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Photochemical Formation of Silver Nanoparticles in Elastomer Films

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Abstract—Photochemical deposition of silver nanoparticles in poly(butyl acrylate) and poly(butadiene–styrene) under the action of monochromatic UV light (254 nm) was studied. Changes in the polymer structure in the course of photolysis were revealed and analyzed. A mechanism of formation of silver nanoparticles was suggested. Electron microscopic examination showed that the efficiency of the particle formation is determined by the residual moisture content of the polymer films. Physicomechanical properties (tensile strength and relative elongation) of the elastomer films containing silver nanoparticles were studied.

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Development of materials based on silver nanoparticles and polymers is of interest from both basic and application research viewpoints. Hybrid composites prepared by the reduction of metal ions to zero valence state in polymer matrices are used in the development of materials for electronics, laser optics, absorption and emission spectroscopy, military industry, and corrosion-protective coatings [1–3]. Particular attention was given recently to the use of properties of metal colloids in biochemical research [4–6].

Filled polymer materials are mainly prepared by microencapsulation of metal particles obtained in advance [7] and by thermolysis of metal-containing compounds in a polymer matrix [8]. The first method is characterized by poor reproducibility and does not ensure uniform distribution of particles in the polymer bulk; as for thermolysis of metal compounds, it is often accompanied by degradation of the matrix.

The goals of this study were photochemical preparation of silver nanoparticles in poly(butyl acrylate) and poly(butadiene–styrene) matrices and examination of the structure of these nanoparticles and of the properties of the composites.

Figure 1 shows changes in absorption spectrum of a film of B-160 butyl acrylate latex modified with Ag^+ ions in the course of UV irradiation. As can be seen, the plasmon absorption band of silver starts to form within the first minute of irradiation. This

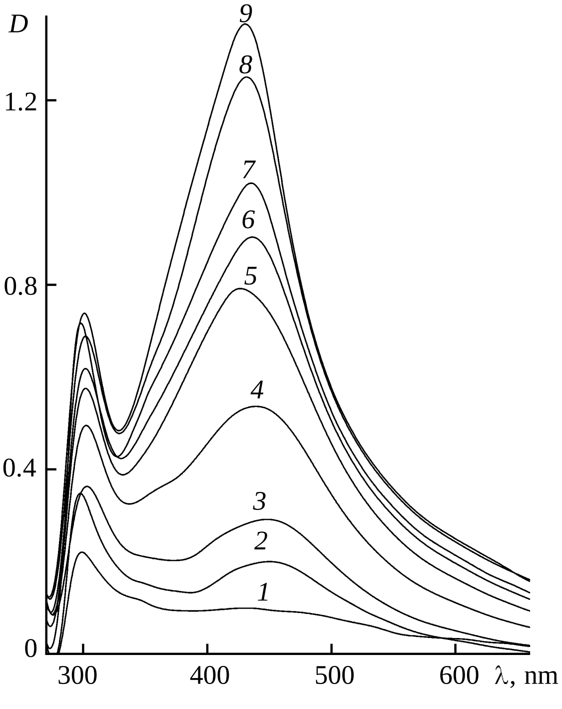


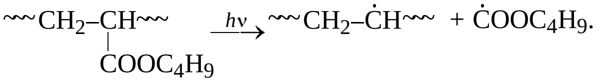
Fig. 1. Evolution of the absorption spectrum of an elastomer film obtained from B-160 latex and containing 1×10^{-2} M $AgNO_3$, observed in the course of photolysis by monochromatic UV light (λ_{exc} 254 nm). Irradiation time, min: (*1*) 0, (*2*) 5, (*3*) 10, (*4*) 30, (*5*) 60, (*6*) 90, (*7*) 120, (*8*) 200, and (*9*) 250.

interval of time corresponds to the induction period in formation of colloidal metal particles. The subsequent irradiation leads to an increase in the intensity of the plasmon band, which is indicative of an increase in the particle concentration. In the process, the plasmon bands are shifted hypsochromically, which in indicative of an increase in the relative content of smaller particles. For example, in the course of irradiation for 60 min, λ_{max} shifts from 457 to 435 nm. Further irradiation does not shift the plasmon absorption band. This fact is caused by the photochemical cross-linking of the polymer, preventing the mass transfer. Structural changes in the polymer are also confirmed by the appearance and gradual growth of the absorption band at 305 nm, belonging to the polymer and assignable to the system of conjugated double bonds formed in the course of the irradiation.

Formation of silver nanoparticles in the polymer matrices based on SKS-65GP butadiene–styrene latex is characterized by the following trends: The induction period in formation of the nanoparticles increases by a factor of 7 and the attainable optical density decreases by a factor of 8–10 relative to the Ag–poly(butyl acrylate) system; λ_{max} of the plasmon absorption band is shifted from 450 to 440 nm in the course of irradiation for 120 min, which suggests a decrease in the particle size. It is interesting that the band shift is observed during the whole period of the photolysis.

