Influence of hybrid carbon nanofillers on the cure behavior and properties of epoxy materials

Honorata Mąka[1)], Tadeusz Spychaj[1), *)], Ryszard Pilawka[1)], Piotr Dziedzic[1)]

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Abstract: The curing process of epoxy compositions with 1-butylimidazole (2 phr as a catalyst) and hybrid carbon nanofillers: multiwalled carbon nanotubes (CNTs) and graphene (GN) (total carbon nanofillers content 0.25—1.0 wt %) has been characterized via rheometry. Thermomechanical measurements of epoxy composites revealed a rather large decrease in the glass transition temperatures depending on CNT/GN weight ratio and total nanofillers content. Electrical volume resistivity of epoxy materials decreased about 8—10 orders of magnitude after modification with 0.25—0.50 wt % CNT/GN hybrids to the range 10^5—10^6 Ω·m.

Keywords: epoxy resin, 1-butylimidazole, hybrid carbon nanofillers, thermomechanical properties, electrical properties.

Wpływ hybrydowych nanonapełniaczy węglowych na proces sieciowania i właściwości materiałów epoksydowych

Streszczenie: Za pomocą pomiarów reometrycznych scharakteryzowano proces sieciowania kompozycji epoksydowych z udziałem 2 phr 1-butyloimidazolu jako katalizatora i 0,25—1,0 % mas. hybrydowych nanonapełniaczy węglowych — wielościennych nanorurek (CNT) i grafenu (GN). Na podstawie badań termomechanicznych wytworzonych kompozytów epoksydowych stwierdzono znaczne zmniejszenie wartości temperatury zeszklenia, zależne od stosunku masowego CNT/GN i zawartości nanonapełniacza. Wartość rezystywności skrośnej materiałów epoksydowych po modyfikacji dodatkiem 0,25—0,50 % mas. nanonapełniacza węglowego zmniejszyła się o 8—10 rzędów wielkości.

Słowa kluczowe: żywica epoksydowa, 1-butyloimidazol, hybrydowe nanonapełniacze węglowe, właściwości termomechaniczne, właściwości elektryczne.

Epoxy materials belong to the most important thermosetting polymers because of their excellent thermal, mechanical, adhesive and chemical properties. For these reasons, they are widely used in adhesives, coatings, electronic and transport areas, including the aerospace industry.

The crosslinking of epoxy resin may be the result of an addition or homopolymerization reaction. Imidazoles are tertiary amines that are often used in a variety of epoxy systems to initiate the curing process. Imidazole and its derivatives are fast curing crosslinking agents applied as catalysts together with other curing reactants such as anhydrides, dicyanamide or phenolics [1—3], as well as sole hardeners [1, 3—7].

Among imidazole derivatives, the most often applied is 2-ethyl-4-methylimidazole (2,4-EMI) [4—6]. 1-Substituted imidazoles are not so commonly used as epoxy resin catalysts as 2,4-EMI even if one could expect a longer pot life for the relevant epoxy systems. 1-Methylimidazole is the most popular [3, 4, 6, 7] such derivative; the other is 1-butylimidazole (1-BI), which is claimed to be industrially used as a catalyst to initiate epoxy resin cure with anhydrides [8].

Carbon nanofillers have been used for manufacturing epoxy nanocomposites with enhanced mechanical and electrical properties, as well as thermal conductivity. To obtain epoxy nanocomposites of good quality, the high dispersion efficiency of carbon nanoparticles is crucial. It is known that imidazolium ionic liquids are catalytic curing agents for epoxy resins [9—12] and simultaneously act as dispersing media for CNT or GN [13—17]. However, the price of ionic liquids is still a limiting barrier in their wide application as epoxy resin catalysts. On the other hand, there are only a few reports on epoxy systems containing non-functionalized carbon nanofillers, crosslinked with imidazole derivatives used as a sole curing agent [18, 19].

Zhou *et al*. [18] studied the effect of multiwalled CNTs on the curing behavior of bisphenol-A diglycidyl ether with 2,4-EMI. It was found that, in the initial curing stage, CNT acted as a catalyst and facilitated curing. That influ-

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1) West Pomeranian University of Technology, Polymer Institute, ul. Pulaskiego 10, 70-322 Szczecin, Poland.

