The Systems Polyamides-Carbon Nanotubes

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Introduction: **Polyamides belong to a new class of heat-resistant polymers, the aromatic nature of which determines their high strength to the decomposition temperature, chemical resistance, fire resistance. Polyamide includes both synthetic and natural polymers containing the amide group –CONH$_2$ or –CO–NH–. Polymer composites reinforced with multiwalled carbon nanotubes, due to their outstanding mechanical properties and low density, are widely used in high-performance applications such as aerospace, automotive, shipbuilding and sports. Therefore, the use of nano-sized particles as fillers for polymers and polymers binder in order to improve the physical and mechanical characteristics of polymer composites is relevant and has been actively researched in recent years. The study of the effect of CNTs on the properties of polymer nanocomposites at the atomic level can be effectively carried out by the methods of computer modelling and quantum chemistry [1-3].**

Multi-walled carbon nanotubes and their deagglomeration

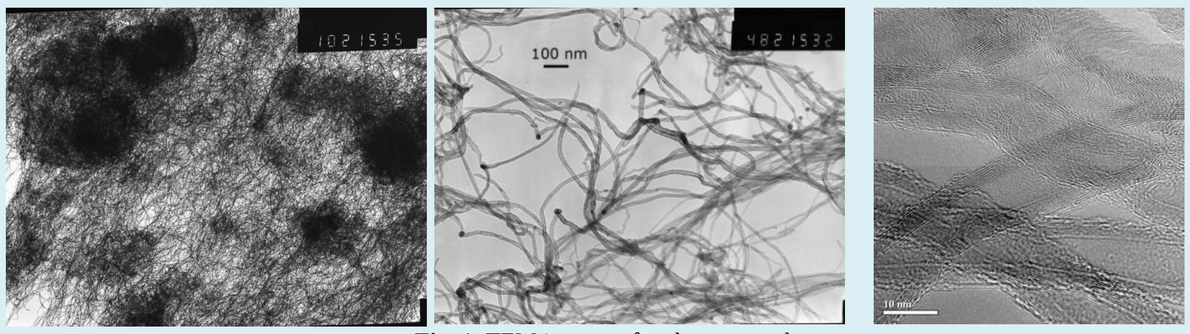

Fig. 1. TEM images of carbon nanotubes

CNT: Young's modulus ~1.8 TPa; Tensile strength ~150 GPa; Aspect ration $\eta \geq 10^3$; Fc ≈ 1/η ~ 0.1% wt.

Deagglomeration of CNTs was carried out in an aqueous solution of surfactant by ultrasonic treatment or in a rotary hydrodynamic homogenizer (Fig. 2).

Fig. 2. Rotary hydrodynamic unit-homogenizer

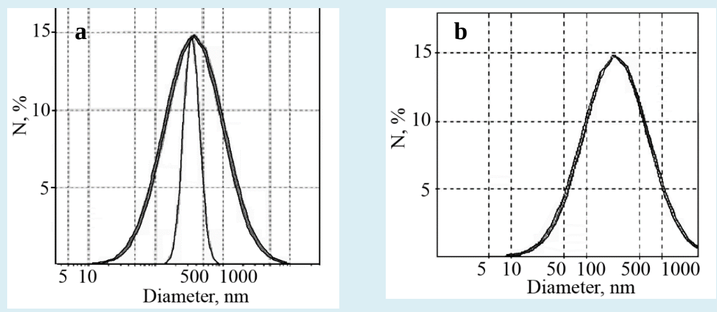

Fig. 3. Laser correlation spectroscopy. Particle size distribution: after obtaining an aqueous dispersion (a) and after holding it for one year (b) Processing in an aqueous solution of acrylic copolymer and isodecyl alcohol ethoxylate.

Production of polyamide-CNTs systems: a stable CNTs dispersion was applied to the surface of granules or polymer powder and dried at a temperature of 110–120 °C in a vacuum cabinet; then the polymer-CNTs mixture was heated to a viscous-fluid state, and the melt was mixed with a twin-screw mixer for 10–20 min at a given temperature. The resulting melt was unloaded and cooled in air. In the study, polyamides of the following brands PA 6, PA 6.6, PA 12.12 (manufactured by the PRC) were used

Mechanicals characteristics

Table 1. Characteristics of samples of polymers hot-pressed from the original polymer and after remelting in two-screw mixers

Sample	Melting point, °C	Density, g/cm^3		Tensile strength, MPa	
		Initial	Melted	Initial	Melted
PA6	250	1.187	1.107	75.1 ± 7.1	25.0 ± 1.2
PA2.12	220	1.319	0.950	41.3 ± 0.4	28.4 ± 1.8

Table 2. Tensile strength characteristics of the PA6-CNTs system depending on the CNTs content (all samples were subjected to the same thermo-mechanical treatment)

