Polymer film materials based on polyethylene containing between 0.5% and 1.0% by wt. nanocrystalline silicon (ncSi) with excellent strength properties have been produced. Specimens of ncSi with a mean core diameter of 7-10 nm were synthesised using plasma chemistry methods and laser-induced breakdown of monosilane. Spectral studies indicate an almost total (up to ~95%) absorption of UV radiation by films 85 microns thick in the 200-400 nm area with a 1.0% by wt. ncSi content in them. Using the method of full-profile modelling of X-ray diffraction patterns, and assuming that the crystallites are spherical in shape and have a log-normal distribution, the particle size distribution density functions in the initial powders and polymer films containing immobilised silicon nano-crystallites were derived. X-ray analysis results show that the distribution function for crystallite dimensions remains virtually unaltered with implantation of initial ncSi specimens in a polymer matrix, while the degree of crystallinity of the initial polymer increases (~10%).

INTRODUCTION

Nanocrystalline silicon (nc-Si) possesses a number of unique optical and electrophysical properties [1], and this, in conjunction with the non-toxicity of silicon and its relatively low cost, makes it an extremely promising material for use in a wide range of areas of science and technology. In order to make effective practical use of this material, and to create new polymer materials based on nc-Si which feature useful properties – sun-protection films [2] and coatings [3], photoluminescent and electroluminescent composites [1, 4] and light-resistant dyes [5] – one important synthetic task is to build these nano-size particles into polymer matrices. In the simplest case, the role of the polymer matrix comes down to providing the requisite physical and mechanical properties of the composite (mechanical strength, elasticity, adhesion to substrate, protection from aggressive environments, etc.). In addition, the matrix must prevent agglutination of nano-particles and create conditions for even distribution of nc-Si through the body of the specimen or fix it at the surface. Finally, if the matrix itself possesses special optical, electrically-conducting and photoelectric properties, when the functional properties of nc-Si particles are added, a material with a whole set of new characteristics will be produced.

UV radiation in the 290-330 nm spectral range is known to reduce the yield of vegetable crops significantly as a result of loss of part of the plant’s growth energy to protect against it [6]. UV radiation in the 200-420 nm range shortens the storage period for food products [7] and causes a deterioration in the use attributes of electronic goods [8]. It has also been found that if an oxygen absorber is used, the freshness of a food product sealed in translucent food packaging may unexpectedly improve if the translucent packaging material contains
a UV radiation absorber [9]. There are various ways of protecting against UV radiation. As a rule, chemicals containing chromophore groups that absorb ultraviolet or convert it into infrared radiation are introduced into polymers [7-9].

The introduction into polymers of nano-particles of oxides of metals and non-metals that feature a screening effect against UV radiation opens up considerable potential for the creation of commercial nano-polymer composites based on thermosoftening plastics of a range of chemical structures with a high level of use attributes. Such materials, in film form, will find a use in agriculture, the packaging industry and medicine.

The objective of the present work was to study film materials possessing UV-protective properties based on low-density polyethylene and a biologically-compatible nano-material [1, 10], nanocrystalline silicon, synthesised using a plasma chemistry method. This process enables an ncSi to be mass-produced that is of adequate purity and at a low enough cost.

MATERIALS

The raw materials for the preparation of film nanocomposites were low-density polyethylene (LDPE) of grade 10803-020 and ultra-disperse crystalline silicon. Silicon powders were produced using the method of plasma chemical recondensation of macrocrystalline silicon to a nanocrystalline powder (ncSi). Synthesis of ncSi took place in argon plasma in a closed gas cycle in a plasma evaporator-condenser operating in low-frequency arc discharge. Following synthesis, the ncSi particles were subjected to micro-capsulation, during which a protective SiO₂ film was created on their surfaces, protecting the subjected to micro-capsulation, during which a protective discharge. Following synthesis, the ncSi particles were subjected to micro-capsulation, during which a protective SiO₂ film was created on their surfaces, protecting the powder from exposure to the atmosphere and rendering it stable for storage. For this work we used silicon from two batches: ncSi-36 with a particle specific surface of ~36 m²/g and ncSi-97 with a particle specific surface of ~97 m²/g, according to BET method data.

