Antistatic polyurethane coats with hybrid carbon nanofillers*)

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Abstract: Thermoplastic coats based on commercial aqueous dispersions of polyurethane and carbon nanofillers (graphite nanoplatelets and/or carbon nanotubes) were prepared and analyzed. The surface resistivity of the samples was in the range of 10^6—10^8 Ω (<1 wt part/100 wt parts of dry coat of carbon nanofillers). Incorporation of carbon nanofillers into coating systems improves the hardness and thermal resistance of dry coats whereas their glass transition temperature is unaffected.

Keywords: water-borne, coating composition, varnish, coat, polyurethane, graphite nanoplatelets, carbon nanotubes.

Antystatyczne powłoki poliuretanowe modyfikowane hybrydowymi nanonapełniaczami węglowymi

Streszczenie: Otrzymano, a następnie zbadano zestaw antystatycznych powłok bazujących na dostępnej w handlu wodnej dyspersji poliuretanowej oraz nanonapełniaczach węglowych — grafenie wielowarstwowym i/lub nanorurkach węglowych. Stwierdzono, że w wypadku zawartości nanonapełniacza węglowego poniżej 1 % mas. rezystywność powierzchniowa powłok wynosi 10^6—10^8 Ω, zwiększają się twardość i odporność termiczna, natomiast nie zmienia się w istotnym stopniu temperatura zeszklenia matrycy poliuretanowej.

Słowa kluczowe: wodorozcieńczalny, kompozycja powłokotwórcza, lakier, powłoka, poliuretan, grafen wielowarstwowy, nanorurki węglowe.

The addition of carbon nanofillers to polymer materials enhances their mechanical, electrical and thermal properties. Graphene (GN) exhibits high thermal and electrical conductivity, high transparency and, moreover, its manufacturing is potentially less expensive than carbon nanotubes (CNT). Generally, graphene is most often commercially prepared from graphite and offered in the form of layered agglomerates [1]. Such carbon nanofillers are often called graphite nanoplatelets (GNP). Nevertheless, CNTs are still the most popular and useful carbon nanofiller applied in polymeric materials. These carbon structures, mainly of the multi-walled type, are widely offered by a number of commercial institutions in a powdered form and as aqueous dispersions. Despite this, there are very few reports on polyurethane-based coating materials (PUR) with carbon nanofillers, so a brief overview of the topic is presented below.

Although unfilled polyurethane coats usually exhibit good thermal, mechanical [2] and electrostatic properties (especially in the case of ionomeric PUR) [3], the introduction of carbon nanoparticles significantly improves these features and sometimes allows the retention of transparency at a high level of ca. 80 % [4—9]. Polyurethane compositions filled with CNT, GNP or GN are described in the literature but they are generally applied as cast films. There are no reports on hybrid CNT/GNP carbon nanostructures applications in polyurethane coating materials.

Ha and Kim investigated polyurethane-acrylate coats modified with multi-walled carbon nanotubes (MWCNTs) and crosslinked via UV irradiation [4]. The low content of MWCNT (0.1 wt %) diminished the electrical resistivity by about 7 orders. Moreover, the presence of MWCNT decreased the yield of the UV photocuring reaction.

Song et al. prepared polyurethane coats with tolylenediisocyanate functionalized MWCNTs [5]. An addition of 1 wt % of nanofiller improved the abrasion resistance by about 100 %, as well as surprisingly increased the value of the friction coefficient.

Jung et al. produced PUR films using graphene formed from expandable graphite after a long-lasting sonication process in N-methylpyrrolidone (NMP) [6]. PUR solution in NMP and GN/NMP dispersion were mixed together for 24 h and cast. The final films with

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0.1 wt % of GN (thickness 150 μm) exhibited a high transparency (85 %) and electrical conductivity ($2 \cdot 10^3$ S/cm).

Liao et al. obtained solvent-borne polyurethane-acrylate coats with graphene. An electrical percolation threshold was achieved for a very low (0.15 wt %) loading of GN [7].

