loss			temperature at 20 % mass loss			temperature at 50 % mass loss		
	P9E17											
EOC, wt.p.	0 wt.p. ZnO	0,02 wt.p. ZnO	0,05 wt.p. ZnO	0 wt.p. ZnO	0,02 wt.p. ZnO	0,05 wt.p. ZnO	0 wt.p. ZnO	0,02 wt.p. ZnO	0,05 wt.p. ZnO	0 wt.p. ZnO	0,02 wt.p. ZnO	0,05 wt.p. ZnO
0	324	342	340	345	358	355	369	378	373	392	393	391
0,1	346	346	352	357	358	363	374	369	380	397	391	397
0,3	311	353	342	317	365	360	330	382	377	398	405	406
0,5	334	353	365	346	371	377	364	388	388	411	442	424
1	445	453	451	456	459	457	468	470	463	480	482	480

Destruction rate of POM, EOC and their blend compositions is decreased by rising ZnO content because of the nanoparticles acting as effective barriers preventing gas exchange near the zone of burning. As one can see in Fig. 19 (a), main evolved gases from POM degradation are formaldehyde and methyl formate, while methanol is formed at smaller amounts. Main evolved gases from EOC17 and EOC38 are ethylene and higher oligomers (propylene, butene, pentene, etc.), which arise from hydrogen transfer to different positions along the polymer chain. The amount of the evolved gases from POM/EOC compositions, in its turn, is proportional to the volumetric contents of EOC and POM in the compositions, as it is clearly shown in Fig.19 (b). As one can see in Fig.19 (c), liberation of gaseous species from POM/EOC/ZnO nanocomposites occurs at higher time values than from POM/EOC blends.

