Technical Physics, 2024, Vol. 69, No. 8

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Impact Resistance of Epoxy-based Materials Filled with Carbon Nanotubes

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Received December 12, 2023
Revised April 30, 2024
Accepted May 19, 2024

The resistance of polymer composite materials based on epoxy resin with multi-walled carbon nanotubes (MWCNTs) as modifying additives under high-velocity impact effects was studied. Samples consisting of layers with different concentrations of MWCNTs in the polymer matrix were synthesized and studied. It was shown that carbon nanotubes improve the resistance of composites to impact effects. The highest values of the impactor kinetic energy absorption capacity are achieved by composites at a concentration of 7 wt.% CNTs (~ 3 times higher than without MWCNT filler).

Keywords: Polymer nanocomposites, high- velocity impact, impact resistance.

DOI: 10.61011/TP.2024.08.59012.304-23

Introduction

Polymer composite (PC) materials based on epoxy resins are actively used in various fields of production and household use. In this regard, an urgent task is to increase the impact strength, improve the mechanical and operational characteristics of such materials. Modification of polymer matrices with nanoparticles is one of the ways to improve composites [1]. Nanocomposites are materials that differ from conventional composite materials in the particle size of the dispersed phase modifier. Nanoparticles can improve the most important characteristics of materials: electrical conductivity [2,3], thermal conductivity [4], magnetic characteristics [5], mechanical properties (elastic limit, strength, impact strength, hardness [6–10]). Carbon nanotubes (CNT) are the most promising fillers of nanocomposites [8–10]. Our previous studies have shown that the impact resistance significantly increases at certain concentrations of reinforcing CNT [11]. The development of new materials with high resistance to high-speed impact and at the same time low specific gravity is one of the tasks of space materials science (see, for example, [11,12]), the development of new army protection gear [13]. We studied in this paper the change of the resistance to high-speed impacts of composite materials in case of introduction multi-walled carbon nanotubes (MWCNT) into the polymer matrix at impact velocities of ~ 100 m/s. The velocities of this range are low compared to the velocities characteristic of micrometeorites and space debris $\sim 10-70$ km/s in near-Earth space, however, they are quite comparable with the velocities of solid particles in near-lunar space, the pace of which increases. The velocities of the impactor were measured in this paper with high accuracy before and after impact with the test sample. Thus, the loss of kinetic energy during passage through the sample was determined, which is a characteristic of the impact resistance of the target. In addition to single-layer samples of polymer composites filled with MWCNT with various concentrations up to 10 mass.%, three-layer monolithic samples with varying concentrations of MWCNT in layers were tested. It was shown that multilayer structures with varying concentrations can significantly (by ~ 3 times) increase the absorption of the kinetic energy of the impactor, indicating their high resistance to high-speed impacts.

1. Materials and methods

1.1. Formation of polymer-composite structures

Polymer materials obtained on the basis of epoxy resins (ER) are rather brittle reactoplastics. Number of studies using standard mechanical methods or low-speed test methods showed that the addition of MWCNT to a polymer matrix can significantly increase the viscoelastic strength properties of composites [7–11,13–16].

The impact on the samples is initialized by a high-speed impact of the test body in our experiments discussed below. In this case, stresses are localized on the structural and compositional inhomogeneities of the material, which leads to the formation and growth of cracks. The formation of cracks can result in significant destruction of samples in materials that do not contain CNT additives. The addition of CNT to the polymer matrix in this case allows reducing these effects because CNT themselves have high mechanical properties, prevent the development of cracks and, in addition, can effectively interact with the polymer matrix [17–20]. A significant effect in enhancing mechanical characteristics can be achieved even with small amounts of added CNT due to their high specific surface area. For instance, the tensile strength of the polymer composite was increased by 35% to 84 ± 2.3 MPa by increasing the MWCNT concentration from 0.1 to 0.5 mass.% in Ref. [15], while the tensile strength of an unmodified polymer has the value of 66.1 ± 2.4 MPa. The tensile strength reached the maximum value (89.6 ± 4.1 MPa) in an epoxy composition with the addition of fluorinated CNT. Young's modulus for a composite with an addition of 0.1 mass.% of fluorinated CNT also reached the maximum value of 1644 ± 76 MPa among all studied composites, exceeding the Young's modulus of a composite without additives by 30%. The authors of the paper [15] conclude that the optimal degree of filling is about 0.10 mass.%, at which a simultaneous increase of elastic-strength characteristics such as compressive modulus of elasticity and modulus of elasticity for tension, compressive strength and impact strength is observed. The growth of the modulus of elasticity continued to CNT concentrations of 7 mass.% in a number of other papers [8,14]. A significant increase of the parameters of mechanical characteristics with an increase of the concentration of CNT without visible signs of weakening of growth to 2 mass.% was observed in Ref. [21,22]. We recorded the highest resistance to the impact of the Charpy machine in the CNT concentration range of 2.5–3.9 mass.% in a polymer composite with a MWCNT additive (PC-CNT) in our previous paper [11]. An increase of the absorption of the kinetic energy of the indenter in case of an impact at speeds of 50 and 280 m/s in the PC-CNT target was observed in the entire studied range of CNT concentrations from 0 to 10%.