Water-borne polyurethane coats with covalently functionalized GN were prepared using the sol-gel method by Wang et al. [8]. An increment in the tensile strength (70—90 %) and Young's modulus of polyurethane matrix with 2 wt % content of GN was observed.

A polyurethane two-component solvent-borne coating system, covalently bound with silicone-modified graphene, was obtained by Ma and coworkers [9]. The incorporation of 0.2 wt % of functionalized GN increased the tensile strength (ca. 200 %), elongation at break (70 %), thermal degradation temperature (50 °C), thermal conductivity (40 %) and reduced the glass transition temperature (T_g) by 9 °C in comparison to the reference coat.

Yu et al. prepared UV-cured polyurethane-acrylate coats with covalently functionalized graphene oxide. The incorporation of the mentioned carbon nanoparticles at an amount of 1 wt % increased the thermal degradation temperature (17 °C), tensile strength (73 %) and storage modulus of the polymeric matrix [10].

The aim of this work was the preparation of water-borne coating compositions and coats based on commercial polyurethane aqueous dispersions and carbon nanofillers, i.e. carbon nanotubes, as well as hybrid CNT/GNP systems, exhibiting electrical surface resistivity below 10^8 Ω, i.e. classifying such coats as antistatic materials.

EXPERIMENTAL PART

Materials

The following materials were used:

— Incorez W2205, commercial aqueous dispersion of polyurethane with polycarbonate backbone, 40 wt % of solids, viscosity 125 mPa·s, contains *N*-ethylpyrrolidone and diethylene glycol monobutyl ether as cosolvents (Incorez, UK);

— Aquacyl AQ0101, 1 wt % aqueous dispersion of multi-walled carbon nanotubes NC7000, average length 1.5 μm (Nanocyl, Belgium);

— ZUT-CNT, 1 wt % aqueous dispersion of NC7000 carbon nanotubes, prepared at Polymer Institute (ZUT in Szczecin) via a sonication process;

— ZUT-GNP, 0.7 wt % aqueous dispersion of commercially available graphite nanoplatelets (650—700 m²/g, 10—15 carbon layers, Cheap Tubes Inc., USA), prepared at the Polymer Institute via a sonication process;

— BYK-345, silicone surfactant for aqueous coating compositions (BYK-Chemie, Germany).

Sample preparation

Water-borne polyurethane varnishes with carbon nanofillers were prepared as follows. Polyurethane aqueous dispersions were mixed with BYK-345 at a ratio of 0.1 wt part of surfactant / 100 wt parts of coating composition by mechanical stirring (300 rpm, 15 min). Then, an appropriate amount of nanofiller dispersion (Aquacyl, ZUT/CNT and/or ZUT-GNP) was added and the composition was mixed (450 rpm, 30 min). After that, the coating composition was applied onto a glass or poly(ethylene terephthalate) (PET) substrate using a gap applicator (Zafil, Poland) and dried for 24 h at *RT* (room temperature). The formulation scheme is graphically presented in Fig. 1. Four series of samples with different carbon nanostructures content (CNT or CNT/GNP) were prepared; the composition and sample symbols are presented in Table 1.

T a b l e 1. Composition of polyurethane coats based on Incorez W2205 aqueous dispersion and carbon nanofillers

Sample symbol	CNT		GNP	
	dispersion type	content wt part [a]	dispersion type	content wt part [a]
RS-0	—	0	—	0
A-0.5	Aquacyl	0.5	—	0
A-0.8		0.8		0
A-1.0		1.0		0
A-1.5		1.5		0
A/GNP-0.8/0.2	Aquacyl	0.8	ZUT-GNP	0.2
A/GNP-0.6/0.4		0.6		0.4
A/GNP-0.4/0.6		0.4		0.6
A/GNP-0.2/0.8		0.2		0.8
Z-0.5	ZUT-CNT	0.5	—	0
Z-0.8		0.8		0
Z-1.0		1.0		0
Z-1.5		1.5		0
Z/GNP-0.8/0.2	ZUT-CNT	0.8	ZUT-GNP	0.2
Z/GNP-0.6/0.4		0.6		0.4
Z/GNP-0.4/0.6		0.4		0.6
Z/GNP-0.2/0.8		0.2		0.8

a — wt part/100 wt parts of dry coat.

