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Structure and properties of polyurethane/YAG:Tb³⁺ nanocomposites with luminescence properties

Summary — Elastic polyurethanes films with luminescent properties have attracted increasing attention, both as a subject of fundamental and applied research. In the present study, polyurethane nanocomposites containing 0.05 to 0.2 wt. % of nanofillers were prepared by *in situ* polymerization. These nanocomposites were subsequently used to investigate the influence of the nanoparticles' content on their structure and properties. PUR was synthesized using polycaprolactone diol (PCL diol) and dicyclohexylmethane-4,4'-diisocyanate (HMDI) with addition of diols as chains extenders. The nanofiller in the form of yttrium-aluminum-garnet (YAG) containing 10 wt. % of Tb³⁺ was added and samples of composites were synthesized employing prepolymer fabrication route. Series of nanocomposites with exhibited high luminescence and intensity of emission. Microstructure of these composites was investigated using atomic force microscopy (AFM) in a tapping mode. The grain size analysis of nanofillers was performed with high resolution scanning electron microscopy (HRSEM) and high resolution transmission electron microscopy (HRTEM). The mechanical and optical properties of the specimens have been correlated to their microstructure.
Key words: polyurethane, nanocomposite, morphology, optical properties, thermal properties, mechanical properties.

STRUKTURA I WŁAŚCIWOŚCI NANOKOMPOZYTÓW POLIURETAN/YAG:Tb³⁺
Streszczenie — Elastyczne folie poliuretanowe o właściwościach luminescencyjnych są przedmiotem dużego zainteresowania ze względu na różnorodność ich zastosowań. Jedną z potencjalnych możliwości ich wykorzystania jest zabezpieczanie dokumentów. W ramach tej pracy zbadano wpływ zawartości nanonapełniacza na strukturę oraz właściwości otrzymanych kompozytów. Do syntezy nanokompozytów użyto poli(ε-kaprolaktano)diolu (PCL diol), 4,4'-diizocyjanian dicykloheksylometanu (HMDI) oraz dioli jako przedłużaczy łańcucha. Nanokompozyty otrzymano metodą *in situ* z mieszaniny substratów w procesie syntezy prowadzonej metodą prepolimerową. Jako nanonapełniacza użyto kryształów granatu itrowo-glinowego (YAG) domieszkowanego 10 % mas. Tb³⁺, dodając go w ilości od 0,05 do 0,2 % mas. w stosunku do całej masy polimeru. Otrzymane nanokompozyty z różną zawartością nanonapełniacza charakteryzowały się wysoką przeświecalnością oraz intensywnością emisji (tabela 1, rys. 3). Za pomocą mikroskopu sił atomowych (AFM) wykonano analizę mikrostruktury otrzymanych próbek (rys. 2). Analizę wielkości ziarna nanonapełniacza przeprowadzono za pomocą wysokorozdzielczego skaningowego mikroskopu elektronowego (HRSEM) oraz wysokorozdzielczego transmisyjnego mikroskopu elektronowego (HRTEM) (rys. 1). Określono korelację pomiędzy właściwościami mechanicznymi (tabela 4) i optycznymi otrzymanych kompozytów, a mikrostrukturą nanokompozytów.
Słowa kluczowe: poliuretan, nanokompozyt, morfologia, właściwości optyczne, właściwości termiczne, właściwości mechaniczne.

Nanocomposites based on non-conducting polymers have been the subjects of interest over last decade [1—4] as materials for light-emitting and photovoltaic devices similarly to conductive materials. Because of their low density and excellent mechanical properties, they are good candidates for applications which require portability. The ease of processing and flexibility of thin films of polymers contrast with the stringent requirements of vacuum epitaxial growth of monocrystalline semiconductor structures. Polymers have also another important advantage — they are cheap.

In the present work, polyurethane (PUR) was used as a nanocomposite matrix. Transparent PUR based materials are of considerable interest for both applied and fundamental reasons [5]. Polycaprolactone polyurethanes from aliphatic diisocyanates show superior light stability and transparency and could be used in optical ap-

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plications. Earlier investigation showed that these polyurethanes could be made transparent in 86 % [6, 7].