Properties	Content of CNTs, % wt.			
	0	0.125	0.25	0.50
Tensile strength (σ_b), MPa	25.0 ± 1.2	31.2 ± 11.2	41.2 ± 1.0	37.5 ± 0.4
Tensile fracture, %	1.5	2.0	3.0	2.5
Modulus of elasticity, MPa	1700	2200	1900	1700

Thermo characteristics

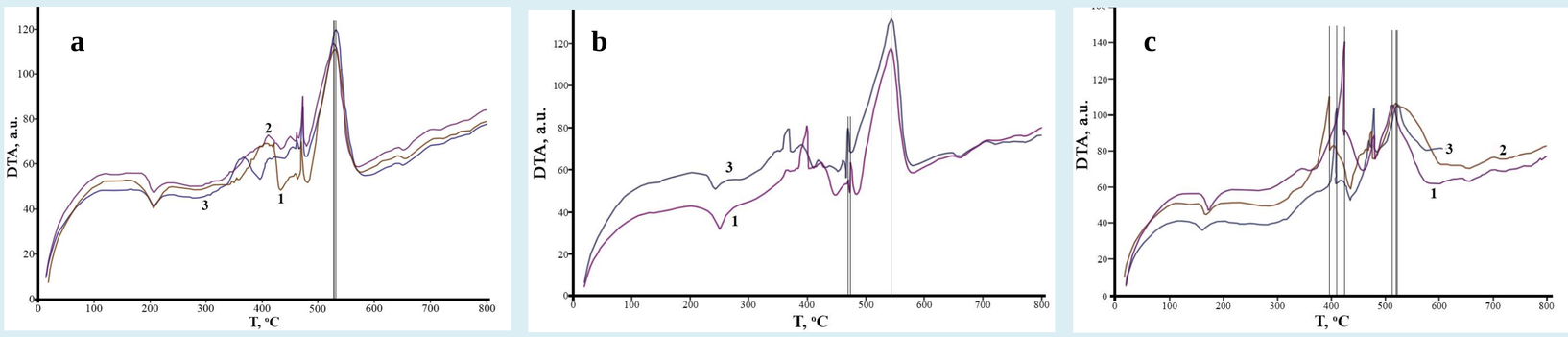

Fig. 3. DTA curves of samples of polyamide brand: a - PA6: 1 — initial; 2 — re-melting at 250 °C for 10 min; 3 — mixing of the melt with CNTs (0.5 % wt.) at 250 °C for 10 min; b - PA6.6: 1 — initial; 3 — mixing of the melt with CNTs (0.25 % wt.) at 270 °C for 10 min; c - PA12.12: 1 — initial; 2 — re-melting at 250 °C for 10 min; 3 — mixing of melt with CNTs (0.25 % wt.) at 250 °C for 10 min

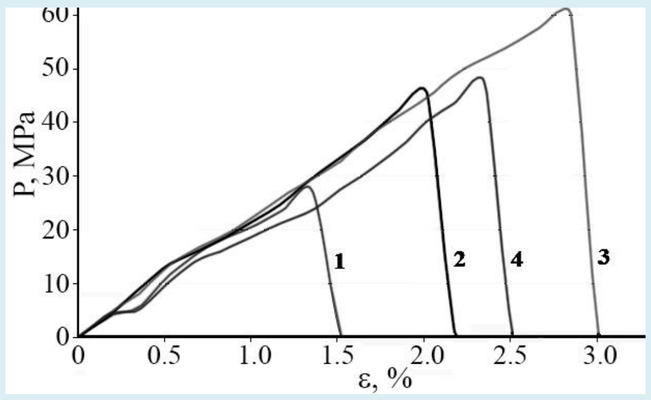

Fig. 4. Load diagrams in the coordinates "stress–strain" for PA6 samples with different mass content of CNTs: 1 — 0%; 2 — 0.125%; 3 — 0.25%; 4 — 0.5%

Table 3. Characteristics of tensile strength of the system, consisting of three layers of fiberglass and two layers of polymer: fiberglass-PA6 and fiberglass-PA6-0.25 % wt. CNTs

Sample	Tensile strength characteristics		
	Strength limit (σ_b), MPa	Fracture deformation, %	Elasticity modulus, MPa
Fiberglass–PA6	209 ± 6	17 ± 3	1230
Fiberglass–PA6-0.25 % wt. CNTs	391 ± 2	12 ± 1	3255

Table 4. Hydrogen bonds lengths of between polyamide fragments and the intermolecular interaction energy for the corresponding complexes

