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EFFECT OF FUNCTIONALIZED CARBON NANOTUBES ON PROPERTIES OF HOT MELT COPOLYAMIDE

Hot melt copolyamide was mixed by the melt-blending process with 7 wt.% non-functionalized multi-walled carbon nanotubes and with amine modified multi-walled carbon nanotubes. The main goal of this work was to analyze the effect of functionalization of the properties of hot melt copolyamide. The rheological properties of the nanocomposites were examined by the dynamic oscillatory test using an oscillatory rheometer. Macrodispersion of both types of multi-walled carbon nanotubes within the copolyamide matrix was examined qualitatively by a light microscope and quantitatively using ImageJ Software. The thermal stability and characteristic temperatures such as the melting point and crystallization temperature were determined by thermogravimetric analysis and differential scanning calorimetry, respectively. It was found that the addition of 7 wt.% functionalized multi-walled carbon nanotubes increases the viscosity of copolyamide but to a lesser extent than in the case of non-functionalized multi-walled carbon nanotubes. Moreover, mixing copolyamide with amine functionalized multi-walled carbon nanotubes resulted in larger agglomerates which resulted in worse thermal stability than for non-modified multi-walled carbon nanotubes. Finally, the electrical conductivity measured by dielectric spectroscopy was lower in the case of nanocomposites with amine-functionalized multi-walled carbon nanotubes which indicates that the affinity to copolyamide was not improved by the amine groups.

Keywords: copolyamide, carbon nanotubes, dispersion, electrical conductivity

WPLYW FUNKCJONALIZOWANYCH NANORUREK WĘGLOWYCH NA WŁAŚCIWOŚCI TERMOTOPLIWEGO KOPOLIAMIDU

Opisano nanokompozyty wytworzone techniką wytłaczania z kopolimidu należącego do grupy klejów termoplastycznych oraz wielościennych nanorurek węglowych. Zastosowano dwa typy nanorurek węglowych - niemodyfikowane oraz modyfikowane grupami aminowymi. Głównym celem wykonanej pracy była analiza wpływu zastosowania funkcjonalizowanych nanorurek węglowych na właściwości wybranego kopoliamidu, szczególnie na jego właściwości elektryczne i porównanie z nanorurkami niemodyfikowanymi. Badania właściwości reologicznych czystego kopoliamidu oraz obu typów nanokompozytów wykonano z użyciem reometru oscylacyjnego. Makrodyspersja obu typów wielościennych nanorurek węglowych w osnowie kopoliamidu została zbadana jakościowo za pomocą mikroskopu prześwietleniowego oraz ilościowo przy użyciu oprogramowania ImageJ. Stabilność termiczną oraz temperaturę topnienia i krystalizacji wyznaczono, odpowiednio, z analizy termogravimetrycznej i skaningowej kalometrii różnicowej. Stwierdzono, że dodatek funkcjonalizowanych wielościennych nanorurek węglowych zwiększa lepkość kopoliamidu, ale w mniejszym stopniu niż w przypadku niefunkcjonalizowanych wielościennych nanorurek węglowych. Nanokompozyty domieszkowane wielościennymi nanorurkami węglowymi modyfikowanymi grupami aminowymi posiadały aglomeraty o większych średnicach, co skutkowało gorszą stabilnością termiczną i niższą temperaturą topnienia niż w przypadku nanokompozytów z niefunkcjonalizowanymi nanorurkami węglowymi. Ponadto przewodnictwo elektryczne nanokompozytów z nanorurkami węglowymi funkcjonalizowanymi grupami aminowymi było niższe niż w przypadku nanokompozytów z nanorurkami bez grup funkcyjnych. Wskazuje to na fakt, że użycie funkcjonalizowanych nanorurek węglowych nie poprawia oddziaływań kopoliamid-nanorurki węglowe, a tym samym właściwości końcowych nanokompozytów.

