Poly(butylene terephthalate)/carbon nanotubes nanocomposites
Part I. Carbon nanotubes functionalization and *in situ* synthesis

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Abstract: Functionalization of multi-walled carbon nanotubes (MWCNTs) has been carried out. As a functionalization agent epoxy peroxide was used. The success of the MWCNTs functionalization was confirmed by Raman spectroscopy and thermogravimetric analysis (TGA). The poly(butylene terephthalate) (PBT) based nanocomposites have been prepared by a two-step melt polycondensation method (*in situ* synthesis). The nanocomposites containing from 0.1 to 0.3 wt % of modified (EpMWCNTs) and unmodified (MWCNTs) carbon nanotubes were prepared.

Keywords: nanocomposites, poly(butylene terephthalate), carbon nanotubes.

Nanokompozyty poli(tereftalan butylenu)/nanorurki węglowe. Cz. I. Funkcjonalizacja nanorurek węglowych i synteza *in situ*

Streszczenie: Przeprowadzono funkcjonalizację wielościennych nanorurek węglowych (MWCNT) przy użyciu epoksynadtlenku i potwierdzono jej efektywność metodami spektroskopii Ramana i analizy termograwimetrycznej (TGA). Następnie metodą polikondensacji w stanie stopionym (synteza *in situ*) otrzymano nanokompozyty na osnowie poli(tereftalanu butylenu) (PBT) z udziałem 0,1—0,3 % mas. modyfikowanych (EpMWCNT) lub niemodyfikowanych wielościennych nanorurek węglowych (MWCNT).

Słowa kluczowe: nanokompozyty, poli(tereftalan butylenu), nanorurki węglowe.

Polymer nanocomposites have become a prominent area of current research, they represent a viable alternative to conventional composite materials. A particular interests is focused on the application of carbon nanotubes as a nanofiller for polymers due to their extraordinary mechanical, thermal and electrical properties [1—7]. The incorporation of CNTs into a polymer system may improve selected properties of the composite such as tensile strength [8], tensile modulus [9], toughness [10], thermal properties [11, 12] and electrical conductivity [13, 14].

The key issues to achieve superior performance of CNT filled polymer composites are homogenous dispersion of the CNTs within the polymer matrix and strong interactions between the CNTs and the matrix [2—5]. A preparation of nanocomposites by introducing CNTs into a polymer during the synthesis (*in situ* method) was first performed for multiblock poly(ether-ester)s elastomer and carbon nanotubes [15]. It has been proved that *in situ* polymerization is a very effective method to achieve a homogenous distribution of a nanofiller in the polymer matrix [12, 15—17].

The main approaches for the surface modification of CNTs can be grouped into two categories: one is a non-covalent attachment of molecules and the other is a covalent attachment of functional groups to nanotubes walls [6, 18, 19]. Functionalized nanotubes might have mechanical, optical or electrical properties that are different from those of the original nanotubes [20]. Herein, we describe the functionalization of MWCNTs by covalent sidewall attachment of free radicals thermally generated from epoxy peroxide.

Poly(butylene terephthalate) (PBT) is a semicrystalline thermoplastic polyester with high stiffness, hardness, dimensional stability, good resistance to chemicals and excellent processability. PBT is applied in components for automotive, electrical and electronic industries [21—23]. There are a few drawbacks, which limit the applications of PBT: low impact strength and heat distortion temperature. For these reason in recent years many

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experiments were devoted to obtain desirable properties of PBT for example by blending it with other polymers or by using different nanofillers [21—25]. Especially carbon nanotubes have emerged as potentially attractive materials for the PBT reinforcement [21, 22]. In addition the epoxy compounds has been proven to be effective as a chain-extenders. The epoxide compounds react with the carboxyl groups which are products of polyester destruction, increasing the molar mass and the polymer quality [26, 27]. Taking all above into consideration, introduction of epoxy functionalized CNTs can induce regeneration and enhance thermal and mechanical properties of polymer at the same time.

The experimental work in this article deals with modification of MWCNTs with epoxy peroxide. The nanocomposites with functionalized and unfunctionalized MWCNTs weight concentration from 0.1 % to 0.3 % were prepared by a two-step melt polycondensation method (*in situ* synthesis).

EXPERIMENTAL PART

Materials

The following chemicals were used for the preparation of a polymer nanocomposite matrix: dimethyl terephthalate (DMT, Sigma-Aldrich); tetramethylene glycol (1,4-butanediol) (BASF) and tetrabutyl orthotitanate (TBT, Sigma-Aldrich) as the polymerization accelerator.

