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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Nanostructured Carbon Coatings on Polyethylene Films

A. P. Alekhin, A. G. Kirilenko, R. V. Lapshin, R. I. Romanov, and A. A. Sigarev

Lukin Research Institute of Physical Problems, Federal State Unitary Enterprise, Moscow, Russia

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Abstract—The properties of medical low-density polyethylene films with carbon coatings improving the biological compatibility of the polymer were studied by electron and scanning atomic-force microscopy, as well as by IR, Raman, visible, and UV spectroscopy.

A promising line in development of hemocompatible materials is modification of the polymer surface by deposition of coatings having the desired biochemical properties [1]. Understanding of the formation mechanism of hemocompatible surfaces requires studying the properties of the modifying coating.

Among the materials suitable for modification of medical polymers, in particular, low-density polyethylene (LDPE), is carbon [2] with its unique properties, above all, the occurrence in various chemical modifications: sp^3 (diamond), sp^2 (diamond-like), and sp (carbyne). Carbon is expected to be well compatible biologically with blood plasma proteins and living cells of the human body, because these cells consist, primarily, of organic, i.e., carbon-containing compounds. Lastly, it is possible to build on the surface of a polymer support the required cluster formations from carbon (nanostructured carbon), matching in the thermodynamic and geometric parameters a certain type of molecules of blood plasma proteins. This makes possible formation of a high-quality polymer–blood interface when using carbon as the modifying coating.

In this work, we studied LDPE-supported nanostructured carbon by physical methods.

EXPERIMENTAL

As the model material for the support we used a 50-μm-thick film of LDPE [GOST (State Standard) 10354–82]. Rectangular 25 × 20-mm pieces of the LDPE film were cut out in a such way that their longer sides made the same angle with the axis of film extension during its preparation.

Carbon coatings were deposited onto the polymer films in a working chamber of a UVNIPA-1 vacuum setup (manufactured by the Kvarts Kaliningrad Machine-Building Plant) by pulse plasma-arc spraying of a graphite target at the residual gas pressure of ca. 7.5×10^{-4} torr. The LDPE sample was fixed in a holder at a distance of 35 cm from the carbon target surface; the working surface of the polymer was perpendicular to the direction of propagation of the carbon ion flow.

The ignition electrodes in the UVNIPA-1 setup were used for initiating a ~0.01-s pulse electric-arc discharge on the surface of a cold in the bulk graphite cathode. The discharge produced carbon plasma whose ions were then accelerated in an electric field with a potential difference of 450 V and condensed on the working surface of the support. The sample surface was modified at various frequencies f of the pulses generated by the carbon plasma generator (0.1, 0.3, and 1 Hz).

The pulsed condensation of the carbon coating (with the pause being more than 10 times longer than the plasma discharge period) improves the heat removal from the carbon coating condensation zone. This makes less probable melting of the structural elements of the polymer matrix and favors stabilization of the surface modification process. The setup used by us provided the carbon film deposition rate of ~0.15 nm per pulse. We estimated the rate constant of the coating thickness growth by X-ray photoelectron spectroscopy using the procedure from [3]. For comparing the modified and initial LDPE film surfaces, a segment of the sample was shielded from the ion beam. The thickness of the deposited carbon films was 1.5–15 nm on the average, which corresponds to $N = 10–100$ pulses of the coating deposition.

The LDPE film surface morphology was examined by scanning probe atomic-force microscopy (AFM)

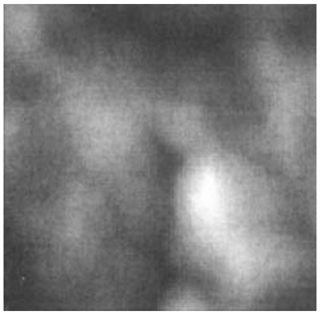

Fig. 1. Unmodified (with carbon) LDPE surface with a characteristic developed random structure.

using a Solver P4 NT-MDT microscope. We used a cantilever (Lukin Research Institute of Physical Problems, Federal State Unitary Enterprise) with the elasticity coefficient of 20 N m^{-1}, resonance frequency of ~132 kHz, and needle tip radius less than 10 nm. The measurements were run in the tapping mode in air at room temperature. The limiting resolution of the microscope was estimated from the minimal discernible film surface elements at 20–30 nm. The maximal scanning field was 6 × 6 μm in size.

The morphology of the surface of the modified films was preliminarily studied by raster electron microscopy (REM). We used an Camscan 4, Cambridge, microscope with a typical magnification of ×3500–5400 corresponding to the examined fields with a size of tens of micrometers. Based on analysis of the features of REM relief image typical for this scale, we made express estimates of the performance of the process equipment when optimizing the parameters of the pulse process of carbon deposition.