Słowa kluczowe: kopoliamid, nanorurki węglowe, dyspersja, wytłaczanie, właściwości elektryczne

INTRODUCTION

For many years, nanocomposites with carbon nanotubes (CNTs) have been studied owing to their extraordinary properties and possible applications routes. Till now most thermoset and thermoplastic polymers have been reinforced with all types of CNTs, i.e. single-walled carbon nanotubes (SWCNTs), double-walled

carbon nanotubes (DWCNTs) and preferably with multi-walled carbon nanotubes (MWCNTs) [1]. It has been observed that to use the potential of CNTs in relation to the properties of the final nanocomposites, it is necessary to achieve well-dispersed CNTs in the polymer matrix. The high tendency of CNTs to form

agglomerates can be overcome by modification of their structure. In order to improve the interfacial interactions between the polymer and nanotubes it is necessary to damage the chemically stable C-C bond in the tubes by surface modification. Hence, the covalent linkage of functional moieties such as amino, alkyl, carboxylic or hydroxyl groups can increase the affinity of the nanotubes to the polymer macromolecules [2, 3]. Nevertheless, the surface modification of CNTs can help to achieve better dispersion and distribution in the polymer matrix. In addition, the presence of linked groups on the CNT surface leads to a decrease in their length and may deteriorate the electrical properties of nanocomposites [4].

Hot melts belong to the group of thermoplastic polymers which are rarely studied as a matrix to disperse CNTs. These polymeric materials consist of a few main components such as a polymer base, tackifier, wax and other additives. As the polymer base, styrene-butadiene, polyurethanes, ethylene-propylene, butyl rubber, polyolefins, polyamides, or copolymers can be used. The tackifier is the most abundant (40%) and is responsible for the sticky properties of hot melts and control of their viscosity [5, 6]. In this work, the main polymer in hot melts is random copolyamide (coPA) consisting of PA6 and PA66 segments and other components not specified by the supplier. Owing to this, hot melt thermoplastics are characterized by lower melting points than polyamides. Furthermore, as in a typical copolymer, the crystallization process occurs in a different way than in homopolymers and will be additionally disturbed by the presence of other components [7, 8].

Hot melt coPAs are able to form fibres and therefore they are used in manufacturing nonwoven fabrics. Such materials have many applications in the agriculture, automotive, hygiene, medical and building sectors as well as in the composites industry. Due to their high compatibility with epoxy resin, thermoplastic nonwovens are applied as interlayers in carbon fibre reinforced polymers (CFRP) to increase their fracture toughness and prevent delamination or cracks [9, 10]. Typical thermoplastic polymers used in technical nonwovens for composites includes polysulfone, polyether-sulfone, polyetherimide, polyphenylene sulfide, polyetheretherketone and polyamides [11, 12].

Looking at the current trends in the field of composite materials, it is highly desired to search for a way to provide textile materials with a new functionality such as electrical conductivity [13]. Due to their light weight, high flexibility, good mechanical performance and presence of CNTs or graphene, thermoplastic textile materials can be a good candidate to be placed as interlayers in CFRP resulting in a new functionality. Therefore, the main goal of this work is to show the effect of two types of MWCNTs on the properties of thermoplastic coPA which could be used further as an initial material to produce nonwoven fabrics for CFRP.

