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Polymers doped with metal oxide nanoparticles with controlled refractive index**)

Summary — Polymer nanocomposites for optical applications, with controlled refractive index in the range 1.46—1.78 were prepared by chemical route and sol-gel process, starting from poly(methylmethacrylate) (PMMA), hydroxyethylmethacrylate (HEMA), polyvinyl alcohols (PVA-1 and PVA-2) and metal oxides from alkoxides or inorganic compounds. The properties of these materials modified by metal oxide nanoparticles depend on the composition, metal oxide concentration, particle size and dispersion homogeneity. Ellipsometric method was used to analyse the changes in the refractive index of the nanocomposites with respect to increasing particle concentration and the spectrophotometry to determine the optical transmittance. The size and dispersity of the nanoparticles in the polymer matrix were evaluated using atomic force microscopy (AFM). As expected, the refractive index of the polymer thin films, spin coated onto substrates, increases with increasing oxide concentration for the polymers modified with TiO_2, ZrO_2 or CuO in the entire visible region and decreases with increasing oxide concentration when the polymers are modified with SiO_2. For the all compounds the transmittance remains above 90 % in the visible wavelength spectra. The particle dimensions are in the range 10—70 nm and were controlled through the method and the parameters of syntheses.

Key words: polymer nanocomposites, refractive index, transmittance, particle size, atomic force microscopy.

POLIMERY SZCZEPIONE NANOCZĄSTKAMI TLENKÓW METALI W CELU KONTROLOWANYCH ZMIAN WSPÓŁCZYNNIKA ZAŁAMANIA ŚWIATŁA

Streszczenie — Metodą chemiczną i sol-gel otrzymano nanokompozyty polimerowe do zastosowań optycznych charakteryzujące się współczynnikiem załamania światła w przedziale 1.46—1.78. Nanokompozyty syntezowano z poli(metakrylanu metylu) (PMMA), metakrylanu hydroksyetylu (HEMA) lub poli(alkoholi winylowych) (PVA-1 lub PVA-2) z dodatkiem tlenków metali otrzymywanych z alkoholanów lub innych związków nieorganicznych (tabela 1). Właściwości polimerów modyfikowanych nanocząstkami tlenków metali zależą od rodzajów i stężenia tlenków metali, rozmiarów cząstek oraz homogeniczności dyspersji. Badania współczynnika załamania światła wykonano metodą elipsometryczną, a transmitancji metodą spektrofotometryczną w zakresie długości fali 200—900 nm. Rozmiary i dyspersję nanocząstek w matrycy polimeru określano za pomocą mikroskopii sił atomowych (AFM). Zgodnie z oczekiwaniami współczynnik załamania światła badanych nanokompozytów rośnie ze wzrostem stężenia TiO_2, ZrO_2 i CuO, natomiast maleje, wraz ze wzrostem SiO_2 (rys. 3—8). W zakresie światła widzialnego transmitancja wszystkich próbek jest większa niż 90 % (rys. 1 i 2). Rozmiary otrzymanych cząstek zależnie od metody i parametrów syntezy zawierają się w przedziale 10—70 nm (rys. 9—11).

Słowa kluczowe: nanokompozyty polimerowe, współczynnik załamania światła, transmitancja, rozmiary cząstek, mikroskopia sił atomowych.

Most organic polymers show a limited refractive index, in the range 1.35—1.5. For optical applications, polymers with higher refractive index are required [1]. In the last years, the polymer doped with metal oxide nanoparticles have been studied as alternative materials for optical applications, including planar waveguide devices and microoptical elements [2—5]. The polymers modified by metal oxide nanoparticles have been prepared by sol-gel process, by polymerization of monomer containing nanoparticles and by dispersing of nanoparticles in a polymeric matrix [6—9].

The presence of nanoparticles in polymer improves the mechanical, electrical and optical properties of the material and it is possible to control these properties, including the refractive index, by concentration and size of the particles [1, 10—12].

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In this paper we report the experiments performed in order to increase the refractive index of poly(methyl methacrylate) (PMMA), 2-hydroxyethyl methacrylate (HEMA) and polyvinyl alcohol (PVA) by doping with oxide nanoparticles (TiO_2, ZrO_2, SiO_2) from alkoxides or inorganic materials (CuO).