Certain structural features of the LDPE films were analyzed by optical spectroscopy (IR, visible, and UV). We measured the transmission spectra of the samples under normal incidence of the light onto the surface. Polarization IR spectra at 500–4000 cm^{-1} were measured on a Michelson 100 (Bomem) IR Fourier spectrometer equipped with a cooled HgCdTe detector and a lattice polarizer on a KRS-5 plate (SPECAC). The UV and visible spectra of the samples at 200–900 nm were recorded with a U3000 Hitachi spectrophotometer.

The electronic structure of the carbon coatings was studied by Raman spectroscopy at 100–1800 cm^{-1}. These spectra were measured using a depolarized radiation from an argon laser at 488 nm (5 mW power) by the procedure from [4]. The focus spot was 50 μm in size. The Raman spectra obtained were typical for solid diamond-like films [4, 5].

We preliminarily compared the morphologies of the modified surfaces of LDPE samples by scanning electron microscopy [frequency of generation of the discharge pulses in plasma $f = 1$ Hz; number of pulses 10 and 50; carbon film thickness (one pulse corresponds to ~0.15 nm) 1.5 and 7.5 nm (samples I and II, respectively)]. The morphology of the samples proved to be globular-fibrillar for sample I and fibrillar for sample II; the fibrils were predominantly oriented along the image diagonal.

The procedure developed by us allows reliable reproduction of the morphology of the modified polymer surface. On the sample I surface, there were globular-fibrillar structures 0.5 to 2.0 μm in size, and on the sample II surface, fibrillar structures 3–4 μm in size. Presumably, the structures with a typical size close to that of thrombocyte will strongly influence the adhesion of thrombocytes.

The sample surface morphology was examined in more detail by AFM. The samples were divided into three groups comprising samples whose modified layer was formed at f of 0.1, 0.3, and 1.0 Hz. From each group we took samples with coatings obtained at different numbers of pulses N, 10, 50, and 100, corresponding to the coating thicknesses of 1.5, 7.5, and 15 nm, respectively.

For coatings with these thicknesses, the carbon layer is not continuous; it consists of clusters (islands) tens and hundreds of nanometers in size. The size of the carbon-free areas in the sample depends on the number of the carbon deposition pulses N and the frequency of their generation f. To ensure high-precision and linear measurements, we developed a method of active scanning and positioning. This implies the use of specific structures on the surface under study (in our case, carbon clusters) as the reference points in movings. This eliminates the effect of the thermal drift, nonlinearity, and nonorthogonality of the piezoscanner on the results of examining the nanostructures.

The image of the initial LDPE surface demonstrates a characteristic developed random structure (Fig. 1).

The image of the carbon-modified polyethylene surface obtained with the carbon plasma generator operating at $f = 0.1$ Hz reveals the presence of elongated carbon clusters, 70–200 nm in size on the average. It should be noted that, at $N = 10$, the length and width of a surface element are in a ratio of approximately 1 : 3; the distance separating the clusters is approximately equal to the size of the clusters, and at $N = 50$ this distance decreases to 20–100 nm.

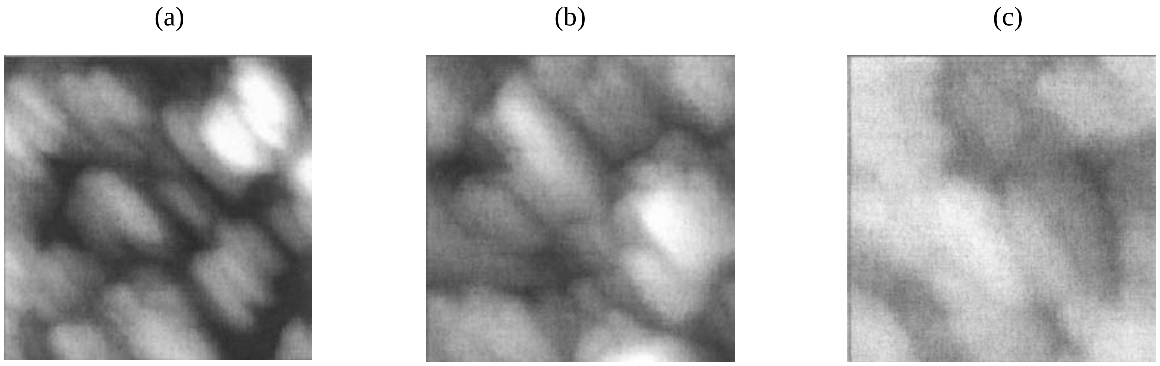

Fig. 2. Carbon-modified LDPE surface; the frequency of pulse generation by the carbon plasma generator 1 Hz. Number of pulses *N*: (a) 10, (b) 50, and (c) 100. Coating thickness, nm: (a) 1.5, (b) 7.5, and (c) 15.0.