Multi-walled carbon nanotubes (MWCNTs) with an average diameter of 9.5 nm, an average length of 1.5 μm and carbon purity higher than 90 % (Nanocyl NC 7000, Belgium, datasheet ref: NC7000 – 10 March 2009 – V05) were used as a nanofiller. As a modification agent epoxy peroxide (Scheme A) was used. Epoxy peroxide was synthesized at the Department of Petroleum Chemistry and Technology, Lviv Polytechnic National University.

The cobalt(II) 2-ethylhexanoate (Sigma-Aldrich) was used as a graft catalyst. For NMR studies, chloroform-d (Sigma-Aldrich) with an isotopic purity of 99.8 atom % D was used as a solvent and tetramethylsilane (Sigma-Aldrich) as an internal reference. Phenol/1,1,2,2-tetrachloroethane (60/40 by weight) was used as a solvent in intrinsic viscosity studies.

MWCNTs functionalization procedure

The MWCNTs were dispersed in ethylene glycol by using a magnetic stirrer with a heating hot plate (T = 50 °C, t = 30 min). The compatibilizer (1 wt % of the total monomer mass) was dissolved in 60 cm^3 of butanone and added to the reaction mixture. The mixture was stirred (250 rpm) under a reflux condenser for 24 h in a temperature of 50 °C. Cobalt(II) 2-etylhexanoate was added dropwise to the reaction mixture as a catalyst.

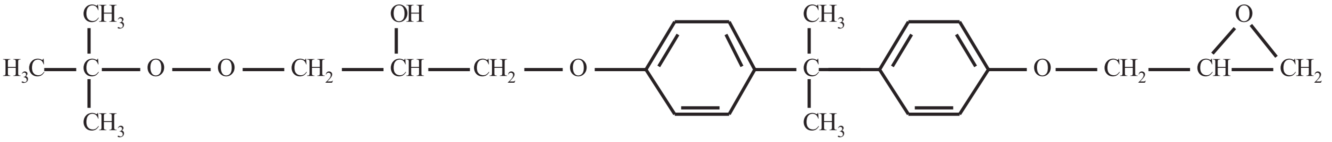
Synthesis of polymers and polymer composites

The poly(butylene terephthalate) and PBT nanocomposites were prepared by a two-step melt polycondensation method. The DMT and 1,4-butanediol were charged into a 1 dm^3 steel reactor (Autoclave Engineers Pennsylvania, USA) equipped with a condenser, a stirrer and a gas inlet applicator. The desired amount of MWCNTs or epoxyperoxide functionalized MWCNTs (EpWMCNTs) were dispersed in 1,4-butanediol through ultrahigh speed stirring with a high-speed stirrer (Ultra-Turax T25) and ultrasonication using a laboratory homogenizer (Sonoplus HD 2200). Dispersion was carried out by turns in cycles (5 min each) and total time of dispersing was 30 min. The dispersion was introduced into the reaction mixture of tetramethylene glycol and melted DMT. In the first step the transesterification reaction was carried out at 160—165 °C. In the presence of the catalyst (TBT) DMT transesterified with tetramethylene glycol and the released methanol was distilled out of the reaction mixture at atmospheric pressure. Then, the temperature was increased slowly to 220 °C and maintained for half hour to reach the endpoint of transesterification. The second step of melt polycondensation was carried out at an increased temperature (250 °C), under reduced pressure (25—30 Pa). During the process the stirring torque changes were monitored to evaluate the viscosity of the product. All synthesis were finished when melting reached the same value of viscosity at 250 °C. The molten polymer or nanocomposite was extruded from the reactor under compressed nitrogen, cooled down to room temperature in water and granulate.

Methods of testing

— For ^1H NMR measurements a Bruker 400 MHz spectrometer was used. Chloroform was used as a solvent and tetramethylsilane (TMS) as an internal reference.

— Functionalized MWCNTs were characterized by Raman spectroscopy and thermogravimetric analysis. Raman analysis was carried out using a micro-Raman Renishaw spectrometer equipped with a CCD detector. To excite samples, a 785 nm laser line (red laser) was



Scheme A

used. All measurements were performed at ambient temperature.

— Thermogravimetric analysis (TGA) was conducted to determine the decomposition temperature of the functionalized MWCNTs. TGA was carried out using an SETARAM TGA 92-16 thermal analyzer under an atmosphere of argon and air (the flow rate was 20 cm^3/min), with a heating rate of 10 °C/min.