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA with molecular weight M_w = 120 000), 2-hydroxyethyl methacrylate (HEMA), polyvinyl alcohols (PVA-1 with M_w = 31 000—50 000 and PVA-2 with M_w = 124 000—186 000), titanium(IV) isopropoxide (97 wt. % purity), zirconium(IV) propoxide (70 wt. % solution in 1-propanol), trimetyloxypropylsilane (98 wt. % purity), zirconium oxide nanoparticles, acetylacetone (99 wt. % purity), methylmethacrylate (MMA), ammonium dichromate and other chemicals used in the experiments were purchased from Aldrich.

Preparation of nanocomposites

To prepare the polymer nanocomposites by low temperature sol-gel process, initial PMMA was dissolved under stirring in chlorobenzene and in methylmethacrylate (MMA) to obtain 7 wt. % or 2.5 wt. % solutions. Titanium(IV) isopropoxide (Aldrich) was chelated with acetylacetone in molar ratio 1:2 (1:0.68 by volume) under nitrogen atmosphere and the solution was agitated for homogenization. Also, in order to lower the reactivity of zirconium precursor and to prevent oxides' precipitation, zirconium(IV) propoxide was mixed with isopropanol and was chelated with acetylacetone in molar ratio 1:10:2 (1:1.7:0.4 by volume). Trimethoxypropylsilane was mixed with isopropanol and deionized water in molar ratio 1:4:4 (1:1.7:0.4 by volume). The alkoxides and PMMA solutions were mixed under nitrogen atmosphere in different metal alkoxide and polymer ratios and were stirred to become homogeneous. Then the resulting solutions were spin-coated onto glass substrates or silicon oxide/silicon wafers at 500—3000 rpm. The coated films on substrates were stored for 24 hours at room temperature and then 1 hour at 100 °C. Also, PMMA-ZrO_2 thin films were prepared by direct mixing of zirconium oxide nanoparticles in PMMA solution.

PVA-1 and PVA-2 were dissolved in deionized water, heated at 70 °C under stirring and then filtered through serigraphic silk to yield two PVA aqueous solutions having 7 wt. % of PVA. A 5 wt. % solution of CuO in acidulated water, 20 wt. % solution of $FeCl_3$ in water or silicon alkoxide solutions direct by mixing in polymer solutions were used as dopant solutions and 2 wt. % aqueous solution of ammonium dichromate as photosensitive material. The thin films spin-coated (at 500 to 3000 rpm for 60 seconds) composed from PVA, CuO and dichromate were dried at 60 °C for 10 min and then UV exposed at 365 nm with dose 3.5 mW/cm^3 for 6—8 min. The solubility difference between the crosslinked polymer matrix and nonexposed matrix is good enough to allow channel waveguide fabrication using UV exposure and development.

HEMA-MMA (3:2 by volume) was mixed with chelated titanium alkoxide and with an organic peroxide (*e.g.* benzoyl peroxide, methyl-ethyl ketone peroxide or Irgacure 184). The titanium alkoxide was used to increase the refractive index and the peroxide to initiate the polymerization reaction.

Methods of testing

The transmittance spectra were measured using UV-VIS Specord M42 (Carl Zeiss Jena) spectrophotometer in the range 200—900 nm.

A Sentec ellipsometer model SE 800 XUV with an operational software SPECTRAY II was used to determine the thickness and the refractive index of the thin film.

The size and dispersity of the nanoparticles in the polymer matrix were determined using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Some of the compositions of investigated samples are presented in Table 1.

The spectral transmittance was determined for the thin layer spin-coated on glass substrate. The results are shown in Figure 1 and 2. The reflectivity of the film surface was not accounted. One can observe that the doped PVA and PMMA films show transmittance of about 90 % for wavelengths in the range 350—800 nm.