Recently, it has been shown that polycrystalline powders of yttrium aluminum garnet doped with Nd^{3+}, Yb^{3+} or Er^{3+} ($Y_3Al_5O_{12}$), can be used successfully for ceramic lasers fabrication [8—10]. On the other hand, Tb^{3+} ions are known to emit a visible radiation in the green regions and are widely used as dopants for phosphorus materials [11]. In this work the powder of yttrium-aluminum-garnet (YAG) doped with Tb^{3+} [12] were used as a filler material. The results published in [13, 14] proved that the composites based on the polymer used here and nanofillers showed optical properties dependent on the nanofillers grain size and its dispersion in the matrix.

The aim of the study was to obtain nanocomposites for optoelectronic applications [15, 16]. The paper describes morphology and basic properties of the nanocomposites obtained. The focus of the study was the influence of nanofiller distribution on the structure of hard domains of polyurethanes and on the properties of nanocomposites.

EXPERIMENTAL

Materials

The following reactants were used in the syntheses of polyurethanes: dicyclohexylmethane-4,4'-diisocyanate (HMDI), polycaprolactone diol (PCL diol) with molecular weight 2000 both purchased from Aldrich Chemical Co. Germany and 1,6-hexanediol (1,6-HDO) and glycerol (G) from Merck-Schuardt Co. Germany.

The powders of yttrium-aluminum-garnet (YAG) doped with 10 mol. % of Tb^{3+} (YAG:10 % Tb^{3+}) used as the filler were prepared by Pechinie method described in detail in [17, 18]. This method has advantages of sol-gel techniques and decomposition based on crystallization [19].

Syntheses of nanocomposites

Nanocomposites were synthesized by prepolymer method. Polyurethanes composed of PCL diol:HMDI: 1,6-HDO:G with a molar ratio 1:5:3:1 and a constant isocyanate index were synthesized. PCL diol with YAG:Tb^{3+} were mixed under a vacuum for one hour at temp. 110±5 °C. The reaction was kept at temp. 120±5 °C for 16 h.

Nanocomposites containing 0.05, 0.1, 0.2 wt. % of nanopowder were fabricated from YAG powder and substrates by *in situ* polymerization method.

Method of characterization

Nanofiller density was measured using helium pycnometer AccuPyc 1330. Specific surface was determined using surface analyzer Gemini 2360.

Analyses of nanofillers structures were performed using a high resolution transmission electron microscopy (HRTEM) and a high resolution scanning electron microscopy (HRSEM).

The morphology of PUR and nanocomposites was characterized by atomic force microscopy (AFM). Topographic images were obtained in tapping mode. The microstructure of PUR was investigated using microsections.

The emission spectra were measured at a room temperature using spectrophotometer equipped with a photomultiplier detector. As an excitation source, 308 nm line of an excimer laser was used. The recorded spectra were corrected for the spectrophotometer response. The emission lifetimes were measured with a Le Croy Wave Surfer 452. The transmittance spectrum was measured at a room temperature with a Cary 5E spectrophotometer (Varian).

Thermogravimetric analysis (TGA) was carried out using samples of 5 mg in an alumina crucible at a heating rate of 10 deg/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed using an instrument equipped with a liquid nitrogen cooling unit.

The density was measured according to ISO 2781 and hardness using an indentation tester according to ASTM D2240-75. Elastic constant was measured according to DIN 53512 and abrasive wear according to ISO 4649. Tensile tests were performed at the rate of 500 mm/min according to ISO 527.

RESULTS AND DISCUSSION

A YAG powder doped with 10 mol. % of Tb^{3+} was investigated by TEM and SEM methods and images obtained are presented in Figure 1. The average YAG particle size determined on the basis of SEM images was below 100 nm.

Specific surface of the powdered nanofiller determined after the synthesis was equal 32.5195 m^2/g and helium density 4.4184 g/cm^3.

In order to evaluate the degree of nanofiller dispersion, microscopic observations were carried out. AFM images of the section surfaces of polymer and nanocomposites are shown in Figure 2.

As one can see from images in Fig. 2, PURs are built from soft and hard domains. In AFM images oval hard domains distributed in the soft domain matrix are seen. Hard domains of PUR (Fig. 2a) form large agglomerates of about 4—6 μm. An addition of 0.05 wt. % of nanofiller (nanocomposite 1) results in a disperstion of hard domains in the soft domain matrix. The size of aggregate increases with an increase in the amount of nanofiller from 0.2 μm for PUR with 0.01 wt. % of nanofillers (nanocomposite 2) up to 0.4 μm for PUR with 0.02 wt. % of YAG (nanocomposite 3).