The scans of the carbon-modified polyethylene surface obtained at $f = 0.3$ Hz reveal oval clusters 70–150 nm in size. The cluster length-to-width ratio is close to 2. The degree of filling of the polyethylene surface with the clusters increases relative to the case of $f = 0.1$, and the distance separating the clusters decreases to 10–70 nm.

The carbon coatings formed at $f = 1$ Hz exhibit a nanostructure with disk-like clusters 120–150 nm in size; the distance separating the clusters decreases to 5–20 nm.

Figure 2 presents the most typical images for different numbers of pulses.

The optical spectroscopic studies showed that the initial and modified polymer films obtained with 10, 50, and 100 pulses have different spectra within 200–900 nm. The transmission is inversely proportional to the number of the carbon deposition pulses or the thickness of the film formed. The transmission band edge is located at $\lambda \sim 200$ nm, which is due to strong light absorption by the polymer at $\lambda \leq 200$ nm.

Figure 3 shows the relative transmission T/T_0 spectra of the modified polymers (T_0 is the transmission of the initial samples of this polymer). It is seen that, with the growth of the carbon coating, the transmission tends to substantially decrease, especially in the UV range. Possible reasons for the characteristic decrease in transmission of the samples are light absorption and scattering on the carbon clusters. Analysis of the characteristic decrease in the relative transmission T/T_0 allowed estimation of the size of the carbon clusters. For example, the carbon clusters of the modified sample obtained at 100 pulses can be 100–200 nm in size. The sizes of the carbon clusters estimated from the spectral and AFM data agree well.

It should be noted that the samples modified at different pulse generation frequencies (0.1, 0.3, and 1.0 Hz) show similar trends in variation of the relative transmission T/T_0 spectra in the UV and visible ranges with the number of pulses.

In the middle IR range, we revealed a number of the most intense characteristic absorption bands of the CH_2 groups in the spectra of LDPE. The IR spectra of the modified polymer films are very close to that of the initial polymer film. The observed modulation of the baseline in the transmission spectrum is due to interference of the IR radiation in the polymer film, which complicates analysis of weak absorption bands in the differential spectra.

Studies of the optical properties of carbon films showed that the band gap for them can be estimated by the procedure from [6] at 2.1 eV; the extinction coefficient ε is determined as

$$\ae = \alpha\lambda/4\pi,$$

where $\alpha = 0.06$ is the absorption coefficient at $\lambda = 550$ nm.

These parameters also correspond to diamond-like films [7].

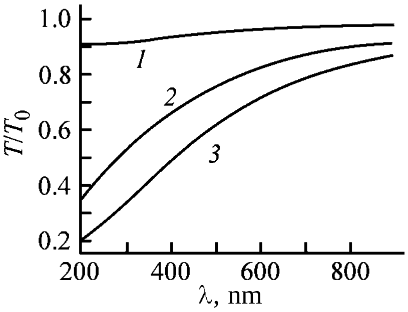

Fig. 3. Relative transmission T/T_0 of the LDPE films with carbon coatings of different thicknesses. (λ) Wavelength. Coating thickness, nm: (*1*) 1.5, (*2*) 7.5, and (*3*) 15.0.

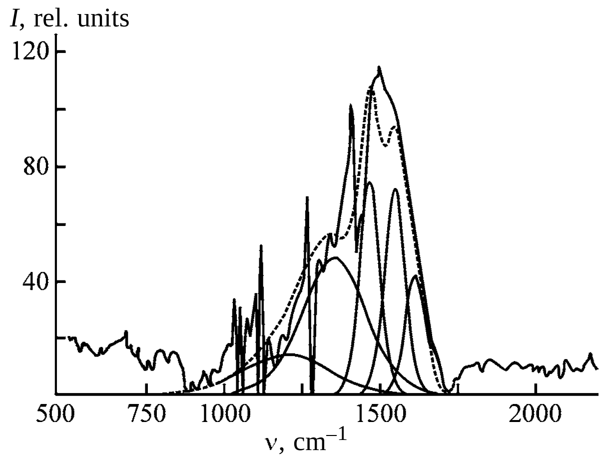

Fig. 4. Raman spectra of the carbon layers obtained by arc pulse-plasma spraying of graphite. $N = 50$, $f = 1.0$ Hz. (*I*) Intensity and (ν) wave number.