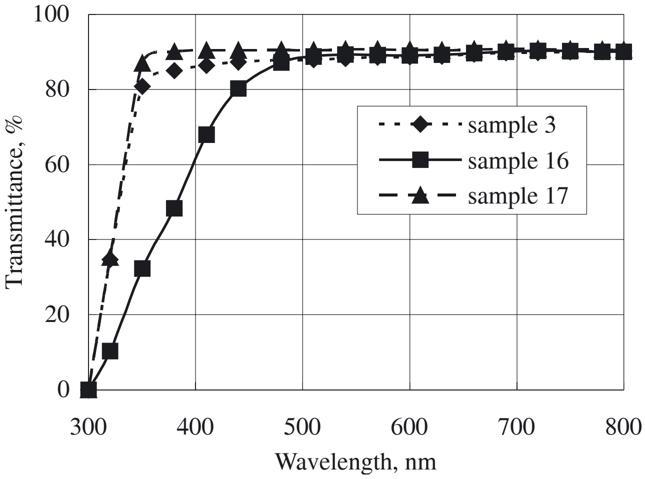

Fig. 1. Transmittance spectra of doped PVA thin films; description of samples in Table 1

T a b l e 1. Method of preparation and compositions of samples investigated

Symbol of sample	Method of preparation	Composition	Investigations
1	direct mixing of solutions	10 ml of 7 wt. % aqueous solution of PVA-1, 0.5 ml of 5 wt. % acidulated aqueous solution of CuO, 1 ml of 2 wt. % aqueous solution of $(NH_4)Cr_2O_7$	transmittance, refractive index
2	direct mixing of solutions	10 ml of 7 wt. % aqueous solution of PVA-1, 1 ml of 5 wt. % acidulated aqueous solution of CuO, 1 ml of 2 wt. % aqueous solution of $(NH_4)Cr_2O_7$	transmittance, refractive index
3	direct mixing of solutions	10 ml of 7 wt. % aqueous solution of PVA-1, 2 ml of 5 wt. % acidulated aqueous solution of CuO, 1 ml of 2 wt. % aqueous solution of $(NH_4)Cr_2O_7$	transmittance, refractive index
4	direct mixing of solutions	10 ml of 7 wt. % aqueous solution of PVA-2, 1 ml of 2 wt. % aqueous solution of $(NH_4)Cr_2O_7$	refractive index
5	direct mixing of solutions	10 ml of 7 wt. % aqueous solution of PVA-2, 0.5 ml of 5 wt. % acidulated aqueous solution of CuO, 1 ml of 2 wt. % aqueous solution of $(NH_4)Cr_2O_7$	refractive index
6	direct mixing of solutions	10 ml of 7 wt. % aqueous solution of PVA-2, 1 ml of 5 wt. % acidulated aqueous solution of CuO, 1 ml of 2 wt. % aqueous solution of $(NH_4)Cr_2O_7$	transmittance, refractive index
7	direct mixing of solutions	10 ml of 7 wt. % aqueous solution of PVA-2, 2 ml of 5 wt. % acidulated aqueous solution of CuO, 1 ml of 2 wt. % aqueous solution of $(NH_4)Cr_2O_7$	higher dopant concentration
8	sol-gel	10 ml of 2.5 wt. % solution of PMMA in MMA, 0.1 ml of chelated Zr-propoxide	refractive index
9	sol-gel	10 ml of 2.5 wt. % solution of PMMA in MMA, 0.1 ml of chelated Zr-propoxide	refractive index after UV expos.
10	sol-gel	10 ml of 2.5 wt. % solution of PMMA in MMA, 2 ml of chelated Ti-isopropoxide	refractive index
11	polymerization of monomers doped with alcoxide	10 ml of HEMA-MMA (3:2 by volume), 4 ml of Ti-isopropoxide, 3 ml of 20 wt. % solution of IRGACURE 184 in HEMA-MMA	refractive index
12	direct mixing of ZrO_2 nanoparticles in PMMA solution	20 ml of 2.5 wt. % solution of PMMA in MMA, 0.055 g ZrO_2 nanoparticles	transmittance, AFM
13	direct mixing	7 wt. % PMMA in MMA	transmittance
14	sol-gel	10 ml 2.5 wt. % PMMA in MMA, 0.5 ml chelated Ti-isopropoxide	AFM
15a	direct mixing of solutions	20 ml 7 wt. % PVA-1, 1 ml 1 wt. % CrO_3	AFM
15b	direct mixing of solutions	20 ml 7 wt. % PVA-1, 2 ml 5 wt. % CuO, 1 ml 1 wt. % CrO_3	refractive index, AFM
16	direct mixing of solutions	20 ml of 7 wt. % aqueous solution of PVA-1, 2 ml of 20 wt. % aqueous solution of $FeCl_3$, 1 ml of 1 wt. % aqueous solution of CrO_3	transmittance, refractive index
17	sol-gel	10 ml of 7 wt. % aqueous solution of PVA-1, 2 ml of chelated Si-trimethoxypropyl	transmittance, refractive index
18	sol-gel	10 ml of 7 wt. % solution of PMMA in MMA, 1 ml of chelated Si-trimethoxypropyl	transmittance, refractive index
19	direct mixing of solutions	10 ml of 7 wt. % of aqueous solution of PVA-1, 0.1 ml of Ti-isopropoxide, 1 ml of 2 wt. % aqueous solution of $(NH_4)Cr_2O_7$	refractive index

