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X-Ray diffuse scattering investigation of polytetrafluorethylene surfaces**)

Summary — We present the X-Ray Diffuse Scattering (XDS) technique which can determine, except for the surface roughness, the distribution of in-plane fluctuations and fractal dimension on the surface. The scattering intensity is calculated using Distorted-Wave Born Approximation (DWBA) and depends on the quantities related both to 1st and 2nd order surface statistics like, surface roughness σ, lateral correlation length ξ and "Hurst coefficient" or "roughness exponent" h ($0 < h < 1$). The samples were prepared by spraying a PTFE dispersion directly on preheated Si wafer, at three different spraying times, following by an annealing process. The aim of this work is to study the effect of spray duration on the surface morphology. Firstly, the amorphization induced due to the annealing was observed by X-ray diffusion measurements. The analysis of the XDS rocking scans gave that the mass density is increased with the spraying time and the roughness is almost the same. However, the surface morphology described also by the distribution of the vertical fluctuations, through the correlation length ξ, showed that the narrow distribution was realized at middle, while broad one at long or short spraying times. Furthermore, the surface exponent h, calculated by XDS off-specular scan, is constant and low, meaning that the low smoothness of the surface is not affected by the spraying time.

Key words: polytetrafluoroethylene, X-Ray Diffuse Scattering, surface assessment, roughness, grain size.

BADANIE POWIERZCHNI POLITETRAFLUOROETYLENU METODĄ ROZPRASZANIA PROMIENIOWANIA RENTGENOWSKIEGO

Streszczenie — Przedstawiono teoretyczne podstawy wykorzystywanej metody, ze szczególnym uwzględnieniem oddziaływania promieniowania Rtg z charakteryzowanymi powierzchniami. Przedmiotem badań były powierzchnie niewygrzewanych i wygrzewanych (w temp. do 350 °C, w obojętnej atmosferze) próbek politetrafluoroetylenu (PTFE). Stosując dwa warianty wymienionej w tytule metody rozproszeniowej (*X-Ray Diffuse Scattering — XDS*), mianowicie XDS *Longitudinal Scans* i XDS *Rocking Scans*, oceniono wpływ wygrzewania oraz regulowanej szybkości nanoszenia ilości naniesionej próbki na szorstkość powierzchni (σ), wymiary cząstek, długość korelacyjną (ξ) i współczynnik Hursta (h) (rys. 1—4, tabela 1). Ustalono, że wygrzewanie powoduje zmniejszenie cząstek, przy czym w przypadku próbek niewygrzewanych wymiary cząstek maleją liniowo wraz ze zwiększaniem ilości materiału (szybkości nanoszenia), a w odniesieniu do próbek wygrzewanych zależność ta wykazuje maksimum (rys. 2). Szorstkość wygrzewanych próbek nie zależy od szybkości nanoszenia (tabela 1) i jest niewielka (stałe i małe wartości σ oraz h).

Słowa kluczowe: politetrafluoroetylen, rozpraszanie promieniowania rentgenowskiego, ocena powierzchni, szorstkość, wymiary cząstek.

Polytetrafluoroethylene (PTFE) has applications in many technological areas due to the low frictional coefficient, high stability against heat and chemical reagents, and high electric resistance. For example, in the products like medical cutting tools and heart stents, insulators in microelectronics, pistons and bearings PTFE coatings are used to improve their performance. So, the PTFE surface morphology is crucial for all the applications mentioned above and the use of surface characterization techniques are more than useful.

Among the numerous surface characterization techniques the X-Rays Diffuse Scattering (XDS) is used because it is non-destructive and can characterize the surface in short length scales (nm). The XDS of rough surfaces has been the object of research for many years [1—5]. In most investigations done so far the specularly reflected contribution of the scattering has been used in

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order to deduce the rout mean square (rms) of roughness (σ) because it exponentially reduces the Fresnel reflectivity by a Debye-Waller-type damping factor. However, specular reflectivity measurements give no information on the correlation length (ξ) with which the roughness decays laterally. This information can be obtained from the diffuse component of scattering, which is observed in a small angular range around the specularly reflected beam.

Sinha *et al.* have described the diffuse scattering in the first distorted-wave Born approximation. Surface roughness is treated as a small perturbation of the smooth surface for which the exact solution is known from Fresnel theory [5].

