Mechanoactivation of fullerites

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Using neutron and synchrotron X-ray diffraction we studied structure of ultradispersion amorphous fullerites C_{60} and mixture C_{60}-C_{70}, produced by different modes of the mechanoactivation (milling in a ball mill with agate balls), changing speed of grinding and in different environments (air, argon, helium).

In case of low speed of milling on the places of Bragg's reflexes, characteristic for initial crystalline fullerites we can observe diffuse gallo, that corresponds to reduction of the sizes of particles. After 30 hours of grinding the picture remains invariable.

In case of high speed milling ($\approx$500 r.p.m) transition from crystalline fullerite to new crystalline phase was observed. It has graphite-like hexagonal crystal lattice with characteristic parameters $a \approx 2a_{gr}$, $c \approx c_{gr}$.This structure looks like graphite intercalates with alkali metals. The phase with similar structure (with ferromagnetic properties) was found out at studying interaction of hydrogen and amorphous fullerites under high pressure and temperature [1]. So it is possible to assume that transitions are caused by influence of light atoms.

[1] S.S. Agafonov, G.I.Borisov, I.F. Kokin , S.A. Lushnikov, N.N. Parshin , V.A. Somenkov. Magnetic hydride of carbon. IWFAC'2007, Book of Abstracts, p. 80.

Polyamorphous transition in amorphous fullerenes

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Samples of amorphous fullerenes were produced by application of the mechano-activation treatment and their structure was investigated. By a method of diffraction of neutrons it is established, that amorphization comes after two-daily milling. Structural stability of amorphous fullerenes in relation to temperature influences is investigated.

At high-temperature (600-1600K) annealing amorphous fullerenes show a polyamorphous transition from a molecular glass in atomic one. Fullerene gallo are narrowed, gradually coming back to a picture, characteristic for an initial crystalline phase. However, at the further increase of temperature of annealing the first fullerene gallo, corresponding to intermolecular distances, decrease and disappear, while gallo at the big corners of scattering remain invariable or even increase. Comparison of this picture to the data for other amorphous phases of carbon (amorphous graphite, nanodiamond) [1] shows that gallo positions of high-temperature phase coincide with those only for nanodiamond, but they are washed out more wide that corresponds to the smaller sizes of particles. From the received results follows that unlike crystal in amorphous fullerene at 800°C polyamorphous transition from molecular (fullerenelike) phases in atomic (diamondlike) takes place. Similar situation and in mixes C_{60}-C_{70}, with that only a difference that in this case temperature of transition a few higher (on 50-100°C) in comparison with pure C_{60}.

The high-temperature phase as against crystalline fullerite appears stable up to T≈1700°C.

At interaction of this phase to detonation diamond nanopowder there is a disappearance of a reflex of detonation diamond which, apparently, is dissolved in a high-temperature amorphous phase.

The various potential application connected to formation of a high-temperature phase amorphous fullerenes are considered.

[1]   S.S. Agafonov, V.P. Glazkov, V.A. Nikolaenko, V.A. Somenkov, JETP Letters **81**, 154 (2005).

Synthesis of long multiwalled carbon nanotube strands

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There has been much interest in the production and processing of carbon nanotubes since their discovery. For some applications, the mechanical and electrical properties of nanotubes can only be harnessed if long continuous nanotubes can be synthesized; for example, such structures may be used as strong, highly conducting microcables or as mechanically robust electrochemical microactuators. However, the creation of such continuous macroscopic strands of nanotubes during production still remains a challenge.

We report the direct synthesis of long strands of multiwalled carbon nanotubes by an optimized catalytic chemical vapor deposition technique with a hot filament method in a horizontal furnace. N-hexane solution with a given composition of ferrocene and thiophene was introduced into the reactor after heating the reactor to the pyrolysis temperature (1273K), with hydrogen as the carrier gas.