Preliminary mixing of polyethylene and ncSi powder took place using a closed hammer-mill chamber made by Branberder (Germany) at a temperature of 135±5 °C for a period of 10 minutes and a rotor speed of 100 rpm. Two LDPE+ ncSi composites were produced: (1) a PE + 0.5% ncSi-97 composite based on ncSi-97, containing 0.5% by wt silicon; (2) a PE + 1% ncSi-36 composite based on ncSi-36, containing 1.0% by wt. silicon.

The moulding of films 85±5 microns in thickness was carried out on a semi-industrial extrusion rig for the production of ARP-20-150 sleeve film (Russia) at temperatures of 120-190 °C in the extruder and extrusion head zones, and a screw speed of 120 rpm. The nanocomposite process parameters were selected on the basis of the thermal stability conditions and recommended characteristic polymer melt viscosity for processing.

METHODS

Tests were performed on the mechanical properties and optical translucence of the polymer films, their phase composition and crystallinity, and also on the link between mechanical and optical properties and the microstructure of the polyethylene and the grain-size composition of the ncSi modifying powders.

The physical and mechanical properties of the films under tension (in the direction of extrusion) were measured using an EZ-40 universal tearing machine (Germany) in line with GOST 14236-71. The tests were carried out on rectangular specimens 10 mm wide and with a working area of 50 mm. The clamp movement speed was 240 mm/min. The tests were performed on a sample of 5 parallel specimens.

The optical translucence of the films was assessed from the absorption spectra. The absorption spectra for the films produced were measured using an SF-104 spectrophotometer (Russia) in the 200-800 nm wave length range. To produce the absorption spectra for polyethylene films and composite films (PE + 0.5% ncSi-36 and PE + 1% ncSi-36), specimens 3x3 cm in size were used, which were fastened in a special holder to ensure even tension on the film.

To study the phase composition of the materials, the degree of crystallinity of the polymer matrix, the size of the monocristalline blocks in the nc-Si powders and in the polymer matrix, and also the size distribution density function (SDDF) of the crystallites in the initial nc-Si powders, we used X-ray structural analysis from data for wide-angle dispersion of monochromatic X-rays.

X-ray diffraction measurements were carried out on a diffractometer with Guinier layout (focusing diffraction photography of stationary specimen by transillumination): G670 Huber camera [11] with curved Ge(111) primary-beam monochromator extracting the Kα₁ line (wave length λ = 1.5405981 Å) of the characteristic radiation of an X-ray tube with copper anode. The diffraction picture in the range of 2θ angles from 3 to 100 was recorded using a plate with optical memory (IP-detector) curved following the circumference of the camera. The measurements were made for initial ncSi-36 or ncSi-97 powders, for pure LDPE film, subsequently referred to as PE, and for PE + 0.5% ncSi-97 and PE + 1.0% ncSi-36 composite films. To eliminate the effect of instrumental distortions, a diffraction pattern was measured for an SRM660a NIST standard made of crystalline LaB₆ powder certified for this purpose by the US Standards Institute, and this diffraction pattern was subsequently used as the diffractometer instrumental function.
The specimens of initial ncSi-36 and ncSi-97 powders for X-ray diffractometry were prepared by applying a thin layer of powder to a substrate of special film 6 microns in thickness (MYLAR, Chemplex Industries Inc., Cat. No. 250, Lot No. 01 1671). The LDPE film specimens and LDPE composite specimens were fastened in the diffractometer holder without any substrate, but to minimise the texture effect, two layers of film were used, oriented by extrusion directions perpendicular to each other.