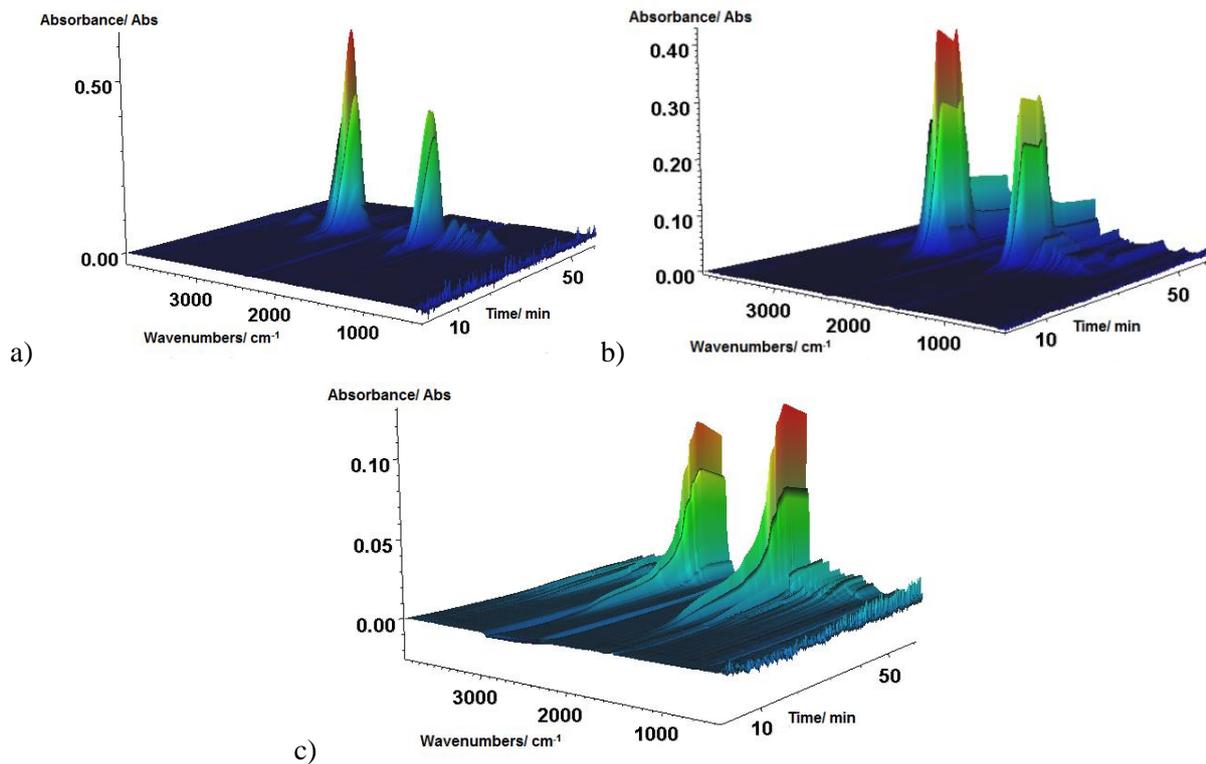


Fig.19. FTIR spectra of evolved gases from P9 (a), P9E17 0,5/0,5 (b) and P9E17 0,5/0,5+0,02 wt.p. ZnO (c)

8. Aging of polyoxymethylene blends

In last part of the work stress-strain properties the investigated composites are characterized under the influence of various environment conditions, which should be considered at possible practical applications

Considering that the range of POM applications, especially, outdoors, is limited due to its sensitivity under ultraviolet light (UV), weathering test of POM and its blends was carried by using Q-Lab QUV accelerated weathering tester. As one can see in Fig. 20, tensile stress-strain characteristics of POM and POM/EOC drastically decrease at the highest UV irradiation time because of crystallinity degree changes of both of the polymers and cleavage of macromolecules.

Under the influence of UV irradiation increase in the intensity of spectral vibrations of hydroxide and carbonyl groups have been also observed, testifying about formation of oxygen containing end-groups generated during the UV irradiation.

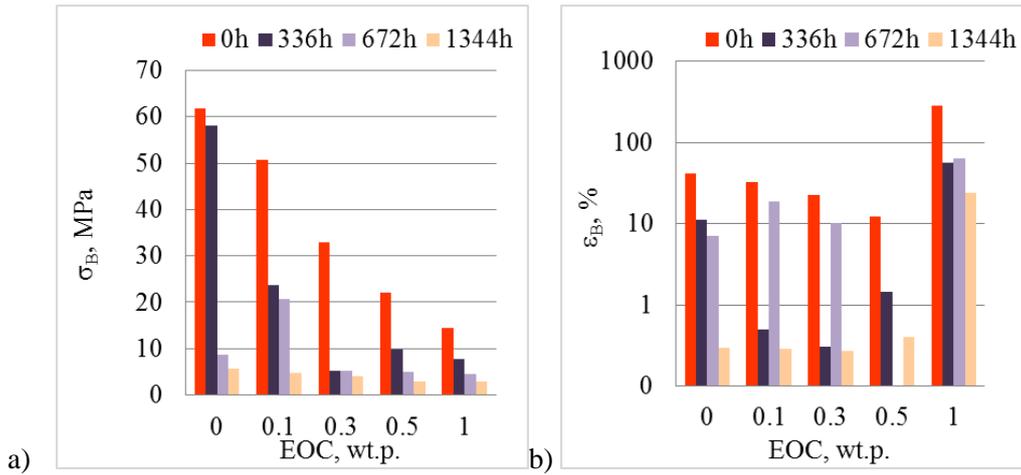


Fig.20. Tensile stress-strain characteristics before and after UV irradiation for 366, 672 and 1344 hours: stress at break (a) and elongation at break (b) of POM/EOC blends at different EOC weight contents

After addition of ZnO to the investigated nanocomposites considerable improvement in stress-strain behavior is observed, due to the fact, that ZnO is an efficient UV absorber, as testified by corresponding decrease in the intensities of hydroxyl and carbonyl absorption peaks (Fig. 21).

