Comparison of organic – inorganic nano-compositions created by different deformation – chemical techniques

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Abstract. Comparative studies of compositions from polystyrene and inorganic crystals of cesium sulfate and cesium iodide obtained by different methods gave new experimental facts and versions about particularities of structures and properties of these materials. The methods of creation of these compositions were based on two deformation – chemical techniques: solidification of micro-fibers from solutions of polystyrene with cesium sulfate and cesium iodide particles and introduction of polystyrene as the doping substance into single crystals of cesium iodide and potassium chloride by means of a ball rolling. In both cases micro- and nanosize singularities of the mass transfer were observed during the forming of these compositions. The microfibers formed by solidification of doped solutions of polystyrene turned out to be split to sets of nano – filaments. In the process of the dynamical centrifuging they formed the bundles parallel to the axis of the fiber, whereas the slow pulling of the fibers from the solution with a thin glass stick created saw-like chains of short pieces of the nano-filaments going along the axis of the fiber. These geometries were regulated by the ratios of compressive and tensile internal stresses, the chemical content of the components, lengths of the polystyrene molecules, viscosity of the solution. Superfast and superdeep mass transfer in the form of nano- and micro-filaments observed in our experiments is attributed to the soliton-like propagation provided by non-linear changes of the properties of the matrix in the vicinity of the filament. Hence wide sets of various nanostructures required by new trends of electronics, optics, etc. can be prepared by rather economic techniques.

1. Introduction

The actuality of studies of various compositions from organic and inorganic components is growing continuously [1–7]. It is explained by widening of applications of these materials for various aero-space constructions, electronics, optical devices, etc [8]. Adequate procedures of preparation of these compounds provide accumulation and enhancement of the positives properties of the components and elimination of their negative characteristics. For example recent results on the development of new scintillators from organic phosphors impregnated with inorganic nanoparticles providing record parameters of a new kind of radiation detectors [9,10] confirm wide prospects of combining of organic and inorganic nanocomponents. On the other hand substitution of micro-components of these compositions by their nano-analogs multiplies by many times the influence of the interfaces between organic and inorganic on the total properties of the materials [11–16]. The structure and properties of interfaces of this kind have not been
studied in detail up to now. So the studies of the relations between forming procedures and properties of these compositions are highly actual either for practical needs or for creation of new knowledge about structures and properties of condensed matter.

2. Experimental results and discussion

The experimental part of this paper is a prolongation of our previous work published in the Journal of Physics C earlier [17]. So the methods of experiments are the same and their detailed description can be found there. Concerning the micro-fibers our main attention now has been paid to detailed studies of the dependence of the fine structures of the compositions produced by solidification of solutions of polystyrene with or without inorganic fillers on the compositions, the viscosity of the solutions and the parameters of the pulling techniques (dynamical centrifuging with the rate from 10 to 100 m/s or slow handle pulling with the rate about 0.03 m/s). In the both cases splitting of the micro-fibers to nano-dimensional filaments has been found. But the detailed patterns of this splitting were quite different. The centrifuging processes resulted in transforming of the fibers to bundles of long filaments being parallel to the axis of the microfiber and covered partially with external core (Fig. 1).

Figure 1. Polarization-optical microscopy (left) and electron scanning microscopy (right) of a polystyrene fiber obtained from its solution in toluene by centrifuging [17]

In addition to the optical anisotropy of the filaments splitting the fibers formed by centrifuging these fibers demonstrate polarization anisotropy in the infrared region in the bands of absorption of phenyl groups of polystyrene and C-H bonds (550 cm\(^{-1}\) and 2900 cm\(^{-1}\) correspondingly, Fig. 2). The absorption at 550 cm\(^{-1}\) is higher for the polarization parallel to the fiber axis whereas at 2900 cm\(^{-1}\) the absorption is higher for the perpendicular polarization. Usually the optical anisotropy of polystyrene is attributed to its crystallization [18, 19]. The ordinary polystyrene (atactic) has random distribution of the phenyl groups around the axis of C-H bonds and its crystallization was not observed. Two other forms of polystyrene (isotactic and syndiotactic) has regular distributions of the phenyl groups and their crystallization takes place below 230 °C for isotactic and below 270 °C for syndiotactic forms [20]. So due to the appearance of the optical anisotropy of the fibers we can suppose that the dynamical pulling out of polystyrene solutions transforms its molecules either to isotactic or to syndiotactic forms with subsequent crystallization to micro- and nano- filaments.

