

In recent years, considerable efforts have been devoted for search new functional nanocomposite materials with unique properties that are lacking in their traditional analogues. Control of these properties is an important fundamental problem. The use of nanocrystals as one of the elements of a polymer composite opens up new possibilities for targeted modification of its optical properties because of a strong dependence of the electronic structure of nanocrystals on their sizes and geometric shapes. An increase in the number of nanocrystals in the bulk of composites is expected to enhance long-range correlation effects on their properties. Among the known nanocrystals, nanocrystalline silicon (nc-Si) attracts high attention due to its extraordinary optoelectronic properties and manifestation of quantum size effects. Therefore, it is widely used for designing new generation functional materials for nanoelectronics and information technologies. The use of nc-Si in polymer composites calls for a knowledge of the processes of its interaction with polymeric media. Solid nanoparticles can be combined into aggregates (clusters), and, when the percolation threshold is achieved, a continuous cluster is formed. An orderly arrangement of interacting nanocrystals in a long-range potential minimum leads to formation of periodic structures. Because of the well-developed interface, an important role in such systems belongs to adsorption processes, which are determined by the structure of the nanocrystal surface. In a polymer medium, nanocrystals are surrounded by an adsorption layer consisting of polymer, which may change the electronic properties of the nanocrystals. The structure of the adsorption layer has an effect on the processes of self-organization of solid-phase particles, as well as on the size, shape, and optical properties of resulting aggregates. According to data obtained for metallic [1] and semiconducting [2] clusters, aggregation and adsorption in three-phase systems with nanocrystals have an effect on the optical properties of the whole system. In this context, it is important to reveal the structural features of systems containing nanocrystals, characterizing aggregation and adsorption processes in these systems, which will make it possible to establish a correlation between the structural and the optical properties of functional nanocomposite systems. Silicon nanoclusters embedded in various transparent media are a new, interesting object for physicochemical investigation. For example, for particles smaller than 4 nm in size, quantum size effects become significant. It makes possible to control the luminescence and absorption characteristics of materials based on such particles using of these effects [3, 4]. For nanoparticles about 10 nm in size or larger (containing $\sim 10^4$ Si atoms), the absorption characteristics in the UV and visible ranges are determined in many respects by properties typical of massive crystalline or amorphous silicon samples. These characteristics depend on a number of factors: the presence of structural defects and impurities, the phase state, etc. [5, 6]. For effective practical application and creation on a basis nc-Si the new polymeric materials possessing useful properties: sun-protection films [7] and the coverings [8] photoluminescent and electroluminescent composites [9, 10], stable to light dyes [11], embedding of these

nanosized particles in polymeric matrixes becomes an important synthetic problem. The method of manufacture of silicon nanoparticles in the form of a powder by plasma chemical deposition, which was used in this study, makes possible to vary the chemical composition of their surface layers. As a result, another possibility of controlling their spectral characteristics arises, which is absent in conventional methods of manufacture of nanocrystalline silicon in solid matrices (for example, in SiO₂) by implantation of charged silicon particles [5] or radio frequency deposition of silicon [2]. Polymer composites based on silicon nanopowder are a new object for comprehensive spectral investigation. At the same time, detailed spectral analysis has been performed for silicon nanopowder prepared by laser induced decomposition of gaseous SiH₄ (see, for example, [6, 12]). It is of interest to consider the possibility of designing new effective UV protectors based on polymer containing silicon nanoparticles [13]. An advantage of this nanocomposite in comparison with other known UV protectors is its environmental safety, i.e., ability to hinder the formation of biologically harmful compounds during UV-induced degradation of components of commercial materials. In addition, changing the size distribution of nanoparticles and their concentration in a polymer and correspondingly modifying the state of their surface, one can deliberately change the spectral characteristics of nanocomposite as a whole. In this case, it is necessary to minimize the transmission in the wavelength range below 400 nm (which determines the properties of UV-protectors [13]) by changing the characteristics of the silicon powder. Objects of research In this study, the possibilities of using polymers containing silicon nanoparticles as effective UV protectors are considered. First, the structure of nc-Si obtained under different conditions and its aggregates, their adsorption and optical properties was studied in order to find ways of control the UV spectral characteristics of multiphase polymer composites containing nanocrystalline silicon. Also, the purpose of this work was to investigate the effect of the concentration of silicon nanoparticles embedded in polymer matrix and the methods of preparation of these nanoparticles on the spectral characteristics of such nanocomposites. On the basis of the data obtained, recommendations for designing UV protectors based on these nanocomposites were formulated. Nc-Si consists of core-shell nanoparticles in which the core is crystalline silicon coated with a shell formed in the course of passivation of nc-Si with oxygen and/or nitrogen. nc-Si samples were synthesized by an original procedure in an argon plasma in a closed gas loop. To do this, we used a plasma vaporizer/condenser operating in a low-frequency arc discharge. A special consideration was given to the formation of a nanocrystalline core of specified size. The initial reagent was a silicon powder, which was fed into a reactor with a gas flow from a dosing pump. In the reactor, the powder vaporized at 7000 – 10000 °C. At the outlet of the high-temperature plasma zone, the resulting gas-vapor mixture was sharply cooled by gas jets, which resulted in condensation of silicon vapor to form an aerosol. The synthesis of nc-Si in a low-frequency arc discharge was described in detail in [3]. The