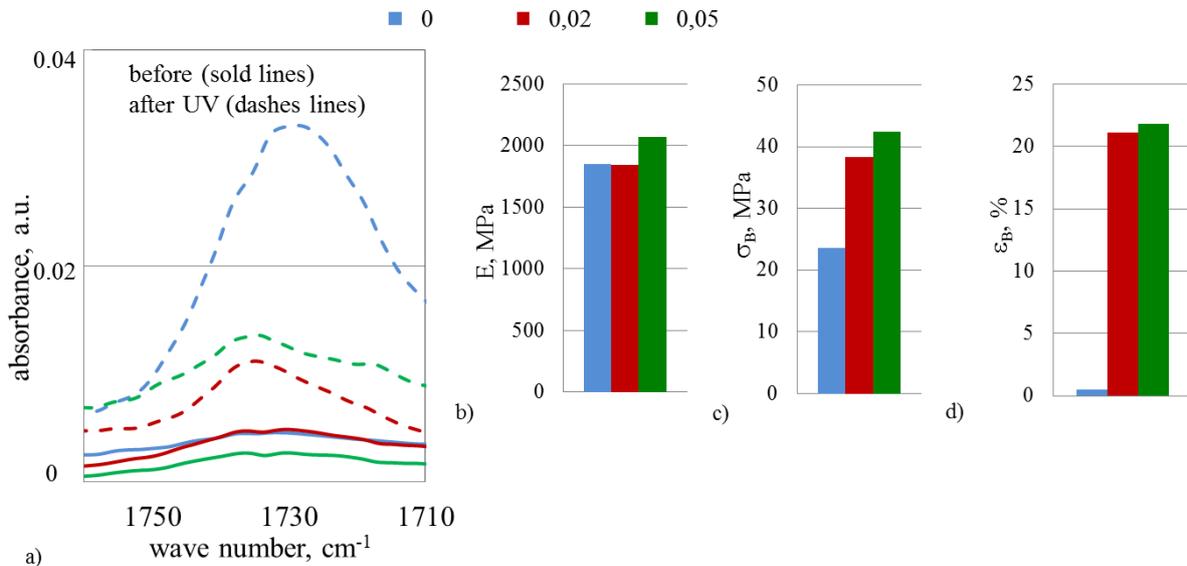


Fig.21. FTIR spectra in the carbonyl absorption region (a), tensile modulus of elasticity (b) stress at break (c) and elongation at break (d) of neat and UV impaired (336h) P9E17 0,9/0,1 blend nanocomposites with ZnO

An important aspect in materials applications is durability under the influence of aggressive media such as moisture, chemicals, technical fluids etc. By considering this fact the effects of water and hydraulic oil on the certain characteristics of POM/EOC blends have been investigated.

As expected mass changes of the specimens of the investigated compositions fully immersed in the test liquids are proportional to the wt.-to-wt. ratio of the constituents (see

Fig.22.) and solubility parameters δ of the polymers in respect to that of water or oil (POM $\delta = 20,9- 22,5 \text{ MPa}^{1/2}$, EOC $\delta = 15,8- 17,1 \text{ MPa}^{1/2}$, water $\delta = 46,4 \text{ MPa}^{1/2}$ and oil $\delta = 16 \text{ MPa}^{1/2}$). After aging in water specimens of the blends with higher EOC content show smaller mass change, whereas after aging in hydraulic oil the same specimens show greater mass changes.

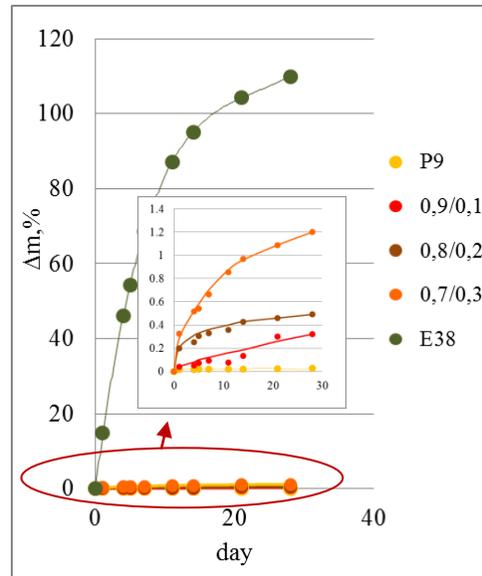


Fig.22. Mass change of P9E38 blends as a function of storage time in hydraulic oil

