Thermal and mechanical properties of polyamide 12/modified carbon nanotubes composites prepared *via* the *in situ* ring-opening polymerization

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Abstract: In this study polyamide 12 (PA12) based composites prepared *in situ via* an ring-opening polymerization of lauryl lactam in the presence of raw and functionalized carbon nanotubes (CNTs) are characterized. This method has been widely applied for thermoplastic based composites, resulting in materials with relatively small amounts and uniform nanofiller distribution. The effect of multi-wall carbon nanotubes chemically modified with hydroxyl or amine groups on PA12 matrix is discussed in terms of the phase structure, thermal, mechanical, and water vapor barrier properties as well as the state of CNTs dispersion in composites. The obtained results confirm, that in general the physical properties of PA12 are noticeably affected by the presence of 0.35 wt % CNTs, whilst the benefits from nanotubes modification are observed in changes of phase transition temperatures and composite mechanical performance, whilst the thermooxidative stability and water absorption the CNTs chemical modification is less pronounced.

Keywords: polymer composites, carbon nanotubes, chemical modification, polyamide 12, *in situ* polymerization.

Termiczne i mechaniczne właściwości kompozytów poliamid 12/modyfikowane nanorurki węglowe otrzymanych *in situ* metodą polimeryzacji z otwarciem pierścienia

Streszczenie: Określono właściwości kompozytów na osnowie poliamidu 12 (PA12), napełnionych niemodyfikowanymi lub modyfikowanymi nanorurkami węglowymi (CNTs), otrzymanych *in situ* w polimeryzacji z otwarciem pierścienia. Metoda ta, szeroko stosowana do wytwarzania kompozytów na osnowie termoplastów, daje możliwość uzyskania materiałów o względnie małej zawartości i jednorodnej dyspersji nanonapełniacza. Omówiono wpływ modyfikacji wielościennych nanorurek węglowych grupami hydroksylowymi lub aminowymi na strukturę fazową, właściwości termiczne, mechaniczne i barierowe osnowy poliamidowej oraz na stopień dyspersji nanocząstek w kompozycie. Wyniki badań potwierdziły wpływ dodatku 0,35 % mas. nanorurek na właściwości fizyczne PA12, przy czym korzyści wynikające z modyfikacji chemicznej obserwowano w wypadku temperatury przemian fazowych oraz wytrzymałości mechanicznej kompozytów, natomiast w odniesieniu do stabilności termooksydacyjnej i właściwości barierowych wpływ funkcjonalizacji był mniejszy.

Słowa kluczowe: kompozyty polimerowe, nanorurki węglowe, modyfikacja chemiczna, poliamid 12, polimeryzacja *in situ.*

Polymer composites containing carbon nanomaterials are still of great interest for research and business due to their high potential to improve polymer matrix performance at a very low filler content [1–4]. Since the first reports on the physical properties of carbon nanotubes (CNTs) in '90 s, they have been widely studied as the re-

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inforcing component. However, CNTs are incompatible with polymers, which affects weak wetting and adhesion between phases as well as unsatisfactory distribution of a nanofiller. CNTs surface functionalization with reactive groups helps to overcome these problems *via* improvement in polymer-CNT physical interactions or even chemical bonds between side groups and polymer chains [5–7].

There are several review papers that describe the non-covalent and covalent methods of carbon nanotube functionalization [8–10]. The former relies on adsorption of molecules through non-covalent interaction using surfactants, aromatics, and other reagents [11, 12]. The latter involves chemical reactions with various reagents in order to introduce chemical groups on the CNT surface. The most popular method is oxidation by nitric acid, sulfuric acid, or their mixtures [13, 14] to generate defects on sidewalls and tube tips. The introduction of oxygen-containing groups (mainly carboxy, hydroxy, and carbonyl) on the nanotube surface enhances their solubility in aqueous or organic solvents and reduces the van der Waals interactions between them [15, 16]. Oxidation may be also an intermediate stage, that allows for the subsequent fixation of more complex functional groups. CNTs with carboxy groups can be treated with thionyl chloride or oxalyl chloride for converting to acyl chloride groups, which then react with amines to form amide groups [17]. Other methods such as halogenation have been also used for CNTs functionalization [18, 19].