The slow pulling of the fibers produced much more sophisticated patterns of their splitting (Fig. 3 a, b). The straight pieces of the filaments formed by means of the splitting of the initial continuous morphology are shorter significantly and the distributions of their orientations with respect to the axis of the fiber are not so strict. These differences of the distributions of the orientations correspond to the scattering of the directions of local stresses induced in the materials of the compositions during their solidification. The centrifugal pulling involves the
Figure 2. The infrared absorption spectra of the bundle of polystyrene fibers produced by centrifuging of the solution of polystyrene in toluene. The red spectrum corresponds to the polarization of the light perpendicular to the fibers, the black spectrum corresponds to the parallel polarization.

emission of the drop of the solution from the edge of the disk due to its fast rotation. The emitted drop is flying away from the disk rather quickly pulling the jet of the solution out of the disk. The end of the jet opposite to the drop being attached to the disk is involving the jet in the direction opposite to the direction of the drop flight. Hence the tensile stress is induced inside the jet in the direction parallel to its axis. This stress is orienting the polystyrene molecules in the same direction. Due to the fast elongation of the jet the intensive evaporation of the solvent from its lateral surface began. The more the curvature of the lateral surface the faster the evaporation proceeds. Due to acceleration of the evaporation with the increase of the local curvature of the surface the circular lateral surface can not preserve its stability. Any random protuberance at the surface increasing the local curvature will accelerate the local evaporation of the solvent. So the solidification of the solution in this region will be accelerated as well. This solidification will induce local contraction of the substance. This contraction will soak in its turn the liquid portions of the material from the neighbor regions. The rate of the soaking will be limited by delivering of polystyrene by diffusion and convection. The forming of analogous filaments in the neighbor regions will compete with the delivery to the filaments created earlier. Thus the process of the development of the instabilities of the solvent will induce the splitting of the continuous materials to separate filaments. The orientation of all of these filaments in the direction parallel to the fiber is determined by the initial orientation of the molecules of polystyrene induce by fast elongation of the jet.

In the second case of slow gradual pulling of the fibers out from the solution the tensile stresses along the fibers do not prevail so the orientation of the molecules of polystyrene is not definite. These orientations are determined by the orientations of combined local stresses which can be modified from point to point. The preferential directions of the orientations of polystyrene molecules will be determined by the direction of maximal tensile stress in this point [21]. Due to much slower rate of the pulling of the jet the rate of the transverse contraction will be comparable with the rate of elongation. So the resulting local stresses orienting the polystyrene molecules can be deviated severely from the axis of the fiber. Consequently the pieces of nano-filaments formed during the solidification of the solution will have essential deviations as well. These deviated pieces of the nano-filaments are observed at Figs. 3, 4 either at the lateral surfaces of the fibers or in their volume. It should be emphasized that the distributions of these pieces are
Figure 3. Scanning electron microscopy of the polystyrene fiber obtained by slow pulling out from the solution. Rather complicated structures of the pieces of nano-filaments are attributed to local variations of the ratio between tensile and compressive stresses characterized by ordering of orientations and inter-filament mean distances. This ordering is attributed to Prigogine principle of the minimization of the entropy production working in the systems with strong deviations from equilibrium [22]. Directional and coordinate orderings of these super-structures are dependent on the acting stresses, viscosity of the solution, lengths and orientations of the molecules polystyrene molecules present in the solution. These parameters can be modified by variations of external conditions of the solidification. Hence the nanodimensional superstructures of nano-filaments can be regulated for preparation of materials for various applications in electronics, nano-optics, elements of constructions, etc. For example Fig. 4 demonstrates saw-like micro-modulation of optical anisotropy of the fiber obtained by slow pulling out interesting for optical systems with distributed optical feedback [23]. The analogies between the images of this structure presented by optical (left) and electron microscopies are clear.