An important problem affecting the characteristics of the PC-CNT is the agglomeration tendency of the MWCNT, which prevents the homogeneous and uniform distribution of the MWCNT over the entire volume of the matrix and limits the necessary adhesion of the working surfaces of the MWCNT to the polymer matrix. The agglomeration factor limits the further growth of the functional characteristics of PC-CNT with an increase of the MWCNT concentration. The limit value of the optimal concentration without significant MWCNT conglomeration is determined by the methods used for pretreatment of MWCNT and homogenization of the composite before polymerization.

A polymer bond of epoxy-diane resin (ER) of grade L (manufactured by PoxySystems, Germany) and hardener 285 (manufactured by HEXION, supplier „Grafit PRO") was used to fabricate PC-CNT samples. The polymer matrix was mixed with pretreated MWCNT of the brand „Taunit-M" (manufactured by LLC „Nanotechcenter", Tambov) with an outer diameter of 10–20 nm, an inner diameter of 4–8 nm, with a length of more than 10 μm with a total impurity content of no more than 1 mass.%, that had reinforcing functions in the polymer matrix of the composite. The pretreatment consisted of mechanical grinding of possible MWCNT conglomerates in a mortar with the addition of a small amount of ethyl alcohol, which quickly evaporated. An alcohol-free MWCNT powder was added to the polymer matrix. No additional steps were taken to purify the amorphous carbon fraction or to functionalize the MWCNT since the supplied powder practically did not contain an amorphous fraction. Mechanical mixing with a spatula and ultrasonic exposure were carried out for 10 min in an ultrasonic dispersant bath for uniform distribution of MWCNT in the polymer matrix. The viscosity of the polymer composite became high with the increase of the concentration above 10–12 mass.%, which limited the possibility of obtaining homogeneous distribution of MWCNT. There were no problems with the homogeneity of the MWCNT distribution and their agglomeration below this concentration, however, the impact of possible MWCNT agglomeration requires special studies which is planned in our future work. The resulting material was formed into thin discs with a diameter of 42 mm and a thickness of 3 mm using collapsible plastic molds. The curing was carried out at room temperature for 24 h. The synthesis process made it possible to vary the content of MWCNT in the polymer matrix in a controlled manner. The appearance of some samples with CNT concentrations of 0, 3, 7 and 10 mass.% is shown in Fig. 1, respectively.

Multilayer composites of various configurations were manufactured based on the above-mentioned method of forming single-layer samples:

1) MWCNT–0–MWCNT (i.e. a sample containing three layers: upper and lower with 7 mass.% MWCNT content and intermediate middle layer with 0% MWCNT);

2) 0–MWCNT–0 (i.e., a sample containing three layers: upper and lower with 0% MWCNT content and an intermediate middle layer with 7 mass.% of MWCNT);

3) MWCNT–MWCNT–MWCNT (all three layers with MWCNT concentration of 7 mass.%).

Three-layer samples from polymers with different nanotube contents were made as follows: a composite of the 1st layer was poured into the mold; a pause was maintained for 5 min for partial polymerization of the polymer of the first layer, then the next layer with a different CNT content was poured on top. Partial polymerization of the first layer prevents the polymer of the second layer from penetrating into the matrix of the first layer, since the first layer has a higher viscosity than the second. At the same time, there were no air gaps between the layers. Interpenetration

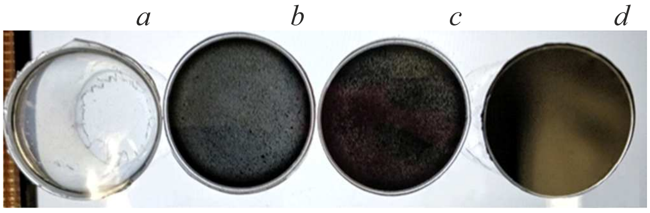

Figure 1. Experimental samples of ER + MWCNT with MWCNT content: *a* — 0, *b* — 3, *c* — 7, *d* — 10 mass.%.