*) Author for correspondence; e-mail: Tadeusz.Spychaj@zut.edu.pl

ence was noticeable at the lowest investigated carbon level (1 wt %) — the catalyzing action was saturated above this level. Moreover, the presence of CNT resulted in a decrease of the overall degree of the cure and glass transition temperature of composites [18].

There are numerous reports on using functionalized CNT with carboxyl groups [19, 20] or amino groups [21, 22] for epoxies cured with 2,4-EMI. However, chemical functionalization of the carbon nanofiller resulted in a decrease in the electrical properties while the mechanical features of the relevant epoxy composites were improved.

According to our best knowledge, no data on the electrical properties of epoxy composites containing CNT or GN cured with 1-alkylimidazoles only have been reported. In this work, 1-butylimidazole was used as an epoxy resin curing agent in the presence of CNT/GN hybrid nanofillers. The rheological characteristics during the curing process of a neat, as well as carbon nanofiller modified, epoxy compositions were investigated using dynamic temperature modes at various temperature gradients: 1, 5 and 20 °C/min. The thermomechanical and electrical properties of the nanocomposites were evaluated as a function of hybrid carbon nanofiller type and content. The purpose of hybrid CNT/GN filler application, instead of CNT or GN used separately, is the lower price of GN and expected easier resin system processing (*i.e.* lower viscosity of epoxy resin with CNT/GN than with CNT itself), as well as high level of electrical conductivity [23, 24].

EXPERIMENTAL PART

Materials

Epoxy resin: bisphenol A based low molecular weight Epidian 6 (E6); epoxy equivalent 185 g (viscosity 18 Pa·s at 23 °C), Organika Sarzyna, Poland and 1-butylimidazole (BI), 98 %, Sigma-Aldrich were used. Multiwall carbon nanotubes, Nanocyl NC7000, with a specific surface area of 250—300 m^2/g, average length 1.5 μm, average diameter 9.5 nm, carbon content 90 wt % (Nanocyl, Belgium) and graphene, xGnP type C750, with average surface area 750 m^2/g, volume density 0.10—0.14 g/cm^3, 1—5 nm thick, particle diameter less than 2 μm (XG Sciences Inc., USA) were applied for epoxy system preparations.

Preparation of epoxy compositions, carbon nanofiller dispersion and epoxy composites

The neat epoxy composition was prepared by mixing the epoxy resin with BI at ambient temperature; a constant weight ratio of BI/E6 was kept at 2 phr in all experiments. The procedure of carbon nanofiller–modified epoxy compositions preparation was as follows: (i) introduction of CNT, or relevant CNT/GN mixture, into a beaker with liquid epoxy resin and preliminary manual mixing with a glass rod for a few min and then, (ii) sonication for 2 h (amplitude 50 %, frequency 50 Hz, UP 200S, Hielscher GmbH, Germany) and, (iii) introduction of BI to epoxy resin with CNT (or CNT/GN) and manual mixing for 10 min.

Table 1. Designation of epoxy compositions with carbon nanofillers and viscosity measured directly after components homogenization

Symbol sample	E6	BI	CNT	GN	Viscosity (23 ± 2 °C)
	phr		wt %		Pa·s
E6	100	2	-	-	12.9 ± 0.3
E6_CNT0.15/GN0.1			0.15	0.1	15.8 ± 0.1
E6_CNT0.25			0.25	-	17.1 ± 0.1
E6_CNT0.3/GN0.2			0.3	0.2	76.5 ± 0.2
E6_CNT0.4/GN0.1			0.4	0.1	114.2 ± 0.4
E6_CNT0.5			0.5	-	153.7 ± 0.5
E6_CNT0.4/GN0.6			0.4	0.6	161.5 ± 0.9
E6_CNT0.5/GN0.5			0.5	0.5	193.4 ± 0.8
E6_CNT0.6/GN0.4			0.6	0.4	318.6 ± 1.7
E6_CNT0.8/GN0.2			0.8	0.2	325.8 ± 1.1
E6_CNT1.0			1.0	-	354.1 ± 1.5

Eventually, the epoxy compositions were cured in a Teflon mold at 120 °C for 2 h. The resultant samples were used for further investigations. In Table 1, all the prepared and investigated compositions/composites are presented.