In this work we present the study on PTFE surfaces, grown with spray coating, using X-Rays techniques and more precisely we examine to the surface morphology with respect to the material quantity.

THEORETICAL BACKGROUND

Surface statistics

The perpendicular fluctuations on a surface are described by the mean-square width, termed roughness $\sigma=<z(x,y)^2>^{1/2}$; $z(x,y)=h(x,y)-<h(x,y)>$, where $h(x,y)$ is the height function and $<h(x,y)>$ the reference plane. The roughness is termed „Gaussian" when $z(x,y)-z(x',y')$ is a Gaussian random variable which distribution (1st order statistics) depends only on relative coordinates $(X,Y)\equiv(x'-x,y'-y)$. Additionally to the 1st order, 2nd order statistics can be used to describe the surface morphology. Thus, complementary to the surface roughness, two other quantities, the Hurst coefficient *h* and the lateral length scale of the surface fluctuations can be calculated. For these surfaces the height-height correlation function is defined by $g(R)=<[z(x',y')-z(x,y)]^2>$; $R=\sqrt{X^2+Y^2}$, where the average is taken from all pairs of points on the surface which are separated horizontally by the length R.

If the surface exhibits self-affine roughness, g(R) will scale as $g(R)\propto R^{2h}$ for short R, and $g(R)=2\sigma^2$ for large R where $0<h<1$ is referred to as the „roughness" exponent. Sinha *et. al.* [5, 6] proposed an empirical expression which was consistent with this asymptotic behavior:

$$g(R)=2\sigma^2\left(1-e^{-(R/\xi)^{2h}}\right) \tag{1}$$

and which for $R\ll\xi$ has the same form as g(R) without cut-off, as expected. The function g(R) is related to the auto-correlation function $C(R)=<z(R)z(0)>$ by $g(R)=2\sigma^2-2C(R)$, thus

$$C(R)=\sigma^2 e^{-(R/\xi)^{2h}} \tag{2}$$

The auto-correlation function will be used in the expression of the scattering intensity below.

X-Rays interaction with the surfaces

The interactions taking place between an electromagnetic radiation and a surface are: transmittance, absorption, specular and non-specular reflection (diffuse scattering). The critical quantity in these phenomena is the refractive index (n) of the material, which in X-rays energy region is a complex quantity given by

$$n=1-\delta+i\beta \tag{3}$$

with the real part corresponds to the dispersion and the imaginary to the absorption of X-rays, in the matter. The value of δ ranges between 10^{-6} and 10^{-5} and is proportional to the electron density. This parameter is also related to the critical angle of total reflection θ_c through the expression $\sin\theta_c^2=2\delta$. The parameter β is one or two orders of magnitude smaller than δ.

In this work we focused on the off-specular reflection. In this case the intensity is proportional to the differential scattering cross-section, which is the solution of the Schrödinger equation under the appropriate boundary conditions:

$$-\frac{\hbar^2}{2m}\left(\nabla^2\Psi(\vec{r})+k^2\Psi(\vec{r})\right)=V(\vec{r})\Psi(\vec{r}) \tag{4}$$

where: $\hbar$ — *Plank constant*, m — *the electron mass*, ∇^2 — *the second derivative*, $\Psi(\vec{r})$ — *function of the electron field*, $k=2\pi/\lambda$ (λ — *the wave lengths of X-rays*) — *the magnitude of wave vector*, $V(\vec{r})$ — *interaction potential.*

Distorted-Wave Born Approximation (DWBA) is one of the solving method [5]. Sinha *et. al.* [5—7] derived the expressions for the differential scattering cross section, by splitting the interaction potential $V(\vec{r})$ into two parts: the unperturbed part corresponds to smooth surface and the perturbation corresponds to the roughness. Thus, the non-specular (diffuse) part of the differential scattering cross section from a bare substrate is then given by:

$$\frac{d\sigma_{diffuse}}{d\Omega}(q)=\frac{Ak^4}{16\pi^2}\left|(1-n^2)\right|^2\left|t_F(k_1)\right|^2\left|t_F^*(k_2)\right|^2 S(q_{tz}) \tag{5}$$

where: $t_F(\mathbf{k}_1)$ *and* $t^*_F(\mathbf{k}_2)$ — *the Fresnel transmission coefficients of the incident and scattered wavevectors* k_1 *and* k_2, *respectively*, A — *the illuminated area*, Ω — *the solid angle of the detector*.