Complex	*l*(N-H··O=C), Å	ΔE, kJ/mol
Monomer ··monomer	2.08	-86.0
Dimer ··dimer	1.91	-302.2
Monomer ··$C_{96}H_{24}$	-	-117.4
Monomer ··$C_{110}H_{26}$	-	-121.2
2 Monomer ··$C_{96}H_{24}$	2.06	-219.0
2 Monomer ··$C_{110}H_{26}$	2.03	-228.1
Monomer ··monomer - $C_{96}H_{24}$	2.06	-187.6
Monomer·· monomer - $C_{110}H_{26}$	2.03	-192.0
Dimer ··$C_{96}H_{24}$	-	-180.5
Dimer·· $C_{110}H_{26}$	-	-188.4
2 Dimer·· $C_{96}H_{24}$	1.86	-346.2
2 Dimer·· $C_{110}H_{26}$	1.87	-345.6
Dimer·· dimer - $C_{96}H_{24}$	1.86	-461.8
Dimer·· dimer - $C_{110}H_{26}$	1.87	-459.7

Conclusion. It has been experimentally shown that thermomechanical processing of polyamides in an oxidizing atmosphere (in air) leads to structural degradation and loss of mechanical characteristics of the polymer.

Quantum chemical study of the influence of the presence of a graphene-like cluster on the energy of covalent bonds of a polyamide fragment in a nanocomposite

The density functional theory (DFT) method with the functional B3LYP [4, 5], taking into account the dispersion correction Grimme D3 [6, 7]. and the basis set 6-31G(d,p), using the GAMESS (US) program [8], was used to calculate the energy of interaction (ΔE) between adjacent polyamide fragments (two fragments of polyamide consisting of single elementary link are used, see Fig. 5 a), as well as that of the interaction between two larger fragments, each of which consists of two elementary units, see Fig. 5 b (hereinafter referred to as monomers and dimers).

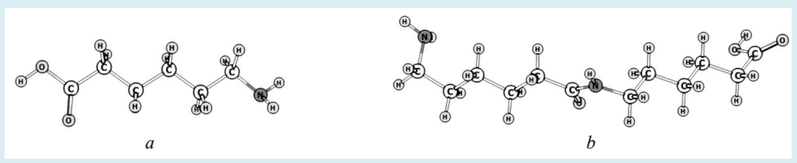

Fig. 5. Models for fragments of polyamide, consisting of: a – monomer, b – dimer

The energy of the intermolecular interaction (ΔE) between:
the two polyamide fragments were calculated by the formula (1):

$$\Delta E = E_{tot}(AB) - 2*(E_{tot}(A)) \quad (1)$$

where $E_{tot}(A)$ – the total energy of the monomer or dimer of amide, $E_{tot}(AB)$ is the total energy of the intermolecular complex of fragments polyamide;

one polyamide fragment (monomer or dimer) and GC were calculated by the formula (2):

$$\Delta E = E_{tot}(AB) - ((E_{tot}(A)+E_{tot}(B)) \quad (2)$$

where $E_{tot}(A)$ is the total energy of the polyamide fragment, $E_{tot}(B)$ is the total energy of the GC, $E_{tot}(AB)$ is the total energy of the intermolecular complex of a fragment of polyamide with a graphene-like cluster;

a graphene-like cluster and a complex consisting of two monomers or dimers was calculated by the formula (3):

$$\Delta E = (E_{tot}(ABC) - (E_{tot}(AB)+E_{tot}(C)) \quad (3)$$

where $E_{tot}(AB)$ is the total energy of the intermolecular complex consisting of polyamide fragments, $E_{tot}(C)$ is that of the graphene-like cluster, $E_{tot}(ABC)$ is the total energy of the intermolecular complex of polyamide with a graphene-like cluster;

the two polyamide fragments, taking into account the graphene-like plane, was calculated by the formula (4):

$$\Delta E = (E_{tot}(ABC) - (E_{tot}(A)+E_{tot}(BC)) \quad (4)$$

where $E_{tot}(A)$ – is the total energy of a polyamide fragment, $E_{tot}(BC)$ is the total energy of an intermolecular complex containing one fragment of polyamide and a graphene-like cluster, $E_{tot}(ABC)$ is the total energy of an intermolecular complex consisting of two identical fragments of polyamide and a graphene-like cluster.

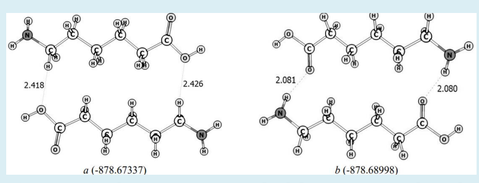

Fig. 7. The most probable intermolecular complexes formed from two monomers of amide (a) and (b) (here and further the distances between atoms in Å, and the total energy of the complexes in Table 4.)