Interpretation of the X-ray diffraction data for phase and grain-size analysis was carried out using two different methods of full-profile analysis [12, 13]: (1) a method of approximation of the diffraction pattern profile by analytical functions, polynomials and splines with breakdown of the diffraction pattern into its component parts; (2) a method of modelling of the diffraction pattern on the basis of the physical principles of X-ray scattering. For approximation and breakdown of the diffraction pattern profile, the WinXPOW ver. 2.02 software package was used (Stoe, Germany) [14], and modelling of diffraction patterns for analysis of particle distribution by size was carried out using the PM2K programme (2009 version) [15].

RESULTS

The results of mechanical tests on the materials prepared are shown in Table 1, from which it may be seen that adding ncSi particles improved the mechanical characteristics of the polyethylene.

The results given in the table show that adding silicon powders improves the mechanical characteristics of films, with the improvement effect on mechanical properties being more marked in the case of the PE + 0.5% ncSi-97 composite, for which, compared to pure polyethylene, the breaking elongation rose substantially.

The transmission spectra for the films tested are shown in Figure 1.

It may be seen that adding ncSi powders reduces the translucence of the films over the entire range of wave lengths studied, but a particularly strong reduction in transmission (by nearly 20 times) is observed in the 220-400 nm wave length range, i.e. in the UV area.

The phase composition of the materials tested and their components was studied from the aspect of wide-angle X-ray scattering data. In terms of the strength and position of the Bragg peaks, the X-ray diffraction patterns measured for the ncSi-36 and ncSi-97 initial powders fully matched the pure crystalline silicon phase (cubic elementary cell of diamond type – spatial group \(Fd\bar{3}m\), cell parameter \(a_{\text{Si}} = 0.5435 \text{ nm}\), the X-ray diffraction picture for which has been well studied, so it is not given here.

For the purposes of this study, interest lay in the grain-size composition of the initial ncSi powders. The size distribution density function (SDDF) of the crystallites in the powder was recovered for the X-ray diffraction pattern from the powder using the PM2K software [15], which puts into practice the method [16] of full-profile diffraction pattern modelling based on the theory of the physical processes of X-ray diffraction. Modelling was performed on the assumption that the crystallites were spherical in shape and their size distribution was log-normal, and the deformation effects from planar and linear defects in the crystal lattice were taken into account. The SDDF obtained for the initial ncSi powders are graphically illustrated in Figure 2, the legend to which gives the statistical parameters for the distributions found. These distributions feature such important parameters as \(Mo(d)\) – the position of the SDDF peak (distribution mode); \(<d>_v\) – the mean crystallite size through the specimen volume (arithmetic mean size) and \(Me(d)\) – the distribution median, which governs the size \(d\) which indicates that particles with diameters smaller than this size constitute half of the volume of the powder.

The results given in Figure 2 show that the initial ncSi powders have in their composition particles less than 10 nm in size, which particularly effectively absorb UV radiation. The SDDF modes for the two powders are very similar, but the SDDF median for ncSi-36 powder is considerably greater than that for ncSi-97. This leads us to conclude that the number of crystallites with diameter less than 10 nm per unit of volume of ncSi-36 powder

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tensile strength, kg/cm²</th>
<th>Breaking elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>100 ± 12</td>
<td>200-450</td>
</tr>
<tr>
<td>PE + 1% ncSi-36</td>
<td>122 ± 12</td>
<td>250-390</td>
</tr>
<tr>
<td>PE + 0.5% ncSi-97</td>
<td>118 ± 12</td>
<td>380-500</td>
</tr>
</tbody>
</table>

Figure 1. Transmission spectra for LDPE film and PE + 0.5% ncSi-97 and PE + 1.0% ncSi-36 nanocomposite films
is perceptibly smaller than per unit of volume of ncSi-97 powder. The composition of ncSi-36 powder contains quite a lot of particles with diameter over 100 nm, and there are even particles larger than 300 nm, whereas the size of the particles in ncSi-97 powder does not exceed 150 nm, with the bulk of the crystallites having a diameter below 100 nm.