On structural features of fullerene C_{60} dissolved in carbon disulfide: complementary study by small-angle neutron scattering and molecular dynamic simulations

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Small-angle neutron scattering (SANS) from fullerene C_{60} in carbon disulfide (CS_2) is analyzed with respect to possible cluster formation. In contrast to previous experiments [1], where some kind of clusterization was revealed, in the given case fullerene is dissolved in equilibrium conditions, i.e. any mechanical influence (shaking, stirring, ultrasound treatment) is avoided. As a result, no significant clusterization is observed. The curves are well treated in terms of the Gunier approximation, which gives the value of 3.85 E for the radius of gyration of C_{60}. However, this is about 10% larger than the value calculated using atomic coordinates of C_{60} from X-ray diffraction (3.55 E). We apply the molecular dynamics simulation of the studied system for analyzing a possible influence of the solvent organization at the interface with C_{60} on the apparent size of fullerene in the scattering. A single C_{60} molecule is placed in the cubic solvent cell (4069 molecules of CS_2 per one molecule of C_{60}). The almost spherical symmetry of the fullerene molecule makes it possible to compare the solvent organizations in bulk and around fullerene surface in terms of isotropic scattering length distributions with respect to the center of C_{60}. It is shown that a specific shell of CS_2 molecules around fullerene with about 20 % excess over the bulk density of the solvent is observed, which explains the increase in the apparent size of fullerene in the SANS experiments.

[1] T.V. Tropin, M.V. Avdeev, V.L.Aksenov, *Fullerenes, Nanotubes and Carbon Nanostructures* **16**, 616 (2008).

Effect of high-temperature annealing on the structure and properties of the superelastic hard carbon particles obtained from fullerenes under pressure

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The thermal stability of the metallic composite materials reinforced by the particles of superelastic hard phase (SHP) is determined by the stability of structure and properties of the reinforcing particles. There are little published data on the thermal stability of the products of the fullerite transformation under pressure. It was established that the 3D-polymerized structures upon heating to 650K return to the initial pristine state, while the amorphous structures undergo partial graphitization [1].

The methods of optical microscopy, Raman spectroscopy, and hardness measurements were used for the study of the effect of annealing temperature (up to 900°C) on the structure and properties of the SHP particles obtained from fullerenes in metallic matrix. The samples were obtained by high-temperature quasyisostatic pressing at 1200°C at a pressure of 3-5 GPa from the mixtures of metal powders (Fe, Ni, Co) and 5-10 wt.% fullerites C_{60} or soot extract (SE). Such conditions provide the synthesis of superelasic hard carbon particles (of up to 0.5 mm in size) and simultaneous compacting (sintering) of the powder composite materials (CM), which contain ~15 vol.% of such particles relatively uniformly distributed in the metallic matrix.

The optical-microscopic examination with polarized light showed that the structure of the carbon particles in the annealed CM is the same as the initial SHP structure looks like deformed coarse crystals or aggregates of fine crystals inherited from the initial fullerites C_{60} or SE, respectively. The Raman profiles show an increase in the content of the graphite component in the particles of the CM annealed at temperatures above 700°C. The hardness of the reinforcing carbon particles in CM decreases with increasing annealing temperature. However, even after annealing at 900°C, the unique SHP properties are retained: the hardness (measured according to the indentation depth under loading) exceeds 10 GPa, and, due to the anomalously high elastic recovery, no indent is visible in optical microscope after the Vickers hardness measurement at a load of 50 N.

[1]   S. Buga, V. Blank, A. Fransson, N. Serebryanaya, B. Sundqvist, *Journal of Physics and Chemistry of Solids* **63**, 331 (2002).

Polyhedral nanosize carbon particles at high pressures and temperatures

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Pressure-temperature-induced transformations of polyhedral nanosize carbon particles (PNCP) at 8.0 GPa and different temperatures up to 1600°C were studied by X-ray diffraction (XRD), small-angle X-ray scattering (SAXS), scanning (SEM) and transmission (TEM) electron microscopies.

The PNCP powder produced through heat treatment of carbon soot at 2700°C in He atmosphere was used as starting material in the present work. According to TEM analysis, the as-produced powder is a mixture of isometric and elongated forms of PNCP with a mean particle size of about 50 nm. A characteristic feature of the pristine PNCP is the availability of internal cavity located in the centre of each particle. The mean size of such cavities was estimated to be ~ 16 nm.

High-pressure high-temperature treatment of the PNCP was carried out in the Toroid-type high pressure apparatus. High-pressure states formed at different p,T parameters of treatment were quenched under pressure to room temperature and then studied by the above-mentioned characterization methods at ambient conditions.