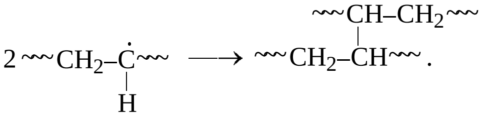
Such differences in the kinetics of the particle formation are associated with the structures of the polymers. In butyl acrylate latex, the silver ions can be reduced by the electron density transfer to the metal from the ester groups of the polymer. This process increases the efficiency of particle formation compared to the butadiene–styrene latex of rigid structure.

An XPES study of the films revealed changes in their structure in the course of irradiation. After the irradiation for 10 min, a band appears at 369.0 eV (Fig. 2). The Auger parameter of this band, 722.9 eV, is close to that of $\underline{\mathrm{Ag}}$–O–C (723.1 eV) and $\underline{\mathrm{Ag}}$–O–S (723.0 eV). However, the Ag $3d_{5/2}$ binding energy in compounds containing these fragments (367.8 eV) is appreciably lower than the measured value. An increase in the binding energy to 369.0 eV may be due to formation of small clusters (e.g., Ag_2^+–O–C, Ag_4^{2+}–O–C) in which the photoionized silver atoms exhibit relaxation effects. Also, a band at 368.2 eV, corresponding to the formation of metallic silver particles, is observed. Longer irradiation of the films (60 min) causes the intensity of the Ag $3d_{5/2}$ line to gradually decrease. This may be caused by gradual migration of the forming colloidal particles into the bulk of the polymer under the influence of the UV-induced surface cross-linking. In particular, irradiation of B-160 films for 60 min causes a gradual decrease in the intensity of the O 1*s* signal at 532.2 eV, corresponding to the $C{=}\underline{O}$ and $O{-}C{=}\underline{O}$ bonds, and of the C 1*s* signal at 286.4 eV, corresponding to the $\underline{C}{-}O{-}C$ bonds. We believe that these changes are caused by detachment of the poly(butyl acrylate) ester groups [Eq. (1)] and formation of “inner” radicals $\sim\sim\sim CH_2{-}CH_1\sim\sim\sim$.



$$\sim\sim CH_2{-}\underset{\substack{|\\ COOC_4H_9}}{CH}\sim\sim \xrightarrow{h\nu} \sim\sim CH_2{-}\dot{C}H\sim\sim + \dot{C}OOC_4H_9. \quad (1)$$

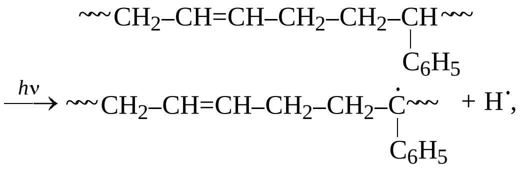
The arising radicals recombine, causing “dark” cross-linking of the polymer [Eq. (2)], which is manifested in enhancement of the C 1*s* signal at 285.0 eV corresponding to the C–C and C–H bonds.



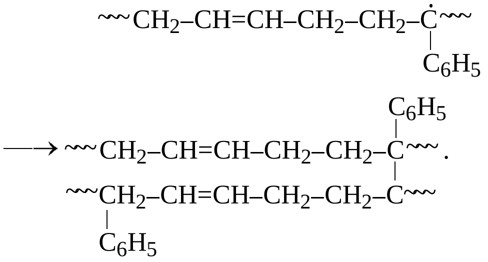
$$2\sim\sim CH_2{-}\underset{\substack{|\\ H}}{\dot{C}}\sim\sim \longrightarrow \sim\sim CH_2{-}\overset{\substack{\sim\sim CH{-}CH_2\sim\sim\\ |}}{CH}\sim\sim. \quad (2)$$

In the process, the concentration of carbon participating in the formation of these bonds increases from 49.49 to 55.17 at. %. Presumably, the reactions yield volatile products, e.g., CO and CO_2, and the irradiated matrix may contain products of the stabilization of the $^{\cdot}COOC_4H_9$ radical, e.g., butanal, butanoic acid, etc. The arising radicals act as potential reductants of silver ions.