(binding) of the boundary regions of the polymer layers took place, but not their mixing.

1.2. Ballistic test bench

To determine the ballistic loss of kinetic energy of the trial body (TB) during flight through a flat nanocomposite sample, an experimental test bench was developed consisting of a pneumatic TB accelerator, a sample holder and devices for determining the velocity of TB before and after the sample. Figure 2 shows a block diagram of the experiment, and Figure 3 — a general view of the test setup.

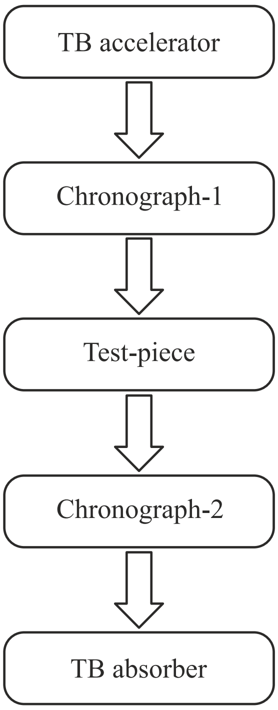

Figure 2. Block diagram of an experimental setup for determining kinetic energy loss.

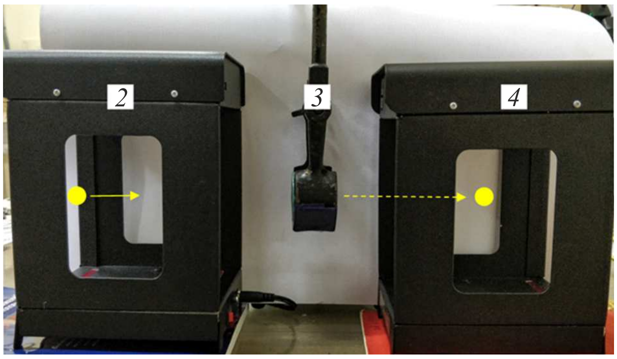

Figure 3. Experimental test bench: *1* — pneumatic TB accelerator (not shown in the figure); *2* — chronograph-1 for determining the input speed; *3* — sample holder; *4* — Chronograph-2 for determining the output speed; *5* — TB absorber (not shown in the picture).

An air gun was used as an accelerator of the trial body, accelerating the TB to speeds of 100−115 m/s with an impact energy of up to 3 J. TB was a copper-plated steel ball with a diameter of $d = 4.50 \pm 0.05$ mm and a mass of $m = 0.355 \pm 0.005$ g. The speed of the ball was measured before and after interaction with the sample using two chronographs. ASS-0022 optical chronographs were used in this setup, which record the speed of any body passing through the sensitive area of the instrument. Highly sensitive optical sensors located at two fixed points of the chronograph at a known distance from each other read the shadow (refraction of light) of a body flying between them and displayed the speed value according to the formula „speed = distance/time“. The initial velocity of the ball V_0 determined the initial energy reserve K_0 (initial kinetic energy $K_0 = mV_0^2/2$. After impact, the velocity decreased to V_1 with energy expenditure for deformation and destruction of the sample to the value $K_1 = mV_1^2/2$. Accordingly, the absorption of kinetic energy by the target (KEA) of TB for deformation and destruction of the sample was determined as $A = K_0 - K_1$.

Obviously, the destructive effect of the impact of the impactor on the target will depend on many factors, in particular on the shape and transverse dimensions of the impactor. With the same kinetic energy of the TB, the nature and degree of damage to the target at a higher cross-section will differ from what can be expected with a more focused impact. For a better comparison of the effects of impact for different calibers of the impactor, we considered it advisable to introduce such an impact characteristic as the specific absorption of kinetic energy, defined as the ratio of the work spent on the destruction of the sample to the cross-sectional area of the TB:

$$a = \frac{4A}{\pi d^2}, \quad \left[\frac{\mathrm{J}}{\mathrm{mm}^2}\right],$$

where d — the diameter of the ball, mm.