Combined analysis of the high-pressure states showed that no substantial changes of the PNCP are observed for the samples obtained at temperature up to 800°C. Further increase of treatment temperature causes a disordering (amorphization) of the initial PNCP. At 1600°C, transformation processes complete by conversion of the PNCP into spherical onion-like particles. The PNCP onionization is accompanied by filling of the internal cavities and isometrization of the nanoparticles shape. As the result, the content of elongated shape particles in the samples falls drastically. The mechanism of pressure-temperature-induced onionization of PNCP and the problem of relative stability of different nanosize carbon forms at high pressure are discussed in this work.

Ostwald rule of stages applied to the supercooled liquid carbon

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With use of pulse laser heating in a gas vessel there had been obtained various liquid carbon states – the equilibrium one (with the total absence of temperature fluctuations on the melting curve plateau and no supercooling) and the metastable supercooled one. Techniques to control the metastable liquid state and the quenched phases structure are studied.

The carbon structure formed after the meta-stable liquid phase solidification contained the diamond superdense C_8 phase, chaoit and carbine crystals, also meta-stable at normal conditions. The hardened graphite together with the hexagonal phase also contained the highly compressed one [1]. Due to these reasons the transformation of the meta-stable carbon liquid to the equilibrium graphite is assumed to occur according to the Ostwald rule of stages via a number of meta-stable intermediate states. The thermodynamical aspects of this transition are discussed.

[1]   A.Y. Basharin, V.S. Dozhdikov, V.T. Dubinchuk, A.V. Kirillin, I.Y. Lysenko, M.A. Turchaninov. *Pisma v ZhETF*. **35**, 84 (2009).

Electric field-enhanced charge transport in amorphous carbon films

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The hard nanocluster carbon films [1] continue to attract attention during last decades. However the character of the electron transport in these materials still remains controversial. This is especially related to the case of the films, doped by different elements, such as silicon, nitrogen, etc., which modify the properties of the films and extend the range of industrial applications.

The transverse charge transport in the hydrogenated nanocluster carbon films, doped by silicon and oxygen, over the temperature range $77 \div 450K$ and applied electric field up to 10^6 V/cm was studied. The films were deposited by PECVD from the vapors of the heavy silicon-organic polymer $((CH_3)_3SiO(CH_3C_6H_5SiO)_3Si(CH_3)_3)$ in the DC stimulated discharge. To control the deposition energy of the films the RF bias (1.76 MHz) was applied to the substrate holder.

It is shown that in the amorphous nanocluster carbon films, grown at deposition energies over the range 50-600 eV, the temperature dependences of the conductivity being well linearized on the Mott scale in low electric fields tend to saturate at temperatures below 150K in high electric fields $(F > 2\times10^5$ V/cm). The current-voltage characteristics demonstrate the power-like behavior, which allows to identify the electron transport mechanism as the space-charge limited current in the presence of the exponentially distributed localized states in the mobility gap. The characteristic energy of the distribution (disorder parameter) determined in this model by the value of the power exponent depends on the deposition energy by the non-monotonic way over the range $0.05 \div 0.1$ eV, with a minimum at the value of deposition energy close to 150 eV. The estimated values of disorder parameter are consistent with that used in the model of the hopping conductivity along the transport energy level which allows to interpret correctly the charge transport mechanism in low electric fields applied.

The applicability of this model is confirmed by the observation of the analogue of the Meyer-Neldel rule, which states in this case the linear relation between the logarithm of pre-exponential factor of the conductivity σ_0 and the characteristic temperature $T_0^{1/4}$, estimated from the conductivity-temperature dependences plotted on the Mott scale.

[1]   J. Robertson, *Mat. Sci. Eng.* **R37**, 129 (2002).

Cluster formation and solvatochromism in fullerene C_{60} solutions based on nitrogen-containing solvents

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The solutions of fullerene C_{60} in nitrogen-containing solvents (pyridine, N-methyl-2-pyrrolidone, benzonitrile and acetonitrile) are of current interest due to the formation of clusters of C_{60} with time. In fact, some kind of transition from molecular to colloidal solutions takes place in these systems depending on the solvent polarity (higher polarity of the solvent the more intensive cluster growth is observed). The reason for the final cluster stability in some cases is not clear. In this connection, the possible appearance of donor-acceptor complexes between C_{60} and solvents molecules on the cluster surface can be considered.