The X-ray photoelectron spectra of SKS-65GP films containing Ag^+ ions, recorded after the irradiation for 10 min, are also indicative of the polymer cross-linking. In the process, the concentration of carbon participating in the formation of C–C bonds increases from 58.23 to 62.02 at. %. The assumed cross-linking mechanism is as follows. Atomic hydrogen is abstracted from butadiene–styrene rubber with the generation of radicals, which subsequently recombine [schemes (3), (4)].



$$\sim\sim CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\substack{|\\ C_6H_5}}{CH}\sim\sim \xrightarrow{h\nu} \sim\sim CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\substack{|\\ C_6H_5}}{\dot{C}}\sim\sim + H^{\cdot}, \quad (3)$$



$$\sim\sim CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\substack{|\\ C_6H_5}}{\dot{C}}\sim\sim \longrightarrow \begin{array}{l} \sim\sim CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{\substack{C_6H_5\\ |}}{C}\sim\sim. \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \sim\sim\underset{\substack{|\\ C_6H_5}}{CH_2}{-}CH{=}CH{-}CH_2{-}CH_2{-}C\sim\sim \end{array} \quad (4)$$

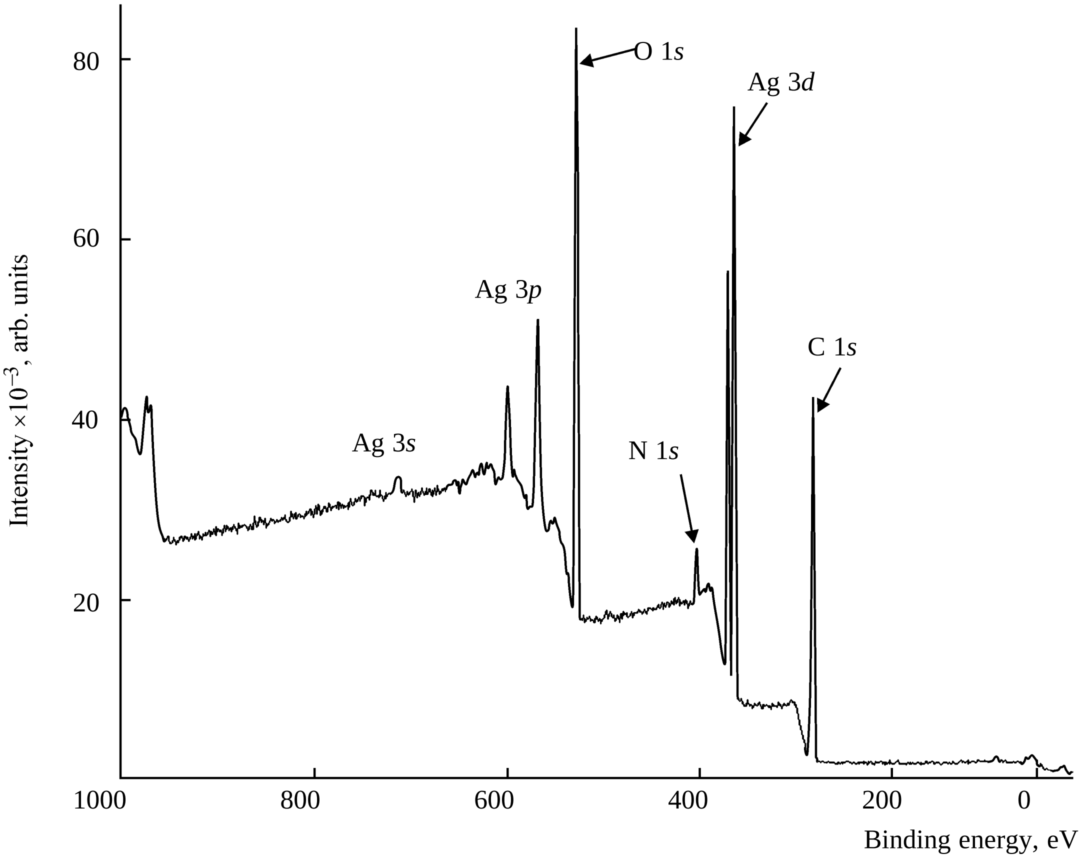
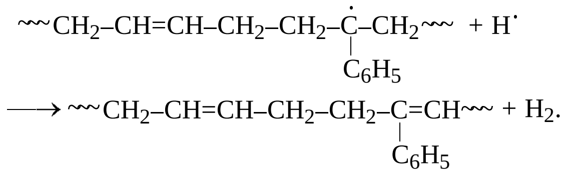


Fig. 2. X-ray photoelectron spectrum of a poly(butyl acrylate) film modified with $AgNO_3$ upon irradiation for 10 min.

Elimination of an H atom from the adjacent C atom results in the formation of a double bond [Eq. (5)]:



$$\sim\!\sim CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle C_6H_5}{\overset{\cdot}{C}}{-}CH_2\sim\!\sim \; + H^{\cdot}$$

$$\longrightarrow \sim\!\sim CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle C_6H_5}{C}{=}CH\sim\!\sim + H_2. \quad (5)$$

Propagation of the process along the chain results in the formation of a system of conjugated double bonds [9]. This is confirmed by the growth of the absorption band at 305 nm in the spectrum of the silver-free films (Fig. 3). In addition, the stabilizer, sodium alkylarylsulfonate, can also participate in the cross-linking. After the irradiation for 10 min, the intensity of the S $1p_{3/2}$ peak at 168.5 eV and O 1s peak at 531.8 eV, corresponding to S=O bonds in alkylarylsulfonate groups, decreases, which is apparently due to evolution of SO_2. The $C_6H_5{-}R{-}O^{\cdot}$ radicals generated in the process recombine with alkyl radicals [Eq. (5)], giving rise to a peak at 533.0 eV corresponding to the formation of $C{-}\underline{O}{-}C$ bonds.