MATERIALS AND METHODS

Hot melt coPA with the trade name Griltech®1330A (EMS Griltech, Switzerland) was selected as the polymer matrix. Its melting point lies between 125–135°C, melt viscosity 1200 Pa·s (160°C/2.16 kg) and the melt volume rate equals 9 (160°C/2.16 kg). Two types of MWCNTs synthesized via catalytic carbon vapor deposition (CCVD), trade name NC7000 from Nanocyl, Belgium were used. The first ones are non-modified MWCNTs and the second ones are amine modified MWCNTs (MWCNT-NH₂). Their average diameter was 9.5 nm, length 1.5 μm and purity 90%. Melt blending of coPA pellets and powder 7 wt.% MWCNTs and 7 wt.% MWCNT-NH₂ was performed by the industrial twin-screw extrusion method by Nanocyl. For both nanocomposites, the extrusion temperature was 200°C and the rotational speed was 200 rpm. All the materials were dried under vacuum at 60°C for 12 h. The nanocomposite pellets were analyzed by their macrodispersion, understood as the dispersion and distribution of CNT agglomerates, with a transmitted light microscope (Biolar-PL, PZO Poland). For this, slices with a thickness of 2–3 μm were cut directly from the pellets using an ultramicrotome (EM UC6, Leica, Austria). For the quantitative analysis of the agglomerates in the nanocomposites, image software (ImageJ) was applied. The number of agglomerates expressed by the area ratio (A_A) was calculated by dividing the area of all agglomerates by the total working area. For each nanocomposite, a minimum of 7 images was analyzed and agglomerates with an area below 1 μm were excluded from the calculation.

The cross sections of the nanocomposites were analyzed by keeping the pellets in nitrogen atmosphere for 30 minutes and then cutting the slides with a knife. Microscopic observations were performed using a SU-70 scanning electron microscope (Hitachi, Japan) to analyze the state of the MWCNTs and MWCNT-NH₂.

Rheological property tests were conducted in the parallel plate geometry mode using an ARES rheometer (Rheometric Scientific Inc., TA Instruments, USA) by a dynamic oscillatory stress-controlled rotational test. The strain value was selected as 1% from the amplitude sweep test, the temperature was 200°C and frequency from 0.1 to 100 Hz. For rheological analysis, round samples with a thickness of 2 mm and diameter of 1.5 mm were prepared directly from the pellets by injection molding using the HAAKE™ MiniJet Pro Piston Injection Molding System (ThermoScientific, Germany).

The effect of MWCNTs and MWCNT-NH₂ on the thermal stability of coPA was examined by thermogravimetric analysis (TGA) using a TGA Q500 (TA Instruments, USA). Pellets of 10 mg were placed in an aluminum crucible and heated from 0 to 1000°C in nitrogen atmosphere at the heating rate of 10°C/min and flow rates of 10 ml/min and 90 ml/min. From the ob-

tained curves, the degradation temperatures of 2% ($T_{2\%}$) and 5% ($T_{5\%}$) weight loss, and maximum peak (T_c) were determined.

The characteristic temperatures of glass transition (T_g) and melting point (T_m) were determined by performing differential scanning calorimetry (DSC) using a Q1000 differential scanning calorimeter (TA Instruments). Pellets with a weight of 8.5 ± 0.2 mg were placed in an aluminum hermetic pan and first heated from -60 to 250°C , then cooled to 0°C , and again heated to 250°C at a scan rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Due to the lack of data on the enthalpy of fusion of 100% crystalline coPA, the crystallinity content was not calculated. The electrical properties of all the materials were measured by broadband dielectric spectroscopy using an LCR HP4284A meter (Keysight Technologies, USA) at room temperature. Samples in the form of pellets were covered with silver paste for better contact with the electrodes. The test under alternating current (AC) was conducted with a 1 V electric field. The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' is the permittivity and ε'' is the dielectric loss, was measured as a function of frequency from 10^1 Hz to 10^6 Hz while electrical conductivity σ_{AC} was calculated from the equation $\sigma = 2\pi\nu\varepsilon_0\varepsilon''$, where ε_0 is the vacuum permittivity, $\omega = 2\pi\nu$ and ν is the measurement frequency.

RESULTS AND DISCUSSION

The average agglomerate diameters versus the number of agglomerates and sample images from the light microscope are presented in Figure 1. In both types of nanocomposites, the MWCNT and MWCNT-NH₂ agglomerates have similar diameters below $50\mu\text{m}$ with slightly lower values for the non-modified MWCNTs, about $30\mu\text{m}$. It can be stated that the applied extrusion process destroyed the primary agglomerates of the MWCNTs and MWCNT-NH₂ to uniform-size secondary agglomerates. In the case of coPA+7 wt.% MWCNTs, most of the agglomerates have diameters below $10\mu\text{m}$, while for coPA+7 wt.% MWCNT-NH₂ the agglomerates are of various sizes.