Methods of testing

The electrical surface resistivity of dry coats (on a glass substrate) were measured using an Electrometer 6517A with electrode set Keithley 8009 (Keithley Instruments, Inc.) according to the Polish Standard PN-E-04405:1998 (at 10 V). The pendulum hardness (three measurements of each sample) and the gloss value at 20° were tested on dry coats (glass substrate) using a König pendulum (AWS-5, Dozafil, Poland) according to the Polish Standard PN-EN ISO 1522:2008 and Mi-
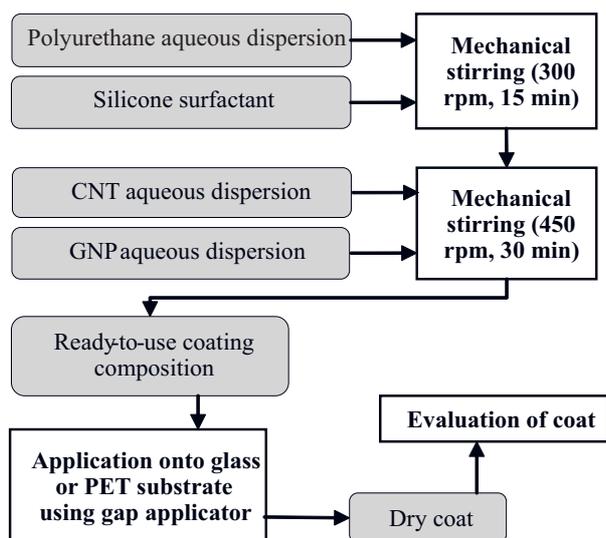
Fig. 1. Formulation scheme of polyurethane coating compositions and coats with carbon nanofillers

T a b l e 2. Surface resistivity and hardness of polyurethane coats with carbon nanofillers

Sample symbol (see Table 1)	Surface resistivity, Ω	Hardness a.u.	Trans-parency, %
RS-0	$9.0 \cdot 10^{14}$	100 ± 1	89
A-0.5	$1.0 \cdot 10^{10}$	100 ± 1	– [a]
A-0.8	$3.0 \cdot 10^{8}$	101 ± 1	38
A-1.0	$5.3 \cdot 10^{7}$	100 ± 1	35
A-1.5	$1.7 \cdot 10^{7}$	105 ± 1	23
A/GNP-0.8/0.2	$2.7 \cdot 10^{7}$	103 ± 1	38
A/GNP-0.6/0.4	$4.1 \cdot 10^{7}$	106 ± 1	39
A/GNP-0.4/0.6	$1.2 \cdot 10^{10}$	100 ± 1	– [a]
A/GNP-0.2/0.8	$2.1 \cdot 10^{14}$	104 ± 1	– [a]
Z-0.5	$3.6 \cdot 10^{12}$	105 ± 1	– [a]
Z-0.8	$2.4 \cdot 10^{7}$	109 ± 1	38
Z-1.0	$7.0 \cdot 10^{6}$	101 ± 1	37
Z-1.5	$1.0 \cdot 10^{6}$	101 ± 1	– [a]
Z/GNP-0.8/0.2	$1.5 \cdot 10^{7}$	102 ± 2	38
Z/GNP-0.6/0.4	$7.3 \cdot 10^{7}$	101 ± 1	39
Z/GNP-0.4/0.6	$2.4 \cdot 10^{12}$	104 ± 1	– [a]
Z/GNP-0.2/0.8	$1.3 \cdot 10^{13}$	103 ± 1	– [a]

a — not tested.