Because the electric field reaches a maximum of twice the incident field at the interface when **k** makes an angle equals to the critical angle θ_c, $|t_F(\mathbf{k})|^2$ is maximum in this case. Hence, whenever θ_1 or θ_2 equals θ_c, Eq. (5) predicts the presence of maxima in the diffuse scattering. These are known as the anomalous (Yoneda) scattering or "angel wings". The factor $S(\mathbf{q}_{ts})$, with $\mathbf{q}_{ts}=(q_x,q_y,q_{sz})=\mathbf{k}_{2s}-\mathbf{k}_{1s}$ being the wave vector transfer in the substrate, is written

$$S(q_{tz})=\frac{e^{\left(-\mathrm{Re}\{q_{tz}^2\}\sigma^2\right)}}{\left|q_{tz}\right|^2}\int_0^\infty\left(e^{\left|q_{tz}\right|^2 C(x)}-1\right)\cdot\cos(q_x x)dx \tag{6}$$

where: Re — *the real part of the complex quantity* q_{tz}.

The intensity of the scattered beam is directly related to the type of scan. There are two types of scans for measuring diffuse scattering: the rocking scan and the longitudinal scan (offset or diffuse near specular scan). In the case of rocking scan the detector has a fixed position and the sample is being rocked under the condition $\theta_1+\theta_2=\theta_d$. The measured intensity (I) then is normalized to the intensity at specular position:

$$I_{norm} = \frac{1-ro}{I_{max}} \cdot \left(\frac{d\sigma}{d\Omega}\right)_{diff} + ro \tag{7}$$

where: *ro — the average between the first and the last point of the spectrum, I_{max} — the maximum intensity at specular position.*

In the case of longitudinal scan ($\theta_i=\theta_s\pm\Delta\theta$) and for $\theta>\theta c$ $q_{tz}\approx q_z$ the scattered intensity is given by [7]

$$I \propto q_z^{-\left(3+\frac{1}{h}\right)} \tag{8}$$

Equations (7) and (8) are used for the analysis of the XDS spectra to obtain the surface features such as the roughness, the correlation length and the Hurst coefficient.

EXPERIMENTAL

Samples preparation

The samples were prepared by liquid spray coating of PTFE diluted in isopropyl alcohol containing 10 % of solids, having molecular weight equal to 30 000, density 2.2 g/cm^3 and average bulk size 3.7 μm. The melting point of these solids is in the range 322—326 °C [8]. The PTFE suspension was sprayed directly on preheated (~120 °C) Si wafers. After the spraying the samples were annealed in inert atmosphere up to 350 °C.

The spraying process is performed as follows: on a moving sample holder the samples are passing through a preheat process with maximum temperature ~120 °C. The substrate is placed at angle ~20° with respect to the direction of the movement. Afterwards the heated samples are passing in-front of a spraying plume with specific velocity and due to the high temperature of the substrate the solvent is vaporized and a white powder of PTFE is spread all over the surface. The experiments were carried out at three different velocities 1.8, 2.5 and 3.2 m/min, thus the study will be focused on the effect of the material quantity (inversely proportional to velocity) on the surface morphology. For convenience the samples after the spraying are named as follows: A1 (1.8 m/min), A2 (2.5 m/min), A3 (3.2 m/min) and after annealing — B1 (1.8 m/min), B2 (2.5 m/min), B3 (3.2 m/min).

Measurements

The X-rays characterization was performed using a D-5000 Siemens diffractometer [8, 9] equipped with a conventional Cu K_α source, a reflectometry sample stage (RSS) and a Goebel mirror [10]. The Goebel mirror transforms a divergent X-ray beam into a parallel and high brilliant one. No monochromator was necessary because CuK_β is suppressed by the mirror. The RSS consists of a translation stage on which an edge diaphragm and a vacuum-held holder are mounted. The edge diaphragm is placed on the sample surface for suppression of the direct source beam. The zero point is calibrated to ensure reproducible results of the measurements.

XRD measurements were applied in the range from 16° to 20°, with $\Delta\theta=0.04$. The diffuse scattering can be measured with two different types of scan: the off specular XRR (XDS Longitudinal Scans), where the scattering angle is slightly different from the incidence angle and Rocking Scans (XDS Rocking Scans), where the detector is at fixed position and the sample is rotated. The XDS Longitudinal Scans were applied in the range 0—1° with offset 0.05° and the XDS Rocking Scans were performed with the detector fixed at position 1° and the sample rotating from 0° to 1°.