— The intrinsic viscosity [28] of the samples was measured using capillary Ubbelohde type 1c (K = 0.03294) at 30 °C. To eliminate the influence of the nanofiller, samples were dissolved in a mixture of phenol/1,1,2,2-tetrachloroethane (60/40 by weight) and filtered through a membrane filter with 0.8 μm pore size. Then samples were precipitated with methanol. The obtained precipitate was dried in vacuum at 60 °C for 12 h and redissolved. A polymer solution with a concentration of 5 g/dm^3 in the mixture of phenol/1,1,2,2-tetrachloroethane (60/40 by weight) was used. The viscosity average molar mass M_v of the samples was calculated according to the Mark-Houwink equation:

$$[\eta] = KM^a \qquad (1)$$

where: $K = 1.17 \cdot 10^{-2}$ cm^3/g, $a = 0.871$ [28].

Measurements were focused on neat PBT and samples with the highest nanofiller content.

RESULTS AND DISCUSSION

Preparation and characterization of functionalization agent

Peroxide-modified resin was employed to functionalize MWCNTs and then prepare thermally stable CNT/poly(butylene terephthalate) nanocomposites via *in situ* polymerization with the assistance of sonication methods.

As a functionalization agent epoxy peroxide was used. Scheme A illustrates the modified resin under discussion. To confirm the structure of functionalization an agent spectroscopic characterization was carried out.

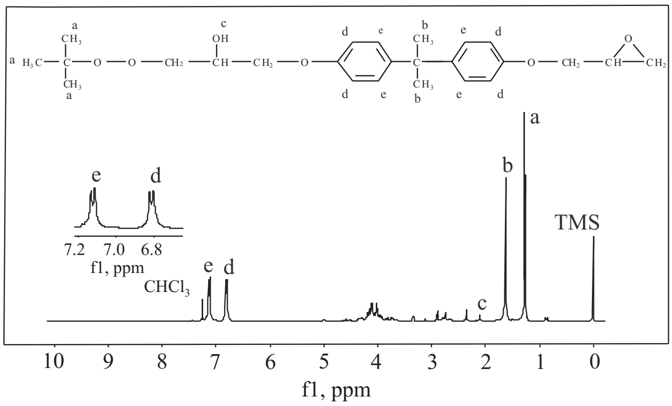


Fig. 1. ^{1}H NMR spectrum of epoxy peroxide in $CDCl_3$

In the aromatic region of ^{1}H NMR spectrum (Fig. 1) two doublets of equal intensity were observed. The integration of the signals observed for the *tert*-butyl group and the aromatic ring gave as expected 8:9 ratio. A single peak at 2.25 ppm may be attributed to one proton of the hydroxyl group. The intense peak at 1.75 ppm clearly indicates the presence of methyl group in the bisphenol A which is a part of epoxy resin. The ^{1}H NMR spectrum confirmed unambiguously the assigned structure of epoxy peroxide (Scheme A).

Characteristics of functionalized MWCNTs

Scheme B illustrates the scheme of MWCNTs functionalization procedure. The functionalization agent has a peroxide group which dissociates into free radicals as classic polymer initiators under the influence of elevated temperature. Presumably, both of them (radical with epoxy group and radical with *tert*-butyl group) link to CNT.

Before proceeding to the preparation of nanocomposites, functionalized MWCNTs were extensively characterized by the following techniques: Raman spectroscopy and thermogravimetric analysis (TGA).

Raman spectroscopy is a very valuable tool in the characterization of carbon nanomaterials. It is highly sensitive and able to investigate the extent of disorder in functionalized MWCNTs [29—31]. Raman spectra of pristine and functionalized MWCNTs were recorded (Fig. 2). The representation shows two important features, the disorder — band (D band) and the graphite — band (G band). The D band located at ~1312 cm^{-1} is usually attributed to defects in the disorder-induced modes or sp^3 hybridized carbons in CNT samples. The G band located at ~ 1611 cm^{-1} is attributed to in plan vibrations of the graphite wall (sp^2 hybridized carbons) [30, 31]. For pristine MWCNTs we can observe an additional line an overtone of D band — G band located at ~ 2620 cm^{-1} [29]. The area