After ageing in water or oil tensile modulus and tensile strength of the investigated compositions decrease, while deformations increase. The change of tensile parameters as function of elastomer content, however, keep the same trend - modulus of elasticity E and yield strength σ_Y decrease, while ultimate deformation ε_B (especially for E38 containing systems) increases. Impact strength of water soaked compositions considerably depends on the component ratio of the investigated systems. Although due to plasticizing effect, impact strength of water soaked POM is higher than that of untreated polymer, by increasing the content of nonpolar E38 increment of impact strength of the water soaked compositions decreases.

Conclusion

Following most important conclusions can be formulated.

1. Technological approaches for development and processing of POM/EOC as well as POM/EOC/ZnO compositions are developed. The investigated composites depending on the ratio of the components form a group of thermoplastic materials possessing broad range of mechanical, tribological, rheological, thermal and barrier properties.

2. One of the most important indicator of the rheological behavior, relationship of shear stress from shear rate $\tau(\dot{\gamma})$ of POM and EOC melts, used for manufacturing of the investigated compositions, testifies that both components show pseudoplastic behavior in the investigated shear rate range 0,01- 1,8 s⁻¹. Rheological behavior of EOC is closer to the Newtonian fluid (flow behavior index $n_{tec}=0,99$) than that of POM ($n_{tec}=0,92$). In the investigated $\dot{\gamma}$ range τ of POM/EOC blends cannot be described by single linear relationship in logarithmic coordinates whereas the flow behavior index n_{tec} values of the compositions (n_{tec} until 0,7) are significantly lower than for neat components.
3. Melt compounded POM/EOC compositions possess heterogeneous structure. Dispersed phase of EOC is characterized by broader particle size distribution and larger average particle sizes (up to 5,7 μm) than POM (particle sizes up to 1,4 μm). Largest sizes of the disperse phase particles are characteristic for the blends in the phase transition region (from 0,3 to 0,7 wt.p. EOC). Components hinder each other's crystallization during formation of the composites.
4. Clearly expressed interface between POM and EOC phases exist in the composite. Development of compatible boundary layer between both polymers is not observed in a molecular level.
5. Stress-strain properties of the investigated composites depend on it content. Tensile modulus of elasticity and yield strength of EOC modified POM blends decrease, while ultimate deformation increases along with raising the content of the elastomer. At similar morphology stress-strain parameters strongly depend on the morphology, as well as crystallinity degree of the composites. Tensile stiffness, strength at yield and strength at brake are increasing, but strain at yield and strain at brake are decreasing, if particle size of the dispersed phase is smaller or crystallinity degree is greater. Lower values of tensile deformations for compositions of phase transition range (0,3 to 0,7 wt.p.) are because of the reduced contact area between the incompatible polymer phases.
6. Only strictly defined amount of EOC (up to 0,1 wt.p.) allows considerably improve impact strength of the investigated compositions. Increment of impact strength (by 39%) of the compositions, containing less crystalline elastomer - E38, is greater because of its smaller particle sizes and better impact absorption efficiency in comparison to E17.
7. Selected POM/EOC compositions can be safely used in contact with aggressive chemical agents (water or oil).

8. Modification of POM and POM/EOC blends with nanosized ZnO (up to 0,02 wt.p.) allows increase tensile stiffness and strength, improve thermal stability, reduce coefficient of friction and decrease permeability due to anisodiametric shape of the nanoparticles as well as their effect on the crystallinity (acts as a nucleation agents) of the investigated composites.
9. Addition of ZnO considerably improves stability of the investigated compositions under the influence of ultraviolet radiation.