Polyamides constitute a large group of semi-crystalline thermoplastics suitable for many industrial sectors due to a wide variety of physical properties and easy processability. Polyamide 12 (PA12) is increasingly finding more applications as an engineering material to produce precisely molded parts for devices, fuel and brake systems, gas and oil transportation, medical instruments, sport equipment, and many others. It is because of its many interesting properties as compared to more popular polyamides 6 or 6.6, *i.e.*, lower water absorption resulting in higher electrical resistance and better dimensional stability; lower melting temperature, but higher elasticity at very low temperatures as well as very high impact strength, resistance to chemicals, and hydrolysis, low friction coefficient, *etc*. [20–22]. Considering polyamide/CNTs composites, PA12, however, is not extensively investigated as a matrix contrary to PA6 and 6.6, and in most papers composites are obtained by direct mixing of CNTs with commercially available polymers in melt [23–25].

The *in situ* polymerization has been proved to be an effective method of composite preparation with relatively small amounts and uniform distribution of a nanofiller [2, 4, 26, 27]. It brings a bulk composite materials, which can be processed and characterized in many ways to reflect the real properties of a potential product. Hänsch *et al.* [28] compared PA12/MWCNTs composites prepared by *in situ* polymerization *via* reactive extrusion with those obtained by direct mixing and the *in situ* composites surpassed melt-mixed materials in significantly better CNTs dispersion and improvement in mechanical performance.

In this study we report on polyamide 12 based composites prepared *via* ring-opening polymerization in the presence of carbon nanotubes (*in situ*). Commercially available multi-wall nanotubes (MWCNTs) were subjected to chlorination in the gas phase followed by treatment with sodium hydroxide or reaction with ammonia in the gas phase in order to induce on CNTs surface hydroxyl or amine groups, respectively. The effect of carbon nanotube functionalization on PA12 matrix is discussed in terms of their thermal, and physical properties as well as the state of CNTs dispersion.

EXPERIMENTAL PART

Materials

The monomer for composites synthesis (lauryl lactam, LL) and the molecular weight stabilizer (sebacic acid, SA) were purchased from Sigma Aldrich. Multi-wall carbon nanotubes used for a further modification were Nanocyl^{TM} NC7000 (Belgium) with the average diameter of 9.5 nm, the average length of 1.5 μm, and carbon purity > 90 %. For the CNTs modification chlorine 2.8 (GHC Handels GmbH), ammonia 3.8 (Messer, Poland) and sodium hydroxide pure p.a. (Chempur) were used.

Chemical modification of carbon nanotubes

The chemical modification of MWCNTs was carried out and two types of carbon material were obtained. First CNTs were subjected to the chlorination. A sample was placed in a quartz batch reactor. When the temperature increased to 400 °C, chlorine was introduced. After 2 h the gas was cut off and residues were pumped out within 0.5 h at the process temperature. Next obtained nanomaterial was boiled in distilled water, filtered and dried in a vacuum oven at 110 °C for 24 h. After chlorination the sample was placed in a flask and treated under reflux with 5 M sodium hydroxide solution. After 2 h the content of the flask was cooled and filtered. The resulting material was dried in vacuum at 110 °C for 24 h.

The second material also underwent chlorination under the same conditions as described above. When chlorination was completed, chlorine was replaced with ammonia and the process continued at 400 °C. After 1 h the gas was cut off and residues were pumped out within 0.5 h at process temperature. The obtained material was also boiled in distilled water, filtered and finally dried at the same conditions as previously. Carbon nanotubes after chlorination and hydroxylation are denoted as NC_OH, while after chlorination and reaction with ammonia as NC_NH_2.

Preparation of PA12 based composites

Polymer composites were obtained *via* a two-step polymerization of LL in the presence of CNTs, preceded by the water induced lactam ring opening. Before synthesis the required amount of CNTs was dispersed in LL/methanol solution at 120 °C, applying sonification and ultra-high speed stirring alternately for 0.5 h. After that LL was crystallized, and heated to evaporate alcohol.