The results of transmittance and luminescence analyses are presented in Table l and in Figure 3. The results
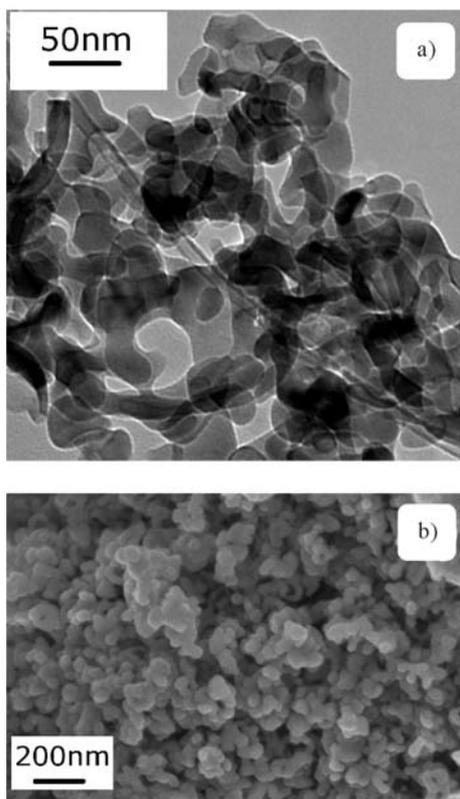
T a b l e 1. Luminescence lifetime (τ) and transparency of PUR, nanofiller and nanocomposites

Type of material	τ, ms	Transparency (λ = 400 nm), %
PUR	—	86
Nanofiller	6.3	—
PUR + 0.05 wt. % of nanofiller (Nanocomposite 1)	3.1	77
PUR + 0.1 wt. % of nanofiller (Nanocomposite 2)	3.1	53
PUR + 0.2 wt. % of nanofiller (Nanocomposite 3)	2.8	33

indicate a significant shortening of luminescence lifetime of about 50—60 % after introduction of nanocrystals into the polymer, compared to Tb^{3+} ions. This is mainly due to the difference in refractive nanocrystal-matrix index and nanofiller's tendency to agglomerate
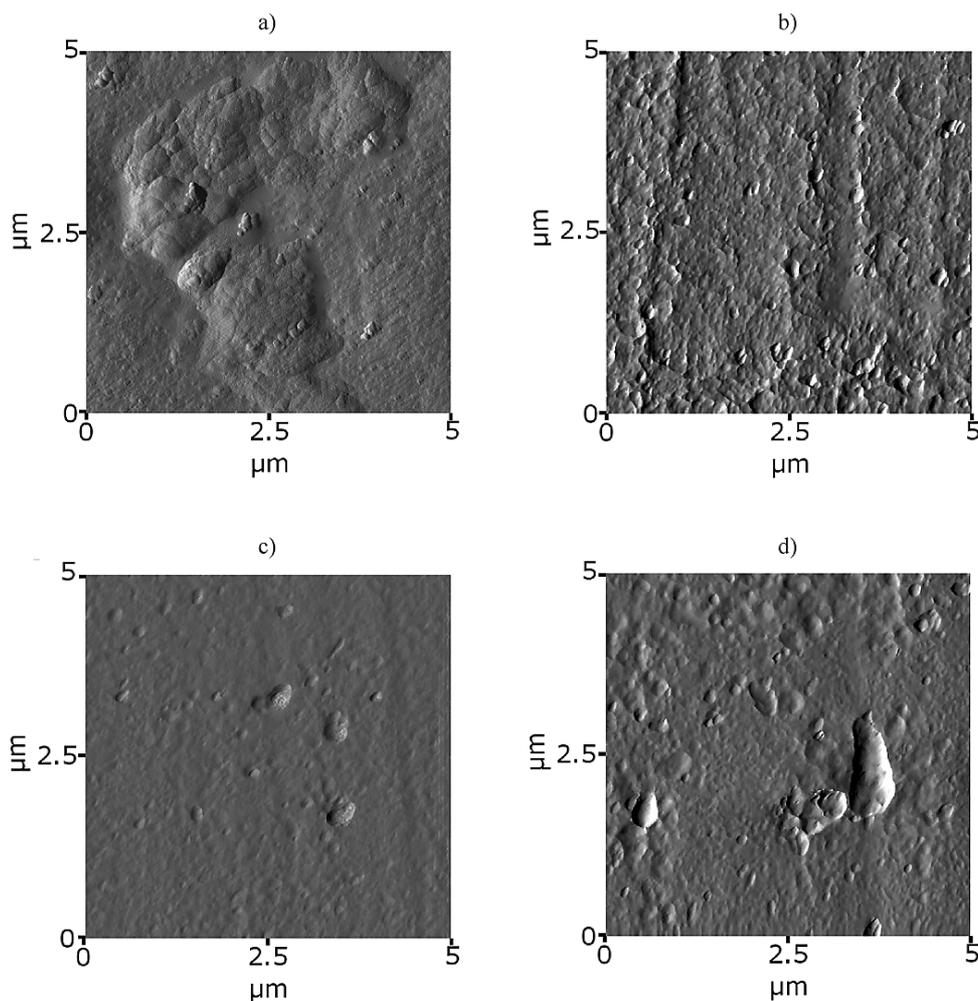

