Nanostructured Composites of Explosives and Single-Walled Carbon Nanotubes

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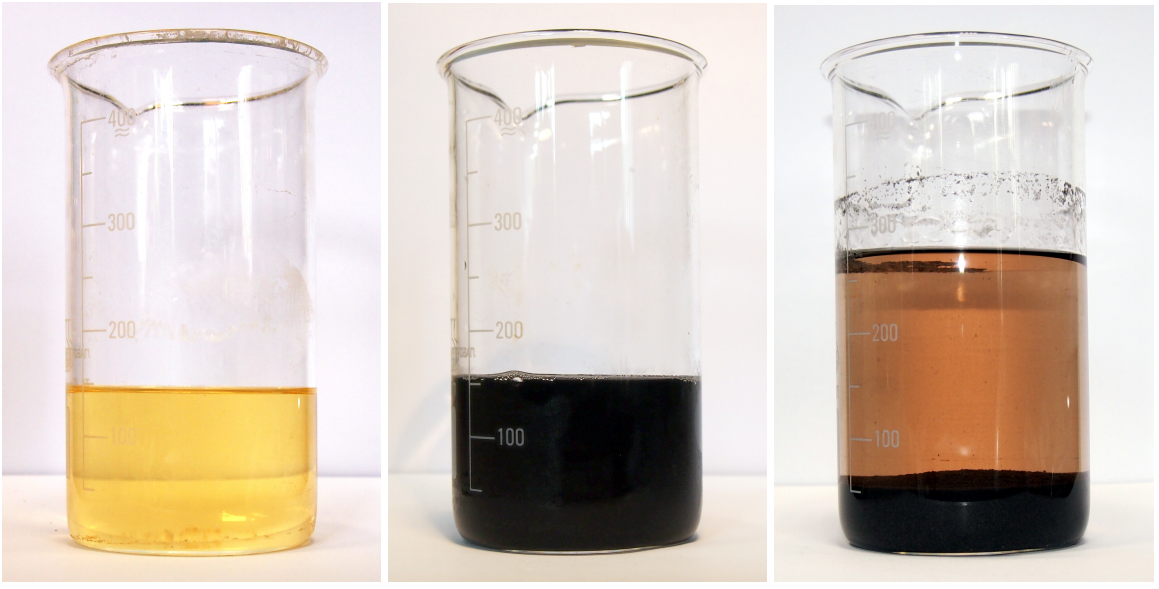
Abstract. Physical properties of many dielectric materials may be changed significantly by addition of small amount of carbon nanotubes. It is reasonable to expect that nanotubes can be used to modify the characteristics of explosives. This paper presents the results of static and dynamic measurements of the properties of such explosive nanocomposites. The composites have rather high electrical conductivity. In the structure of the composites, the pores, which are tens of nanometers in size, were observed. For the RDX-based composition, the chemical reaction behind the front is somewhat faster as compared to the pure recrystallized hexogen. The dynamics of small-angle x-ray scattering of synchrotron radiation during detonation was measured. Nanotubes in detonation products are not observed by high-resolution transmission electron microscopy.

Introduction

The parameters at the detonation front of high explosives (HEs), as well as the sensitivity to external action, significantly depend on the initial structure of the charge. The influence is exerted both by the porosity of the charge as a whole and by the particle size of the explosive. The size of the initial particles of HEs determines to a considerable extent detonation parameters of pressed charges close to the maximum density. Submicron particles can be relatively easily obtained by mechanical particle size reduction or in the process of recrystallization. Getting smaller particles down to tens of nanometers requires a much more complex process. At the same time, this scale of the microstructure of HEs is of greatest interest. The sensitivity tests carried out by Yi Wang et al[1] showed that when RDX was pulverized to nanoparticles, its mechanical and shock sensitivities decreased by more than 45%. Surprisingly, the decrease in the critical thickness of detonation of RDX charges was also observed,[2] which indicates significant changes at the process of detonation transformation in nanostructured explosive materials.

This suggest that the important scale of processes in the detonation front might be tens of nanometers. Modification of the microstructure of explosive charges at this level may significantly influence the process of detonation transformation. Nanostructured composites may open the perspective of miniaturization of explosive elements and increase the safety of their use.