APPROBATION OF THE THESIS

Publications

Results are presented in the 7 scientific journal articles (6 SCI journals):

1. A. Grigalovica, J. Zicans, R. Merijs Meri, T. Ivanova, J. Grabis. „Polioksimetilēna un etilēnu kopolimēru kompozīciju pārstrādes un struktūras īpašības. RTU zinātniskie raksti Materiālzinātne un lietišķā ķīmija, 2011, 23.sējums.
2. A. Grigalovica, J. Zicans, R. Merijs Meri, T. Ivanova, H.-P. Heim, C. Berger. „Relaxation properties of polyoxymethylene and ethylene- octane copolymer blends in solid and melt state”, Proc. Estonian Acad. Sci. Chem. 2012,61,3;ISSN 1406-0124
3. A. Grigalovica, I. Bochkov, R. Merijs Meri, J. Zicans, J. Grabis, R. Kotsilkova, I. Borovanska. „The effect of nanosize ZnO on the properties of the selected polymer blend composites”, IOP Conference Series: Materials Science and Engineering 2012, 38,012053;
4. R. Merijs Meri, I. Bochkov, A. Grigalovica, J. Zicans, J. Grabis, R. Kotsilkova, I. Borovanska. „Nanocomposites based on ZnO modified polymer blends” Macromolecular Symposia, 2012, 321-322,130-134
5. A. Grigalovica, R. Merijs Meri, J. Zicans, T. Ivanova, J. Grabis. Thermal stability of polyacetal/ethylene-octene copolymer/zinc oxide nanocomposites”, IOP Conf. Ser.: Mater. Sci. Eng. 49 012004 doi:10.1088/1757-899X/49/1/012004
6. A. Grigalovica, R. Merijs Meri, J. Zicans „Elastic properties and phase transition of polyoxymethylene and ethylene-octene copolymer composites”, Key Engineering Materials, 2014, Vol.604, 114- 117
7. A. Grigaloviča, R. Merijs Meri, J. Zicāns, J. Grabis, A. Aniskevich „Aging of nanosized ZnO modified polyoxymethylene blends with ethylene octene copolymer”, Polymer-Plastics Technology and Engineering, doi:10.1080/03602559.2014.1003227

International conferences

Results of doctoral thesis have been presented at the following international scientific conferences:

1. Grigalovica, R. Merijs Meri, J. Zicāns, A. Aniskevics. Mechanical properties of modified polyacetal blends with various elastomers. *RTU 55nd International Scientific Conference*, Latvia, Riga, October 14-17, 2014, pp.59.
2. A.Grigalovica, R. Merijs Meri, J. Zicans, M.Kalnins, J.Grabis, A.Aniskevics. The effect of ageing on the structure and mechanical properties of modified polyoxymethylene composites. *Baltic Polymer Symposium 2014*, Estonia, Laulasmaa, September 24-26, 2014, pp.30.
3. A.Grigalovica, R. Merijs Meri, J. Zicans, J. Grabis, M. Kalnins, A. Aniskevics. Aging of nanosized zno modified polyacetal blends with ethylene octene copolymer. *22nd Annual International Conference on Composites/Nano Engineering*, Malta, July 13-19, 2014.
4. A.Grigalovica, R. Meri Merijs, J. Zicāns, M. Kalnins, R. Maksimov, J. Jansons. Mechanical properties of modified polyoxymethylene composites. *Eighteenth international conference mechanics of composite materials*, Latvia, Riga, June 2-6, 2014, pp.76.
5. A.Grigalovica, R. Merijs Meri, J. Zicans, J. Grabis. Development of nanostructured zinc oxide modified composites based on polymer blends. *22nd International Baltic Conference of Engineering Materials & Tribology*, Latvia, Riga, November 14-15, 2013, pp.74.
6. A.Grigalovica, E. Sauss, R. Merijs Meri, J. Zicāns, T. Ivanova, J. Grabis. Polyoxymethylene and ethylene octene copolymer composites structural and exploitation properties. *RTU 54nd International Scientific Conference*, Latvia, Riga, October 14-16, 2013, pp.72.
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14. R.Merijs Meri, I.Bochkov, A.Grigalovica, J.Zicans, J.Grabis, R.Kotsilkova. Nanocomposites based on ZnO modified polymer blends. *Book of Abstract 11th European Symposium on Polymer Blends*, Spain, San-Sebastian-Donostia, March 25-28, 2012, pp. 259-260.
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