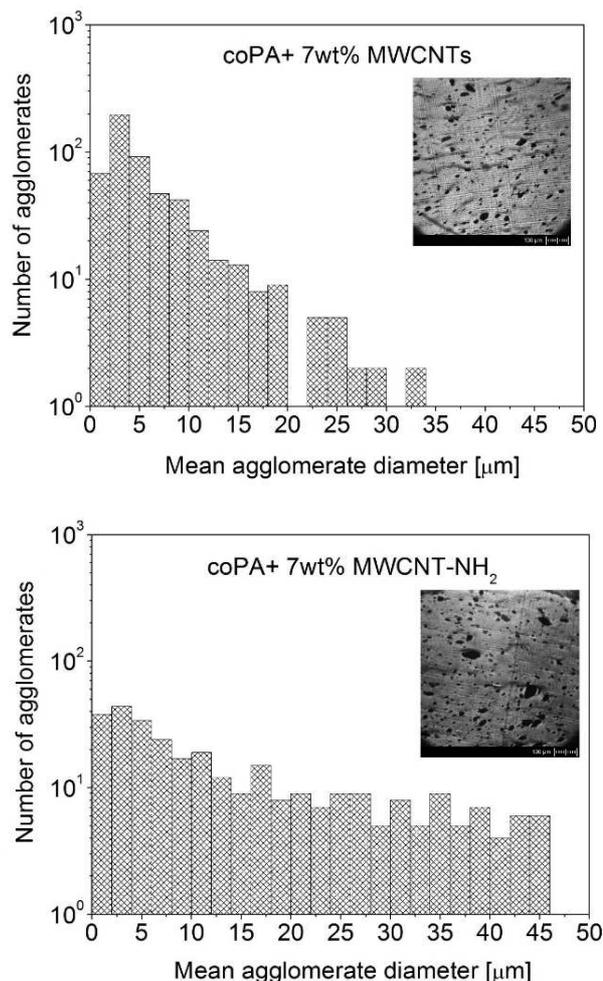


Fig. 1. Dependence between agglomerate diameter and number of agglomerates in coPA mixed with 7 wt.% non-modified and amine functionalized MWCNTs. Inserts are images from light microscope showing MWCNT/MWCNT-NH₂ agglomerates as black dots

Rys. 1. Zależność pomiędzy średnicą a ilością aglomeratów w coPA domieszkowanym 7% wag. niemodyfikowanych i modyfikowanych MWCNTs. Na rysunku umieszczono zdjęcia z mikroskopu prześwietleniowego pokazujące aglomeraty MWCNT/MWCNT-NH₂ jako czarne kropki

The MWCNT and MWCNT-NH₂ agglomerates in coPA were also observed on the cross sections of the nanocomposite pellets using SEM (Fig. 2).