RESULTS AND DISCUSSION

All the stages of the experimental procedure affect both bulk and surface properties of PTFE coating. Thus, due to the annealing the PTFE powder is undergoing a phase transition. From the literature PTFE is known to occur in four crystal forms [11—13]: at normal pressure and a temperature of 19 °C, PTFE transforms from form-II (triclinic) to form-IV (hexagonal), at 30 °C form-IV transforms to I (pseudohexagonal). Form-III can be obtained from II or I at a pressure of about $5.5 \cdot 10^8$ Pa and at temperature of 80 °C. The crystal structure of PTFE is consisted of hexagonally packed zigzag, twisted helices of a linear chain polymeric molecules $(\text{-}CF_2CF_2\text{-})_n$ [13]. Additionally [14, 15], the phase transition of II→IV was shown to consist of a decrease in screw frequency from 13_6 (13 units at 6 full spiral rotations) to 15_7. The further conversion (at 30 °C) is considered to be a loss of ordering in the mutual-rotation of separate adjacent spirals and the polymeric chains undergo entanglements, which result in the total loss of the crystalline phase.

The XRD patterns of the samples before (samples A) and after sintering (samples B) are given in Fig. 1. As it can be observed from Fig. 1a, the A samples are semi-crystalline showing a peak at ~17.98° corresponding to the (100) reflection for phase IV. The 1b graph shows the XRD patterns of the sintered B samples. As it can be seen from the lowering of the peaks there is an evidence of the amorphous state of the material after the sintering process from RT to 350 °C and back to RT.

The mean grain size L of PTFE can be determined from the broadening full width at half maximum (FWHM) of the XRD peaks which correspond to Miller indices (hkl) through Scherrer's formula and depicted in Fig. 2:

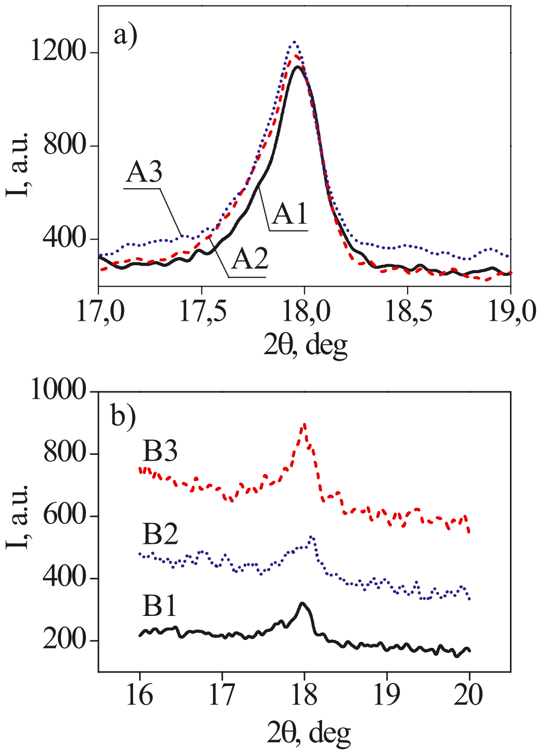

Fig. 1. PTFE XRD pattern for the three different sample velocities [before (a) and after annealing (b), see samples symbols in Experimental]

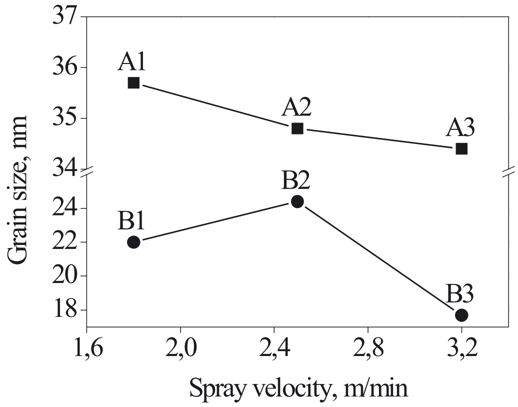

Fig. 2. Grain size dependence on the spray velocity and annealing of the samples

$$L = \frac{0.9 \cdot \lambda}{\mathrm{FWHM} \cdot \cos\theta_B} \tag{9}$$

where: λ — *wavelength*, θ_B — *Bragg angle of diffraction that corresponds to the (hkl) lattice planes.*