Always, the cluster growth in the discussed solutions is accompanied by the temporal solvatochromism (change in the absorption UV-Vis spectrum with time). The question under study in the present work is to what extent the solvatochromism is determined by the cluster formation. We study the solution C_{60}/N-methyl-2-pyrrolidone (C_{60}/NMP), where the formation of large (up to 500 nm in size) and stable clusters are reported. The important feature of this solution is the cluster reorganization after addition of water in the system [1,2]. It is shown [3] that water addition leads to the decomposition of fullerene clusters in the solution, which is a result of the detachment of monomers from the clusters. This reorganization is reflected in the change of absorption UV-Vis spectra.

Two main possibilities of the solvatochromic effects in the systems C_{60}/NMP, C_{60}/NMP/H_2O, namely, the appearance of new bonds between fullerene molecules in the clusters or the mentioned above donor-acceptor complexes on the cluster surface, are discussed.

[1]   Aksenov, V.L. Avdeev, M.V. Tropin, T.V. et al. *Physica B : Condensed Matter.* **385-386**, 795S (2006).
[2]   Aksenov, V.L. Avdeev, M.V. Kyzyma, O.A. et al. *Cryst. Rep.* **52**, 479 (2007).
[3]   Kyzyma, O.A. Bulavin, L.A. Aksenov, V.L. et al. *Fullerenes, Nanotubes and Carbon Nonstructures* **16**, 610 (2008).

Modeling of water clusters formation processes in the inner atmosphere of 67P/Churyumov-Gerasimenko comet

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The Rosetta project of European Space Agency (ESA) provides investigation of the 67P/Churyumov-Gerasimenko comet by spacecraft and landing probe. The success of mission depends on many factors including preliminary estimation of inner atmosphere parameters. For landing mission it is very important to know intensity of jets which formed by evaporation of dusty-ice nucleus surface under solar radiation. Different physical-chemical processes like condensation can influence on the structure and parameters of such jets.

The powerful tool for numerical investigation of rarefied comet atmospheres is the direct simulation Monte Carlo (DSMC) method [1]. The model of water clusters formation for the DSMC technique was developed on the base of the kinetic approach [2,3]. The model takes into account hierarchy of kinetic processes from water dimer formation under three body collisions up to molecule-cluster and cluster-cluster associations. The probabilities of association acts under particles collisions, the influence of intra-molecular vibrations of water molecules in clusters on cluster decay rate were analyzed.

We used data about gas productivity rates of nucleus of 67P/Churyumov-Gerasimenko comet at the different distances between comet and Sun and formulated model of jets formation. The influence of gas productivity on intensity of cluster formation process in jets was investigated using the developed clusterization model and the DSMC technique. The data on resulting condensation mass, size distributions of observed water clusters, velocities, internal energies of clusters were obtained. The effect of condensation on flow structure was discussed.

[1]   G. A. Bird. Molecular gas dynamics and the direct simulation of gas flows Clarenton Press, Oxford, 1994, 456 p.
[2]   N. Yu. Bykov and G. A. Lukyanov. Direct simulation Monte Carlo of pulsed laser ablation of metals with clusterization processes in vapor Thermophysics and Aeromechanics, 2006, № 4, V. 13. pp. 523-535.
[3]   N. Y. Bykov, D. V. Leshchev, O.I. Simakova. The direct simulation Monte Carlo of near-continuum flows with condensation process In Proc. of XXXVI summer school Advanced Problems in Mechanics, 2008, Saint-Petersburg: Comilfo, pp. 159-166.

Collision models of monomer-cluster and cluster-cluster interaction for the direct simulation Monte Carlo method

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The direct simulation Monte Carlo (DSMC) method [1] is powerful tool for numerical research of gas flows with physic-chemical processes. Recently some models of clusters formation and growth processes were developed for the DSMC technique. Models of condensation allowed investigation of condensation phenomena in rarefied jets formed under expansions of different nature, for example under laser ablation phenomenon [2, 3]. The models of clusterization are usually based on kinetic approach and provide description of whole hierarchy of collision processes which lead to formation and growth/decay of clusters.