The phase composition of the films produced was assessed from the wide-angle X-ray scattering diffraction patterns only in a qualitative way, since the complexity of the dispersion diffraction pictures and the presence of texture makes quantitative phase analysis of polymer films virtually impossible [17]. During phase analysis of polymers one often has to content oneself with a comparative qualitative analysis, which enables the evolution of structure to be traced in relation to specific production process parameters.

The diffraction patterns measured for wide-angle X-ray scattering by the films under study are shown in Figure 2. The diffraction patterns are of the form that is typical of polymers. Polymers are generally two-phase systems comprising an amorphous phase and zones

Figure 2. Density distribution functions for size of crystallites in ncSi powders produced from X-ray diffraction patterns using the RM2K programme: (a) – ncSi-97 Mo(d) = 35 nm, Me(d) = 45 nm, <d> = 51 nm; (b) – ncSi-36 Mo(d) = 30 nm, Me(d) = 54 nm, <d> = 76 nm.

Figure 3. Diffraction patterns for composite films studied compared to diffraction pattern for pure polyethylene. The vertical lines at the bottom show the standard positions of the diffraction lines for silicon, with their interference indices (hkl)
of long-range order, known conventionally as crystals. Their diffraction patterns constitute [17] a superposition of the intensity of scattering of the amorphous phase, which has the form of a broad halo, in the low-angle area (in the case in point, in zone 2 between 10 and 30), and peaks of the intensity of Bragg scattering by the crystalline phase.

The data in Figure 3 are shown on a relative intensities scale (the intensity of the highest peak in the diffraction pattern is taken as 100%). For convenience of examination, the curves are shown with a shift along the Y-axis. If scattering graphs are shown without a shift, the diffraction pattern profiles for composite films coincide exactly with the diffraction pattern for pure LDPE film, apart from the peaks for crystalline silicon, which are not present in the PE diffraction pattern. This indicates that adding ncSi powders had virtually no effect in altering the crystalline structure of the polymer.

On the diffraction patterns for films with silicon, the crystalline silicon peaks are readily discernible (their standard positions with the corresponding Miller indices are shown below as vertical lines). The heights of analogous peaks for silicon (i.e. peaks with identical indices) on the diffraction patterns for PE + 0.5% ncSi-97 and PE + 1.0% ncSi-36 films differ by almost a factor of two, which matches the ratio of the mass Si concentrations set for their manufacture.

The degree of crystallinity of the polymer films (the proportion by volume of zones of crystal ordering in the material) in this study was determined from the diffraction patterns in Figure 3 for a series of specimens in only a semi-quantitative way (more/less). The essence of the method of determining crystallinity consists in an analytical separation of the diffraction pattern profile into Bragg peaks from crystalline zones and a diffuse amorphous phase peak [17], as shown in Figure 4.

The peak profiles, in this case including the amorphous phase peak, were approximated by a pseudo-Voigt function, and the background by 4th-order Chebyshev polynomials. A non-linear least-squares method was used to minimise the difference between the intensity of the points on the experimental and approximating curves. The breadth and height of the approximating functions were refined, along with the positions of their peaks and integral areas, and also the background parameters. The ratio of the integral intensity of the amorphous phase scattering profile to the full integral scattering intensity by all phases apart from crystalline silicon particles gives the proportion of amorphism of the specimen, and the degree of crystallinity is obtained as the difference between one and the proportion of amorphism.