The polymerization process was carried out in a steel reactor, where LL/MWCNTs dispersion, SA (0.67 wt %) and distilled water (20 g) were heated up to 280 °C. The quantities of reagents were calculated on the weight average molecular weight of the polymer matrix as 30 000 g/mol. The first stage of synthesis was carried out at *ca.* 260 °C under the pressure of 3.4 MPa for 5 h. After that time the pressure was reduced removing water and the synthesis was continued in the temperature range of 260–280 °C under the nitrogen flow up to an appropriate value of the stirrer torque was reached. A composite in melt was then extracted from the reactor under nitrogen pressure. All investigated materials were granulated, methanol purified through Soxhlet extraction, dried overnight, and injection molded into dog-bone shaped pieces according to ISO 37:2005 type 3.

Composites containing 0.35 wt % of both unmodified (NC) and chemically modified MWCNTs (NC_OH and NC_NH_2) are discussed in this study.

Methods of testing

A qualitative assess of the state of MWCNTs dispersion in the matrix was done using scanning (SEM) and high-resolution transmission (HRTEM-FEI) electron microcopies (SU-70 Hitachi and Tecnai F20, respectively). The composite samples for SEM were cryofractured and sputtered with a gold, whilst TEM analysis was done on very thin cuts prepared with a ultramicrotome.

The characteristics of carbon nanotubes using Raman spectroscopy were obtained from Renishaw InVia Raman Microscope spectrometer by excitation laser of 785 nm (1.58 eV).

The weight average molecular weight $\overline{M}_w$ of the composite polymer matrices were calculated based on the values of intrinsic viscosities [η] according to the Mark-Houwink equation with $K = 4.6 \cdot 10^{-4}$ and $\alpha = 0.75$ [23]. The viscosity tests were performed on a capillary Ubbelohde viscometer (type Ic, $K = 0.03294$) at 25 °C. Nanocomposite samples were first dissolved in *m*-cresol (99 %, Sigma Aldrich) in the concentration of 5 g/dm^3, and then filtered to remove carbon nanotubes from the solution.

A differential scanning calorimeter (DSC, TA Instruments Q 100) was employed to characterize thermal transitions and the crystalline structure of polymer matrix. The samples were analyzed in heating – cooling – heating cycles in the temperature range of -30 to 220 °C with the standard heating rate of 10 °C/min. The melting (T_m), crystallization (T_c), and glass transition (T_g) temperatures were determined from the exothermic and endothermic peaks at DSC thermograms.

The mass degree of crystallinity (X_c) was calculated as the ratio of composite melting enthalpy (ΔH_m) and the enthalpy of 100 % crystalline PA12 ($\Delta H_m^o = 209.2$ J/g [22]).

The thermooxidative stability of composites was analyzed using thermogravimetric analysis (TGA, TA Instruments SDT Q600). The measurements were carried out with the heating rate of 10 °C/min up to 900 °C in the atmosphere of air.

Tensile tests were performed on a universal testing machine (Instron 5566) equipped with an optical extensometer. The injection molded samples were stretched with the speed of 20 mm/min using 5 kN force transducer at the room temperature and minimum of six tests were made for each material. The tensile properties of composite materials were determined according to ISO 527-1, -2:2012.

The absorption of composite materials in cold and boiling water was determined according to ISO 62:2008 using injection molded samples. Before measurements the samples were dried at 80 °C within 24 h to a constant mass. Ten measurements were made for one material. Water vapor permeability was measured using a moisture analyzer (MAC 50, RADWAG, Poland) equipped with Sampler 2000. Water vapor permeability is defined as the quantity of water (expressed in %), that permeates through a sample (thin film) in defined conditions of temperature and time, referring to loss of water mass, that evaporated from a sampler without any sample ("0" test). The measurements were carried out at 40 °C within the time of 10 h for one sample.

RESULTS AND DISCUSSION

Carbon nanotubes functionalization

The effect of MWCNTs chemical modification is presented in Fig. 1. The Raman spectra of both raw and modified carbon nanotubes indicates two typical graphite bands – D and G as well as the intensity ratios of these bands (I_D/I_G), known as a ratio of amorphous/disordered carbon (*sp*^{3}) relative to graphitic carbon (*sp*^{2}). The G band is the first order Raman mode, which appears around