The dependence of refractive index on the dopant and polymer compositions is presented in Figures 3—8.

The refractive indices of the doped polymers were determined from ellipsometric data, according to the effective medium approximation (EMA) method. In this method the polymer-oxide film is considered as a multilayer of the polymer and oxide assembled one on the top of the other. The properties of the each layer determine

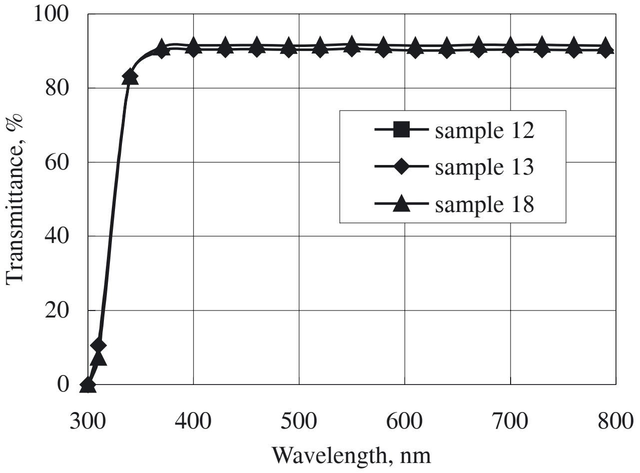

Fig. 2. Transmittance spectra of doped PMMA thin films; description of samples in Table 1

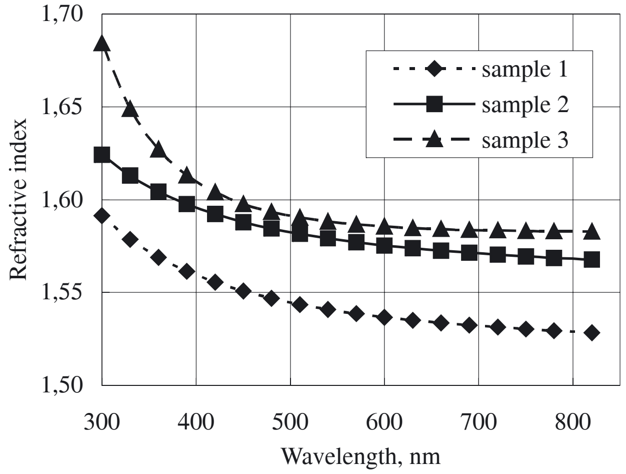

Fig. 3. Refractive index spectra of PVA-1 samples doped with CuO; description of samples in Table 1

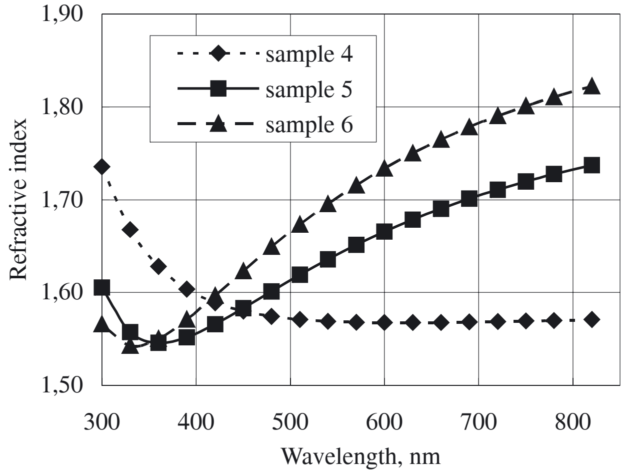

Fig. 4. Refractive index spectra of PVA-2 samples doped with CuO and $(NH_4)_2Cr_2O_7$