Figure 4. Polarization optical (left) and scanning electron microscopy copy (right) of a saw-like chain of nano-filaments pieces formed during solidification of the polystyrene micro-fiber

The active influence of tensile stresses on forming of the nano-filaments is confirmed by scanning electron microscopy of the fibers presented at Fig. 5. The filaments of sub-micron diameters are observed at the edges of the cracks produced by the tensile stresses in the rigid cores of the polystyrene fibers formed during solidification of the solution of polystyrene in toluene.

Fig. 6 presents the optical microscopy of the region of the semi-liquid fiber corresponding to the right photo at Fig. 4 at the initial stage of forming of the crack. The vertical flow of the gel
Figure 5. Scanning electron microscopy of creation of nano-filaments during cracking of the cores of polystyrene micro-fibers

preceding to the cracking contains the micro-filaments created by the motion of the gel.

Figure 6. Optical microscopy of the initial stage of forming of oriented polystyrene molecules before the cracking of the fiber core

Our experiments showed that a wide set of superstructures from nano-filaments can be obtained by variations of the ratios between tensile and compressive stresses. Fig. 7 presents a piece of a bended polystyrene fiber. At the upper side the compressive stress prevails along the axis whereas the bottom side is subjected to the longitudinal tensile stress. The transverse folds are observed at the top. The longitudinal filaments substitute these folds lower to the bottom.

Moreover, the magnified image of the lower part of the fiber from Fig. 8 shows that at the concave sections of the lateral surface the longitudinal filaments prevail whereas at the
Figure 7. Scanning electron microscopy of a bended piece of polystyrene microfiber. Upper side – compression, bottom side – tension

Figure 8. The magnified image of the lower part of the fiber at Fig. 4. The convex parts – the transverse filaments, the concave parts – longitudinal filaments

convex part they are substituted by the transverse filaments (Fig. 5). When the tensile stresses are prevailing the superstructure of the splitting filaments acquires good periodicity (Fig. 9). The period of this set of filaments is about 1 micrometer being in good correspondence with requirements to optical resonators of high quality.

We found that the micro- and nano-particles of cesium sulfate (as at Fig. 9) and cesium iodide create strong chemical bonds with the molecules of polystyrene. The infrared spectra of the fibers from polystyrene with fillers of particles of cesium sulfate and cesium iodide confirm the creation of these bonds. Fig. 10 presents the infrared spectra of two fibers of polystyrene:
Figure 9. The periodical superstructure of parallel micro-filaments formed by the tensile stress for pure polystyrene (black spectrum) and for the fiber with the filler of cesium iodide (red spectrum). It is seen clearly that the band of IR absorption corresponding to vibrations of C-H bonds of polystyrene after introduction of CsI particles is broadened asymmetrically.

Severe broadening of the absorption band with the center at about $2900 \text{ cm}^{-1}$ observed in the fibers with CsI filler reveals strong interaction of C-H bonds of polystyrene and the particles of cesium iodide. Our measurements of the same spectra with better spectral resolution using plane films of the same composition showed that this broadening is induced by splitting of the absorption band.

The results presented above concern self-organization of micro- and nano-filaments induced by crystallization of oriented polystyrene molecules. In addition we have observed one more kind of nano-filaments during solidification of polystyrene providing an alternative mechanism of their forming (Fig. 11). The mean direction of these nano-filaments is perpendicular to the sub-micron threads of polystyrene formed during its solidification by means of tensile stresses. Due to the curvature of these threads the surface tension induces internal Laplace pressure under the surfaces of the threads [24]. This pressure is inversely proportional to the radius of curvature and for sub-micron radius it can be essential.

This pressure transforms the gel from the molecules of polystyrene and of the solvent to non-equilibrium state when the remnant molecules of the solvent which had no enough time for evaporation should be pushed out from the gel. Due to the principle of minimization of production of entropy for the transition to the equilibrium state the molecules of the solvent are agglomerated to discs of more liquid mixture of the solvent and polystyrene molecules which are extruded to the external surface and their subsequent solidification forms the nano-filaments perpendicular to the micro-treads shown at Fig 11. The transportation of these nano-discs to the external surface can be accelerated by the generation of the phonons localized in these discs which are bombarding and softening the material before the disc [25, 26]. This directed propagation of the self-localized inhomogeneity through the condensed media provided by the non-linear modifications of the media parameters has a set of analogies with the motion of solitons [27].