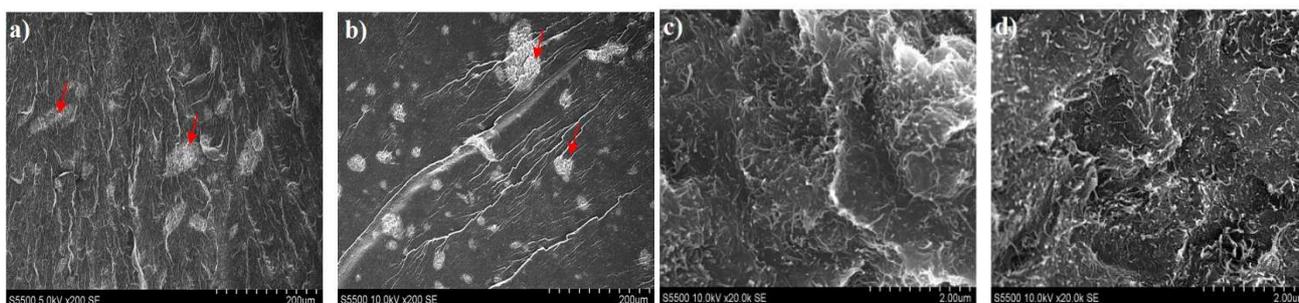


Fig. 2. Cross sections of nanocomposite pellets of coPA+7 wt.% MWCNTs (a, c) and coPA+7 wt.% MWCNT-NH₂ (b, d). Agglomerates are marked with red arrows

Rys. 2. Przelomy z granulatów nanokompozytów coPA+7% wag. MWCNTs (a,c) oraz coPA+7% wag. MWCNT-NH₂ (b, d). Aglomeraty zaznaczone czerwonymi strzałkami

The white dots dispersed in the polymer matrix which indicate the MWCNT and MWCNT-NH₂ agglomerates can be easily seen (Fig. 2 a, b). Some of the nanotubes are well-dispersed in coPA and occur in a curly state as visible in Figure 2c, d. It can be stated that the concentration of 7 wt.% MWCNTs and MWCNT-NH₂ is high enough to create shear stress during extrusion causing breakdown of the primary agglomerates and in effect uniform dispersion of secondary agglomerates in the coPA matrix.

Rheological properties

The effect of MWCNT and MWCNT-NH₂ on the rheological properties of coPA is presented in Figure 3. The complex viscosity of unfilled coPA is around 10³ Pa·s and at low frequencies it exhibits the characteristic Newtonian viscosity plateau. In the presence of non-functionalized MWCNTs the viscosity increased three times and for the amine-functionalized MWCNTs, two times. The character of both curves is typical for non-Newtonian liquids since the viscosity decreases when the frequency increases [14, 15]. Moreover, both nanocomposite systems are above the rheological percolation threshold, which was found to be between 1–2 wt.% MWCNTs for the analyzed coPA [16]. Also visible is a jump in loss modulus G'' (Fig. 3b) and in storage modulus G' (Fig. 3c) after the addition of 7 wt.% nanotubes, whereas for the non-functionalized MWCNTs the increase is higher. Moreover, the loss modulus shows lower values than the storage modulus, which is observed for many thermoplastic nanocomposites doped with CNTs [17]. The rheological properties of the nanocomposites can give information about the interactions of polymer-CNTs as well as the filler dispersion and its orientation [18]. Generally, the higher the rheological properties (complex viscosity and modulus), the stronger the interaction between the polymer and CNTs. In the case of coPA it

is seen that the complex viscosity as well as both moduli are lower for coPA+7 wt.% MWCNT-NH₂ which means that improvement in the interactions between the coPA macromolecules and MWCNTs was not achieved by functionalization of their surface with the amine groups. Similar results were obtained for PA6 nanocomposites prepared with 2 wt.% non- and amine functionalized MWCNTs also using the melt blending process [19].

Electrical properties

Dielectric spectroscopy was applied to determine the σ_{AC} within the frequency range from 10¹–10⁶ Hz, as shown in Figure 4. The real permittivity part does not achieve the plateau for low frequency and it is higher for coPA+7 wt.% MWCNTs. For the coPA+7 wt.% MWCNT-NH₂ nanocomposites the permittivity is lower than for coPA with MWCNTs but is still two times higher than for neat coPA. The permittivity decreases slightly within the applied frequency but the curve for neat coPA has a gentler character. From the σ_{AC} plot it is seen that at frequencies below 10² Hz, there is a plateau which confirms the percolated structure in the studied nanocomposites. It is observed that an addition of 7 wt.% MWCNT-NH₂ did not result in higher electrical conductivity than that obtained for the non-functionalized MWCNTs. In the presence of 7 wt.% MWCNT-NH₂ the σ_{AC} is increased three times from 10⁻⁸ to 10⁻⁵ S/m while for 7 wt.% MWCNT up to 10⁻² S/m. According to the rheological properties, the higher interactions between the polymer and MWCNTs which affect the higher electrical properties were obtained by the non-modified MWCNTs. These results confirm that functionalization of the surface of CNTs decreases the length of individual tubes and causes surface defects leading to a decrease in the electrical properties of the final nanocomposites.