Methods of testing

— The viscosities of epoxy compositions containing CNT or CNT/GN were determined using a stress rheometer (Rheometric Scientific, USA) at room temperature (23 ± 2 °C), a plate-plate system, $\phi = 40$ mm, a gap of 1 mm. Measurements were performed directly after the introduction of BI curing agent into the epoxy composition and component mixing. The curing process of epoxy compositions was investigated using a rheometer at a heating rate of 1, 5 and 20 °C/min, frequency 1 Hz, in the temperature range of 30—300 °C. Onset temperature (T_o), *i.e.* start of epoxy composition gelation, was evaluated.

— The glass transition temperatures (T_g) and tan δ values were determined using dynamic mechanical thermal analysis (DMTA Q-800, TA Instruments) with a dual cantilever at a heating rate of 3 °C/min from 30 to 250 °C, frequency 1 Hz.

— The volume electrical resistance of cured composites with various types and carbon nanofiller(s) content was tested at room temperature in accordance with IEC 93:1980 and ASTM D 257-99 using Keithley Instruments, Inc., USA, with a set of electrodes (Keithley 8009).

RESULTS AND DISCUSSION

Curing behavior analysis

The viscosity change of epoxy compositions containing various total contents of hybrid CNT and GN fillers was measured at ambient temperature (23 ± 2 °C) (Table 1).

Introduction of the lowest amount (0.25 wt %) of carbon nanofiller hybrids into the epoxy resin/catalyst system resulted in a slight viscosity increase (from *ca.* 13 to 17 Pa·s). However, with the carbon nanofiller content increased up to a total of 0.5 wt % (partial CNT content changed between 0.3 and 0.5 wt % and GN 0.2 → 0 wt %, respectively), a more pronounced viscosity increase of the relevant epoxy compositions (*ca.* 76—154 Pa·s) was noted. A similar tendency for higher viscosities was observed when the total filler content was raised to 1 wt % (partial CNT content between 0.4 and 1.0 wt %, and 0.6 → 0 wt % GN, respectively) *ca.* 162—354 Pa·s. Moreover, the viscosity of the epoxy compositions containing hybrid CNT/GN nanofillers could be substantially lowered when compared to that measured for the systems with relevant content of CNT only. For example, the epoxy composition with CNT0.3/GN0.2 exhibited a viscosity of *ca.* 77 Pa·s, while that for CNT0.5 was 154 Pa·s, with CNT0.4/GN0.6 was *ca.* 162 Pa·s and for CNT1.0 it was 354 Pa·s (Table 1).

The beginning of the fast viscosity jump in rheometric measurements, *i.e.* start of epoxy resin gelation, was observed at 96 °C when the lowest temperature gradient (1 °C/min) was applied (Figs. 1a and 1d, and Table 2). With increasing temperature gradient, the onset temperatures, T_o, were shifted to higher temperature ranges: 128—134 °C (5 °C/min) and 183—192 °C (20 °C/min).

Table 2. Curing parameters for epoxy compositions with carbon nanofillers and glass transition temperatures of crosslinked epoxy materials

Symbol sample	Rheometry T_o, °C temperature gradient			DMTA T_g, °C
	1 °C/min	5 °C/min	20 °C/min	
E6	96	128	183	175
E6_CNT0.3/GN0.2	96	134	190	159
E6_CNT0.4/GN0.1	96	133	190	163
E6_CNT0.5	96	131	192	165
E6_CNT0.4/GN0.6	96	133	188	154
E6_CNT0.5/GN0.5	97	132	188	154
E6_CNT0.6/GN0.4	96	134	185	157
E6_CNT0.8/GN0.2	97	131	187	160
E6_CNT1.0	95	131	183	165

As may be seen in Fig. 1, the epoxy systems with or without carbon nanofiller during heating — before reaching gelation point — behaved in different ways. The viscosity of neat epoxy composition with BI decreased from a level of *ca.* 13 Pa·s at ambient temperature to below 1 Pa·s at 80—170 °C (depending on temperature of gelation viscosity jump). On the other hand, the epoxy compositions with carbon nanofillers exhibited a slight viscosity increase with temperature. Generally, epoxy/CNT+GN compositions with total carbon content 0.5 wt % exhibited viscosity 1—3 orders of magnitude higher than the relevant reference system, depending on the heating rate (Fig. 1). The viscosity values changed between *ca.* 20—150 Pa·s, whereas minimum values for neat epoxy system reached 0.2—0.3 Pa·s (at 80, 110 and 130 °C for temperature gradients 5 → 20 °C/min). Higher viscosity values at elevated temperatures (before gelation) were found for epoxy compositions with 1 wt % total carbon nanofiller content (*ca.* 25—290 Pa·s). The order of epoxy composition viscosities before gelation was consistent with that measured at room temperature.