It was assumed that, thanks to the same production process, the films would have identical texture, and this is confirmed by the coincidence of relative intensities of

![Figure 4. Breakdown of diffraction pattern into separate peaks and background with the aid of full profile approximation using analytical functions taking as an example the data for a PE + 1% ncSi-36 specimen (Figure 3). PE-n designates the Bragg peaks for crystalline polyethylene with serial numbers from left to right. Si(111) is the Bragg peak for silicon ncSi-36. The vertical lines show the positions of the tops of the peaks.](image-url)
all peaks on the diffraction patterns in Figure 3, and the specimens consist solely of crystalline and amorphous phases of identical chemical composition. The values obtained for the degree of crystallinity should therefore correctly reflect the trend in its variation when LDPE is modified by ncSi powders, although because of the texture of the films, they may perceptibly differ in quantitative terms from the actual concentration of crystalline zones in the given material. The values found for the degree of crystallinity are given in Table 2.

Another important characteristic of polymer crystallinity is the size $d$ of the ordered zones in it. To determine the size of the crystallites and their maximum deformation $e$ in X-ray structural analysis, the width of the Bragg peaks at half the maximum intensity is often used [18] (Bragg line half-width). In the study in question, the sizes of the crystallites in the polyethylene matrix were calculated from three very distinct peaks on the film diffraction patterns in Figure 3. We used the peaks for polyethylene located at angles of $2\theta$ that were roughly equal to 21.28°, 23.57° and 36.03° (see peaks PE-1, PE-2 and PE-3 in Figure 4). The size $d$ of the ordered zones in the maximum relative deformation $e$ of their lattice were calculated through a joint resolution of the Scherrer-Wilson equations [18] using peak half-widths determined as a result of approximation using analytical functions, and taking into account the experimentally-measured instrumental function of the diffractometer. The calculations were performed using the WinXPOW size/strain programme. The values of $d$ and $e$ obtained, as well as their mean values for the films studied, are shown in Table 2. The table gives the refined positions of the tops of the diffraction peaks used in the calculations.

DISCUSSION

The process put forward here enabled LDPE films and composite LDPE + 1% ncSi-36 and LDPE + 0.5% ncSi-97 films of identical thickness (85 microns) to be produced. The concentration of the modifying ncSi additives in the composite films matched the set composition, as confirmed by X-ray phase analysis.

It was established by direct measurements that adding ncSi powders reduced the translucence of the polyethylene over the entire range of wave lengths studied, but a particularly large reduction in transmission (by almost 20 times) is seen in the 220-400 nm wave length range, i.e. in the UV area. A particularly strong UV radiation suppression effect was found for LDPE + 0.5% ncSi-97 film, although the concentration of the silicon additive in this material is lower. One reason for this fact may be that, according to experimentally-generated SDDFs, the number of particles with sizes below 10 nm per unit of volume/mass in ncSi-97 powder is greater than in ncSi-36 powder.

Direct measurements were used to determine the mechanical characteristics of the films produced – tensile strength and breaking elongation (table 1). The results obtained show that adding silicon powders increases film strength by roughly 20% compared to pure polyethylene. Compared to pure polyethylene, composite films also have a higher breaking elongation, and this improvement is particularly marked in the case of PE + 0.5% ncSi-97 composite. The observed improvement in mechanical properties correlates with the degree of crystallinity of the films and the average sizes of the crystalline blocks in them (Table 2). From the results of X-ray analysis, the highest degree of crystallinity is to be found in LDPE + 0.5% ncSi-97 film, and this film also features the smallest size of crystalline ordered zones, which should support an increase in strength and elasticity.

ACKNOWLEDGEMENT

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REFERENCES


Table 2. Characteristics of ordered (crystalline) zones in polyethylene and composites of it with nc-Si

<table>
<thead>
<tr>
<th>PE</th>
<th>PE + 1% ncSi-36</th>
<th>PE + 0.5% ncSi-97</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallinity</td>
<td>2θ ($^\circ$)</td>
<td>d [Å]</td>
</tr>
<tr>
<td></td>
<td>23.566</td>
<td>151</td>
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<tr>
<td></td>
<td>36.038</td>
<td>191</td>
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<tr>
<td>Av. values</td>
<td>206</td>
<td>9.5x10^{-3}</td>
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</tbody>
</table>


7. RU Patent No. 2000130235.