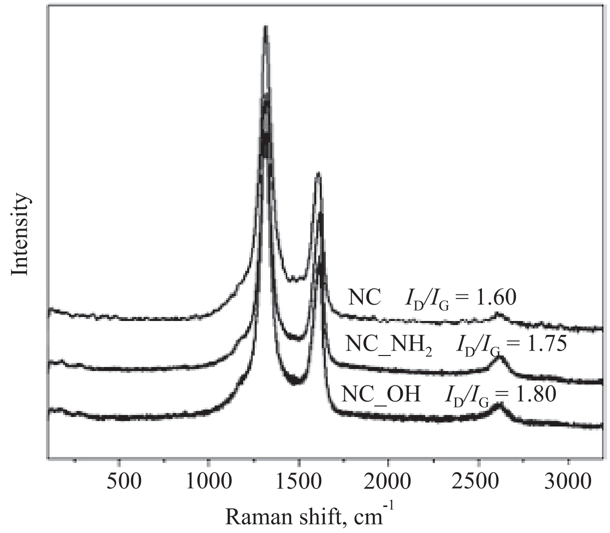

Fig. 1. The Raman spectra of MWCNTs before and after chemical treatment

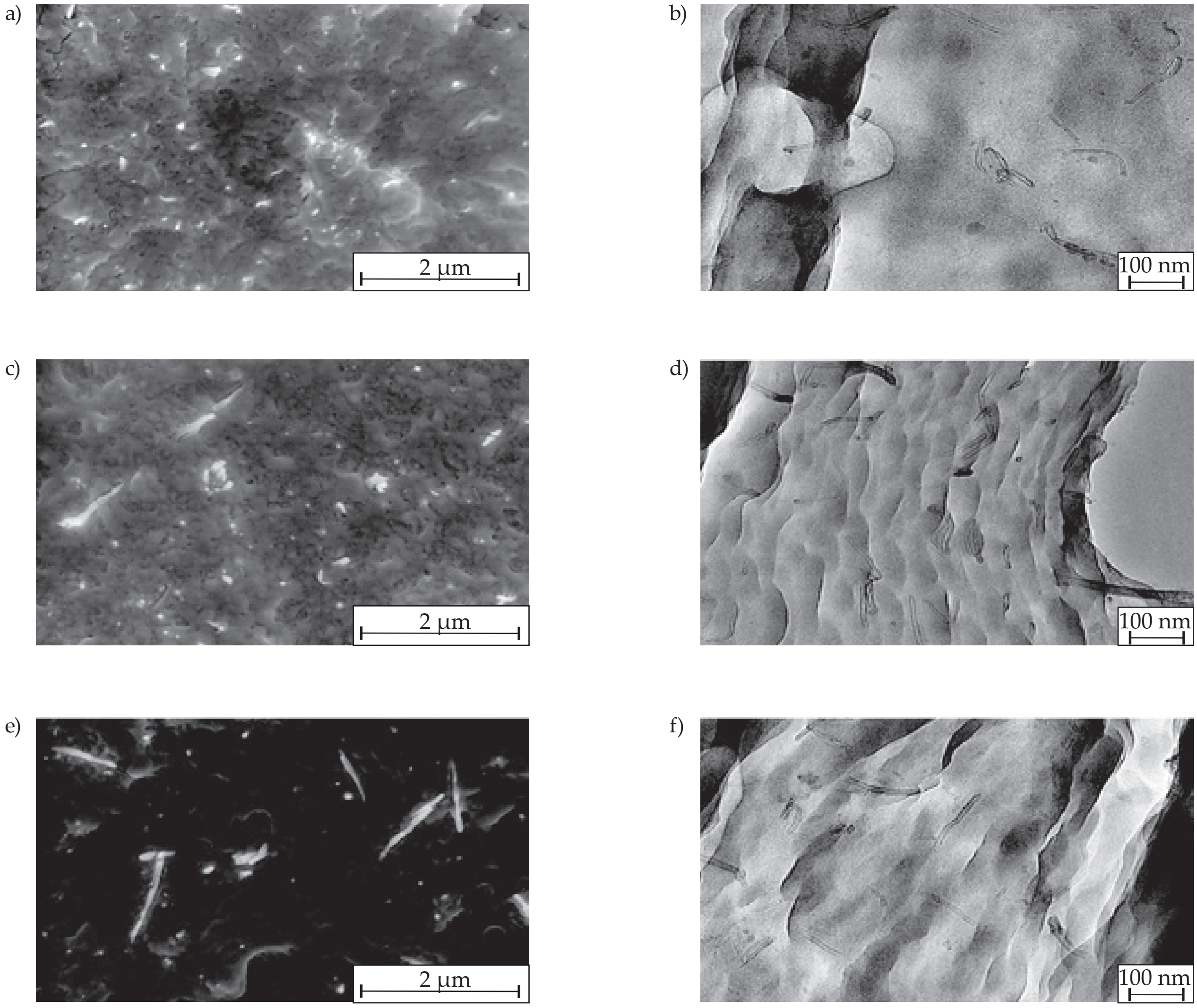

Fig. 2. SEM (left) and TEM (right) micrographs of PA12 composite fractures containing: a), b) NC, c), d) NC_OH, e), f) NC_NH_2 nanotubes