Considering the rheometric curves above the T_0 values, one could see that they followed the same pattern when measured at lower temperature gradients (1 and 5 °C/min) independent of carbon nanofiller type and content. Some differences of the rheometric curve runs were found when the highest heating rate (20 °C/min) was applied, especially with 1 wt % carbon nanofiller. The observed small shifts of rheometric curves (Figs. 1c and 1f) are dependent, to some extent, on the total carbon nanofiller content (3—4 °C, *i.e. ca.* 180—184 °C for 0.5 wt % of total carbon filler content, and 6—7 °C, *i.e. ca.* 178—185 °C for 1 wt % of CNT or CNT+GN). No simple correlation between the shifts of upgrading parts of the rheometric curves and thermal conductivity of epoxy systems filled with carbon nanofillers could be observed. The thermal conductivity of epoxy materials with hybrid CNT/GN fillers should be higher than with the nanocomponents used separately [25]. Some other effect such as different tendency for interphase thin film creation between epoxy matrix and CNT [26] and CNT+GN can influence the curing kinetics in the investigated system.

Moreover, it should be noted that the applied temperature gradient regimes allowed the relevant epoxy compositions to gel at various times, *i.e.* 58 min (1 °C/min), 19 min (5 °C/min) and 8 min (20 °C/min) with little difference between the reference and carbon nanofiller modified systems (Fig. 2). The observed differences of epoxy resin reactivity with increasing heating temperature gradient are caused by the higher catalytic activity of BI with a growing stream of heat supplied into polymerising epoxy system.

Thermomechanical characteristics of epoxy nanocomposites

The glass transition temperatures and tan δ values were determined for epoxy nanocomposites with 0.5 and 1.0 wt % of hybrid carbon nanofillers and collected in Table 2. For the sake of clarity, the T_g dependence as a func-