In the present work, we studied the detonation parameters of explosive nanocomposites prepared by introducing single-walled carbon nanotubes (SWCNTs) into HEs particles. In the composites obtained, pores with diameters of tens of nanometers are observed by scanning electron microscopy (SEM). The samples have a structure with



a b c

Fig. 1. TNT+0.5% wt SWCNTs synthesis, a – solution of TNT in acetone, b – SWCNTs dispersed in water, c – precipitated explosive composite.

characteristic dimensions of tens and hundreds of nanometers.

Currently, SWCNTs are widely used in the industry to modify the properties of various materials. The introduction of SWCNTs in amounts less than 1% wt allows one to achieve high electrical conductivity of initially nonconducting materials, a significant increase in thermal conductivity, and modification of mechanical properties. To obtain maximum effect, a high homogeneity of nanotube insertion into the material is required, which is a non-trivial task. The verification of the homogeneity of nanotube insertion, that is, the constancy of the properties of the composite over the entire volume of the sample, is a serious problem.

The authors of this work have previously proposed a method for synthesizing explosive composites containing 0.5% wt SWCNTs by precipitating explosives from a solution to a dispersed SWCNTs in water.[3] The electrical conductivity of the resulting composite increases by more than 10^{10} times as compared with the initial explosive and reaches values of up to $0.1\ Ohm^{-1}cm^{-1}$, which is comparable to other composites containing a similar amount of SWCNTs.[4] The value of conductivity obtained is practically independent of the choice of the explosive and is fairly well maintained from charge to charge. This allows us to believe that this method of synthesis gives a satisfactory degree of homogeneity of SWCNTs implantation in explosives, as well as a good reproducibility of the results. In some cases, a similar level of conductivity of composites can be obtained with amount of SWCNTs hundreds of times lower, but the method proposed by the authors is easy to implement and does not require any special equipment other than the hands of the experimenter and the ordinary laboratory table.

Despite the fact that the proposed method of synthesis does not directly produce particles with sizes of tens of nanometers, the final composite had a heterogeneity in the structure of the desired scale. This allows us to expect that for the resulting composite, the trends in the properties of the explosive compositions observed when the grain is reduced to tens of nanometers will be valid. In particular, a decrease in the sensitivity to mechanical impacts should be mentioned. In addition to the influence of nanopores on the properties of a composite ex-

plosive, the effect of the nanotubes themselves must also be observed. For example, there is a significant decrease in the sensitivity to shock for samples obtained by mechanical mixing SWCNTs with CL-20.[5] The authors suppose that this is due to an increase in the thermal conductivity of the explosive composite and, as a consequence, a decrease in the local heating of the pores during compression of the substance.

Thus, the use of SWCNTs for the modification of the structure of explosives at the nanolevel is a promising method to achieve a significant change in both the static and dynamic characteristics of the explosive material.

Synthesis and preparation

The method for synthesizing explosive composites is the precipitation an explosive from a solution by adding to it an anti-solvent containing dispersed SWCNTs.[3] In fact, it is the standard solvent/antisolvent method of recrystallization. We used TNT, RDX, PETN or benzotrifuroxane (BTF) to prepare solution in acetone, fig. 1(a). As an antisolvent, a dispersed SWCNTs in water was used (TUBALL™ COAT_E produced by OCSiAl, Novosibirsk), fig. 1(b)). The mixing of the initial components leads to an almost instantaneous precipitation of explosives. In this case, SWCNTs act as centers of crystallization. Initially, the dispersion of SWCNTs in water is the opaque black liquid. After a sufficiently rapid precipitation of the synthesized composite within a few minutes, the remaining liquid becomes transparent and almost colorless, fig. 1(c). The residual coloration depends on the initial concentration of the solution of HEs in acetone, as well as on the content of SWCNTs. As the mass concentration of SWCNTs increases, the black color of the liquid remains. A decrease in the mass concentration of SWCNTs leads to a decrease in the electrical conductivity of the resulting composite. Accordingly, it is expected that the effect of SWCNTs on the structure of the composite will be reduced.

The resulting dried composite is a gray powder. The structure of explosive composites has characteristic nanoscale features observed by scanning electron microscopy. The particles of HEs are coated with nanotubes, fig. 2. Nanotubes fill the pores between the particles and connect them together. In the structure of the particles themselves, pores of tens of nanometers in size are observed, fig. 3. The formation of such pores, is, apparently, due to the shape of SWCNTs. The diameter of SWCNTs usually does not exceed 2 nm, whereas their length is several microns. Therefore, they are usually observed in the tangled globular form. When explosive precipitates from a solution, such globule is the center of crystallization, but the penetration of the material of explosives inside it is difficult.