Some questions arise under calculation of cross-sections of collisions between different kinds of particles. The hard sphere (HS) model or the variable hard sphere (VHS) model is usually employed for description of elastic collision between atoms (molecules). The HS model may be regarded as the special case of the inverse power law potential application. The VHS model provided also some dependence of HS diameter on relative velocity of colliding particles. In this work we discussed the problem of cross-section description for monomer-cluster and cluster-cluster collisions. Three models for collision/reaction cross-section definition were suggested. These models use different potentials of interaction: the potentials of Lennard-Jones and Born-Maier and the potential received from quantum-chemical calculations.

The elaborated models were applied for the problem of 1D plate expansion of Nb atoms from laser ablated target. The data on collision frequencies, size distributions of clusters, parameters of clusters motion and internal state were obtained. The spatial distributions of flow density, velocity and temperature were investigated. The influence of models application on intensity of condensation process and parameters of process were analyzed.

[1]   G. A. Bird. Molecular gas dynamics and the direct simulation of gas flows Clarenton Press, Oxford, 1994, 456 p.

[2]   N. Yu. Bykov and G. A. Lukyanov. Direct simulation Monte Carlo of pulsed laser ablation of metals with clusterization processes in vapor Thermophysics and Aeromechanics, 2006, V. 13, № 4, pp. 523-535.

[3]   M. I. Zeifman, B. J. Garrison, L. V. Zhigilei Combined molecular dynamics — direct simulation Monte Carlo computation study of laser ablation plume evolution J. Appl. Phys. 2002, V. 92, № 4. pp. 2181-2193.

Novel nanocluster systems in superfluid helium

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Impurity-helium condensates, or impurity gels, formed by impurity nanoclusters in superfluid helium, He-II, have been the subject of our intense studies within the last decade. We investigated the temperature stability of the impurity gel samples produced of deuterium and heavy water nanoparticles in superfluid helium He-II. The samples were grown at the temperature below 1.7K, and it was observed that in liquid helium they could exist up to 4.22K. Being extracted above the liquid level at T~1.6K, in helium vapor, the gel samples start to decay with increasing their temperature above 1.8K. This gel sample decay is followed by accumulation of powder on bottom, with the volume of two orders of magnitude smaller than the gel sample volume. If only a fraction of a sample is extracted above the liquid level then only this fraction decays, while another part survives. These observations illuminate restrictions in the growth rate of gel samples in our experimental cell of limited size (with inner diameter of 26 mm).

The size distribution of nanoparticles in freshly prepared gel samples produced of deuterium and heavy water at the temperature of 1.6K was studied by the methods of neutron spectroscopy (small angle scattering of cold neutrons, qusielastic scattering). The q-dependence of the count rate of neutrons scattered at D_2O and D_2 gel samples was measured in the momentum transfer range of q = $(3 \cdot 10^{-3}$-$3 \cdot 10^{-1}$ A$^{-1})$. Those observations have shown occurrence of a well-defined preferred size of the nanoparticles of 10-15 nm in the heavy water gel samples. In the same "q" range no preferred nanoparticles size was observed for deuterium gel samples. However, very large probability of small-angle scattering indicates presence of a large relative density of deuterium nanostructures with a broad size distribution.

The next step included investigations of the dependence of the nanoparticles size distribution on the temperature. The gel temperature during the measurements was fixed in steps in the range of 1.55-4.2K. No significant modification is observed in the whole momentum-transfer range q $\leq 10^{-1}$ A^{-1}, indicating no strong evolution of the main fraction of the cluster sizes. However, we observed a well pronounced increase of the neutron scattering to the range q $\geq 10^{-1}$ A^{-1} with rising the sample temperature from 1.6 to 2.13K for both kinds of gel samples. This fact could be understood as appearance of a large amount of ~1 nm sized nanoparticles, or rather as their separation from the gels samples.

The studies are under continuation now.

Formation of carbonic cluster ions at the ionization of fullerenes and multiatomic molecules of hydrocarbons

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Formation of pure carbon ions and clusters arising from the collisions between multiply charged ions and fullerenes C_{60}, toluene – C_7H_8, benzene – C_6H_6 and butane – C_4H_{10} molecules have been studied. These processes in mediums containing the abovementioned molecules are of interest because of electric conductivity that appears due to ionization of the mediums under-influence of probing ion beams. For the ionization of many atomic molecules the electron capture processes by fast Ar^{6+} projectile ions have been used. The charge state change analysis of projectile ions after a single ion-molecule collision with molecules made it possible to control the number of electrons captured from the target molecule. The fragment ions formed at target molecule dissociation have been analyzed by time-of flight system.