microstructure of nc-Si was studied by transmission electron microscopy (TEM) on a Philips NED microscope. X-ray powder diffraction analysis was carried out on a Shimadzu Lab XRD-6000 diffractometer. The degree of crystallinity of nc-Si was calculated from the integrated intensity of the most characteristic peak at $2\theta = 28^\circ$. Low-temperature adsorption isotherms at 77.3 K were measured with a Gravimat-4303 automated vacuum adsorption apparatus. FTIR spectra were recorded on in the region of 400-5000 cm^{-1} with resolution of about 1 cm^{-1} . Three samples of nc-Si powders with specific surfaces of 55, 60, and 110 m^2/g were studied. The D values for these samples calculated by Eq. (2) are 1.71, 1.85, and 1.95, respectively; i.e., they are lower than the limiting values for rough objects. The corresponding D values calculated by Eq. (3) are 2.57, 2.62, and 2.65, respectively. Hence, the adsorption of nitrogen on nc-Si at 77.3 K is determined by capillary forces acting at the liquid-gas interface. Thus, in argon plasma with addition of oxygen or nitrogen, ultra disperse silicon particles are formed, which consist of a crystalline core coated with a silicon oxide or oxynitride shell. This shell prevents the degradation or uncontrollable transformation of the electronic properties of nc-Si upon its integration into polymer media. Solid structural elements (threads or nanowires) are structurally similar, which stimulates self-organization leading to fractal clusters. The surface fractal dimension of the clusters determined from the nitrogen adsorption isotherm at 77.3 K is a structurally sensitive parameter, which characterizes both the structure of clusters and the morphology of particles and aggregates of nanocrystalline silicon. As the origin materials for preparation film nanocomposites served polyethylene of low density (LDPE) marks 10803-020 and ultradisperse crystal silicon. Silicon powders have been received by a method plazmochemical recondensation of coarse-crystalline silicon in nanocrystalline powder. Synthesis nc-Si was carried out in argon plasma in the closed gas cycle in the plasma evaporator the condenser working in the arc low-frequency category. After particle synthesis nc-Si were exposed microcapsulating at which on their surfaces the protective cover from SiO_2 , protecting a powder from atmospheric influence and doing it steady was created at storage. In the given work powders of silicon from two parties were used: nc-Si-36 with a specific surface of particles $\sim 36 \text{ m}^2/\text{g}$ and nc-Si-97 with a specific surface $\sim 97 \text{ m}^2/\text{g}$. Preliminary mixture of polyethylene with a powder nc-Si firms "Brabender" (Germany) carried out by means of closed hummer chambers at temperature $135 \pm 5^\circ\text{C}$, within 10 minutes and speed of rotation of a rotor of 100 minutes $^{-1}$. Two compositions LDPE + nc-Si have been prepared: (1) composition PE + 0.5 % ncSi-97 on a basis ncSi-97, containing 0.5 weights silicon %; (2) composition PE + 1 % ncSi-36 on a basis ncSi-36, containing 1.0 weights silicon %. Formation of films by thickness 85 ± 5 micron was spent on semiindustrial extrusion unit ARP-20-150 (Russia) for producing the sleeve film. The temperature was 120-190 $^\circ\text{C}$ on zones extruder and extrusion die. The speed of auger was 120 minutes $^{-1}$. Technological parameters of the nanocomposites choose, proceeding from conditions of thermostability and the characteristic viscosity