1580–1600 cm^{-1} and corresponds to vibrations of sp^2 carbon atoms. The D band (disorder induced) comes from the second order scattering process which occurs around 1280–1350 cm^{-1} and provides information on structural defects and the presence of amorphous carbon in the sample. In functionalization studies the higher I_D/I_G means the higher extent of covalent functionalization. As expected, the I_D/I_G of functionalized samples increases from 1.6 for pristine to 1.75 and 1.8 for modified nanotubes, what suggests, that some moieties are covalently introduced onto the surface of MWCNTs. Similar results were observed by other researchers for diamine functionalized CNTs by the microwave method [29] or using water assisted chemical vapor deposition and nitric acid [30].

The effect of the *in situ* polymerization

The *in situ* polymerization for polymer composites preparation, previously applied by our group to thermoplastic polyesters and their copolymers, resulted in a satisfied state of dispersion [2, 4, 27, 31]. The same can be concluded about PA12 composites. SEM and TEM micrographs of composite fractures in Fig. 2 confirm, that the applied procedure of dispergation results in a uniform distribution of CNTs nanotubes are mostly separated, which is particularly seen at NC and NC_NH_2 micrographs, whereas in the case of NC_OH composites the bundles of two/three nanotubes are also observed. Moreover, CNTs are only slightly entangled or bent, which does not decrease their aspect ratio significantly. Some TEM micrographs also depict single nanofibres practically fully covered by the polymer, what confirms good wettability of CNTs by the polymer and possible adhesion between composite ingredients regardless of chemical modification. However the TEM micrographs prove also, that for such a small CNTs concentration (*i.e.* max. 0.35 wt %) and their uniform distribution the possibility of creating conducting paths for electric charges is rather low. Indeed, the investigated materials are not conductive, and the measurements of electrical conductivity are not included in this paper.

T a b l e 1. Thermal properties of PA12/CNTs composites based on DSC and TGA analysis

Sample	$\overline{M}_w \cdot 10^3$ g/mol	T_g °C	T_m °C	T_{conset} °C	T_{cmax} °C	X_c %	$T_{deg\,(5\,\%)}$ °C
PA12 neat	29.3 ± 0.2	49	176	155	151	26	337
PA12/NC	29.9 ± 0.2	54	180	163	155	26	402
PA12/NC_OH	28.8 ± 0.2	55	179	166	156	26	395
$PA12/NC\_NH_2$	30.0 ± 0.2	55	178	167	159	26	398

The standard deviation for DSC and TGA measurements ± 1 °C.

One of the problems, reported in the case of *in situ* composites, is a drop in molar mass of the matrix [27, 31] decreasing the polymer chain length. The weight average molecular weight $\overline{M}_w$ values for composites matrices, collected in Table 1, are very close to each other and practically achieve the theoretical value of 30 000. Slight fluctuations of the values may result from filtration process, when macromolecules, entangled or absorbed with CNTs, could stay at a filtration membrane decreasing the concentration of polymer solution. Presented results indicate a high degree of substrate conversion as well as that the presence of carbon nanotubes modified or not in the polymerization environment does not influence the reaction process.

