

Research Article

Effect of Nanodisperse Carbon Fillers and Isocyanate Chain Extender on Structure and Properties of Poly(ethylene terephthalate)

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The effect of diisocyanate chain extender (CE) on the mechanical, rheological, and relaxation properties, as well as on molecular weight and crystallizability, of starting poly(ethylene terephthalate) (PET) and its composites containing carbon nanomaterials (CNM) such as carbon nanotubes (CNTs) and commercial carbon (CC) has been studied. The composites were compounded in molten PET using twin-screw extruder (screw diameter 35 mm; L/D = 40). To improve the distribution of CNM in the polymeric matrix (before introduction into the melt), they were blended with PET powder and subjected to an ultrasonic treatment in methylene chloride. The salient features of the materials structure were estimated based on DSC and relaxation spectrometry (dynamic mechanical analysis) data. It has been found that CNM additives partly suppress the PET-chain extension reactions which take place during interaction between macromolecular end groups and CE. Besides, both CNT and CC favour crystallizability of the modified PET owing to nucleation of the crystallization process. The influence of CNT appears to be more effective than that of CC. Enhancements in true mechanical strength and deformability of PET/CE/CNM composites, as against PET/CE materials, were found to be most clearly exhibited by the CNT-containing composites.

1. Introduction

poly(ethylene terephthalate) (PET) is one of the most important types among the thermoplastic polymers; its role in the human vital necessity is constantly growing. The major application areas for PET are fibers, films, beverage bottles, containers for food products, and so forth [1].

In recent years—a period of about last twenty years—PET has been widely used more and more often in designing various composites for industrial purposes [2]. Composite materials that have no analogs in their economics and technical characteristics are developed on its base. Such materials include blends with polycarbonate [3, 4]; olefin polymers and copolymers [5, 6]; elastomers, poly(butylene terephthalate), styrene plastics [7, 8] and other polymers; materials reinforced by glass-fibers [2, 9]; fireproof composites [10] as well as systems containing small quantities of hard nanoparticles [11, 12].

An important problem arising during compounding and processing of PET composites—irrespective of their type—is hydrolytic as well as thermal degradation of polyester macromolecules. Breakdown reactions of PET macromolecules cause molecular weight reduction, deteriorate mechanical properties and impair technological characteristics [13].

The most important ways of slowing-down or preventing negative influence of macromolecular degradation on PET properties are incorporation of stabilizers, additional polycondensation of the material in the solid phase, using special chain extenders (CEs) [9]. The latter method is the most economically beneficial and efficient because it prevents macromolecules from both hydrolytic and thermal breakdown. CE mainly interacts with –OH or –COOH– end groups in polymer melt thus preventing molecular weight reduction. The reactions of interaction between CE and PET macromolecules easily take place in the melt in extrusion

mixer-reactor when special catalysts and vacuum treatment are used.

Several researchers have reported [4, 9, 14, 15] that compounds containing isocyanate groups can be excellent CE for heterochain polyesters and their blends. However, together with the increase of PET molecular weight, partial cross-linking of macromolecules which slows down polymer crystallization is observed [15]. As a result, at first, the efficiency of molten PET processing drops because more time is required for crystallization of formed product that ensures its shape stability. Besides, mechanical properties and heat resistance of finished products can be impaired due to decreased crystallinity.

It is well known, on the other hand, that crystallization kinetics of thermoplastics, including PET, can be controlled by small quantities of nanofillers such as nanoclays and/or carbon nanomaterials (CNMs) [15, 16] added to compositions. It is of interest, therefore, to understand the joint influence of CE and CNM on structural transformations in PET, the set of technological relaxation, and physicochemical characteristics of the obtained materials. The present work considers the stated problem using as an example PET composites containing diisocyanate CE along with carbon nanotubes and commercial carbon (CC).

2. Experimental

2.1. Materials. The experiments were conducted using granulated PET of commercial grade supplied by Mogilev-khimvolokno Co. (PET-8200 intended for making beverage bottles, containers or any other packaging items); having intrinsic viscosity in dichloroacetic acid, 0.700 dL/g; concentration of end carboxyl groups, 24 mmol/kg; glass-transition temperature, $T_g = 76.5^\circ\text{C}$. A powdery PET prepared by size reduction of PET-8200 granules in liquid nitrogen was also used. The powder particle size did not exceed 300 μm .