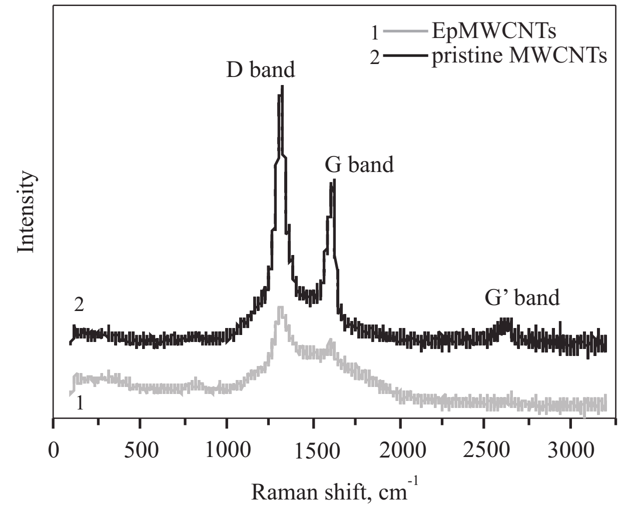
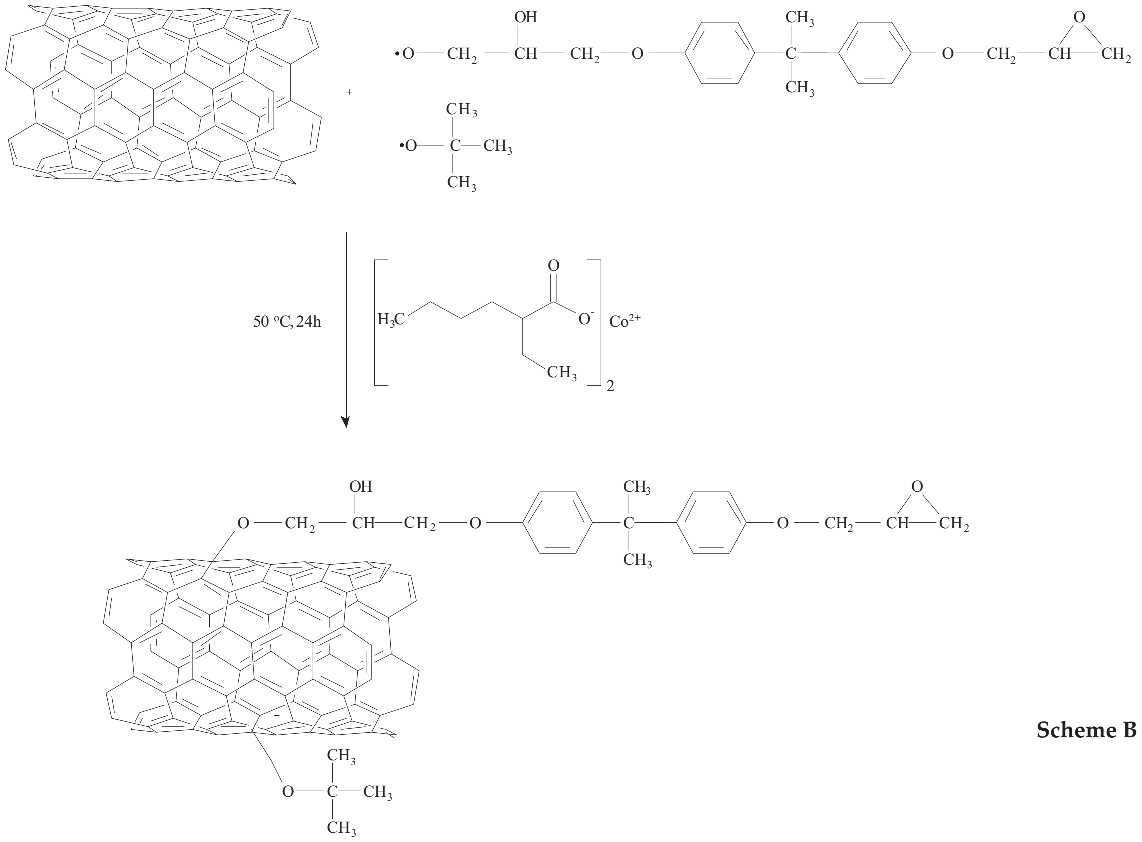


Fig. 2. Raman spectra of pristine and functionalized MWCNTs



Scheme B

ratio of the D band to G′ band (*i.e.*, D_a/G_a) can be taken as the indication of the extent of covalent functionalization [29—32]. The Raman spectra of EpMWCNTs showed the expected increase in the D_a/G_a ratio in comparison to D_a/G_a ratio of pristine MWCNT. The D_a/G_a area ratio increased from 0.63 for pristine MWCNTs to 0.91 for EpMWCNTs (Fig. 2). This suggest that the modification affects the surface structure of MWCNT due to covalent grafting of a epoxy peroxide.