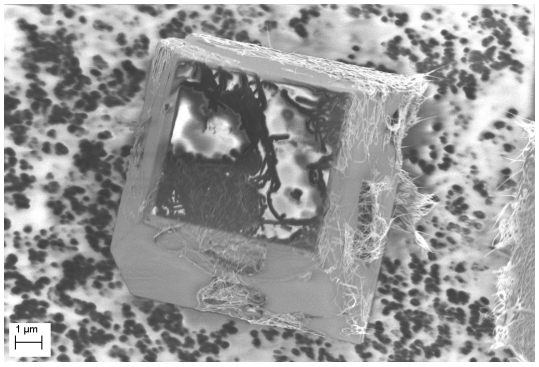


Fig. 2. BTF + 0.5% SWCNTs.

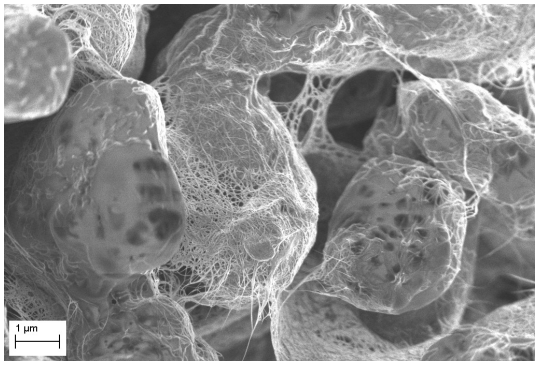


Fig. 3. RDX + 0.5% SWCNTs.

When the electron beam is exposed to a particle for a long time, a sublimation reveals the internal structure. Nanotubes are not only located outside the particle, but also permeate them inside, fig. 4. It is also observed that SWCNTs are reinforcing fibers within the structure of an explosive composite, fig. 5.

The resulting composites were both studied in the initial state and used to make pressed charges.

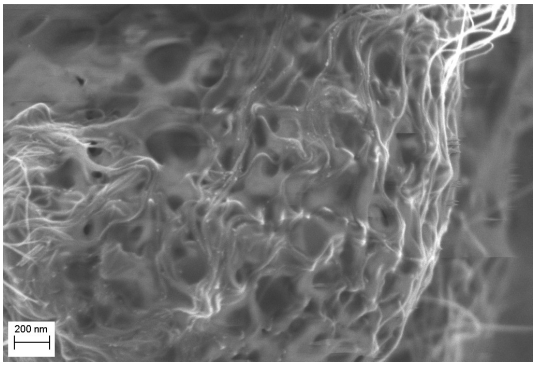


Fig. 4. RDX + 0.5% SWCNTs, partial sublimated.

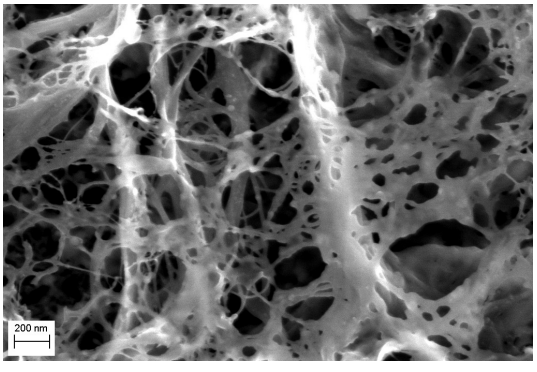


Fig. 5. TNT + 0.5% SWCNTs.

In the detonation products[6] of composites based on PETN and BTF nanotubes in the initial state were not detected by the transmission electron microscopy (TEM). The detonation products contain some carbon fibers, which theoretically could be referred to the products of nanotube decomposition, but this requires an additional detailed study. In general, the detonation products of the initial explosives according to the TEM data are identical to the detonation products of composites based on them.

Electrical conductivity

The process of detonation of a composite based on RDX was studied using the technique developed earlier for measuring the electrical conductivity behind the detonation front of dense explosives.[7, 8] The technique allows us to measure electrical conductivity with a resolution of not worse than $0.1\ mm$. The measurements are made in coaxial geometry with an external charge diameter of $8\ mm$, an internal diameter of $2\ mm$.