cro-TRI-gloss μ (BYK-Gardner GmbH, Germany; ISO 2813), respectively. Digital images of surface micrographs of coats on glass substrates were prepared using a laser scanning microscope (LSM) (VK-9700, Keyence, USA). The transparency of cured coats (on a PET foil) were evaluated by UV-Vis spectroscopy (Specord M40, Medson, Germany). The glass transition temperatures (T_g) of coats were evaluated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) methods. DSC analysis was performed on a small sample (ca. 10 mg) of dried nanocomposite coats; standard Al pans were used with scanning range -20—220 °C and heating rate of 5 °C/min (DSC Q100, TA Instruments, USA). DMA tests were taken under the following conditions: tension test in a range of 0—140 °C, heating rate 3 °C/min, 1 Hz of frequency, amplitude 15 μm (DMA Q800, TA Instruments). The T_g values of samples (PET substrate) on the basis of tan δ peak temperature were determined. Thermogravimetric analysis (TGA) was made using a Q5000 thermoanalyzer (TA Instruments). Small doses (ca. 10 mg) of dried coats were examined in an air atmosphere. The tested temperature range was 20—800 °C with a heating rate of 5 °C/min.

RESULTS AND DISCUSSION

Electrical surface resistivity of coats

The surface resistivity values of polyurethane coats with CNT or CNT/GNP mixtures are given in Table 2. Additionally, the influence of CNT content on the surface resistivity of dry coats is graphically presented in Fig. 2.

As can be seen, the addition of a small amount of CNT (1 wt %) significantly decreased the surface resistivity of polyurethane coats from $9 \cdot 10^{14}$ Ω (reference sample RS-0) to $5.3 \cdot 10^{7}$ Ω (coat with Aquacyl dispersion; A-1.0) and $7 \cdot 10^{6}$ Ω (coat with ZUT-CNT dispersion; Z-1.0). Gene-

rally, higher contents of CNT leads to better electrical conductivities. It should be noted that coats with a ZUT-CNT dispersion exhibited distinctly better electrical properties with CNT concentrations above 0.6 wt % than samples with commercial aqueous dispersions of Nanocyl NC7000 (i.e. Aquacyl AQ0101). The established 10^{8} Ω
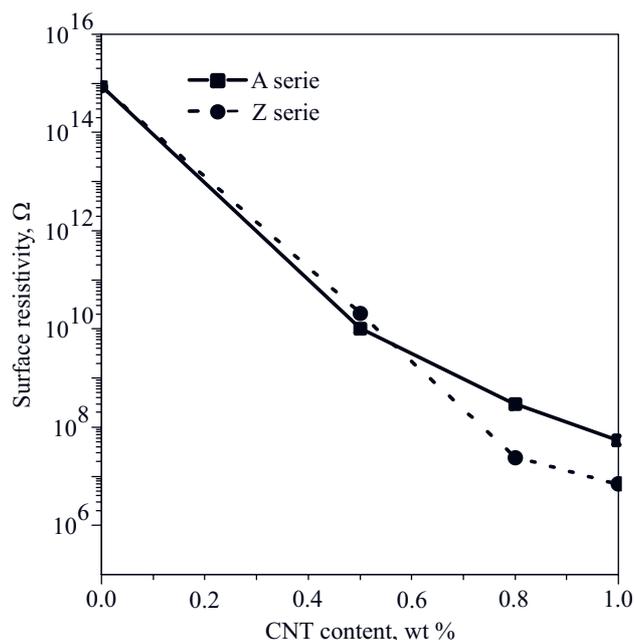
Fig. 2. Electrical surface resistivity of polyurethane coats with CNT (Aquacyl or ZUT-CNT), designation of the samples as in the Table 1
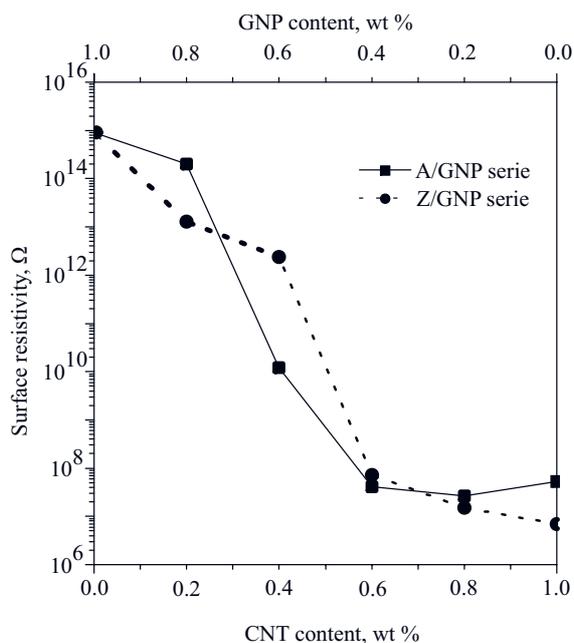
Fig. 3. Electrical surface resistivity of polyurethane coats with CNT/GNP mixtures (A is for Aquacyl, Z is for ZUT), designation of the samples as in the Table 1