Multilayer CNTs produced at Heat-and-Mass Exchange Research Institute, NAS of Belarus, were used as carbon nanofillers. The technology of obtaining CNT is based on reaction of H_2 , CO , and N_2 in the plasma of high-voltage discharge at atmospheric pressure. The CNT were purified from amorphous carbon, diamond, and fullerene fractions by sedimentation and extraction in benzene. CNT dimensions were diameter, 5–30 nm, length, 0.5–3.0 μm (Figure 1). At initial state, CNTs were chaotically intertwined structural units of different lengths and diameters (Figure 1). Besides CNT, technical carbon No. 220 (Specifications 38 41558-97, supplied by Tekhuglerod Co., Omsk) was tested: average particle size, 13–85 nm, pH = 6–8 of aqueous suspension; specific external surface area, 111 m^2/kg ; iodine number, 121 g/kg; dibutylphthalate sorption, 100 $\text{cm}^3/100\text{ g}$.

The modifier APEC-MM (Specifications by 400084698 .151-2004) containing diisocyanate and stabilizer (ST) against thermal degradation of PET macromolecules was used as a CE. The compositions of test materials are listed in Table 1.

2.2. Compounding and Specimens Preparation. Test materials were compounded as follows. The CE powdery PET and

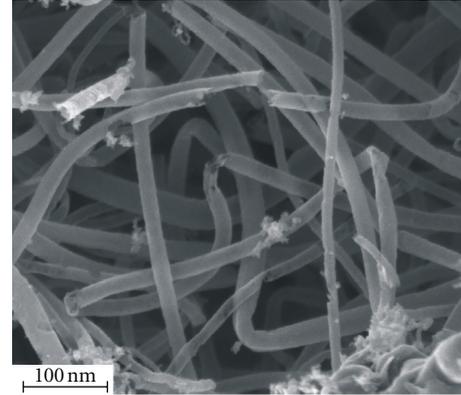


FIGURE 1: Electron photomicrograph of CNT.

TABLE 1: Compositions of test materials.

Number	Components (wt.%)					
	PET	Powdery PET	NT	CC	CE	ST
I	99.00	0.8				0.2
II	98.00	0.9			0.9	0.2
III	97.99	0.9	0.01		0.9	0.2
IV	97.95	0.9	0.05		0.9	0.2
V	97.99	0.9		0.01	0.9	0.2
VI	97.95	0.9		0.05	0.9	0.2

CNM were together subjected to ultrasonic treatment (sonication) in methylene chloride at the following conditions: instrument UZDN-1U32 (Russia), frequency, 22 kHz; duration, 15 min; initial temperature, 23°C . Then, the methylene chloride was “vacuum-evaporated” at $\approx 30^\circ\text{C}$. The powder prepared was added to PET granulate previously dried up to residual humidity below 0.02%; the mix was thoroughly stirred in a high-speed two-blade mixer. After that, the components were reactively mixed in molten PET. The work was done on an extrusion-granulating line based on the twin-screw extruder TSSK-35/40 (China): the screw diameter 35 mm; $L/D = 40$; 10 separate zones of heating the material cylinder; vacuuming zone and the screws of special configuration to provide for a high dispersion degree of the components as well as their uniform distribution throughout PET bulk. The melt temperature in the reactive mixing zone was 270°C . From the material cylinder of the extruder the material appeared as strands; they were water cooled and granulated on a rotor-type granulating device. The granulate produced was used to make test samples and do physicochemical analysis.

The test samples for testing mechanical properties of the materials were injection moulded on a machine EN-30 (Taiwan); screw diameter 35 mm; injection volume 30 cm^3 . The injection mould’s temperature was maintained at $45 \pm 5^\circ\text{C}$.

2.3. Characterization. The relaxation spectrometry technique was employed using test specimens in the form of

TABLE 2: Property values for polyester materials.

Composition	$[\eta]$ (dL/g)	M_n	MFI (g/10 min)	σ_{uf}^b (MPa)	σ_{tt}^c (MPa)	σ_r (MPa)	ε_r (%)	S (%)	
								$S_{ }$	S_{\perp}
I ^a	0.634	16006	23.0	54	199	42	374	0.85	0.54
II	0.746	22626	16.7	54	256	50	412	0.75	0.53
III	0.728	21480	18.8	55	282	55	412	1.23	0.58
IV	0.727	21417	19.5	56	325	60	441	1.21	0.66
V	0.723	21411	18.9	53	270	53	410	0.95	0.56
VI	0.737	22049	18.0	56	300	58	418	0.96	0.54

Here and in subsequent tables and figures, materials markings are as in Table 1. ^aComposition I was subjected to single extrusion at regimes similar to compounding of Compositions II–VI. ^b σ_{uf} is upper flow limit. ^c $\sigma_{tt} = \sigma_r(1 + \varepsilon_r/100)$ is true tensile strength, where σ_r and ε_r are, respectively, strength and relative elongation at break.

plates, $50 \times 5 \times 1$ mm. They were made on a piston moulding machine of laboratory version, the injection volume being 2.5 cm^3 .