The increase of density of pressed RDX leads to the peak value increase, but the width of the conduction zone varies marginally.[9] The widths of the electrical conductivity zones measured in this way are close to the reaction zones behind the detonation front measured by optical method.[10]

It was found that the measured electrical conductivity data of the RDX-based composite significantly differs from the pure RDX obtained by the same method of recrystallization under close conditions (fig. 6). It should be noted that for the nanocomposite, rather good reproducibility of the experimental results is observed.

The initial stage of the conductivity growth in a nanocomposite and pure RDX is very different. At present, the nature of this behavior is not clear. One of the reasons could be the distortion of the current lines due to the presence of a noticeable electrical conductivity (≈ 0.5 Ohm^{-1}cm^{-1}) ahead of the wave front. This is probably a systematic measurement error.

The method of measuring the electric conductivity also gives the velocity of the detonation front. For a pure RDX with a density of $1.8\ g/cc$, the front velocity is $8.44 \pm 0.025\ km/s$. For the composite, the front velocity is slightly higher and is $8.62 \pm 0.059\ km/s$. Both values are lower than the estimated detonation velocity 8.7433[11] km/s for a given density, apparently this is the effect of the small size of the charge.

The region of high electrical conductivity for a nanocomposite seems to be wider. However, after approximately $0.2\ \mu s$, the conductivity becomes the same both in two experiments with the nanocomposite, and in the experiment with the pure RDX. This means that the contribution of nanotubes to the conductivity of products is minimal, i.e. by this time they are probably already destroyed.

Electromagnetic measurements

The velocity history at the interface between the face of cylindrical RDX-based charge and an inert PMMA window was measured. A Π – shaped sensor cut from $9\ \mu m$ thick Al foil was glued to the contact boundary. The experimental assembly was placed in an external magnetic field created by the Helmholtz coil. The velocity of the contact bound-

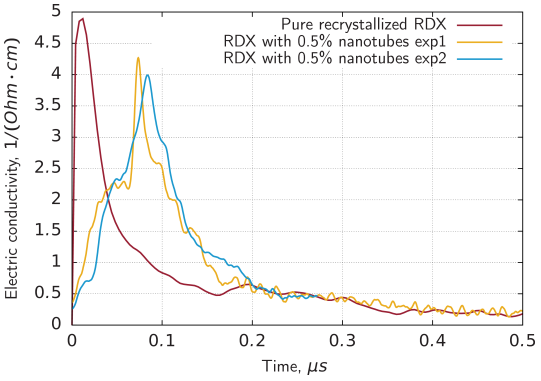


Fig. 6. Electrical conductivity behind the detonation front for a pure RDX and a composite. The charge density in all cases is $1.8\ g/cc$.

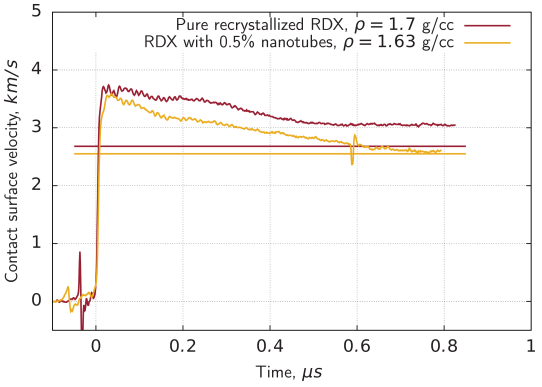


Fig. 7. Velocity of contact boundary HEs – PMMA. The horizontal lines show the calculated velocity levels for the Chapman-Jouguet state.

ary was extracted from the emf generated in the magnetic field. More detailed description of the experimental procedure is presented in a accompanying paper. [12]

Explosive charges 20 mm in diameter were pressed either from pure RDX or from RDX+0.5% SWCNTs. The results of the two experiments are shown in fig. 7. Both charges were compacted under the same maximal pressure. The presence of SWCNTs makes the material more tough so the density of the composite charge is slightly lower. The calculated values of the velocities of the contact boundary, corresponding to the Chapman – Jouguet state for each explosive material, are also given in fig. 7 by horizontal lines. The Chapman – Jouguet parameters for the RDX were taken from the tables[11] and the PMMA shock adiabat was $D = 2.59 + 1.52U$ km/s (here D is the shock velocity and U is the particle velocity). For both pure RDX and a composite containing nanotubes, at the wave front the Chapman – Jouguet levels are exceeded. Then one can see a gradual decrease of velocity, as predicted by the Zeldovich-Neumann-Döring model. Note that the velocity decreases markedly faster (and consequently the reaction rate is higher) for the composition with nanotubes.