threshold (recommended for antistatic materials) was achieved for samples with ca. 0.75 wt % of ZUT-CNT (solid content) or 0.9 wt % of Aquacyl, are presented in Fig. 2.

Fig. 3 shows the influence of CNT and GNP concentrations on the electrical resistivity of dry coats prepared using a total 1 wt % of either Aquacyl/ZUT-GNP or ZUT-CNT/ZUT-GNP mixtures. Although some differences for the resistivity of coats containing 0.1—0.5 wt % of CNT (and 0.9—0.5 wt % of GNP) could be observed, samples with 0.6 wt % of CNT and 0.4 wt % of GNP reached ca. 10^8 Ω for the analyzed parameter irrespective of the type of CNT dispersion used (i.e. $4.1 \cdot 10^7$ Ω for A/GNP-0.6/0.4 and $7.3 \cdot 10^7$ Ω for Z/GNP-0.6/0.4). Nevertheless, it should be noted that coats with 0.6—0.9 wt % of CNT (from Aquacyl) and 0.4—0.1 wt % of GNP exhibited similar (or slightly reduced) electrical resistivity with relation to the A-1.0 coat filled with 1 wt % of CNT. In the case of coating systems based on ZUT-CNT dispersions of carbon nanotubes, the addition of GNP (even 0.1 wt % instead of CNT, Fig. 3) increases that electrical parameter value. The presented results showed that CNT addition had a greater (positive) influence on the electrical properties of coats than GNP. However, a small dose of GNP, i.e. 0.2—0.4 wt %, in the presence of CNT from Aquacyl dispersions (compare data for samples: A-1.0, A/GNP-0.8/0.2 and A/GNP-0.6/0.4; Table 2) could maintain/improve the conductivity of polyurethane coats. The above-mentioned phenomenon was not analogically observed for dry coats prepared using ZUT-CNT and ZUT-GNP dispersions. Probably, the CNT in the former dispersions were dissipated much better than in the Aquacyl system, thus the addition of two-dimensional

GNP to the coating composition based on ZUT-CNT did not significantly affect the electrical conductivity of dry polyurethane coats.

Other coat properties

The hardness test results are presented in Table 2. These values varied between 100 and 109 units. It was revealed that the addition of carbon nanostructures improved the hardness of the obtained coats to some extent. Interestingly, in the case of coats based on Aquacyl dispersions, the best improvement of the analyzed parameter was noted for a sample with the highest CNT content (105 units; A-1.5), while this hardness value was registered for coats containing only 0.5 wt % of ZUT-CNT dispersion. Moreover, taking into consideration the coating system filled with CNT/GNP hybrid nanofiller, the generally higher hardness values were recorded for samples containing either a higher amount of CNT from Aquacyl dispersion, (e.g. A/GNP-0.6/0.4) or lower amount of CNT from ZUT-CNT dispersion (Z/GNP-0.4/0.6 and Z/GNP-0.2/0.8 samples).