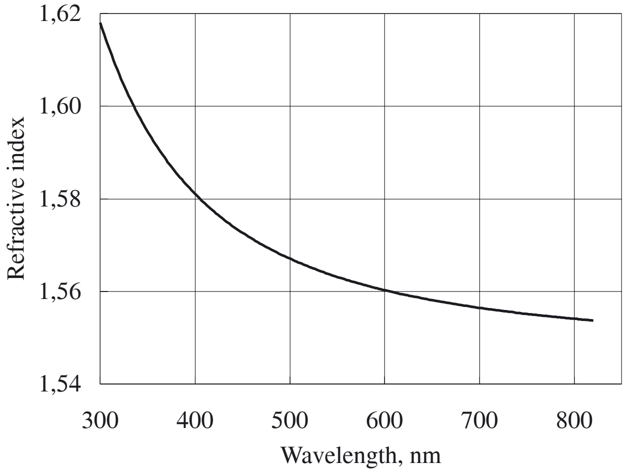

Fig. 5. Refractive index spectrum of PVA-1 sample doped with TiO_2 *(sample 19 in Table 1)*

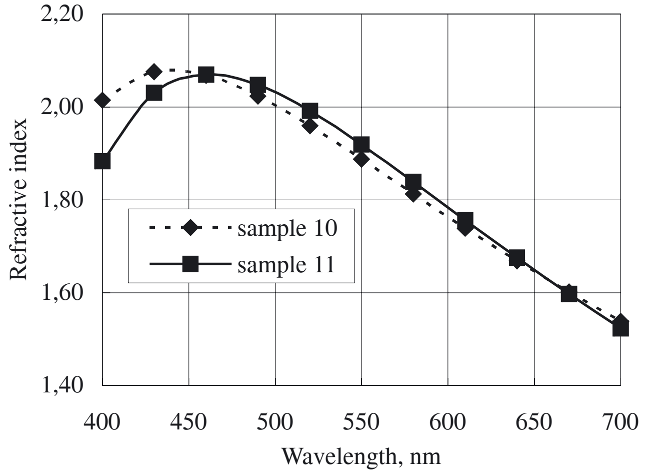

Fig. 6. Refractive index spectra of PMMA and HEMA samples doped with TiO_2

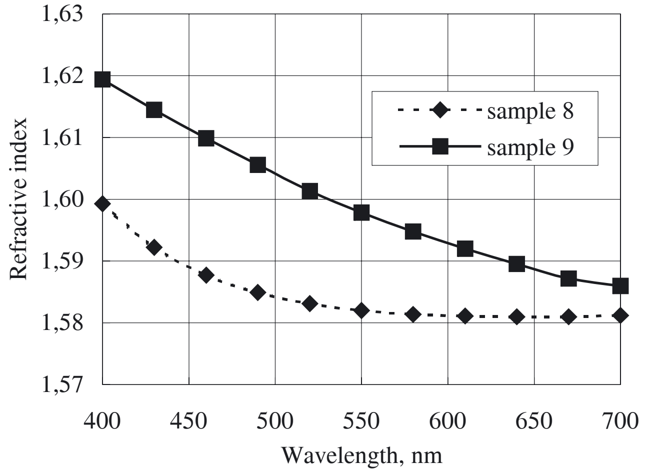

Fig. 7. Refractive index spectra of PMMA samples doped with ZrO_2

the multilayer properties. Because TiO_2, ZrO_2, CuO have a higher refractive index (n > 2.1) than the polymer, one can expected an increase in the refractive index of the polymer doped with these oxides and the decrease when polymer is doped with SiO_2 because of its lower refractive index (n ≈ 1.459).