In addition the creation of micro- and nano-filaments of polystyrene was observed in the
Figure 10. Infrared spectra of non-doped polystyrene fiber (black spectrum) and of the fiber with cesium iodide fillers (red spectrum) with asymmetrical broadening of the red spectrum at 2900 cm$^{-1}$

process of introduction of the polystyrene molecules into the matrix of cesium iodide single crystal by the ball rolling of the surface of this crystal with the solution of polystyrene in benzene poured onto this surface. This process was registered by the polarization-optical microscope equipped with the video-recorder. The optical axis of the microscope during the observations was oriented along the surface subjected to the ball rolling and perpendicular to the direction of the introduction of polystyrene [17]. The spatial resolution of the optical microscopy varied from 2 to 10 micrometers by changing the objectives. Fig. 12 demonstrates two stages of introduction of polystyrene to cesium iodide.

At the initial stage approximately equal participation of quasi-homogeneous penetration of the molecules to the crystal as well as several protuberances in the form of micro-filaments is observed (top photo). Then after 10 minutes of rolling the protuberances became much longer exceeding essentially the quasi-homogeneous mass-transfer (bottom photo). It should be emphasized that the thickness of the protuberances is not increased during their penetration into the subsurface layer. Moreover the observations with improved resolution showed that the broadenings of the basements of these protuberances are explained by creation of new needle-like protuberances. Hence these protuberances are self-localized like solitons. In the case of solitons of various natures the preservation of their localization is provided by non-linear changes of the parameters of the substance before and around the soliton [27]. Analogous processes can take place around the moving of the micro-filaments or micro-needles of polystyrene whose penetration into the crystals of cesium iodide was induced by the ball rolling. For example the soliton – like localization of the mass transfer of the polystyrene molecules into crystals by the ball rolling can be attributed to excitation of localized phonons in the needle-like polystyrene
Figure 11. Scanning electron microscopy of nano-filaments perpendicular to the sub-micron threads

agglomerations as it was supposed earlier for the disc-like agglomerations of the solvent in the polystyrene matrix. In the case of polystyrene agglomerations inside crystals the reason of autoclassical localization of their phonons can be explained by lower elastic moduli of the polymer. In this case the velocities of sound oscillations are lower than in the matrix providing this localization. The motions of the ball will excite the local phonons in the agglomeration of polystyrene. These phonons will in their turn bombard the boundary between the tip of the polystyrene and the matrix softening the crystal in the vicinity and providing penetration of the agglomeration. The additional reason for soliton-like propagation of the agglomerations of polystyrene is connected with the crystallization of polystyrene molecules when the distributions of the phenyl groups around the C-H chains became ordered due to isotactic or syndiotactic type. The both kinds of these conformations of polystyrene can be crystallized at the room temperature. On the one hand this crystallization will increase the hardness of the agglomeration whereas on the other hand the crystallization energy will be emitted locally softening the surrounding matrix. It should be emphasized that the creation of the needle-like micro-inclusions of polymer molecules inside inorganic crystal is a new result providing a wide set of actual studies of this kind of qualitatively new material.

3. Conclusion

Comparative studies of processes of forming and properties of various compositions from organic polystyrene and inorganic cesium sulfate and cesium iodide created by several deformation – chemical techniques showed that non-equilibrium processes of forming of these compositions includes generation and soliton – like propagation of filaments of nanoscopic and microscopic dimensions. These structural particularities provide wide possibilities to achieve qualitatively new level of necessary mechanical, electronic, optical and chemical properties of materials with corresponding new technologies of their preparation.

Superstructures of nano- and micro-filaments formed during solidification of fibers from
Figure 12. Polarization – optical microscopy of the initial and final stages of the introduction of polystyrene molecules into cesium iodide crystal by means of the ball rolling

solutions of compositions of polystyrene with inorganic fillers can be modified essentially by regulation of combinations of tensile and compressive stresses. Dynamical flows of the polystyrene gel during solidification induces transformations of the atactic molecules and syndiotactic forms with subsequent crystallization revealed by optical anisotropy.

Qualitatively new kinds of organic-inorganic compositions have been prepared by the deformation-chemical procedures of the ball rolling: organic polymers of polystyrene introduced in the form of nano – and micro – needles into inorganic matrices of cesium iodide and potassium chloride single crystals.

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