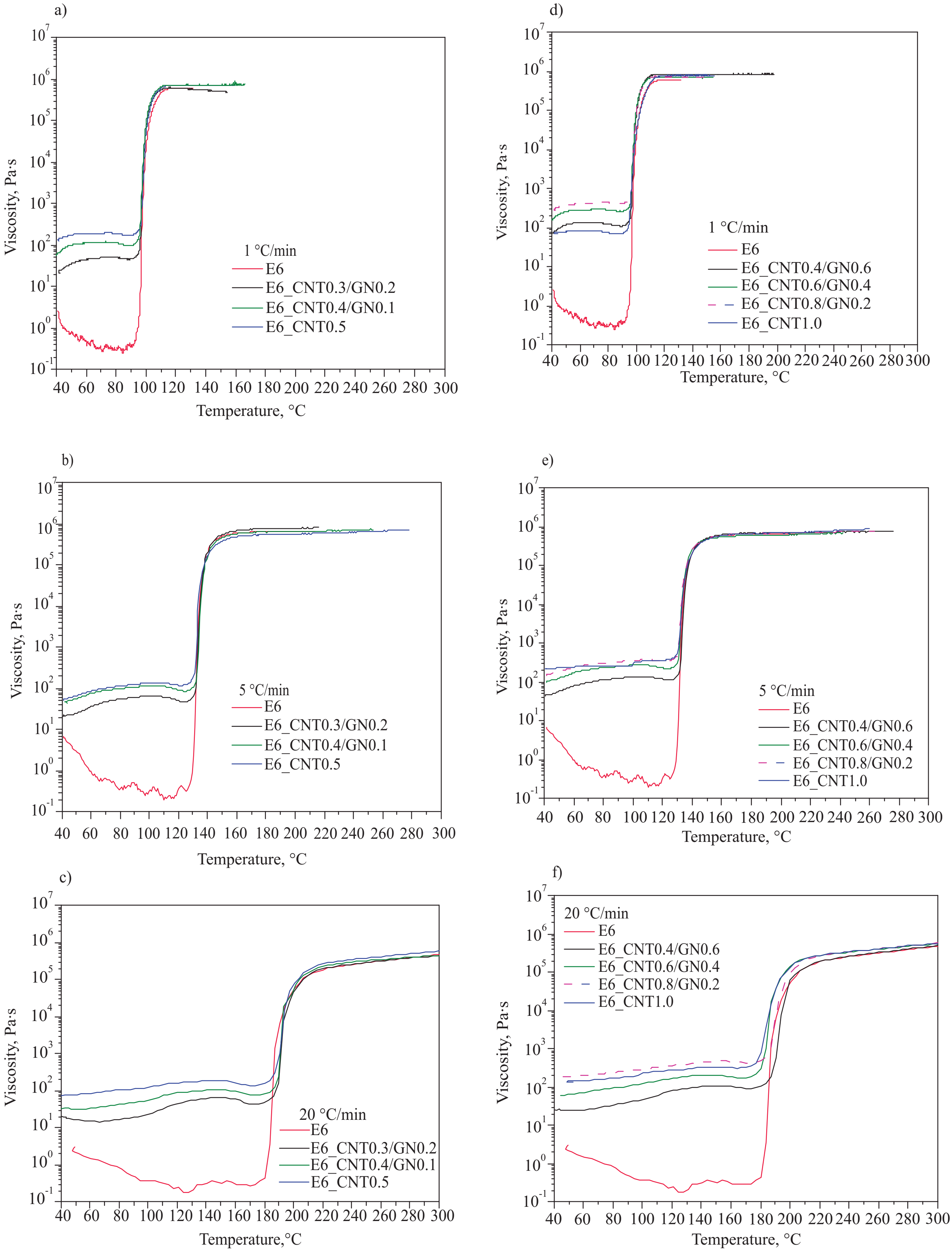


Fig. 1. Rheometric curves of selected epoxy compositions with carbon nanofiller systems at various heating rates: a) and d) 1 °C/min, b) and e) 5 °C/min, c) and f) 20 °C/min