recommended for processing polymer melting. Experimental methods Mechanical properties and an optical transparency of polymer films, their phase structure and crystallinity, and also communication of mechanical and optical properties with a microstructure of polyethylene and granulometric structure of modifying powders nc-Si were observed. Physicomechanical properties of films at a stretching (extrusion) measured in a direction by means of universal tensile machine EZ-40 (Germany) in accordance with Russian State Standard GOST-14236-71. Tests are spent on rectangular samples in width of 10 mm, and a working site of 50 mm. The speed of movement of a clip was 240 mm/minutes. The 5 parallel samples were tested. Optical transparency of films was estimated on absorption spectra. Spectra of absorption of the obtained films were measured on spectrophotometer SF-104 (Russia) in a range of wavelengths 200 – 800 nanometers. Samples of films of polyethylene and composite films PE + 0.5 % ncSi-36 and PE + 1 % ncSi-36 in the size 3x3 cm were investigated. The special holder was used for maintenance uniform a film tension. X-ray diffraction analysis by wide-angle scattering of monochromatic X-rays data was applied for research phase structure of materials, degree of crystallinity of a polymeric matrix, the size of single-crystal blocks in powders nc-Si and in a polymeric matrix, and also functions of density of distribution of the size crystalline particles in initial powders nc-Si X-ray diffraction measurements were observed on Guinier diffractometer: chamber G670 Huber [14] with bent Ge (111) monochromator of a primary beam which are cutting out line $K\alpha_1$ (length of wave $\lambda = 1.5405981 \text{ \AA}$) characteristic radiation of x-ray tube with the copper anode. The diffraction picture in a range of corners 2θ from 3° to 100° was registered by the plate with optical memory (IP-detector) of the camera bent on a circle. Measurements were spent on original powders nc-Si-36 and nc-Si-97, on the pure film LDPE further marked as PE, and on composite films PE + 0.5 % ncSi-97 and PE + 1.0 % ncSi-36. For elimination of tool distortions effect diffractogram standard SRM660a NIST from the crystal powder LaB6 certificated for these purposes by Institute of standards of the USA was measured. Further it was used as diffractometer tool function. Samples of initial powders ncSi-36 and ncSi-97 for x-ray diffraction measurements were prepared by drawing of a thin layer of a powder on a substrate from a special film in the thickness 6 microns (MYLAR, Chemplex Industries Inc., Cat. No: 250, Lot No: 011671). Film samples LDPE and its composites were established in the diffractometer holder without any substrate, but for minimization of structure effect two layers of a film focused by directions extrusion perpendicular each other were used. Phase analysis and granulometric analysis was spent by interpretation of the X-ray diffraction data. For these purposes the two different full-crest analysis methods [15, 16] were applied: (1) method of approximation of a profile diffractogram using analytical functions, polynoms and splines with diffractogram decomposition on making parts; (2) method of diffractogram modeling on the basis of physical principles of scattering of X-rays. The package of computer programs WinXPOW was applied to approximation and profile decomposition diffractogram ver.

2.02 (Stoe, Germany) [17], and diffractogram modeling at the analysis of distribution of particles in the sizes was spent by means of program PM2K (version 2009) [18].

Results and discussion Results of mechanical tests of the prepared materials are presented to tab. 1 from which it is visible that additives of particles nc-Si have improved mechanical characteristics of polyethylene. Table 1 - Mechanical characteristics of nanocomposite films based of LDPE and nc-Si

Sample	Tensile strength, kg/cm ²	Relative elongation-at-break, %
PE	100 ± 12	200 - 450
PE + 1% ncSi-36	122 ± 12	250 - 390
PE + 0.5% ncSi-97	118 ± 12	380 - 500