The thermal properties and crystalline structure of composites

For semicrystalline polymers even a small amount of a nanofiller may affect their thermal transitions as well as crystalline structure, and in consequence the composites performance [4, 27, 32]. The DSC analysis, applied to investigate the effect of CNTs functionalization on glass transition (T_g), melting (T_m) and crystallization (T_c) temperatures as well as crystallinity degree (X_c), is presented on Fig. 3. The results summarized in Table 1 clearly show, that for all materials the changes in characteristic temperatures are observed. The T_g is higher by 5–6 °C and T_m by 2–4 °C as compared to a neat polymer, whilst there is practically no change in crystallinity degrees of composites. It suggests that an increase of temperature is only the result of CNTs-polymer chain physical interactions, which restrict molecular mobility in the glass transition region, and the existing crystalline structure is less defected or more uniform in the presence of nanofillers. It is even more pronounced, when analyzing the melting peak of neat PA12 with longer left shoulder suggesting multiple endothermal effect, not observed for composites. It may result from different manners of crystallization process proceeding in the presence (heterogeneous) and without CNTs (homogeneous) in the melt, or more precisely – different rates of nucleation and crystal growth [33]. For homogeneous crystallization of neat PA12, the highest rate of nucleation may be reached at lower temperature than the temperature of the highest crystal growth. In consequence, between and on the primary formed lamellas, smaller and more defected crystals may grow. When then heated from the solid, smaller crystals may partly melt, then recrystallize on big lamellas, and finally the primary and more perfect crystals melt. It brings an effect of multipeak. In the case of composites, the CNTs promote nucleation in higher temperature. The crystallization peaks are shifted by 7–8 °C for NC and 11–12 °C for modified if compared to the reference. In consequence, the temperature window between nucleation and crystal growth is reduced, and the crystalline structure is more uniform as well as composites endotherms. The CNTs nucleation effect can be considered as an advantage, as it leads to shortens the processing cycle in, *e.g.*, injection molding.

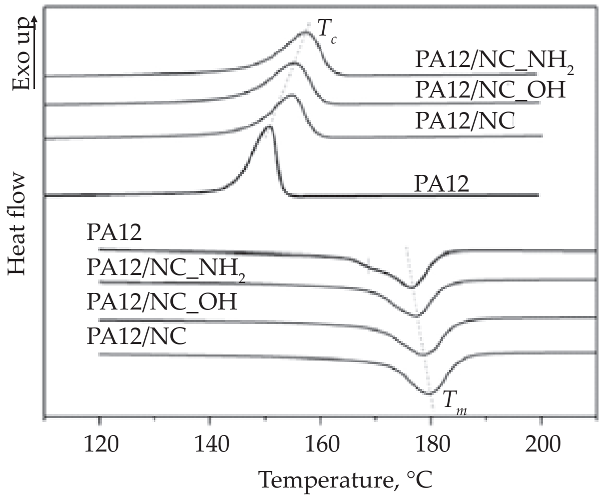

Fig. 3. DSC thermograms for PA12 and PA12/MWCNTs composites during cooling and 2nd heating

The further evidence for macromolecules-nanofillers interactions is the thermooxidative stability of PA composites showed in Fig. 4. In general the decomposition of polyamides proceeds in two steps: depolymerization at chain endgroups, and chain cutting by forming unsaturated nitriles and alkenes, accelerated in the presence of oxygen [34]. In the case of the investigated materials studied in air, the two steps in decomposition were also detected, and the significant improvement of stability in the presence of CNTs is observed. From the values in Table 1 the relatively small content of CNTs shifts the 5 % decomposition temperature to even 65 °C. It can be attributed not only to enhanced molecular interactions, but

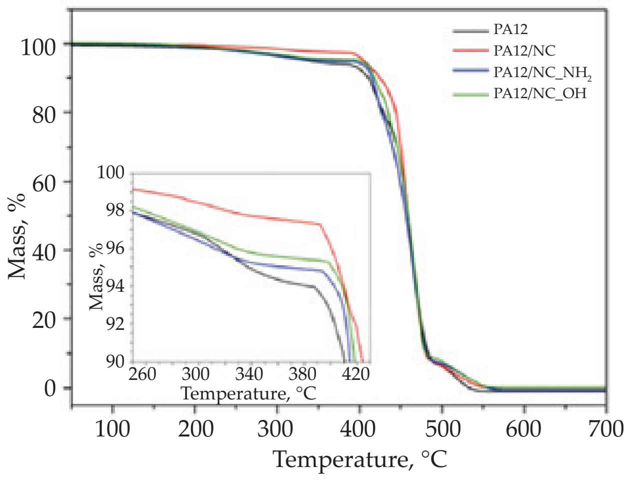

Fig. 4. Thermooxidative stability of PA12 composites containing 0.35 wt % of MWCNTs

also to the effectiveness of nanotubes in capturing free radicals, responsible for polymer degradation. Slightly lower values detected for modified CNTs may result from a decrease in stability of nanotube structures due to the chemical treatment.