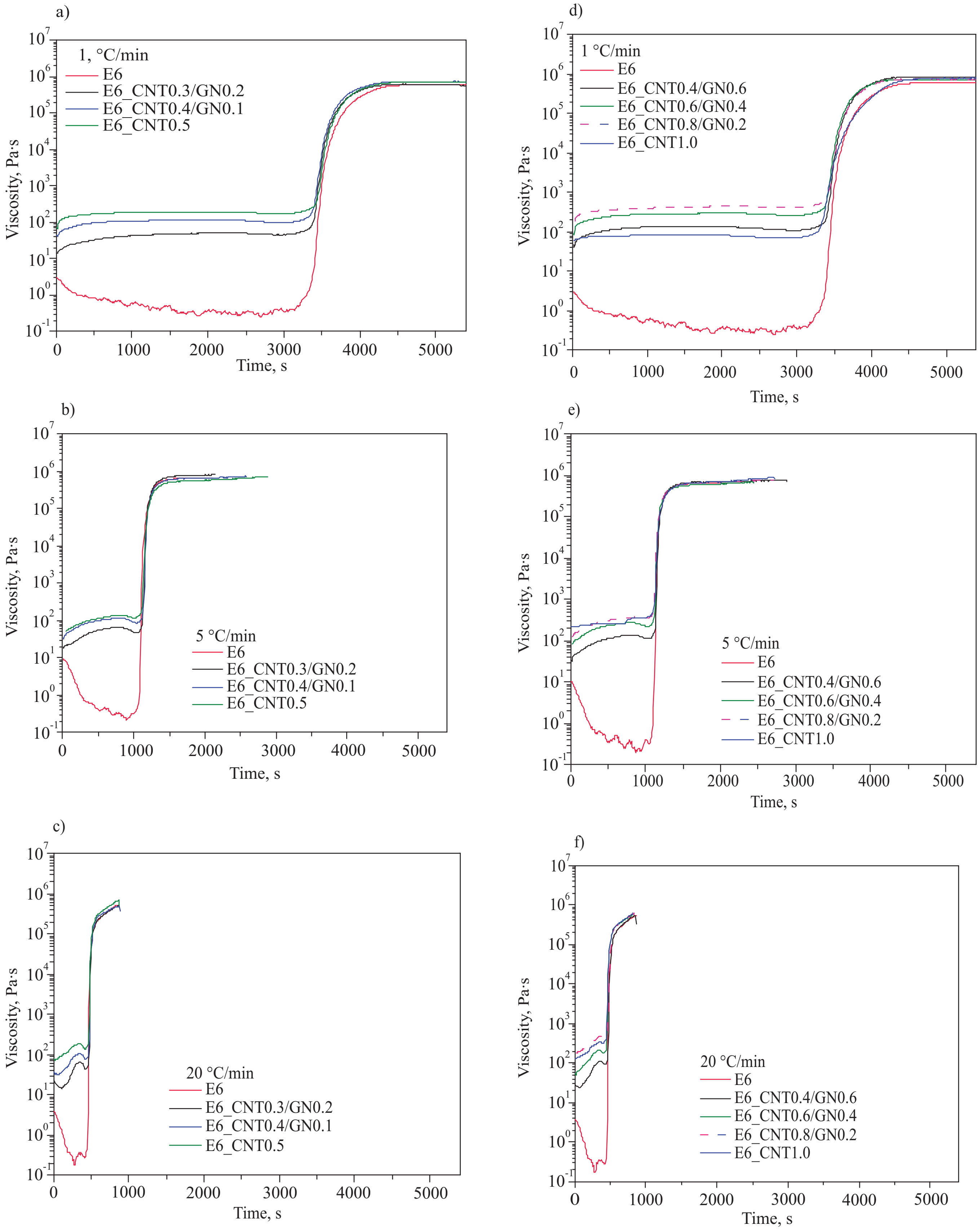


Fig. 2. Rheometric curves of epoxy compositions as a function of time registered during dynamic heating: a) and d) 1 °C/min, b) and e) 5 °C/min, c) and f) 20 °C/min

tion of carbon nanofiller type and content is presented in Fig. 3 and the relevant tan δ graphs in Fig. 4. The relatively high T_g value of 175 °C was found for neat epoxy material cured with 2 phr of BI at 120 °C. It was higher

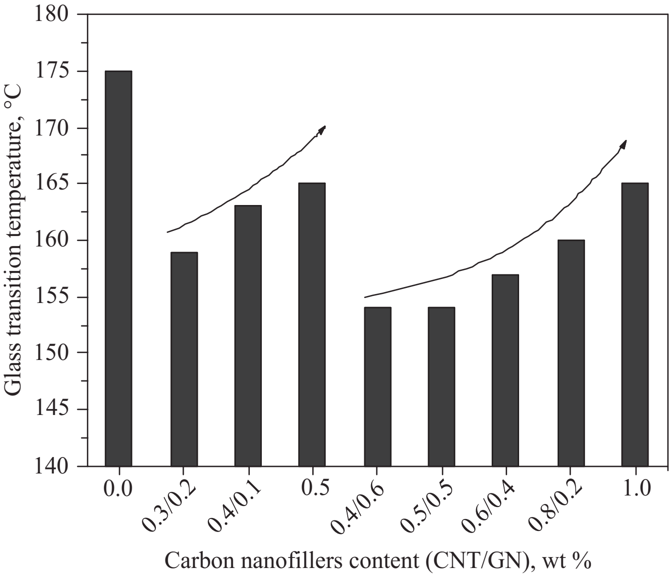


Fig. 3. Dependence of epoxy composites glass transition temperature on type and content of hybrid carbon nanofiller

than data reported for epoxy resin cured with 2,4-EMI (151—154 °C) [6, 18] or 1-methylimidazole (165 °C) [3]. In Fig. 3, a sharper decrease of T_g with GN weight ratio increase in nanofiller hybrids could be observed. For composites with 0.5 wt % total carbon content, the maximum T_g decrease 16 °C (175 → 159 °C) was found for CNT0.3/GN0.2, *i.e.* 40 wt % GN in nanofiller hybrid. With increased CNT contents in the carbon nanofiller system, the ΔT_g between T_g of reference sample and nanocomposites decreased to 12 °C (CNT0.4/GN0.1, *i.e.* 20 wt % GN in nanofiller hybrid) or 10 °C (CNT0.5). The carbon nanofiller total content in epoxy materials 1.0 wt % resulted in an even deeper T_g decrease to 154 °C (*i.e.* ΔT_g = 21 °C when CNT0.4/GN0.6, *i.e.* 60 wt % GN in nanofiller hybrid applied). Lower GN/CNT ratios resulted in lower ΔT_g values; the lowest was 10 °C when CNT 1 wt % only was used.