The results presented in the table show that additives of powders of silicon raise mechanical characteristics of films, and the effect of improvement of mechanical properties is more expressed in case of composite PE + 0.5 % ncSi-97 at which in comparison with pure polyethylene relative elongation-at-break has essentially grown. Transmittance spectra of the investigated films are shown on fig. 1. Fig. 1 - Transmittance spectra of the investigated films LDPE and nanocomposite films PE + 0.5 % ncSi-97 and PE + 1.0 % ncSi-36 It is visible that additives of powders nc-Si reduce a transparency of films in all investigated range of wavelengths, but especially strong decrease transmittance (almost in 20 times) is observed in a range of lengths of waves of 220-400 nanometers, i.e. in UV areas. The wide-angle scattering of X-rays data were used for the observing phase structure of materials and their component. Measured x-ray diffractograms of initial powders ncSi-36 and ncSi-97 on intensity and Bragg peaks position completely corresponded to a phase of pure crystal silicon (a cubic elementary cell of type of diamond - spatial group , cell parameter $a_{Si} = 0.5435$ nanometers). For the present research granulometric structure of initial powders nc-Si is of interest. Density function of particle size in a powder was restored on X-ray diffractogram a powder by means of computer program PM2K [18] in which the method [19] modellings of a full profile diffractogram based on the theory of physical processes of diffraction of X-rays is realized. Modeling was spent in the assumption of the spherical form of crystalline particles and logarithmically normal distributions of their sizes. Deformation effects from flat and linear defects of a crystal lattice were considered. Received function of density of distribution of the size crystalline particles for initial powders nc-Si are represented graphically on fig. 2, in the signature to which statistical parameters of the found distributions are resulted. These distributions are characterized by such important parameters, as $Mo(d)$ - position of maximum (a distribution mode); V - average size of crystalline particles based on volume of the sample (the average arithmetic size) and $Me(d)$ - the median of distribution defining the size d , specifying that particles with diameters less than this size make half of volume of a powder. The results represented on fig. 2, show that initial powders nc-Si in the structure have particles with the sizes less than 10 nanometers which especially effectively absorb UV radiation. The both powders modes of density function of particle size are very close, but median of density function of particle size of a powder ncSi-36 it is essential more than at a powder ncSi-97. It suggests that the number of crystalline

particles with diameters is less 10 nanometers in unit of volume of a powder ncSi-36 much less, than in unit of volume of a powder ncSi-97. As a part of a powder ncSi-36 it is a lot of particles with a diameter more than 100 nanometers and even there are particles more largely 300 nanometers whereas the sizes of particles in a powder ncSi-97 don't exceed 150 nanometers and the basic part of crystalline particles has diameter less than 100 nanometers. The phase structure of the obtained films was estimated on wide-angle scattering diffractogram only qualitatively. Complexity of diffraction pictures of scattering and structure don't poses the quantitative phase analysis of polymeric films [20]. At the phase analysis of polymers often it is necessary to be content with the comparative qualitative analysis which allows watching evolution of structure depending on certain parameters of technology of production. Measured wide-angle X-rays scattering diffractograms of investigated films are shown on fig. 3. Diffractogramms have a typical form for polymers. As a rule, polymers are the two-phase systems consisting of an amorphous phase and areas with distant order, conditionally named crystals. Their diffractograms represent [20] superposition of intensity of scattering by the amorphous phase which is looking like wide halo on the small-angle area (in this case in area 2θ between 10° and 30°), and intensity Bragg peaks scattering by a crystal phase. Fig. 2 - Density function of particle size in powders ncSi, received from x-ray diffractogram by means of program PM2K: (a) - ncSi-97 $M_o(d) = 35$ nm $M_e(d) = 45$ nm $V = 51$ nm; (b) - ncSi-36 $M_o(d) = 30$ nm $M_e(d) = 54$ nm $V = 76$ nm. Data on fig. 3 is presented in a scale of relative intensities (intensity of the highest peak is accepted equal 100 %). For convenience of consideration curves are represented with displacement on an axis of ordinates. The scattering plots without displacement represented completely overlapping of diffractogram profiles of composite films with diffractogram of a pure LDPE film, except peaks of crystal silicon which weren't present on PE diffractogram. It testifies that additives of powders nc-Si practically haven't changed crystal structure of polymer. Fig. 3 - Diffractograms of the investigated composite films in comparison with diffractogram of pure polyethylene. Below vertical strokes specify reference positions of diffraction lines of silicon with their interference indexes (hkl) The peaks of crystal silicon are well distinguishable on diffractograms of films with silicon (the reference positions with Miller's corresponding indexes are pointed below). Heights of the peaks of silicon with the same name (i.e. peaks with identical indexes) on diffractograms of the composite films PE + 0.5 % ncSi-97 and PE + 1.0 % ncSi-36 differ approximately twice that corresponds to a parity of mass concentration Si set at their manufacturing. Degree of crystallinity of polymer films (a volume fraction of the crystal ordered areas in a material) in this research was defined by diffractograms fig. 3 for a series of samples only semiquantitative (more/less). The essence of the method of crystallinity definition consists in analytical division of a diffractogram profile on the Bragg peaks from crystal areas and diffusion peak of an amorphous phase [20], as is shown in fig. 4. Fig. 4 - Diffractogram decomposition on separate peaks and a background by means