Fig. 2. AFM images of the surface sections of: a) PUR, b) nanocomposites 1 (PUR + 0.05 wt. % of YAG:10 % Tb^{3+}), c) nanocomposites 2 (PUR + 0.1 wt. % of YAG:10 % Tb^{3+}), d) nanocomposites 3 (PUR + 0.2 wt. % of YAG:10 % Tb^{3+})
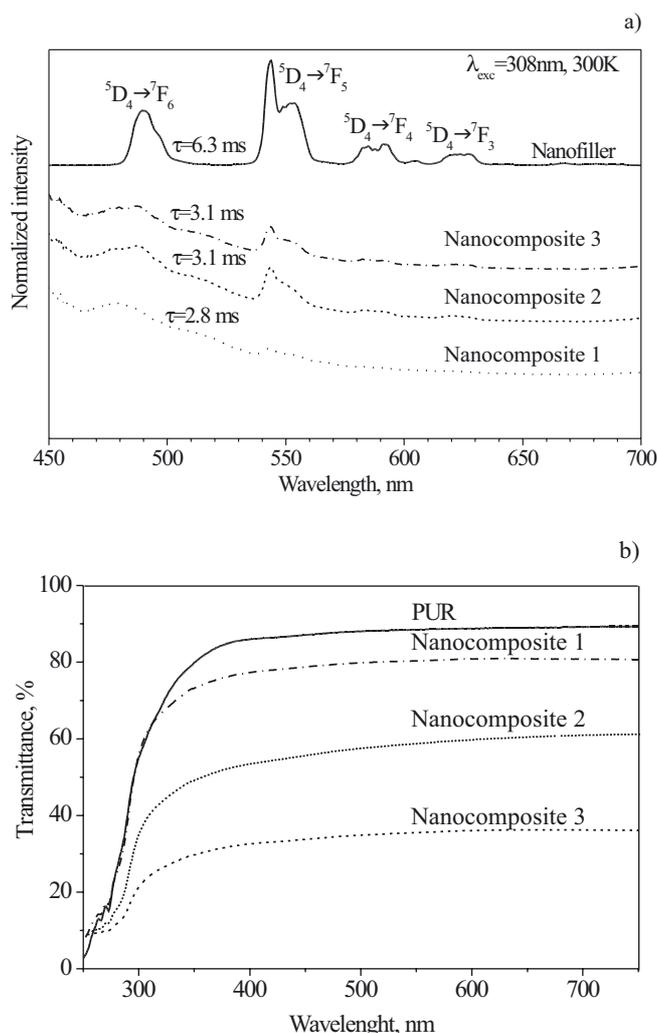
Fig. 3. Spectra of nanocomposites, nanofiller and polymer matrix: a) emission, b) transmittance

in the polymer. The bigger the agglomerate, the shorter, and comparable to the Tb³⁺ doped single crystal, is the luminescence lifetime. This behavior is explained in terms of the host effect enhancing the effective refractive index [20]. Analyses of emissions spectra (Fig. 3) indicate a clear increase in the emission intensity with the increased amount of the nanofillers. With the increase in nanofiller content the transmittance drops. This might be due to a larger number of elements and the size of hard domains, observed in AFM images.