2. Experimental results

2.1. Testing of single-layer samples

Samples of a polymer composite material filled with nanotubes with concentrations of 0, 1, 3, 5, 7 and 10 mass.% MWCNT were fabricated for testing.

The qualitative results of the impact on the PC-MWCNT samples are shown in Fig. 4.

The quantitative analysis of the experimental results is presented in the table. The experimentally obtained dependence of the specific kinetic energy absorption (KEA) on the CNT concentration is shown in Fig. 5.

A visual inspection of the damage pattern of the samples indicates that the polymer without added MWCNT is a rather brittle material, the impact of the impactor on which results in the formation of a grid of radial and annular cracks (Fig. 4, *a*). The addition of MWCNT to the polymer

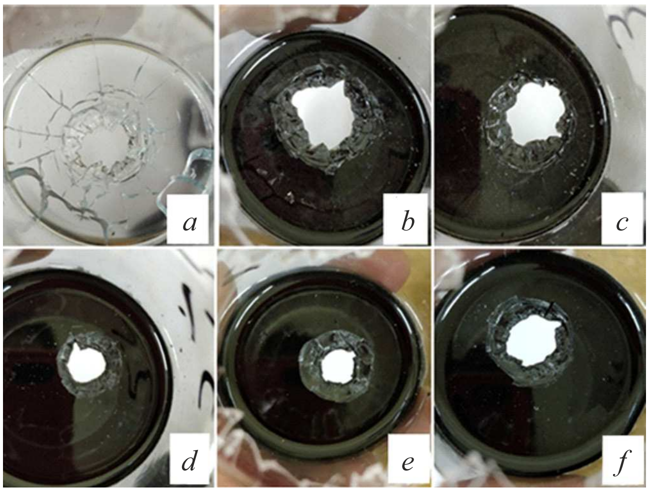

Figure 4. Photos of the destruction of single-layer samples of ER+x% MWCNT: a — $x = 0$, b — 1, c — 3, d — 5, e — 7, f — 10 after the impact of accelerated TB.

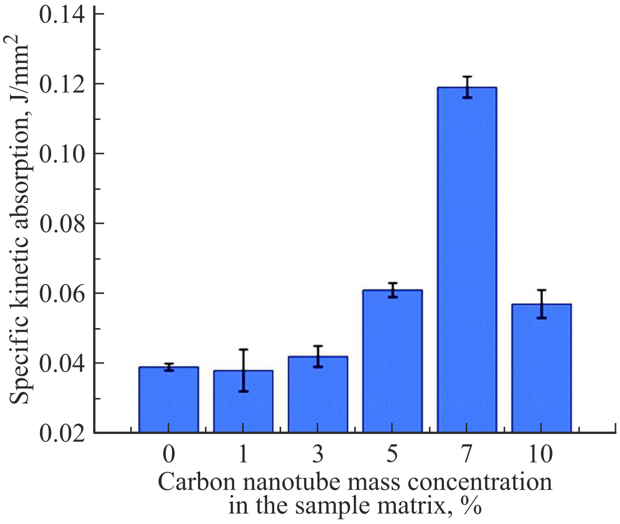

Figure 5. The dependence of the specific KEA of the composite on the MWCNT concentration.

Dependence of the KEA on the concentration of MWCNT in the polymer matrix

N	V_0, m/s	V_1, m/s	m, g	A, J	a, J/mm^2	
	0%					
1	111.4	94.5	0.355	0.618	0.039	0.039
2	111.7	95.6	0.355	0.592	0.037	±0.001
3	110.9	93.3	0.355	0.638	0.040	
	1%					
1	110.1	88.8	0.355	0.752	0.047	0.038
2	106.2	94.3	0.355	0.424	0.027	±0.005
3	104.5	86.2	0.355	0.619	0.039	
	3%					
1	102.2	80.7	0.355	0.698	0.044	0.042
2	93.2	74.1	0.355	0.567	0.036	±0.002
3	104.1	82.5	0.355	0.715	0.045	
	5%					
1	101.4	70.2	0.355	0.950	0.060	0.061
2	103.2	69.7	0.355	1.028	0.065	±0.002
3	102.1	71	0.355	0.956	0.060	
	7%					
1	125.4	72.8	0.355	1.850	0.116	0.119
2	127.3	72.3	0.355	1.949	0.123	±0.002
3	126.4	73.3	0.355	1.882	0.118	
	10%					
1	125.3	99.1	0.355	1.044	0.066	0.057
2	119.2	97.4	0.355	0.838	0.053	±0.004
3	121.3	100.1	0.355	0.833	0.052	