The characteristic times of the decrease of velocity in fig. 7 are noticeably larger than the durations of the conductivity peaks in fig. 6. Actually, the electromagnetic data require gas dynamic simulation to obtain the true reaction zone duration. A primitive estimate of durations by looking at profiles may be several times and even an order of magnitude longer.[13] However, a comparison of profiles obtained under the same conditions is quite reliable. Thus, according to electromagnetic diagnostics, the reaction in the RDX-based nanocomposite is faster than in pure RDX.

SAXS Measurements

The composites were studied in static and dynamic experiments by the technique for diagnosing fast processes using synchrotron radiation (SR), developed by the authors.[14] The density fluctuations inside the studied sample cause scattering of the probing SR beam into small angles – small-angle X-ray scattering (SAXS). The high frequency SR pulses and their stability allows us to register the dynamics of density fluctuations during the detonation of explosives. In the present state of the experimental base, we can measure the density fluctuations in the range from 2 to 100 nm. The presence of such fluctuations behind the detonation front is usually associated with the process of carbon condensation, dynamic measurements make it possible to track the dynamics of particle sizes[15] and, in particular, its phase state.[16]

In the composites, studied nanoscale density fluctuations are present initially, produced by both nanotubes directly embedded in the sample, and the pores formed due to embedding. The transverse sizes of SWCNTs are less than 2 nm, and the

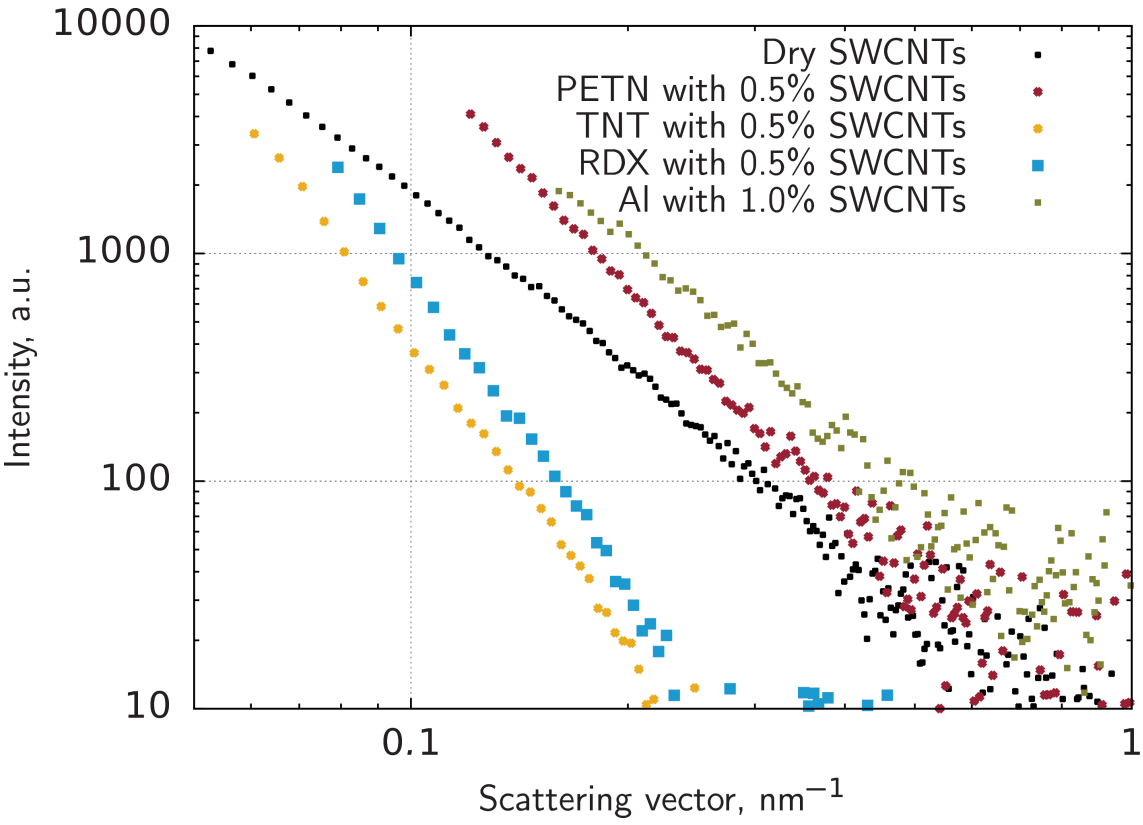


Fig. 8. Static measurements of the SAXS.