TGA analysis was used to analyze the influence of a compatibilizer on the thermal stability of MWCNTs and EpMWCNTs. Different structure forms of carbon can exhibit different oxidation behavior. Degradation of MWCNTs is a multistage process and depends on the available reactive sites. A typical oxidation temperature characteristic for disordered or amorphous carbons is 500 °C, because of their lower activation energy for oxidation or due to the presence of active sites [31, 33]. Unlike them, the graphitic structure of CNTs usually starts to oxidize at higher temperatures between 600 °C and 700 °C [33]. The TGA and DTGA curves of MWCNTs and EpMWCNTs are displayed in Fig. 3. The organic part covalently attached to the surface of MWCNTs is usually removed in the temperature range between 250 °C and 500 °C [30, 31]. At the TGA trace for functionalized MWCNTs (EpMWCNTs) a weight loss below 400 °C can be observed and it can be attributed to the functionalizing agent decomposition. It can be seen from the TGA curves that the total mass loss of pristine MWCNT is 92 % while the total mass loss of EpMWCNT is 88 %. TGA results confirmed the success of the MWCNTs modification.

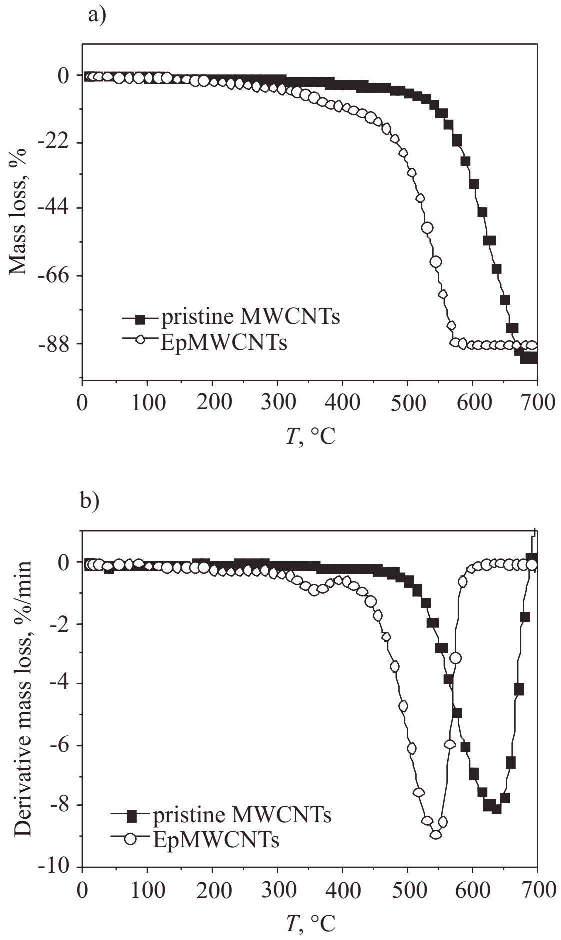


Fig. 3. a) TGA, b) DTGA curves of pristine and functionalized MWCNTs in air atmosphere

The *in situ* polymerization method was applied to obtain PBT nanocomposites with MWCNTs/EpMWCNTs weight concentration from 0.1 % to 0.3 %. Avoiding agglomeration of CNTs in the polymer matrix and forming a strong interactions between the nanotube and the polymer matrix are a key issues in maximizing the advantage of CNTs reinforcements [5, 16, 30]. It has been proved that *in situ* polymerization enables both of them [5, 16, 17]. The essential element of obtaining composites in such a way is good dispersion of a nanofiller in the liquid substrate before synthesis. Here, CNTs were dispersed by sonication and mechanical stirring. Neat PBT was synthesized as a reference. The obtained materials were extruded from the reactor under compressed nitrogen, granulated and injection-molded to prepare dumbbell shaped samples for testing mechanical properties.

Table 1. Physical properties of PBT, PBT/MWCNTs and PBT/EpMWCNTs nanocomposites

Sample	MWCNT / EpMWCNT, wt %	[η] cm^3/g	$M_v \cdot 10^3$ g/mol
PBT	0.0/0.0	89	28.91
PBT/0.3 MWCNT	0.3/0.0	70	21.82
PBT/0.3 EpMWCNT	0.0/0.3	72	22.37

[η] — intrinsic viscosity, M_v — viscosity average molar mass.