The values of mechanical properties of the materials in tension were determined using a multipurpose machine Instron 5657 (UK). Experimental samples were of Type 5 ($50 \times 5 \times 3$ mm). In compliance with Russian GOST 1162 related to the determination of arithmetical mean parameter of mechanical properties, at least five samples were used. The samples, for which deviations from the arithmetical mean values did not exceed 10%, were used in calculations. The shrinkage was determined according to GOST 18616 on bars with size $80 \times 10 \times 4$ mm; were moulded by injecting melt at one butt end of the mould. The measurements were done longitudinally ($S_{||}$) and perpendicularly (S_{\perp}) to the melt flow direction.

Variations in molecular weight of PET were estimated by viscosity measurements conducted at 25°C with a capillary viscometer Ubbelohde; dilute solutions (0.5 parts of PET in 50 mL of solvent); the solvent was dichloroacetic acid of “chemically pure” grade. Every solution was agitated for 60 min at 60°C until PET became completely dissolved. The dependence between intrinsic viscosity ($[\eta]$) and number-mean molecular weight (M_n) of PET was found from Mark-Houwink’s equation [17]:

$$[\eta] = 0.0067 \cdot M_n^{0.47}. \quad (1)$$

Rheological properties of the materials were judged by the melt flow index (MFI) determined on the instrument IIRT-AM (Ukraine) at $T = 265^\circ\text{C}$, load $P = 21.6 \text{ N}$, and capillary diameter, $\varnothing = 2.095 \text{ mm}$.

The material structure was studied by differential scanning calorimetry (DSC) technique using microcalorimeter DSM-10 M (Institute for Biological Instrumentations, RAS, Russia); sample weight, 10 mg; scanning rate, $16^\circ\text{C}/\text{min}$.

The dynamic mechanical (relaxation) properties of the materials were found by analyzing temperature dependences of the mechanical loss tangent ($\tan \delta$) and dynamic shear modulus (G') of the samples. The tests were performed using a reverse torsion pendulum (designed at MPRI NAS of Belarus) [3, 15]; the frequency was 1 Hz. The temperature measurement accuracy was 0.1°C , $\tan \delta$, $\pm 3\%$; G' , $\pm 1\%$.

3. Results and Discussion

3.1. Rheological and Mechanical Properties. It is clear from Table 2 that modification of PET by addition of CE and CNM substantially influences the parameters that characterize molecular structure, along with values of mechanical and technological properties of the materials. There is a noticeable difference in the effects of CE alone and its combination with CNM. Thus, the addition of CE leads to the increase of intrinsic viscosity and noticeable reduction of MFI values, which results from increased molecular weight of PET [4, 15]. M_n ’s growth (MFI reduction) of PET containing CNM is not very substantial. This can be explained by high adsorptive (chemisorptive) surface activity of CNT and CC that causes partly blocking CE’s isocyanate groups, and consequently, the decrease of the output of products of its interaction with ending groups of PET macromolecules [12, 14].

It is worth mentioning that PET containing both CE and CNM shows a higher tensile deformability than the material containing only CE (Table 2, Figure 2). This effect is most pronounced in composites containing CNT (Table 2). With 0.05 wt.% of CNM (CNT or CC), the deformation curve changes because the material becomes stronger owing to orientational stretching of the sample neck. The calculated true strength values of the material (Table 2) show maximum tensile strength σ_{tt} for Composition IV, containing CE and CNT—0.05 wt.% exceeds 300 MPa. It appears that PET containing CE and CNT tends to have orientational stretching and its strength considerably increases. This fact shows a possibility of obtaining stronger PET fiber by modifying polyester with CE and CNT. The reinforcing effect of CE and CNM added simultaneously can be explained as follows.