The LSM observations concerned samples with different GNP and/or CNT content. Micrographs of prepared polyurethane coats were very similar; for example two images with various magnification of the Z/GNP-0.6/0.4 sample (0.6 wt % of CNT and 0.4 wt % of GNP) are presented in Fig. 4.
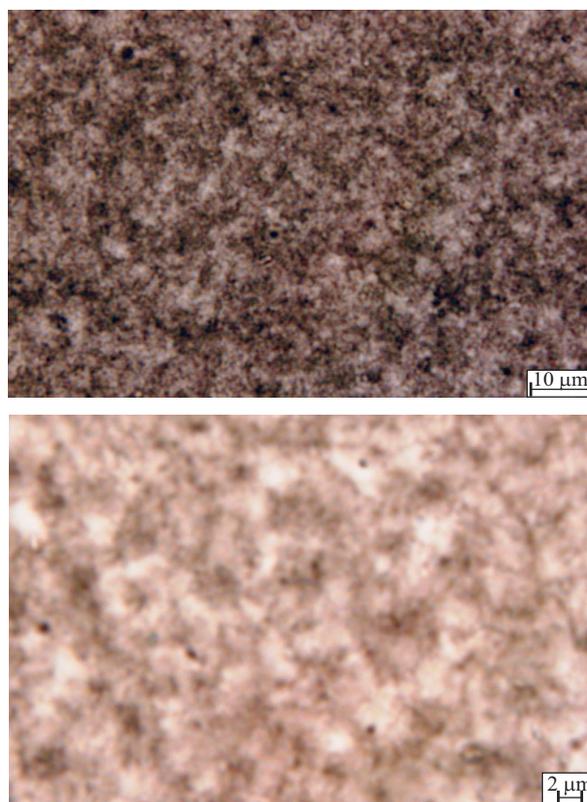
Fig. 4. LSM micrographs of polyurethane coat with CNT/GNP mixture (Z/GNP-0.6/0.4) at different magnifications
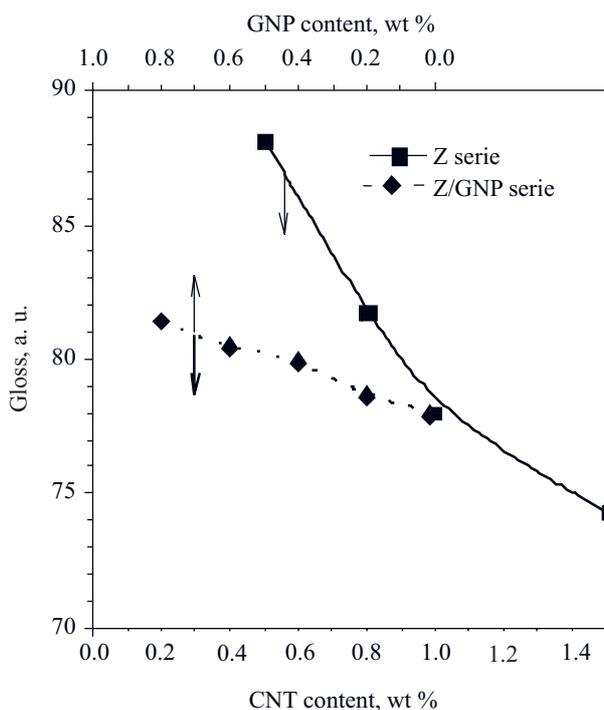
Fig. 5. Gloss of polyurethane coats with CNT and CNT/GNP

Even though darker (CNT, GNP) and brighter areas (binder) were visible, the carbon nanofillers were quite uniformly dispersed in the polymeric matrix. It was confirmed by a relatively low electrical resistivity of all coats filled with the tested nanofillers.

The gloss assessment was performed on coats modified with either ZUT-CNT dispersion or hybrid CNT/GNP systems; the results are graphically presented in Fig. 5.

As can be seen, the carbon nanofillers significantly reduced the coat gloss; in the case of coats with CNT, the highest gloss value was registered for Z-0.5 (88 %) and the lowest for Z-1.5 (74 %). On the other hand, the GNP deteriorated the gloss parameter to a lower extent than CNT, as can be seen for samples with 1 wt % of CNT (Z-1.0) or CNT/GNP mixture. All coats containing both types of carbon nanofillers exhibited higher gloss values (79—82 units) than the above-mentioned sample filled with only CNT (78 units). The highest gloss value among coats with 1 wt % total content of carbon nanofillers was registered for Z/GNP-0.2/0.8 coat.