As it can be observed, there is a clear reduction of the grain size due to the annealing. This behavior is explained by the fact that the polymeric material is heated to temperature higher than its melting point and the resulted entanglements do not allow the chains to be aligned. Additionally, the grain size of the samples before annealing is decreasing when the spraying velocity is increasing as expected, because the quantity of the sprayed material is inversely proportional to the spray velocity. In the case of annealed samples the grain size shows a maximum value.

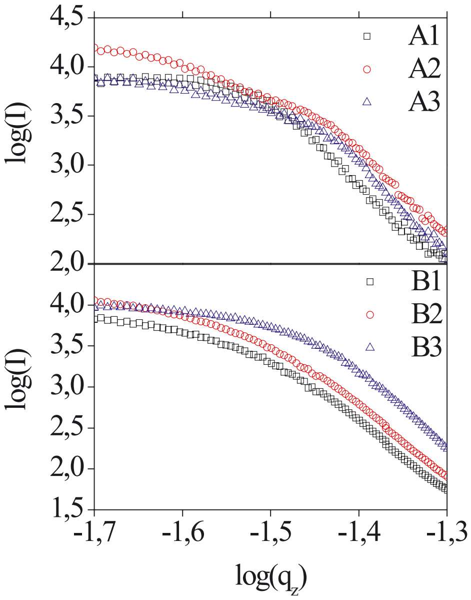

Fig. 3. XDS Longitudinal Scans of the samples before and after annealing

The surface features can be studied using the X-Rays Diffuse Scattering at grazing incidence in two ways: longitudinal and rocking scans. In the case of XDS Longitudinal Scan the angle of incidence is slightly different from the scattering angle and the spectra are depicted in Fig. 3 as $\log_{10}I$ *vs* $\log_{10}q_z$. For $q_z > q_c$ the $\log_{10}I$ decays linearly with the $\log_{10}q_z$, meaning that the intensity depends on q_z exponentially. From the linear fit of this region Hurst parameter h can be calculated through the formula [7]:

$$I \propto q_z^{-\left(3+\frac{1}{h}\right)}.$$

This analysis gave that for the B samples the Hurst coefficient h was the same and equal to 0.15, whereas for the A samples was not much higher and equal to 0.19.

The above results are showing that the surface morphology of the samples after annealing become more jagged. This result agrees with the fact that the annealing enhances the untwisting and the entanglements of the macromolecules and furthermore the local distortions from smoothness and regularity. Additionally, the spraying velocity does not seem to have any effect on the final morphology of the samples.

The second type of scan (XDS Rocking Scan) that can give information about the surface features (correlation length and Hurst coefficient) is the rocking curve and the spectra are depicted in Fig. 4. As it can be observed from these curves the unsintered samples (full points) have identical spectra, what means that the surface morphology is independent on the velocity and thus the quantity of PTFE. On the other hand, the surface morphology of the sintered sample (open points) shows significant dependence on material's quantity. Taking into account the results of the off-specular XRR, the reason of the dif-