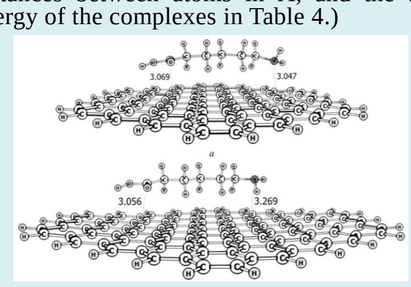

Fig. 9. Possible intermolecular complexes formed from amide monomer and graphene-like clusters of different sizes: a – $C_{96}H_{24}$. b – $C_{110}H_{26}$

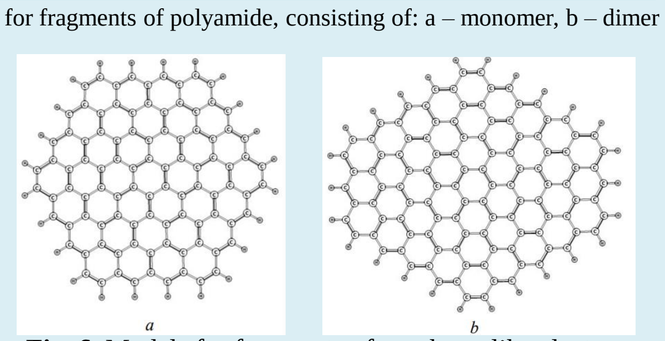

Fig. 6. Models for fragments of graphene-like clusters of gross formula: *a* – $C_{96}H_{24}$, *b* – $C_{110}H_{26}$

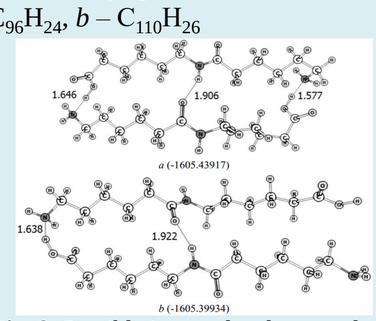

Fig. 8. Possible intermolecular complexes formed of two dimers of amide

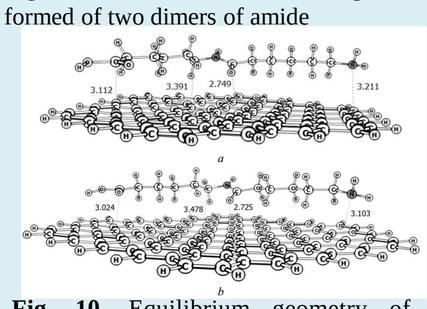

Fig. 10. Equilibrium geometry of intermolecular complexes formed of two monomers of amide and graphene-like clusters of different sizes: a – $C_{96}H_{24}$. b – $C_{110}H_{26}$

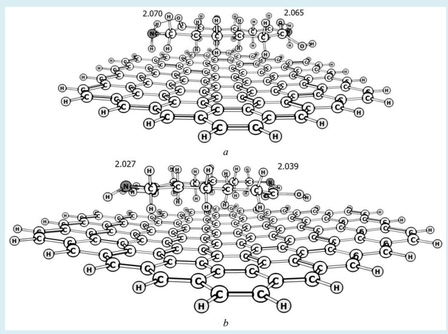

Fig. 11. Possible intermolecular complexes formed of dimer amide and graphene-like clusters of different sizes: a – $C_{96}H_{24}$. b – $C_{110}H_{26}$

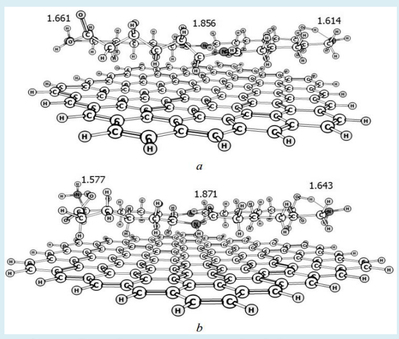

Fig. 12. The most probable intermolecular complexes formed of two dimers of amide and graphene-shaped planes of different sizes: a – $C_{96}H_{24}$, b – $C_{110}H_{26}$

Reinforcement of polyamides PA6, PA6.6, PA12.12 with CNTs up to 0.5% by weight. significantly increases the mechanical characteristics, melting temperature, work of destruction of the nanocomposite (by 3-4 times) compared to the unfilled polymer that underwent the same thermomechanical treatment. According to the results of quantum chemical calculations, in the nanocomposite polyamide - carbon cluster for all studied models, the energy of intermolecular interaction increases compared to the similar value for two fragments of pure polyamide, due to the strengthening of hydrogen bonds in the polymer matrix, which leads to an increase in the thermal stability and mechanical characteristics of the nanocomposite. Thus, the most promising is the reinforcement of CNTs polyamides in the process of their synthesis.

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