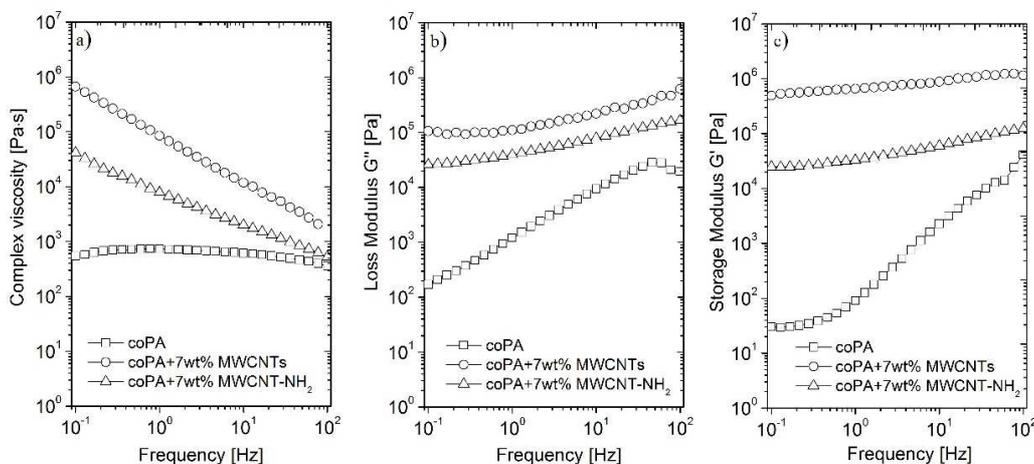


Fig. 3. Log-log plots of: a) complex viscosity, b) loss modulus and c) storage modulus versus frequency for coPA doped with 7 wt.% MWCNTs and 7 wt.% MWCNT-NH₂

Rys. 3. Wykres logarytmiczny: a) lepkości, b) modułu stratności i c) modułu zachowawczego w zależności od częstotliwości dla coPA domieszkowanego 7% wag. MWCNTs i 7% wag. MWCNT-NH₂

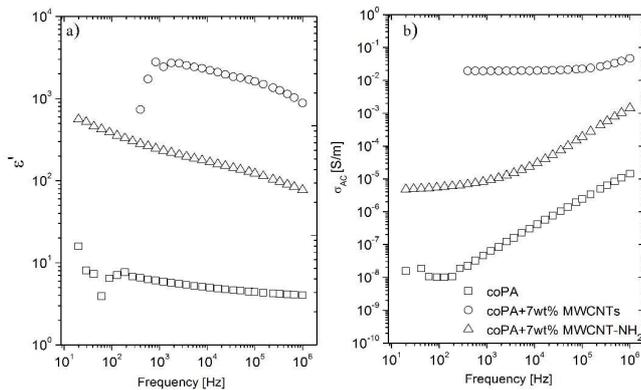


Fig. 4. Dependence of permittivity ϵ' (a) and AC conductivity (b) versus frequency for filled and unfilled coPA

Rys. 4. Zależność przenikalności elektrycznej ϵ' (a) i AC przewodności elektrycznej (b) w funkcji częstotliwości dla napełnionego i czystego coPA