The CNT and CNT/GNP nanofiller additions reduced the dry coat transparency. The results for selected samples, i.e. with electrical surface resistivity values below 10^8 Ω, are presented in Table 2. It can be seen that the presence of CNT in the dry coat directly affects the analyzed feature (higher CNT contents result in lower transparencies). It should be noted that samples based on Aquacyl and ZUT-GNP dispersions (i.e. coats with 1 wt % of these nanofiller mixtures) reached higher transparencies (38—39 % for A/GNP-type samples) than coats with 1 wt % of CNT (0 wt % of GNP; A-1.0; 35 %). In the case of samples with either ZUT-CNT (Z-1.0; 37 %) or

ZUT-CNT/ZUT-GNP mixtures (38—39 %) that phenomenon was not observed. Similar effects of Aquacyl and ZUT-CNT dispersions were registered for the surface resistivity results, i.e. GNP improved the properties of Aquacyl-modified coats, but not the ZUT-CNT-based samples.

The glass transition temperatures were measured for samples based on ZUT-CNT and ZUT-GNP dispersions. The results determined by DSC and DMA techniques are compiled in Table 3.

Detailed DSC thermographs of samples with CNT/GNP mixtures are presented in Fig. 6. As can be seen, an incorporation of carbon nanofillers into the polyurethane matrix did not significantly affect the T_g of dry coats measured by DSC. Although the values of T_g for RS-0 and modified coats were in the narrow range of 14.3—15.7 °C (DSC technique), the span of T_g values (DMA) in some cases was markedly higher (31.0—36.5 °C). This means that the tested carbon nanofillers did not significantly change the thermal features analyzed by DSC but only affected the thermomechanical properties of the polyurethane coats measured by DMA. The differences between the glass transition temperature values determined by these techniques are due to the different physical basis of the T_g measurements. In the DSC method, the increase in specific heat of the material as it passes from the glassy to rubber state is analyzed. The DMA method measures the viscoelastic properties of the material as a function of frequency and oscillatory deformation. In the glassy state, the material will exhibit solid-like characteristics and has a measurable shear modulus. The glass transition can be detected as the temperature where the storage modulus starts to fall rapidly
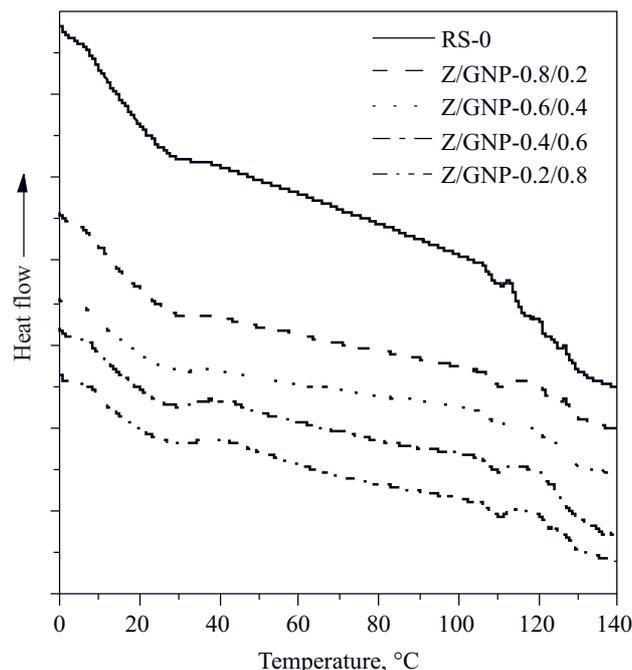
Fig. 6. DSC thermograms of polyurethane coats with CNT/GNP nanofiller mixtures
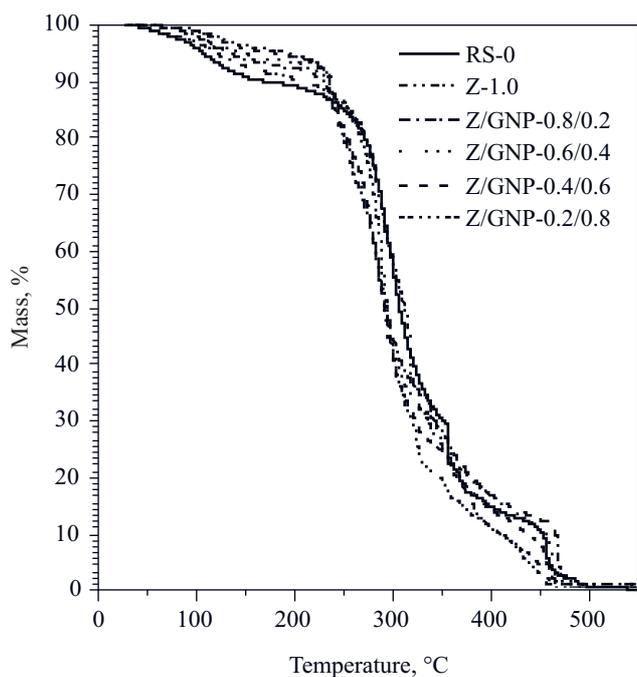
Fig. 7. TGA curves for polyurethane coats with CNT and CNT/GNP