In the literature, some data considering decreased [26, 28] or increased [26—29] T_g values for epoxy materials caused by CNT presence have been reported. Relatively high differences of T_g values for neat epoxy materials and epoxy composites containing low contents of functionalized graphene to 9 °C (0.8 wt % GN) [30] or even to 15—18 °C (0.1—0.2 wt %) [31] have also been recently reported. The declining trend of T_g change may be attributed to reducing the crosslinking density of the epoxy network. The wall effect, caused especially by large GN particles (750 m^2/g, volume density 0.10—0.14 g/m^3), does not allow the buildup of polymer networks like in a neat epoxy resin curing case. Hindering the epoxy curing reaction in the presence of carbon nanofillers (especially with high GN content) enhanced the molecular chain mobility thus lowering T_g. Moreover, the possibility of interfacial thin film creation on the carbon surface/epoxy matrix borderline could also result in a T_g decrease [26].

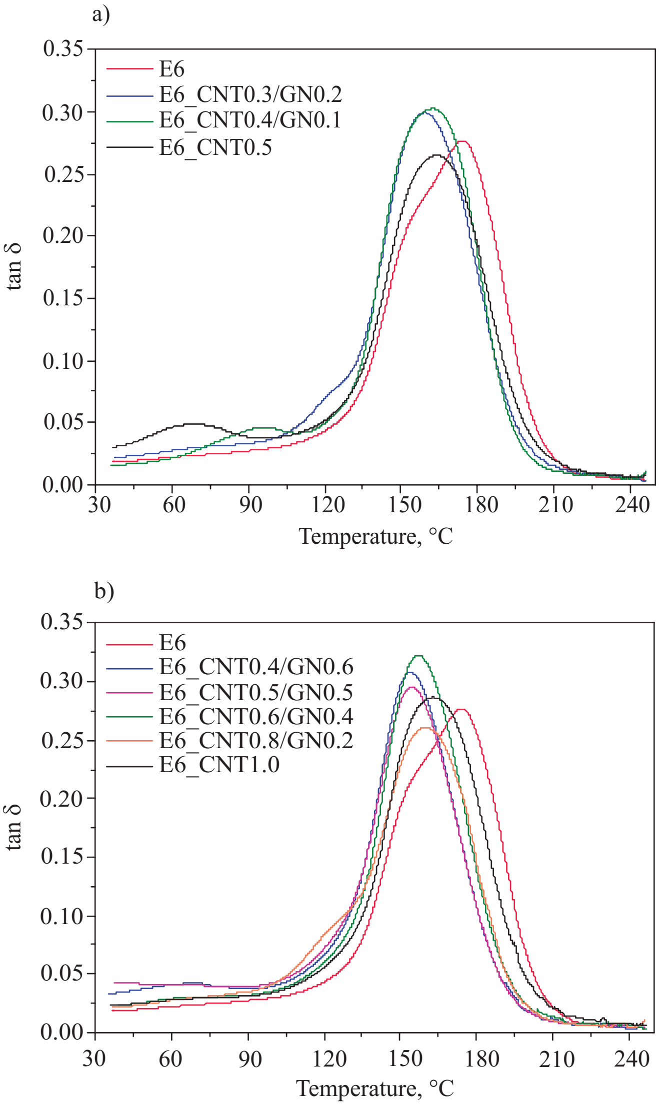


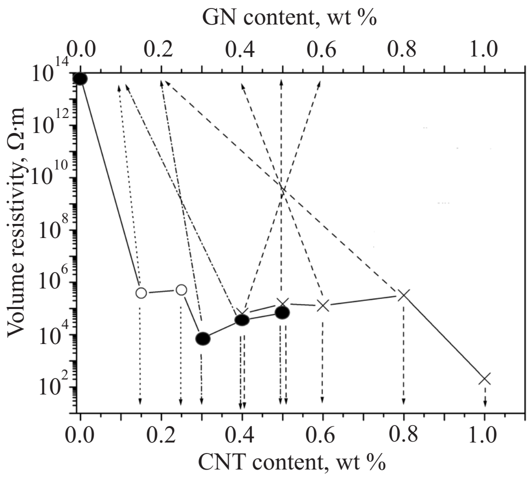
Fig. 4. Dependence of tan δ versus temperature

The results of tan δ lay in a rather narrow range 0.26—0.32 and no clear tendency of changes between reference epoxy material and composites filled with carbon nanofillers was noticed (Fig. 4).