It was found that in the case when three or more electrons are removed from a fullerene molecule the most probable processes lead to the formation of carbon clusters C_n with wide size spectrum of "n" from one to more than ten. In the case of multi atomic hydrocarbon molecule ionization the process connected with the removal of most of hydrogen atoms from molecule and formation of singly charged pure carbon rest fragments C_n^+ has high relative cross section. The subsequent mass-analysis of C_n^+ cluster ions can be applied as efficient way to obtain pure carbon cluster ions with given mass.

Structure state of carbon nanomaterials produced by high-energy electric discharge techniques

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New technologies are developed for manufacturing of novel carbon nanomaterials (CNM), such as fullerene-like clusters, carbon nanotubes, nanodiamonds and amorphous carbon, with use of the methods of electrical wire explosion (EW) and electrical breakdown of organic liquids (EBOL) [1].

Performed X-ray diffraction and spectroscopic investigations of the CNM produced by the EW of graphite rods in different organic liquids (such as toluene, hexane, ethanol) has been shown that the phase composition is controlled by the ratio of the energy w, introduced into graphite, to the energy of sublimation of graphite w_s (w_s= 62 MJ/kg). When $w >> w_s$ the products of EW of graphite in hexane are consist of ordinary graphite and nanodiamonds. In this case the melting process of graphite rod due power current pulse advancing occurs in an axial zone of the rod with postevaporation and ultrafast quenching of carbon atoms. It results in formation of nanodiamonds via graphite-liquid-diamond phase transformation. When the introduced energy is $w \approx w_s$ phase composition consists of mixture of high-dispersive particles of graphite and lonsdalite. When $w < w_s$ graphite rod fractures into separated fragments of graphene sheets with postrolling them into fullerenes (if size of graphene sheet fragment is enough small) or nanotubes.

The technique of EBOL is used for the production of amorphous carbon with different type of short range order. It was found, that the type of short range order of amorphous structure is connected with type of working liquids, namely with degree of hybridization of carbon atoms in molecule of hydrocarbons. In the case of EBOL in kerosene (mixture of hydrocarbons with predominance of sp^2-hybridization of carbon atoms) graphite-like amorphous carbon is produced. But in the case of cyclohexane (hydrocarbon with predominance of sp^3-hybridization of carbon atoms) diamond-like amorphous carbon is produced.

Performed investigation of process of graphitization of amorphous carbon has shown that the graphite-like amorphous carbon is stable up to 1500°C, but diamond-like carbon graphitizes at 500°C.

[1]   A.D. Rud, A.E. Perekos, V.M. Ogenko, et al., *J. Non-Cryst. Sol.* **353**, 3650 (2007).

Kinetics of fullerene cluster growth in nitrogen-containing solvents

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Fullerenes, a new allotropic form of carbon, discovered at the end of last century, exhibit a number of peculiar properties, which may lead to some valuable applications in different fields. Perspective applications (e.g. in biomedicine) require us to study fullerenes in various solutions. An interesting effect, discovered in solutions of C_{60}, is the formation and growth of clusters [1].

From the viewpoint of tendencies in fullerene cluster formation, one can distinguish three different groups of C_{60} solutions. The first group consists of fullerene low-polar solutions. While there is some evidence of the formation of clusters in these systems, experimental data is contradictive. Mostly, concentration of clusters and their sizes are low. The second group includes fullerene solutions in solvents of medium polarity. In these systems one can observe slow growth of large stable clusters (size ~100 nm). The third group consists of fullerene solutions in highly polar solvents, in which fullerenes cannot be dissolved at equilibrium. This group consists of stable colloidal solutions, prepared by a certain method, like powerful ultrasonication.

In this work we present an attempt to develop a kinetic theory of cluster growth in C_{60}/NMP and C_{60}/Pyridine. These solutions can be considered as good representatives of the second group of fullerene solutions. A number of SANS experiments on these systems was performed lately, revealing some interesting properties [2]. We develop a kinetic model, which accounts the competition in time of fullerene cluster growth and the formation of donor-acceptor complexes. The second effect eventually limits the growth of C_{60} aggregates in the system.