The mechanical performance of PA12/MWCNTs

The tensile stress-strain characteristics of investigated materials, presented in Fig. 5a, are typical for polyamides with a clear yield point. The yield stress (σ_y), stress at break (σ_b), the strain at break (ε_b) as well as Young's modulus (E) were determined and are shown in Table 2.

It is clearly seen, that all composites reveal an improvement in mechanical strength if compared to neat PA12, and this effect is better for modified nanotubes. An increase of stress is observed at the yield and during further deformation. The stress at break values, as well as elongation at break, are practically at the same level as neat PA12, only more scattered and statistical. The best results were achieved for oxidized nanotubes with the maximum increase in σ_y of *ca.* 20 % and the stress at 100 % strain ($\sigma_{100\,\%}$) of *ca.* 25 %. For NC_NH$_2$ composites the increase in σ_y of 16 % and in $\sigma_{100\,\%}$ of *ca.* 24 % was recorded, while raw nanotubes induced the increase of 9 % and 13 % in σ_y and $\sigma_{100\,\%}$, respectively. Even a more pronounced effect of CNTs modification is observed for *E* modulus of composites: the increase of *ca.* 18 % for NC, *ca.* 33 % for NC_OH and 26 % for NC_NH$_2$. These results seem to be promising if we consider the relatively low CNTs content. However it is also more likely, that the CNTs modification induces rather an improvement in physical van der Waals or hydrogen interactions than a possible chemical bonding between the composite two phases. It is also confirmed by the SEM micrograph of the composite sample after test (Fig. 5b), which reveals many nanotube bare tips partly pulled out from the matrix. To conclude the enhancement in mechanical performance may result from both CNTs/polymer physical interactions, and more uniform crystalline structure of PA composites, even if no change in crystallinity degree of composites was detected.

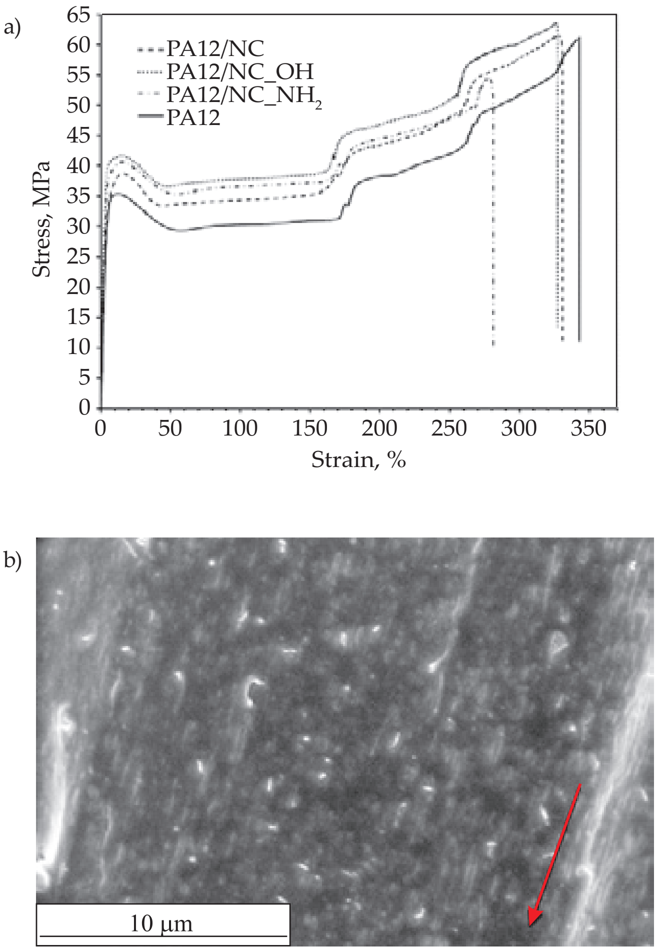

Fig. 5. a) The representative tensile stress-strain characteristics of PA12 based composites, b) the SEM micrograph of composite fracture after tensile tests with an arrow indicating the direction of deformation