Table 1 summarizes the physical properties of neat PBT and 0.3 % loading samples for PBT/MWCNTs and PBT/EpMWCNTs nanocomposites. The synthesized PBT homopolymer has an intrinsic viscosity of 89 cm^3/g and viscosity average molar mass (M_v) of 28.91 · 10^3 g/mol. The presence of a nanofiller, MWCNT and EpMWCNT affects the intrinsic viscosity of the obtained materials. The intrinsic viscosity gradually decreased to 70 cm^3/g for PBT loaded with 0.3 wt % MWCNT and to 72 cm^3/g for PBT loaded with 0.3 wt % EpMWCNT. The changes in M_v of PBT prepared in the presence of MWCNT and EpMWCNT show a similar downward trend in comparison to the M_v of PBT obtained in the absence of a nanofiller. However, the obtained materials have a relatively high molar mass, confirming the correct selection of synthesis parameters.

CONCLUSIONS

Epoxy peroxide functionalized multi-walled carbon nanotubes were prepared (EpMWCNT). Using TGA and Raman spectroscopy the functionalization efficiency was assessed. Nanocomposites consisting of poly(butylene terephthalate) (PBT) and multi-walled carbon nanotubes (MWCNTs) or functionalized multi-walled carbon nanotubes (EpMWCNTs) were prepared by *in situ* polymerization method. The obtained materials have a relatively high molar mass, confirming the correct selection of synthesis parameters.

In next part of our research we will present the effects of unmodified and modified (epoxy peroxide) multiwall carbon nanotubes on the morphology, thermal, mechanical, and electrical properties of PBT.

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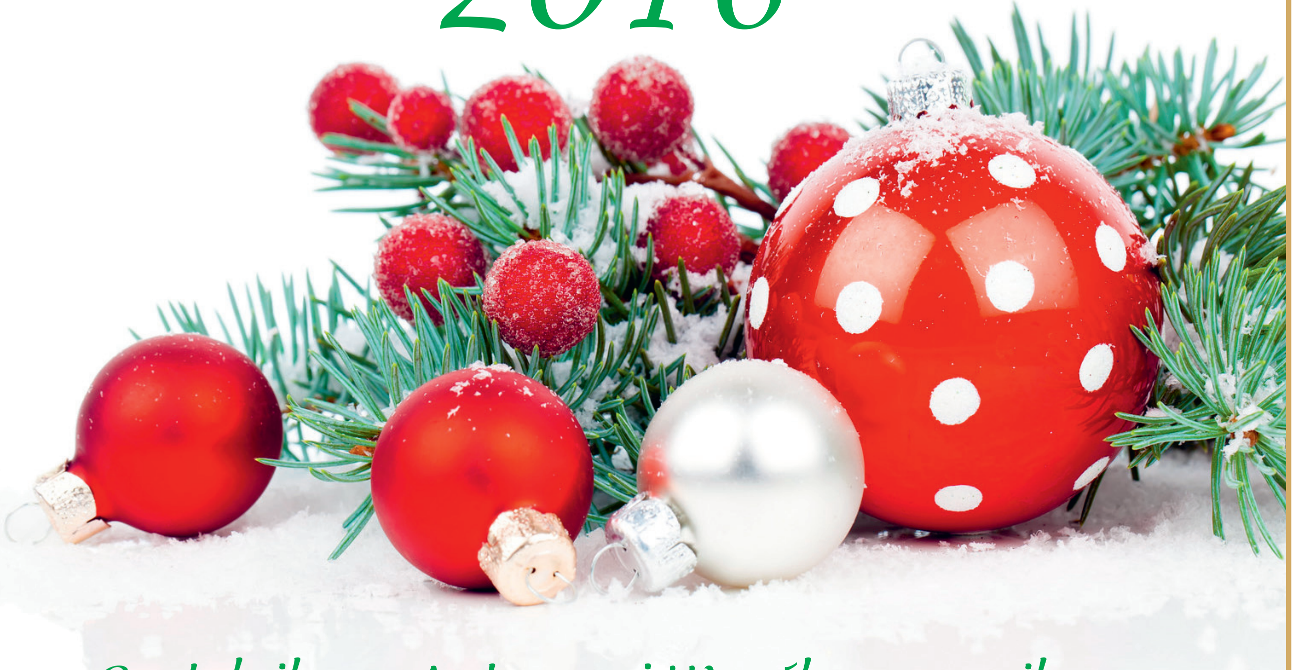

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