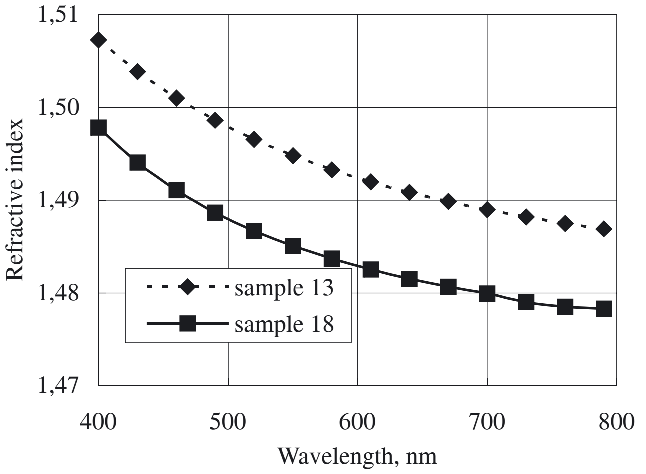

Fig. 8. Refractive index spectra of PMMA and PMMA doped with SiO_2 samples

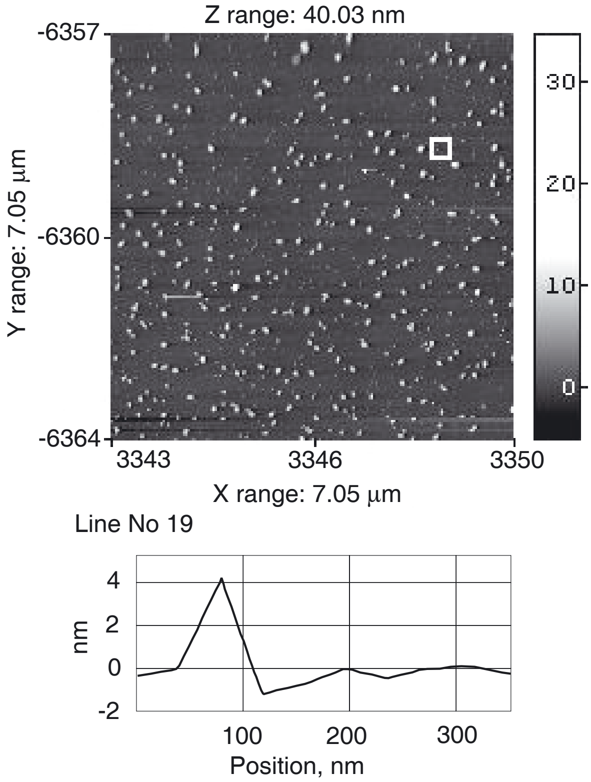

Fig. 9. AFM image of the film prepared by sol-gel process from 2.5 wt. % of PMMA mixture in MMA and titanium isopropoxide chelated with acetylacetone (sample 14 in Table 1)

As it can be seen from figures 3—8 the refractive index measured for the polymer thin films spin-coated onto substrates increases with increasing oxide concentration for the polymers modified with TiO_2, ZrO_2 or CuO in the entire visible region and decreases with growing SiO_2 concentration. We can also observe that the refractive index versus wavelength curves for the hybrid coatings have the same shape as those of the dopants and that the value of the refractive index depends on the polymer structure. The refractive index value for the same polymer structure depends on the chain length of the polymer as can be seen for PVA-1 in Fig. 3 and PVA-2 in Fig. 4.

The maximum refractive index value obtained for the film prepared from PVA-2 and CuO (sample 6) was 1.78 at 700 nm wavelength.

The refractive indices of the acrylic polymers increased with TiO_2 or ZrO_2 as dopants, prepared using sol-gel process, starting from PMMA or from the monomers (HEMA-MMA) and an agent to the initiation of the polymerization of unsaturated monomer (Figs. 6, 7). As it can be seen in Fig. 7, the refractive index can be further increased by UV-exposure (3.5 mW/cm^2). The maximum of the refractive index value was 2.07 at 450 nm for samples obtained from PMMA and TiO_2 (samples 10 and 11).