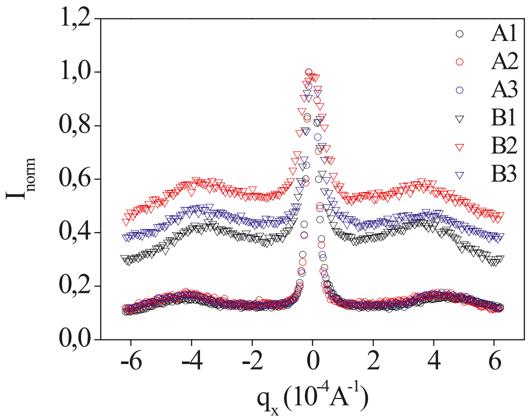

Fig. 4. XDS Rocking curves of both A (o) and B (△) samples

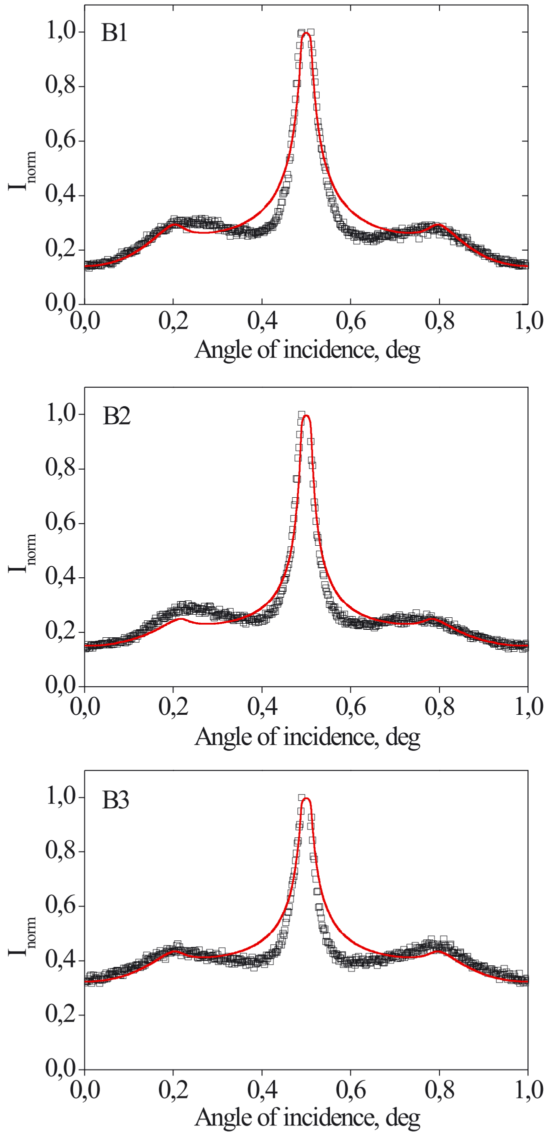

Fig. 5. Experimental points (□) and the fitting (red line) according to Sinha's expression

ferent surface morphology is probably the correlation length which is related to the distribution of the height fluctuations on the surface.

Following Sinha's expression for the data fitting, we can calculate the surface roughness and the correlation length; the results are shown in Fig. 5. The Hurst coefficient that is used in the fitting procedure is already known from the off-specular XRR. The results from the fitting are summarized in the Table 1.

Table 1. Values of surface roughness (σ), correlation length (ξ) and Hurst coefficient (*h*) of sintered PTFE samples

Sample	B1	B2	B3
σ (nm)	0.5	0.5	0.5
ξ (nm)	126	268	103
h	0.15	0.15	0.15

As it is clear from the Table, the correlation length depends on the spray velocity, whereas the other parameters do not. This fact means that although the three surfaces show the same roughness, the distribution of the macromolecules is related strongly to the material's quantity (through spray velocity).

CONCLUSIONS

The above analysis revealed the high potential of X-Rays techniques and especially XDS technique to describe polymeric surfaces grown by spray coating and sintered at high temperature in inert atmosphere. The grain size of PTFE is decreasing with the material quantity and after the annealing. Furthermore, for the annealed samples the grain size does not depend monotonically on the quantity, but has a maximum value. The XDS Longitudinal Scan shows that all the annealed samples have the same surface texture. Finally, the analysis of XDS Rocking Scans spectra showed that the correlation length has the same dependence on the spray velocity as the grain size. Thus, the most significant conclusion from this study is that the surface characteristics do not monotonically or linearly, depend on the spray velocity, but exhibit a maximum value for specific surface features.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

- Piroliza zużytych opon w aspekcie technicznym i ekonomicznym oraz uszlachetnianie otrzymywanych produktów
- Modyfikowany fulerenami poliamid 6 wytwarzany metodą anionowej polimeryzacji ε-kaprolaktamu
- Porównawcze badania skrobi modyfikowanej za pomocą kwasu mlekowego i poli(kwasu mlekowego) (*j.ang.*)
- Wybrane aspekty wpływu oddziaływania przeciwutleniaczy fenolowych z nadtlenkiem dikumylu na właściwości sieciowanych poliolefin
- Otrzymywanie cząstek sferycznych z oligomeru kwasu 3-hydroksymasłowego
- Wpływ ciepła na niektóre właściwości warstwy wierzchniej folii polimerowych przeznaczonych do formowania próżniowego
- Wpływ zmiany warunków brzegowych na charakterystykę przepływu ślimakowego