length is up to several microns, so single nanotubes should not give the SAXS signal. However, SWCNTs practically do not occur in the form of separate particle and usually form something like tangled globular structures, the characteristic dimensions of which are within the range available for measurements at our station. This is confirmed by observing the intense SAXS signal when the SR beam passes through a cuvette with SWCNTs (fig. 8, Dry SWCNTs). A similar shape of the SAXS signal is also observed when a SR beam passes through an aluminum composite with SWCNTs (fig. 8, Al with 1% SWCNTs), provided by our colleague PhD. V.I. Mali.

The shape of the SAXS signal for explosive composites containing nanotubes differs essentially, see fig. 8. At the same time, for all studied explosives composites, the shape of the SAXS signal is close to each other. The fact is that the nanotubes embedded in the explosive material are no longer such bright density fluctuations, as in the case of dry nanotubes in the air. For the same reason, the nanotubes dispersed in water do not form an intense signal of the SAXS when probing with a SR beam.

Taking into account the SEM data, the intense SAXS signal is primarily produced by the pores. Assuming the sphericity of the pores and using the Guinier approximation,[15] the following average pore sizes were obtained for the investigated composites: pressed PETN – 32 nm, powdered RDX – 43 nm, pressed TNT – 40 nm.

Discussion and results

The data obtained by the electromagnetic method and the method of electrical conductivity at first sight seem to be contradictory. In our opinion, the results of these methods can be reconciled as follows. Acceleration of the RDX reaction in the presence of nanotubes can be caused by changing

the material microstructure, which clearly contains more defects, small pores or other nucleis of potential hot spots, and possibly by increasing the thermal conductivity, which can promote propagation of reaction from the hot spots. We suppose that small difference (about 4%) in the density of the charges is of secondary importance. Besides, one can expect that the effect of density alone should be opposite: faster reaction at higher density, see, e.g. [10]. On the other hand, the widening of the electrical conductivity zone in the composition with nanotubes can be explained (apart of the finite conductivity before the front) by their slow burning out or destruction after completion of the main reactions of the RDX. This is confirmed by the absence of SWCNTs in detonation products of composites. Thus, electromagnetic measurements demonstrate the course of energy release in the main reaction, while the conductivity measurements are sensitive to its final stage, which practically does not contribute to energy release.

The method to embed the SWCNTs into explosives proposed by the authors allows one to modify the microstructure of the material. A characteristic feature of the microstructure is a large number of pores with sizes of tens of nanometers. The method of nanocomposite synthesis does not require the use of special equipment, and it has good reproducibility for a wide range of explosives. The structure of explosive materials containing SWCNTs allows one to expect the observation of change of the properties characteristic for nanodisperse explosives.

In the detonation products of the obtained composites, SWCNTs in the initial state are not observed. According to the data on the electrical conductivity behind the detonation front, the nanotubes decompose in about $0.2\ \mu s$.

An acceleration of the reaction behind the detonation front of explosive composites containing nanotubes is observed.

Acknowledgments

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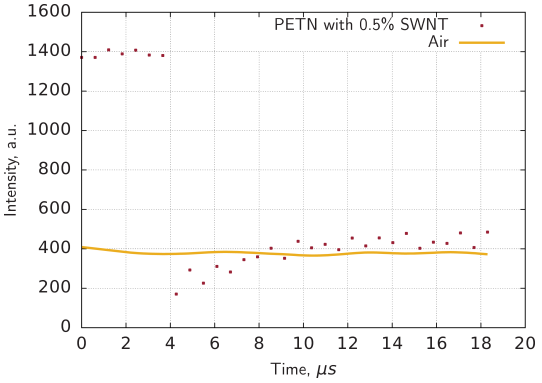

Fig. 9. Integral SAXS during detonation of PETN-based composite.

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Question from Rajen Patel, ARDEC

Did you investigate chirality and how it affects properties? Chirality alters nanotube properties?

Answer from Alexey Kashkarov

Presently, there are no methods for producing SWCNTs with the prescribed chirality. Therefore, in this work we used nanotubes from one produc-tion batch and the effect of chirality on the resulting properties of composites was not investigated. Con-sidering the achievements of recent years in the sep-aration of metallic and semiconducting nanotubes, the study of the effect of chirality is of great interest.