The reinforcing effect of CE and CNM added simultaneously can be explained as follows. The chemisorptive interaction of one of the CE’s diisocyanate groups with CNM surface functionalizes the nanofiller surface. More possibilities arise for strengthening the bond between the nanofiller particles and PET macromolecules. This may happen through interaction of free isocyanate groups in CE chemisorbed on CNM nanoparticles with terminal hydroxyl or carboxyl groups of PET macromolecules, Polar van der Waals interactions with intramolecular ester groups, and so forth. It is quite possible that inter chain bonding of PET

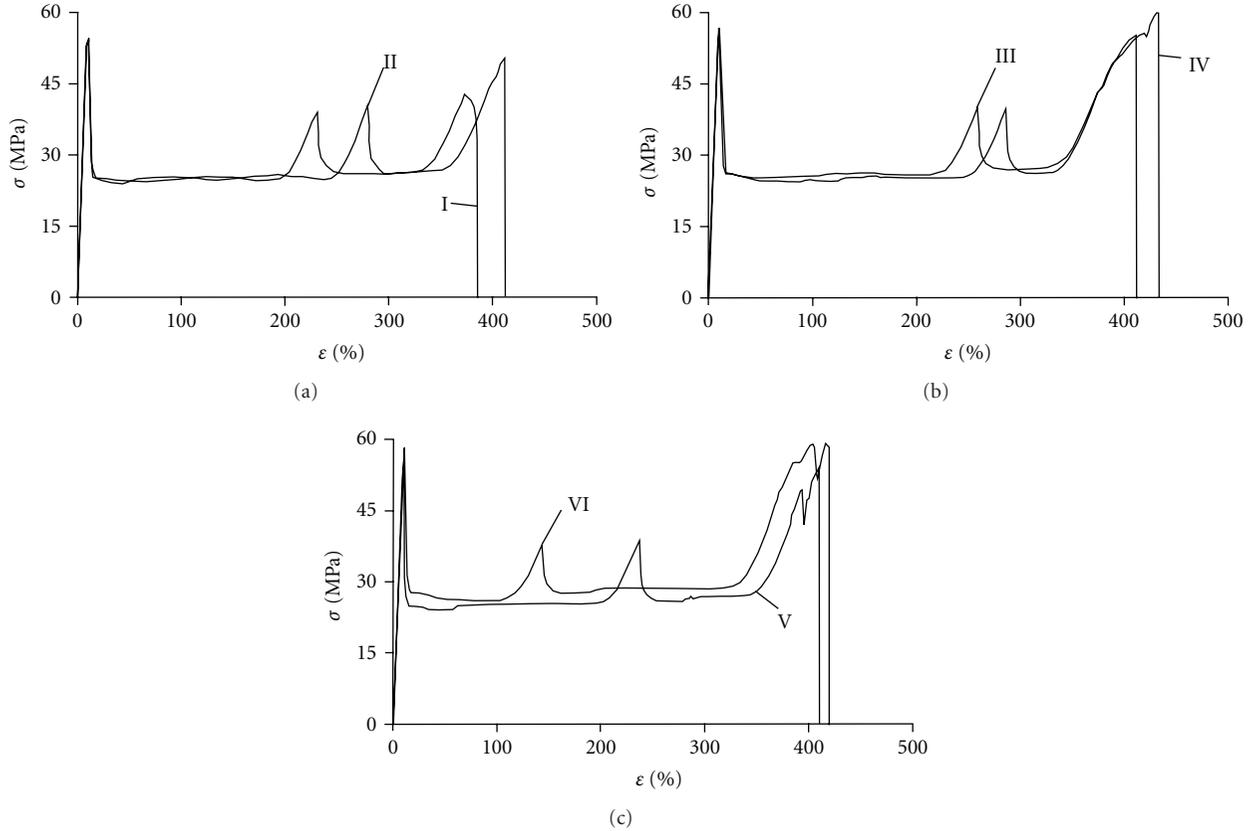


FIGURE 2: Deformation plots for materials.

macromolecules by means of the functionalized filler can happen in the presence of two free isocyanate groups in CE that was chemisorbed on CNM surface. It is obvious from the data in Table 2 and Figure 2 that the influence of CNT is stronger than that of CC.

Schemes of probable reactions for PET/CE, CNM/CE and PET/CNM/CE are shown in Figure 3.

3.2. DSC Observations. It is clear from Table 2 that pure CE added to PET causes shrinkage to reduce, whereas CNM increases the latter; the shrinkage increases more noticeably in case of CNT. This event is explained by specific influence of modifying additives on PET crystallization.