Experimentaly, we observed that zirconium propoxide has a high hydrolysis reaction rate even if it was mixed with isopropanol and chelated with acetylacetone in molar ratio 1:10:2 under nitrogen atmosphere. The sol-gel zirconium alkoxide solution has to be spin coated just after preparation and cannot be stored. For comparison, PMMA-ZrO_2 thin films were prepared by direct mixing of zirconium oxide nanoparticles in PMMA solution. The maximum refractive index was 1.62 at 400 nm for thin films obtained from PMMA and 0.3 wt. % of ZrO_2.

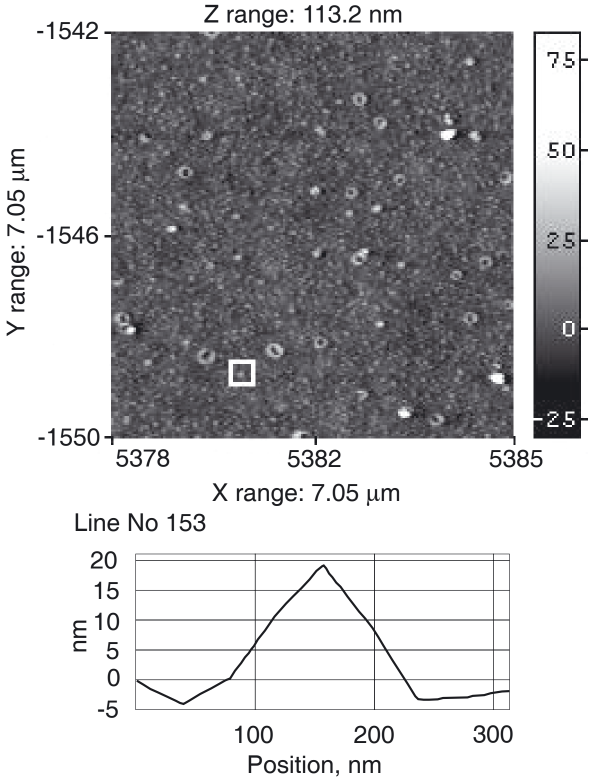

Fig. 10. AFM image of the film prepared by direct mixing of 0.3 wt. % of ZrO_2 nanoparticles in 2.5 wt. % of PMMA mixture in MMA (sample 12 in Table 1)

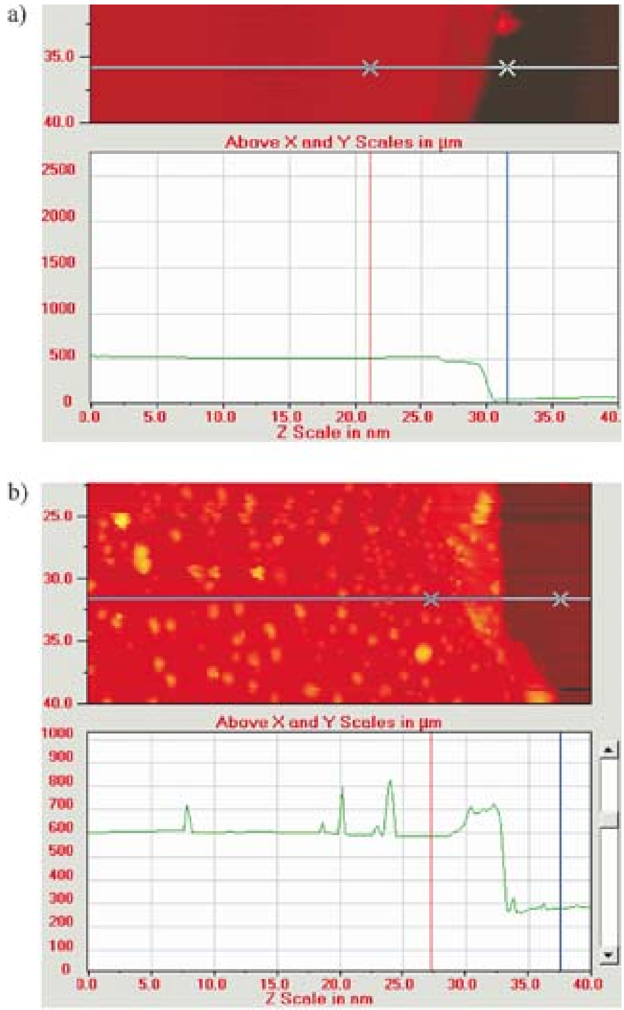

Fig. 11. AFM images of PVA-1 films: a) sample 15a, b) sample 15b

The lower refractive index was obtained when the polymer was doped with SiO_2 prepared from trimethoxypropylsilane by sol-gel process (Fig. 8, sample 18).