of approximation of a full profile by analytical functions on an example of the data from sample PE+1%ncSi-36 (fig. 3). PE-n designate Bragg peaks of crystal polyethylene with serial numbers n from left to right. Si (111) – Bragg silicon peak ncSi-36. Vertical strokes specify positions of maxima of peaks Peaks profiles of including peak of an amorphous phase, were approximated by function pseudo-Foigt, a background 4 order polynoms of Chebysheva. The nonlinear method of the least squares minimized a difference between intensity of points experimental and approximating curves. The width and height of approximating functions, positions of their maxima and the integrated areas, and also background parameters were thus specified. The relation of integrated intensity of a scattering profile by an amorphous phase to full integrated intensity of scattering by all phases except for particles of crystal silicon gives a share of amorphity of the sample, and crystallinity degree turns out as a difference between unit and an amorphity fraction. It was supposed that one technology of film obtaining allowed an identical structure. It proved to be true by coincidence relative intensities of all peaks on diffractograms fig. 3, and samples consist only crystal and amorphous phases of the same chemical compound. Therefore received values of degree of crystallinity should reflect correctly a tendency of its change at modification polyethylene by powders nc-Si though because of a structure of films they can quantitatively differ considerably from the valid concentration of crystal areas in the given material. The found values of degree of crystallinity are represented in table 2.

Table 2 - Characteristics of the ordered (crystal) areas in polyethylene and its composites with nc-Si

Sample	Crystallinity (%)	2 θ [°]	d [Å]	e [Å]	2 θ [°]	d [Å]	e [Å]
PE	46%	21.274	276	8.9	21.285	229	7.7
PE + 1% ncSi-36	47,5%	21.282	220	7.9	23.566	151	12.8
PE + 0.5% ncSi-97	48%	23.582	128	11.2	23.567	123	11.6
Average values		206	9.5	10 ⁻³	174	8.2	10 ⁻³

One more important characteristic of crystallinity of polymer is the size d of the ordered areas in it. For definition of the size of crystalline particles and their maximum deformation e in X-ray diffraction analysis [21] Bragg peaks width on half of maximum intensity (Bragg lines half-width) is often used. In the given research the sizes of crystalline particles in a polyethylene matrix calculated on three well expressed diffractogram peaks fig. 3. The peaks of polyethylene located at corners 2 q approximately equal 21.28 °, 23.57 ° and 36.03 ° (peaks PE-1, PE-2 and PE-3 on fig. 4 see) were used. The ordered areas size d and the maximum relative deformation e of their lattice were calculated by the joint decision of the equations of Sherrera and Wilson [21] with use of half-width of the peaks defined as a result of approximation by analytical functions, and taking into account experimentally measured diffractometer tool function. Calculations were spent by means of program WinXPOW size/strain. Received d and e, and also their average values for investigated films are presented in table 2. The updated positions of maxima of diffraction peaks used at calculations are specified in the table. The offered technology allowed the obtaining of films LDPE and composite films LDPE + 1 % ncSi-36 and LDPE + 0.5 %

ncSi-97 an identical thickness (85 microns). Thus concentration of modifying additives ncSi in composite films corresponded to the set structure that is confirmed by the X-ray phase analysis. By direct measurements it is established that additives of powders ncSi have reduced a polyethylene transparency in all investigated range of lengths of waves, but especially strong transmittance decrease (almost in 20 times) is observed in a range of lengths of waves of 220-400 nanometers, i.e. in UV areas. Especially strongly effect of suppression UV of radiation is expressed in LDPE film + 0.5 % ncSi-97 though concentration of an additive of silicon in this material is less. It is possible to explain this fact to that according to experimentally received function of density of distribution of the size the quantity of particles with the sizes is less 10 nanometers on volume/weight unit in a powder ncSi-97 more than in a powder ncSi-36. Direct measurements define mechanical characteristics of the received films – durability at a stretching and relative lengthening at disrapture (Tab. 1). The received results show that additives of powders of silicon raise durability of films approximately on 20 % in comparison with pure polyethylene. Composite films in comparison with pure polyethylene also have higher lengthening at disrapture, especially this improvement is expressed in case of composite PE + 0.5 % ncSi-97. Observable improvement of mechanical properties correlates with degree of crystallinity of films and the average sizes of crystal blocks in them (Tab. 2). By results of the X-ray analysis the highest crystallinity at LDPE film + 0.5 % ncSi-97, and at it the smallest size the crystal ordered areas that should promote durability and plasticity increase.