composition results in higher resistance to impact with minimization of noticeable cracks (Fig. 4, b–e), and to a higher KEA. Samples with a 7% concentration of CNT demonstrated peak values of the composite's ability to absorb TB kinetic energy (in ∼ 3 times higher than in case of the absence of CNT) under high-velocity impact. A further increase of the CNT concentration in the polymer matrix results in a decrease of the ability of the composite to absorb the TB kinetic energy. Apparently, the oversaturation of the polymer with reinforcing components results in an increase of the fragility of the material, which is associated with the difficulty of penetration of viscous epoxy resin into CNT conglomerates, which become larger and compact at high concentrations. Significant CNT concentrations complicate the task of uniform distribution of CNT in the polymer matrix which naturally results in a degradation of the impact resistance of samples.

2.2. Testing of multilayer samples

When multilayer samples were tested, the available power of the accelerator was sufficient only for through penetration of samples with CNT–CNT–CNT configuration. The penetration of the input layer and the formation of cracks in the input and output layers was observed in 0–CNT–0 and CNT–0–CNT samples, but no complete penetration of the output layer occurred. An illustration of the impact damage of three-layer samples is shown in Fig. 6.

It is obvious that a layered configuration consisting of layers with different concentrations of CNT demonstrates a more efficient impact resistance than a sample of the same thickness consisting only of CNT layers. Therefore, layered structures with a variable composition of layers demonstrate an improvement of impact resistance properties. The reduction of CNT consumption by at least a third is an important factor in addition to the increased impact resistance of CNT–0–CNT and 0–CNT–0 samples compared to CNT–CNT–CNT samples. It should be noted, however,

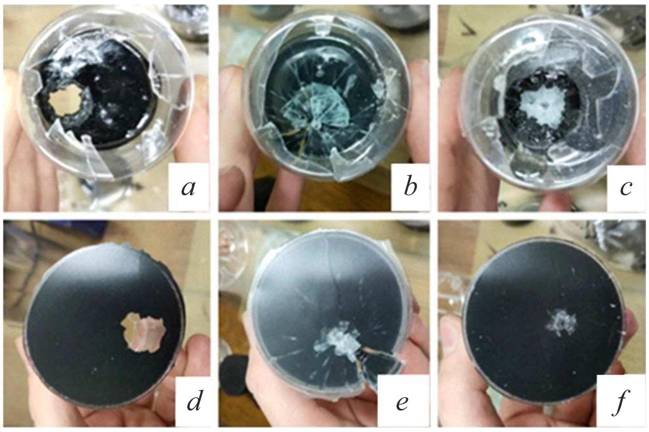

Figure 6. The result of tests of through penetration of multilayer samples. *a–c* — type of sample output surface; *d–f* — type of sample input surface. Through penetration is observed in CNT–CNT–CNT samples (*a, d*); there is no through penetration in 0–CNT–0 (*b, e*) and CNT–0–CNT samples (*c,f*).

that the structure without CNTs, i.e. 0–0–0, turns out to be easily penetrated. Thus, a layered structure absorbs impact energy more efficiently than a homogeneous one.

Conclusion

Adding CNTs to an ER-based polymer matrix is an effective way to enhance the impact resistance of materials. Addition of small amounts of CNT make it possible to improve the properties of composite materials, avoiding an increase of the weight and thickness of the sample, which is extremely important for the practical application of these materials. It was shown that the impactor kinetic energy absorption capacity increases non-linearly with an increase of the CNT concentration in the polymer matrix. The composite demonstrate best absorption capacity at a CNT mass concentration of 7% (~ 3 times higher than without CNT). An increase of concentration above 7 mass.% results in a weakening of the properties of the material.

A further increase of the absorption capacity can be achieved by using multilayer composite materials consisting of layers with different CNT concentrations. Thus, the optimal combination of layers with varying CNT concentrations should increase the impact resistance of composites while reducing the nanofiller consumption.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by A.Akhtyamov