Thermal properties

The changes in the characteristic temperatures of coPA related to 2% ($T_{2\%}$), 5% ($T_{5\%}$) weight loss, decomposition (T_d), glass transition (T_g), melting point (T_m) and crystallization phenomena as an effect of 7 wt.% MWCNTs and MWCNT-NH₂ are shown in Table 1. It can be seen that neat coPA started decomposing at lower temperatures (188.1 and 339.9°C), the while the addition of 7 wt.% MWCNTs improved the thermal stability by around a 100°C jump in $T_{2\%}$ and $T_{5\%}$. In the case of coPA+7 wt.% MWCNT-NH₂ all these values are lower, which suggests less effective blocking of heating flow through the material because of worse dispersion of amine modified MWCNTs. The degradation peak is shifted to higher values by only about 5°C after the addition of both types of MWCNTs, showing the same effectiveness of MWCNTs and MWCNT-NH₂. Similar results were obtained by nanocomposites based on PA6 and 0.5 wt.% of non-functionalized and amine functionalized MWCNTs prepared by the solution mixing method [20].

Based on the DSC results, also included in Table 1, the glass transition temperature T_g (observed only during the first heating) of unfilled coPA occurs at 46°C, characteristic for PA6 segments. In the presence of 7 wt.% MWCNTs the T_g peak is slightly shifted to 50.1°C, but to 80.1°C for 7 wt.% MWCNT-NH₂ corresponding to PA66 segments. The melting point of coPA (124°C) determined from the second heating run is shifted to 132°C for the MWCNTs and to 128°C for MWCNT-NH₂ which could be explained by the nucleation effect of CNTs already reported in the literature for many thermoplastics [21, 22]. The effect of the MWCNTs used on the crystallization of coPA is also confirmed by the appearance of a crystallization peak during cooling, at 93.1°C for the 7 wt.% MWCNTs and at 90.8°C for the 7 wt.% MWCNT-NH₂, which was not detected for unfilled coPA. This is evidence of a heterogeneous nucleation phenomenon induced by CNTs [23]. Furthermore, the increase in enthalpy of melting from 28.8 to 31.8 J/g is observed for MWCNTs and

a decrease to 25.7 J/g for MWCNT-NH₂. This means that the nucleation effect on coPA is higher in the case of non-modified MWCNTs than of amine modified MWCNTs.

TABLE 1. Difference in thermal properties of coPA with non-modified and amine modified MWCNTs

TABELA 1. Różnice we właściwościach coPA domieszkowanym niemodyfikowanymi i funkcjonalizowanymi grupami aminowymi MWCNTs

	$T_{2\%}$ [°C]	$T_{5\%}$ [°C]	T_d [°C]	T_g [°C]	T_m [°C]	ΔH_m [J/g]	T_c [°C]
coPA	188	339	455	46.1	128	28.8	---
coPA+7 wt.% MWCNTs	291	379.1	461	50.1	133	31.8	93.1
coPA+7 wt.% MWCNT-NH ₂	286	377.4	460	81.0	128	25.7	90.8

CONCLUSIONS

In this work, new types of thermoplastic nanocomposites fabricated by melt-blending from hot melt coPA and 7 wt.% non-modified and 7 wt.% amine modified MWCNTs were characterized. It was shown that the addition of MWCNT-NH₂ increased the complex viscosity, storage and loss modulus of coPA but to a smaller extent than the non-modified MWCNTs. In both nanocomposites, the used MWCNTs were well-dispersed but some single agglomerates were also found. They had higher diameters (~50 μm) in the nanocomposites doped with MWCNT-NH₂ than in the nanocomposites with MWCNTs (~30 μm). The worse dispersion of MWCNT-NH₂ resulted in lower values of electrical conductivity ($\sigma_{AC} = 10^{-5}$ S/m) than for coPA mixed with MWCNT ($\sigma_{AC} = 10^{-1}$ S/m). Moreover, a stronger nucleation effect was observed for the non-modified MWCNTs and higher thermal stability than for coPA+7 wt.% MWCNT-NH₂. The presented results show that the use of amine modified MWCNTs does not help to improve the properties of coPA. Moreover, it was revealed that the key factor affecting the properties of nanocomposites is the dispersion of MWCNTs and MWCNT-NH₂ in the coPA matrix.

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