Indeed, it can be seen from Table 3 and Figure 4 that CE rises the temperature of cold crystallization ($T_{c,cr}$) and decreases the temperature of crystallization from the melt (T_{cr}) which results from the delay of crystallization processes owing to higher molecular weight of PET [4]. The addition of CNM together with CE leads to a noticeable enhancement in PET crystallizability. Crystallization proceeds faster when CNT is used: addition of nanotubes accelerates both cold crystallization and that from the melt in comparison with polyester non-modified with CE (Table 3). The use of CC in PET reduces the cold crystallization temperature (by 2.6–4.6°C) of the material as against the starting PET. However, irrespective of filler concentration, however, the T_{cr} -values

TABLE 3: DSC values for polyester materials.

Composition	$T_{c,cr}$ (°C)	$\Delta H_{c,cr}$ (J/g)	T_m^a (°C)	T_{cr}^a (°C)	ΔH_{cr}^a (J/g)
I	130.4	28.2	253.3	194.4	27.7
II	132.3	17.2	248.4	187.7	22.3
III	126.1	12.5	245.0	197.0	35.4
IV	128.3	13.0	246.8	197.6	37.2
V	127.6	9.8	248.9	188.2	35.8
VI	125.8	12.1	244.0	192.9	39.8

^aThe values were obtained after repeated heating (cooling) of samples.

(from the melt) remain somewhat lower in comparison with the initial polymer. It can be concluded that CNT are more advantageous as crystallization nucleator than CC for PET composites containing CE.

Some growth of crystallinity is observed under the influence of CNM what follows from the comparison of latent heat values of crystallization (ΔH_{cr}) of the materials (Table 3). Somewhat lower crystallinity of the materials containing CNT as against those with CC (Table 2) can be explained by the fact that nanotubes generate excessively great number of crystallization nuclei that prevent crystals from growing because of geometric (spatial) limits. Retarded