At higher concentrations we observed the crystals growth on the film surfaces after drying and photocrosslinking reaction when the dopant concentration was high (for example, sample 7). We also observed small droplets of titanium alkoxide when this solution was added to PVA; PVA-titanium alkoxide solution became homogeneous by stirring only for lower concentration of titanium alkoxide (for example, sample 19). We suppose that a dopant at higher concentration cannot be linked in the polymer binder, but more investigations are necessary to prove the nature of this link.

To estimate by AFM the size and dispersion of the nanoparticles in the polymer, very thin films with a thickness in the range 20—80 nm have been spin coated, by application of higher spin speed (3000—5000 rpm) from dilluted solutions (≤ 2.5 wt. %). In this way the films thickness became comparable or even smaller than particles' sizes, thus allowing them to cast in/over the film surface.

The particle dimensions obtained from AFM images (Fig. 9) are in the range 10—70 nm for PMMA-TiO_2 films prepared by sol-gel process and were controlled through the parameters of synthesis.

AFM images (Figs. 10 and 11) show clusters of submicron dimensions on the film surface for PMMA-ZrO_2 films prepared by direct mixing of ZrO_2 nanoparticles in PMMA and for PVA-$(NH_4)_2Cr_2O_7$-CuO films prepared by chemical route. The resolution of SEM image is not sufficient to observe oxide nanoparticles with sizes in the nanometer range.

Unfortunately, due to technical difficulties in AFM imaging, coming from films elasticity and frequent tip contamination by nanoparticles sticking, only large scan size images could be obtained. This fact restricted the accuracy of estimations for particle lateral sizes, but had no effect on the measurements in vertical direction. The AFM images revealed a certain distribution of the dimensions of the particles, which could be partly attributed to clustering. Size measurements aimed at the smaller range of distinguishable particles. As can be seen in Figs. 9 and 10, lateral dimensions differed from the vertical ones by about an order of magnitude. This fact could not be explained only by limited lateral resolution due to scan size and/or tip convolution. Measured vertical dimensions of only 5—15 nm may be attributable to particles being partially embedded in the polymer film and not sticking out of it, as it might appear from Figs. 9—11.

CONCLUSIONS

The experiments showed that the refractive indices of the polymers can be adjusted in the range 1.45-1.78 by controlling the nature and the concentration of the metal oxides incorporated into polymer solutions. This method is simple, inexpensive and the doped polymer seems to be a useful material for optical applications. To prove the nature of the polymer-metal oxide interaction more investigations are necessary.

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

— Przegląd postępów w stosowaniu spektroskopii NMR wysokiej rozdzielczości stanu stałego w badaniach strukturalnych nanokompozytów polimer/glinka (*j. ang.*)

— Zastosowanie spektroskopii ^{27}Al NMR do badań mechanizmów polimeryzacji cyklicznych eterów (*j. ang.*)

— Zastosowanie spektroskopii ^{29}Si NMR do badań polimerów krzemoorganicznych

— Postęp w badaniach strukturalnych białek za pomocą spektroskopii NMR (*j. ang.*)

— Wgląd w dynamikę protein za pomocą magnetycznej relaksacji jądrowej (*j. ang.*)

— Analiza głównych metod badania swobodnej energii powierzchniowej materiałów polimerowych

— Wpływ rozdrabniania poli(tereftalanu etylenu) i polietylenu na właściwości mechaniczne oraz termiczne kompozycji polimerowych

— Fotopolimeryzacja monomeru wielofunkcyjnego inicjowana za pomocą układu redoks barwnik–związki siarki