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[2]   O.A. Kyzyma, L.A. Bulavin, V.L. Aksenov, M.V. Avdeev, T.V. Tropin, M.V. Korobov, S.V. Snegir, L. Rosta, *Materials Structure* **15**, 17 (2008).

Comparative EPR study of monomer and polymer C$_{60}$ phases

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Monomeric (M) and polymeric phases of C$_{60}$ – orthorhombic (O), tetragonal (T) and rhombohedral (R) – were systematically studied by the EPR method. The EPR spectra were observed for all phases. Two types of signal were obtained in the spectra. The main EPR signal, present in all studied phases, is a doublet attributed to paramagnetic centres (PC1) with spin S=1/2. The g-factor observed for the main EPR signal was slightly higher than the g-factor of free electron, g$_e$=2.0023. Corresponding PC1 was attributed to hole-type radical cation C$_{60}^+$. The doublet EPR spectra of the T and R phases (2D phases) were found to be anisotropic. Thus the interaction of unpaired spin with its environment in the layer and in the perpendicular direction is different. Masse concentration, Ns, of PC1 varies from N$_s$=9×10^{13} spin/mg (for M) up to N$_s$= 8×10^{15} spin/mg (for T). The measurements in vacuum and in air at T=77K allow us to conclude that the main part of PC1 is in the bulk of samples. The temperature dependencies of N$_s$ in the interval 293-77K for all studied phases demonstrate the Curie-like behaviour, which is a characteristic of paramagnetic materials.

The second type of EPR signals (triplet) was caused by PC2 with S=1 and was observed for the T and R phases only. PC2 was attributed to the pair of PC1 (S=1/2). The distances between them were found to be different for the T and R phases: 10.5Å for the T phase and 11.3Å for the R phase. The quantity of PC2 is 1% of quantity of PC1. From measurements at 293K, 77K and 11K, the low energetic level of PC2 for the R and T phases was found. Possible models of PC2 are also discussed.

Polymer nanocomposites containing fullerene C_{60} nanofillers

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Polymer nanocomposites have attracted enormous interest of the materials research scientists because these composites promise substantial improvement of mechanical properties at very low filler loadings. Because of excellent physical properties, nanosize in diameter, low density fullerene C_{60} has been considered as an ideal reinforcing filler in multifunctional polymer nanocomposites. In this communication, we describe our investigation of nanocomposites comprised by PA-6, PA-12 and epoxy resins (as matices) and fullerene C_{60}. The challenges for developing high-performance fullerene C_{60}/ polymer nanocomposites are (i) homogeneous dispersion/solution of fullerene C_{60} in the polymer matrix and (ii) strong interfacial interactions so as to effect efficient load transfer from the polymer matrix to the fullerene C_{60}. The nanocomposites were prepared by either simple melt-compounding (for PA-6 and PA-12) or in situ polymerization in the presence of fluorine C_{60} (for epoxy resins, PA-6 and PA-12). The amount of fullerene C_{60} was varied of 0.001-0.1wt.%. Many of the macroscopic properties of nanocomposites crucially depend on their morphology. Electron microscopic imaging was used to elucidate their nanoscale morphology. As we show in all the cases, the fullerene C_{60} is well dispersed/dissolved in polymer matrix used and did not forms large-scale aggregates independently the method of nanocomposite formation. This provides a good load transfer between the matrix and the filler. This leads to substantial improvement of mechanical properties at very low fullerene C_{60} loadings. Mechanical tests show that, compared with neat PA-6, PA-12, and epoxy resins, the tensile modulus, the tensile strength and the hardness of the composite are improved by about 40-50%. The fullerene C_{60} has potential to be a conducting filler in multifunctional polymer composites. Several orders of magnitude enhancement has been achieved in electrical conductivity with a very small loading (up to 0.1 wt% and less) in the polyamide matrix. An improvement in thermal stability of nanocomposites under study was also observed. Detailed studies on the effectivity of addition of fullerene C_{60} on crystalline structure (morphology), mechanical (such as fracture and strengthening mechanisms), thermal and electrical properties of nanocomposites are discussed.