(or tan δ reaches maximum value) with increasing temperature. Thus T_g transitions during DMA measurements are a kinetic, rather than equilibrium, phenomena. Differences between T_g values determined by DSC and DMA can vary by as much as 15 °C (when based on storage modulus changes) up to 25 °C (tan δ peak evaluation) [11].

T a b l e 3. Glass transition temperature values and thermal stability of polyurethane coats with carbon nanofillers

Sample symbol (see Table 1)	T_g [a], °C	T_g [b], °C	T_5 [c], °C	T_{10} [d], °C
RS-0	15.7	32.4	107.2	169.8
Z-0.5	14.7	31.0	95.3	211.2
Z-1.0	15.3	34.2	119.0	208.3
Z-1.5	15.3	33.8	138.8	230.4
Z/GNP-0.8/0.2	15.5	33.4	132.3	228.7
Z/GNP-0.6/0.4	15.0	36.5	142.5	232.9
Z/GNP-0.4/0.6	14.6	32.3	180.4	234.8
Z/GNP-0.2/0.8	14.3	32.7	191.8	239.6

a — determined using DSC technique; b — determined using DMA technique; c — temperature at 5 % mass loss; d — temperature at 10 % mass loss.

A similar set of samples was analyzed by TGA. The results of the thermal stability of polyurethane coats with carbon nanofillers, i.e. temperatures at 5 % (T_5) and 10 % (T_{10}) mass losses are given in Table 3.

TGA revealed that carbon nanostructures significantly improve the thermal stability of tested coats in the temperature range 100—240 °C (Fig. 7). Moreover, the influence of GNP on the observed phenomenon was more significant than that of CNT. The T_{10} value for RS-0 was ca. 170 °C and rose up to ca. 208 °C (Z-1.0) and ca. 240 °C after 0.2 wt % of CNT and 0.8 wt % of GNP addition (Z/GNP-0.2/0.8). The growth of T_5 for the mentioned samples was also observed: the increment was 12 °C (1 wt % of CNT) and 85 °C for the sample with the highest dose of GNP.

CONCLUSIONS

Water-borne varnishes and coats based on thermoplastic polyurethane aqueous dispersion and either CNT or CNT/GNP nanofiller mixtures were prepared and tested. The addition of nanoparticles up to 1 wt % is responsible for electroconductive path formation and decreasing surface resistivity of coats by 8 orders of magnitude in relation to the unfilled coat (i.e. to 10^6 Ω). It is important that the presence of carbon nanostructures improves hardness and the thermal stability of dry coats. Although the influence of GNP on electrical resistivity/conductivity is lower than that of CNT, the addition of GNP causes an increase of gloss and thermal stability of the analyzed materials. It is noteworthy that the CNT and CNT/GNP-based coat preparation process is simple and possible to perform on a larger scale.

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