The results of thermal decomposition analyses are given in Table 2. Typical TGA curves of polyurethanes

showed two distinct stages of degradation (nanocomposite 3). It is known that for poly(ester urethanes) the weight loss in the first stage is related to the degradation of allophanate, biureate and urea linkages of hard segment. The temperature of the first degradation stage, about 350 °C, increases with the increasing amount of the nanofiller. So does the amount of polymer which was degraded in that temperature. The calculated amount of hard domains in polyurethane's matrix is 47 wt. %. With higher amount of nanofiller the weight loss about 42—45 % is similar to that value. The results show that introduction of nanofiller lowers the thermal resistance of hard domains, probably by reduction of hydrogen bond, which helps to increase the arrangement in the domains. In the soft domains, decomposing in higher temperatures, two stages are revealed.

T a b l e 3. Thermal properties of PUR and nanocomposites obtained

Type of materials	T_{g1}, °C	T_{g2}, °C	ΔH, J/g	T_m, °C
PUR	-42.2	239.6	4.5	71.6
Nanocomposite 1	-43.9	210.3	4.0	76.0
Nanocomposite 2	-43.4	208.7	3.6	75.3
Nanocomposite 3	-46.8	234.5	5.9	74.2

Thermal properties of prepared samples are listed in Table 3. Glass transition temperature of soft segment (T_{g1}) of nanocomposite 1 and nanocomposite 2 is slightly lower than that of PUR and significantly lower for nanocomposite 3. This observation is confirmed by the melting enthalpy (ΔH) and is related to the fact, that the matrix of nanocomposite 3 contains more crystalline phase. The introduction of the nanofiller increased the melting point of soft domain (T_m). Similar effects were observed in nanocomposites containing 0.2 wt. % of ZrO₂ [21].

The change in the hard domains structure observed in AFM images is accompanied by a change in glass transition temperature (T_{g2}). For PUR and nanocomposite 3 the glass transition temperature is about 235—240 °C. Values of (T_{g2}) nanocomposites 1 and 2 are lower, about 210 °C. These differences are related to the differences in phase segregation during which hard and soft domains of polyurethanes are formed.

Changes in the soft domain structure in the nanocomposite matrix, in fact, influence the mechanical proper-

T a b l e 2. TGA results for polyurethane and nanocomposites

Type of PUR	$T_{2\%}$[a] °C	First stage of degradation		Second stage of degradation		Third stage of degradation		Weight loss at 500 °C %
		temperature, °C	weight loss, %	temperature, °C	weight loss, %	temperature, °C	weight loss, %	
PUR	285.2	348.1	33.9	374.5	58.9	403.3	77.3	99.4
Nanocomposite 1	273.9	348.1	36.8	375.9	58.6	402.8	78.7	99.2
Nanocomposite 2	271.4	352.6	44.2	374.5	65.4	407.8	88.3	99.4
Nanocomposite 3	274.5	353.3	47.5	373.8	71.1	412.1	91.8	99.1

ties of nanocomposites presented in Table 4. With an increase in the nanofiller content in the nanocomposite the hardness (*H*) increases and the elasticity (η) drops. Nanocomposites 1 and 2 show higher Young's modulus (*E*) than the matrix. However, it is lower than the modulus for nanocomposite 3, which can be related to a change in the form of the flexible segments. Introduction of larger amount of nanofiller decreases the tensile strength (R_m).

T a b l e 4. Mechanical properties of PUR and nanocomposites obtained

Type of materials	Hardness ShA	Elasticity %	Young modulus MPa	Tensile strength MPa
PUR	82.3	15.8	12.8	19.8
Nanocomposite 1	87.0	16.0	15.5	15.4
Nanocomposite 2	91.7	12.0	18.9	15.3
Nanocomposite 3	91.1	11.8	11.8	12.1

CONCLUSION

By addition of YAG into the polymer matrix during *in situ* polymerization, nanocomposites showing luminescent properties were obtained. Introduction of nanofiller influences the structure of polyurethane matrix. Addition of 0.2 wt. % of YAG (nanocomposite 3) results in a significant decrease in mechanical properties of the nanocomposite. For nanocomposites containing 0.05 or 0.1 wt. % of YAG (nanocomposites 1 and 2) the desired mechanical properties were obtained. This is promising for the future applications.

The matrix material offers low cost processing and a wide range of functional possibilities. Combining the characteristic of organic and inorganic materials within a single nanocomposite makes it possible to tune up electronic and optical properties of the materials in question.

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