Electrical properties of epoxy nanocomposites

The volume resistivity results of epoxy composites with various total carbon nanofillers content, *i.e.*: 0.25, 0.5 and 1.0 wt %, as well as various CNT/GN weight ratios are presented in Fig. 5. The reference epoxy material exhibited insulating properties with $\rho = 6.9 \cdot 10^{13}$ Ω·m whereas nanocomposites exhibited values of that parameter 8—11 orders of magnitude lower, indicating higher electrical conductivity. As one would expect, the highest electrical conductivity (*ca.* $2 \cdot 10^2$ Ω·m) was shown by the nanocomposite containing 1.0 wt % CNT.

The electrical percolation threshold was found to be below 0.25 wt % of carbon nanostructures in the epoxy composite (Fig. 5). That value was lower than observed for coating materials based on polyurethane [23] or



	Volume resistivity, Ω·m
E6	$6.9 \cdot 10^{13}$
E6_CNT0.15/GN0.1	$3.9 \cdot 10^{5}$
E6_CNT0.25	$5.1 \cdot 10^{5}$
E6_CNT0.3/GN0.2	$7.2 \cdot 10^{3}$
E6_CNT0.4/GN0.1	$3.6 \cdot 10^{4}$
E6_CNT0.5	$6.8 \cdot 10^{4}$
E6_CNT0.4/GN0.4	$6.3 \cdot 10^{4}$
E6_CNT0.5/GN0.5	$1.5 \cdot 10^{5}$
E6_CNT0.6/GN0.4	$1.3 \cdot 10^{5}$
E6_CNT0.8/GN0.2	$3.2 \cdot 10^{5}$
E6_CNT1.0	$2.1 \cdot 10^{2}$

Fig. 5. Electrical volume resistivity of epoxy composites as a function of hybrid carbon nanofiller type and content

acrylic [24] binders filled with the same type of carbon hybrid nanofillers. From data presented in Fig. 5, it was evident that, depending on the application of the final epoxy composite material, it could be sufficient to use 0.25 wt % of the filler for composites to offer resistivity of $4—5 \cdot 10^5$ Ω·m. Slightly enhanced electrical features could be obtained using higher doses of carbon nanostructures, *i.e.* 0.5 wt %. The observed similar resistivity values (or even slowly increased) for epoxy composites filled with CNT/GN 0.2/0.3 to CNT/GN 0.8/0.2 could be caused by differences in the efficiency of CNT and GN mixtures dispersions and precision of the parameter evaluation (estimated error of measurement is ± 0.2 units in that measurement range).

Two factors of the investigated epoxy systems are important for their possible applications: (i) viscosity of the epoxy composition, (ii) the carbon nanofiller type and content, which not only determines the former parameter but also the composite electrical resistivity, as well as its price. For instance, the epoxy composition viscosity increased twice whereas the electrical resistivity of the composite even slightly increased when the nanofiller type and content was changed from CNT0.3/GN0.2 to CNT0.5 (76.5 → 153.7 Pa·s and $7.2 \cdot 10^3 \rightarrow 6.8 \cdot 10^4$ Ω·m, respectively). The observed change of electrical resistivities can be attributed to a synergistic effect between CNT and GN nanoparticles in the epoxy environment; on the other side some differences in the dispersion efficiency of both types of nanoparticles could also play a role.

CONCLUSIONS

The influence of carbon nanofiller type and content on the viscosity of epoxy compositions was evaluated. The viscosity of epoxy compositions with CNT/GN can be lowered two-fold when compared to those with relevant content CNT only, without deterioration of the electrical properties of the final epoxy nanocomposites. Some shift of onset temperature towards upwards values could be noted for epoxy compositions with carbon nanostructures — more distinct with increasing heating rate. Relatively high decreases in the glass transition temperature values for epoxy composites with carbon nanofillers were found: from 175 °C for neat epoxy materials down to 154 °C. These differences were especially pronounced for hybrid nanofillers with higher GN content in CNT/GN hybrids. Volume electrical resistivity could be decreased about 8—9 orders of magnitude after the introduction of 0.25—0.50 wt % carbon nanofillers. The most effective nanostructure system considering the increase of electrical conductivity whereas keeping viscosity of the epoxy composition on acceptably low level was CNT0.3/GN.02 ($\rho = 7.2 \cdot 10^3$ Ω·m and 76.5 Pa·s, respectively).

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