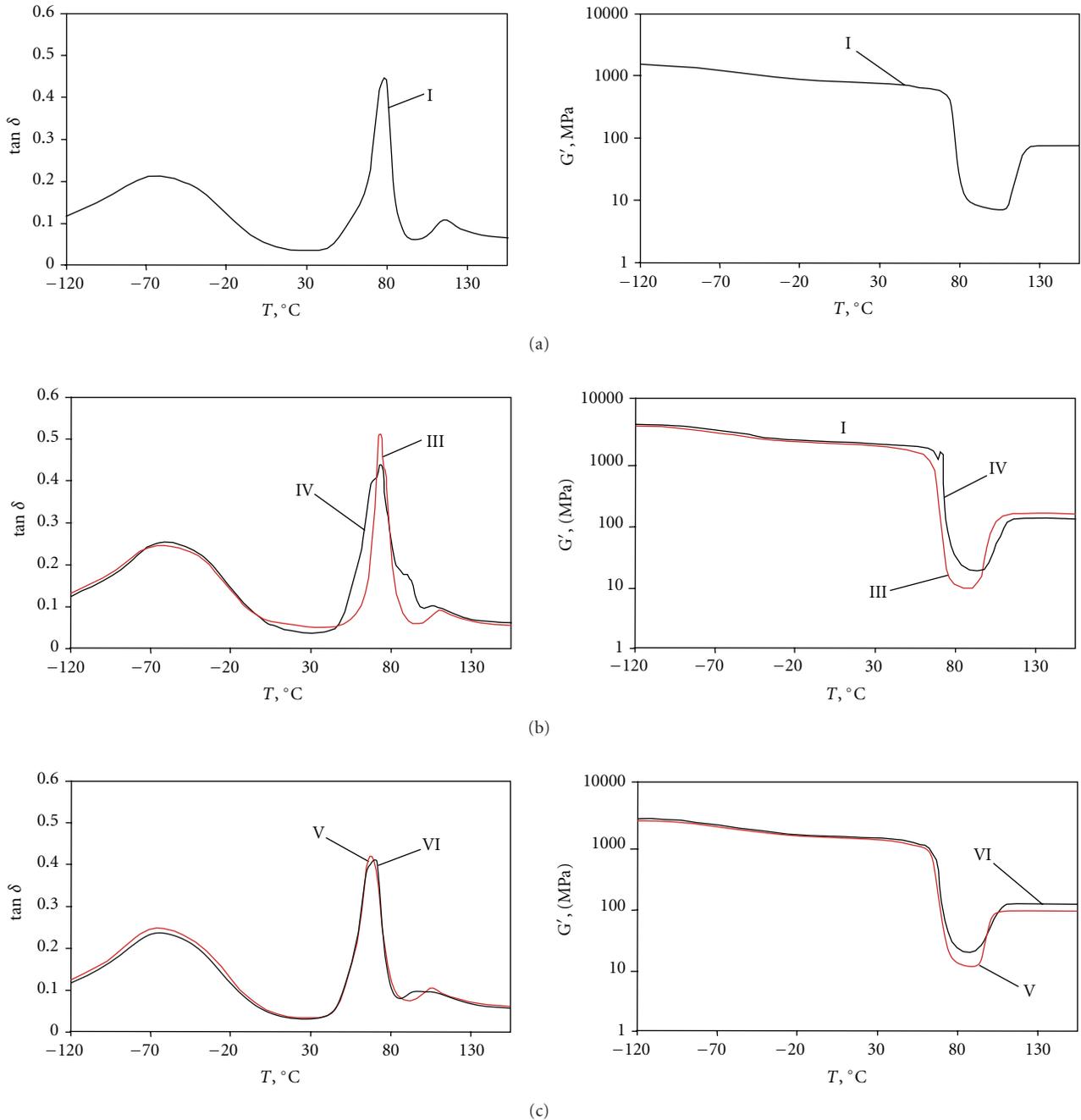


FIGURE 5: Temperature dependence of mechanical loss tangent ($\tan \delta$) and dynamic shear modulus (G') of materials (numbers correspond to compositions in Table 1). (a) I; (b) III-IV; (c) V-VI.

growth of crystals in spite of their accelerated nucleation has been reported elsewhere [18] where polyamide 6 crystallization had been investigated in the presence of nanodispersed clay minerals.

Therefore, simultaneous addition of CE and CNM to PET can result in composites with an increased molecular weight and enhanced crystallizability as against the starting polyester. CNM (especially CNT) levels the inhibiting effect of CE upon PET crystallization.

3.3. Relaxation Spectrometry. It has already been mentioned that adsorptive (chemisorptive) interaction between polymer macromolecules and filler particles surface can explain the influence of CNM on the structure and physicochemical properties of PET composites. The relaxation spectrometry data (Table 4, Figure 5) can prove this statement. The presence of CE and CNM in PET does not change T_g values determined by the temperature location of the glass-transition peak maximum point in the temperature dependence of

TABLE 4: Values of parameters characterizing relaxation properties of polyester materials.

Composition	T_g (°C)	T_β (°C)	G'_{\min} ^a (MPa)
I	76.5	-61.3	8
II	75.5	-64	3
III	75.6	-60.1	11
IV	76.5 (excess at 93.3)	-58.2	15
V	75.7	-60.7	10
VI	75.9 (excess at 90.3)	-60.1	13

^a G'_{\min} is dynamic shear modulus at 90–95°C.

mechanical loss tangent. However, at concentration of CNM = 0.05 wt.%, excesses (Figure 5) in the high temperature portions of the glass-transition peak are observed. Most likely the presence of excesses is due to mobility devitrification of macromolecular segments connected through adsorption with CNM particles surface. Under the effect of CNM, T_β values increase owing to mobility devitrification within an elemental unit of PET macromolecules; the growth of minimal values of dynamic shear modulus G'_{\min} within the zone of high elasticity (at $T \approx 90$ – 95°C) occurs which can also be explained by active adsorptive interaction between macromolecular fragments and CE-modified CNM surface.

These findings are indicative of prospects for designing and testing polyester composites containing CE and CNM. Investigations in this direction are undoubtedly of scientific interest and are of great importance for scientific substantiation of technology for making competitive and advantageous composites intended for industrial applications; also fiber-type materials of new generation.

4. Conclusions

Comparative analysis of molecular structure, relaxation, and mechanical properties of PET and its composites containing carbon fillers like nanotubes or commercial carbon and also diisocyanate CE has been conducted. It has been showed that reactions leading to chain extension proceed easily in the presence of carbon nanofillers. At the same time, retardation of crystallization of PET occurring under the influence of CE is leveled in the presence of carbon nanofillers; this effect is most pronounced in composites containing CNT. PET modified in the melt by CNT and CE appears to be perspective for making block-type articles and reinforced fibers.

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