Table 2. Mechanical properties of neat PA12 and PA12 based composites

Sample	σ_y MPa	σ_b MPa	$\sigma_{100\,\%}$ MPa	ε_b %	*E* MPa
PA12 neat	35.5 ± 0.16	60.7 ± 4.7	30.4 ± 0.26	347 ± 21.0	878 ± 50
PA12/NC	38.7 ± 0.19	61.8 ± 2.7	34.3 ± 0.21	326 ± 13.0	1036 ± 104
PA12/NC_OH	42.8 ± 0.29	62.4 ± 3.0	37.9 ± 0.28	327 ± 3.4	1170 ± 32
PA12/NC_NH$_2$	41.3 ± 0.31	53.6 ± 0.8	37.6 ± 0.21	283 ± 6.2	1110 ± 50

The values are average for six tests and their standard deviations.

The water absorption and vapor permeability of PA composites

Polyamides are known as hydroscopic materials, and their physical properties are strongly related to an amount of moisture absorbed. It was also reported that nanoparticles in a composite may make a barrier against gas/liquid molecule transport, inhibiting their diffusion into and through the polymer [2]. For further characteristics of PA12/MWCNTs composites, the absorption in cold and hot water as well as water vapor permeability were investigated (Table 3). PA12 is characterized by the lowest tendency for water intromission among polyamide family, nevertheless the obtain results bring a clear evidence, that even a small content of CNTs reduces this tendency even more. One can say, that water absorption is dependent on polymer structure (crystalline or amorphous). Although the DSC analysis proved, that the crystallinity degree of composites is at the same level as neat PA12, their more uniform structure may prevent the water molecules penetration into the composite sample. Moreover in both cases (cold and hot water) the lowest values were obtained for NC composites, thus it cannot be excluded, that the hydrophobic nature of carbon nanotubes plays a role, whilst polar groups attached to CNTs surfaces in NC_OH and NC_NH$_2$ attract water molecules, but restrict their further diffusion. The results of vapor permittivity, made on thin films, also indicate an improvement in the barrier effect. The maximum decrease in permittivity is by *ca.* 38 % as compared to neat PA12, regardless of nanotube modification, and it seems to be interesting particularly for packaging applications.

Table 3. The water absorption and vapor permittivity of PA12/MWCNTs composites

Sample	Absorption, %		Water vapor permeability/ film thickness %/μm
	Cold water	Hot water	
PA12 neat	0.39 ± 0.05	0.77 ± 0.05	1.89 ± 0.05/130
PA12/NC	0.26 ± 0.04	0.63 ± 0.02	1.18 ± 0.05/120
PA12/NC_OH	0.29 ± 0.01	0.68 ± 0.02	1.19 ± 0.05/120
PA12/NC_NH$_2$	0.28 ± 0.01	0.65 ± 0.02	1.19 ± 0.05/130

CONCLUSIONS

Polyamide 12 based composites prepared *via in situ* polymerization in the presence of carbon nanotubes were prepared and characterized. This method allowed to obtain bulk composite materials with relatively small amount of CNTs retaining processability typical for a neat polymer. In order to improve polymer-CNTs physical interactions, commercial multi-wall carbon nanotubes were subjected to chlorination followed by a treatment with sodium hydroxide or a reaction with ammonia to induce hydroxyl or amine groups, respectively. The values of $\overline{M}_w$ of the composite matrix confirmed, that the presence of CNTs – modified or not – in the polymerization environment did not influence the reactions, and the polymer matrix did not suffer a drop in molecular weight. The SEM and TEM analysis affirmed likewise, that the applied procedure of composite preparation resulted in an uniform distribution of CNTs. Obtained results proved, that in general the presence of carbon nanotubes affects the physical and thermal properties of PA12, and the chemical treatment of CNTs brings some benefits to polymer-nanofiller interactions if compared to those untreated. The advantage gained from the chemical modification is observed mainly in changes of phase transition temperatures and enhancement of composite mechanical performance, particularly their stiffness and yield stress. Whilst in the case of thermooxidative stability and water absorption the CNTs chemical modification is less pronounced. The level of improvement, promising if only 0.35 wt % content is considered, leads to conclusion, that mainly physical van der Waals or hydrogen interactions dominate between composite constituents. On the other hand one can expect, that for the 0.35 wt % of CNTs content in the reaction mixture the concentration of their side reactive groups is rather small, what also reduces the probability of chemical reactions between growing polymer chains and nanofiller during polymerization.

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