Comparison of the spectra of polyethylene before and after sputtering shows that the line positions and their relative intensities do not change significantly. There is only general decline in intensity, probably due to shielding of polyethylene by the carbon layer. It can be supposed that the surface processes associated with the film deposition produce no changes in the bulk of the polyethylene support.

To gain additional information about the structure of the modifying carbon coatings, we carried out mathematical analysis of their Raman spectra. Figure 4 presents the Raman spectrum of the modifying carbon coatings for $N = 50$ and $f = 1$ Hz (for other N and f, the spectra are similar). This analysis consisted in resolution of the experimental spectrum into three model subspectra determined as mixed Lorenzian–Gaussians by the relationship

$$F(x) = \text{peak height}/[1 + M(x - x_0)^2/\beta^2]$$
$$\times \exp(1 - M)\ln 2(x - x_0)^2/\beta^2,$$

where x_0 is the peak center position and β, a parameter equal approximately to the half of the full width at half maximum (FWHM).

Characteristics of the Raman spectra after resolution ($N = 50$, $f = 1.0$ Hz)

Raman shift of the peak, cm^{-1}	Intensity, rel. units	FWHM, cm^{-1}
1200	15	300
1350	45	250
1450	75	100
1550	70	100
1650	40	75

Such spectra (Fig. 4) are characterized by two wave numbers: 1355 (*D* line) and 1580 cm^{-1} (*G* line) responsible for sp^3 diamond (1322 cm^{-1}) and sp^2 graphite (1580 cm^{-1}) electronic structures, respectively. For certain samples, we sometimes observed another peak with a wave number of 1200 cm^{-1} characterizing the disordering of the sp^3 electronic structure.

The characteristics of the Raman spectra of the samples after resolution are listed in the table.

These data were calculated from the parameter β by the iteration method. The parameter M determines the degree of mixing and is equal to 1 for pure Lorenzian and to 0 for pure Gaussian peaks. We varied such parameters of the model subspectra as intensity, Lorenzain-to-Gaussian ratio, and peak width with the aim to achieve the best agreement between the superposition of the model subspectra and the experimental spectrum. As the criterion of fitting quality we took the χ^2 parameter.

The Raman shift of one of the most intense lines is 1550 cm^{-1}. This suggests predominant graphite modification of the carbon layers under study with the sp^2 hybrid bond. This peak is also significantly shifted relative to the typical position of the *G* line (1580 cm^{-1}). This shift is due to the presence in the carbon layers of sp^3 bonds, along with sp^2 bonds, as well as to angular disorientation for sp^2 bonds [5, 6]. This disorientation is also confirmed by the presence in the resolved spectrum of a broadened peak at 1200 cm^{-1} [7].

The spectra of all the samples studied contained another broadened peak near 1350 cm^{-1}. It is also shifted to larger wave numbers from the typical position of the *D* peak (1332 cm^{-1}). This peak suggests the presence in the obtained layers of carbon with the sp^3 hybrid bond [7].

The presence in the resolved spectra of peaks at 1450 cm^{-1} confirms oxygen bonding with the deposited carbon.

The peak at 1615 cm^{-1} suggests the presence of C–H chemical bonds in the layers.

Analysis of the parameters of the Raman spectra such as the Raman shift and the height and width of the model subspectra using the data from [7] allows the following conclusions about the electronic structure of the layers formed on the polymer supports. These layers contain carbon with both sp^2 and sp^3 hybridizations. According to the general thermodynamic principles, the sp^2 states are integrated into small clusters. Among these, the most probable energetically are clusters in the form of six-membered rings, either single or fused. The average size of the clusters, most probably, does not exceed 2–3 nm. The sp^2 hybrid bonds inside the clusters exhibit disorientation in angles, and the rings have the shape of irregular hexagons. The clusters are linked by sp^3 hybrid bonds and randomly oriented with respect to one another.

This pattern corresponds to the cluster model of amorphous carbon substantiated in [8, 9].

CONCLUSIONS

(1) The optimal conditions for formation of a cluster structure on the polymer surface are the pulse generation frequency of 1–2 Hz and the deposition rate of the carbon-containing films of 0.1–0.2 nm s^{-1}.

(2) The following conditions can be recommended for deposition of a modifying coating onto medical polymers: process temperature no higher than 60°C; pulse generation frequency 1–2 Hz; pulse number 30–50; and thickness of the layer deposited during one pulse 0.15 nm.

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