Along with these processes, in both polymers we observed a progressive decrease in the concentration of nitrate ions (N 1*s* signal at 406.6 eV). The signal is detected only in the initial spectrum. Upon irradiation for 10 min and more, the signal disappears, probably because of evolution of gaseous NO_2 and O_2 [Eq. (6)]:

$$2NO_3^- \longrightarrow 2NO_2 + O_2. \qquad (6)$$

Irradiation of the films for more than 60 min causes an increase in the intensity of the Ag $3d_{5/2}$ signal at 368.2 eV. This may be due to an increase in the concentration of the forming silver particles. Also, upon the irradiation for 60 min, the oxidation of the polymer surface layer becomes noticeable, with break of the carbon chains and uncovering of colloidal silver particles, making them better detectable. The oxidation is confirmed by a decrease in the intensity of the C 1*s* signal at 285.0 eV, caused by the cleavage of the C–C and C–H bonds, and enhancement of the C 1*s* signal assignable to the $\underline{C}{=}O$ and $O{-}\underline{C}{=}O$ groups. The process apparently occurs via intermediate formation of hydroxoperoxy groups, followed by their transformation into carbonyl and carboxy groups. The oxidant can be both atmospheric oxygen and oxygen

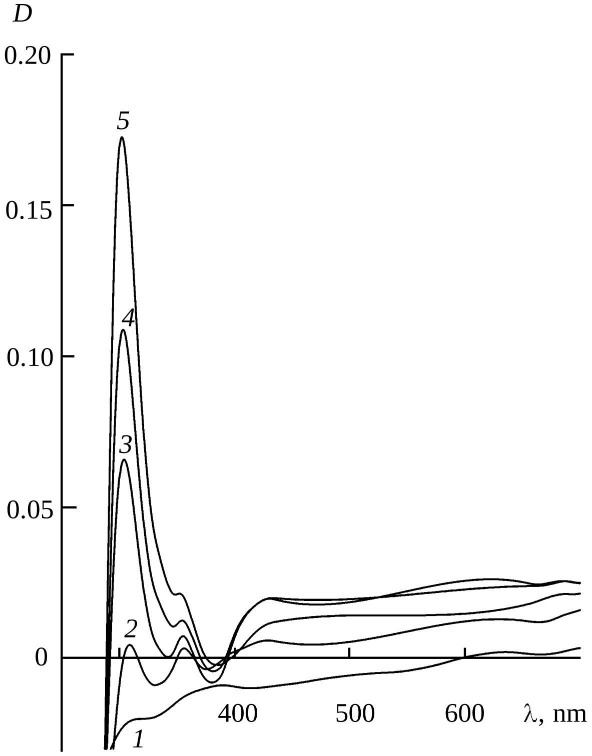


Fig. 3. Evolution of the absorption spectrum of an elastomer film obtained from B-160 latex in the course of photolysis with monochromatic light (λ_{exc} 254 nm). Irradiation time, min: (*1*) 0, (*2*) 10, (*3*) 60, (*4*) 120, and (*5*) 250.

released by decomposition of nitrate ions. The oxidation can also occur by photolysis of ester groups with the cleavage of C–O–C bonds and formation of CO radical groups, which also transform into carboxy or carbonyl groups. The oxidation is the most efficient in butadiene–styrene latex films, which is caused by the presence of double bonds, prone to oxidation even in air, in the backbone. A shift of the polymer absorption maximum to 330 nm suggests formation of quinoid structures in pendant chains [10, 11].

We found that the particle formation depends on the residual moisture content in the films. When this parameter exceeds 15%, a broad absorption band with λ_{max} 440 – 450 nm appears and becomes noticeable in the course of irradiation. This fact is attributable to the disordered structure of the polymer. The diffusion of silver ions in such a film should be relatively fast, which results in rapid uncontrollable growth of silver particles and formation of a polydisperse system. An electron microscopic examination of such films revealed the formation of dendritic metallic structures of size 1–2 μm (Fig. 4a), along with separate spherical particles of size 50 – 70 nm. Nevertheless, the optical density *D* of such systems does not exceed 0.25, i.e., the efficiency of the colloid formation is low (probably because of the decay of the arising radicals on residual water molecules).

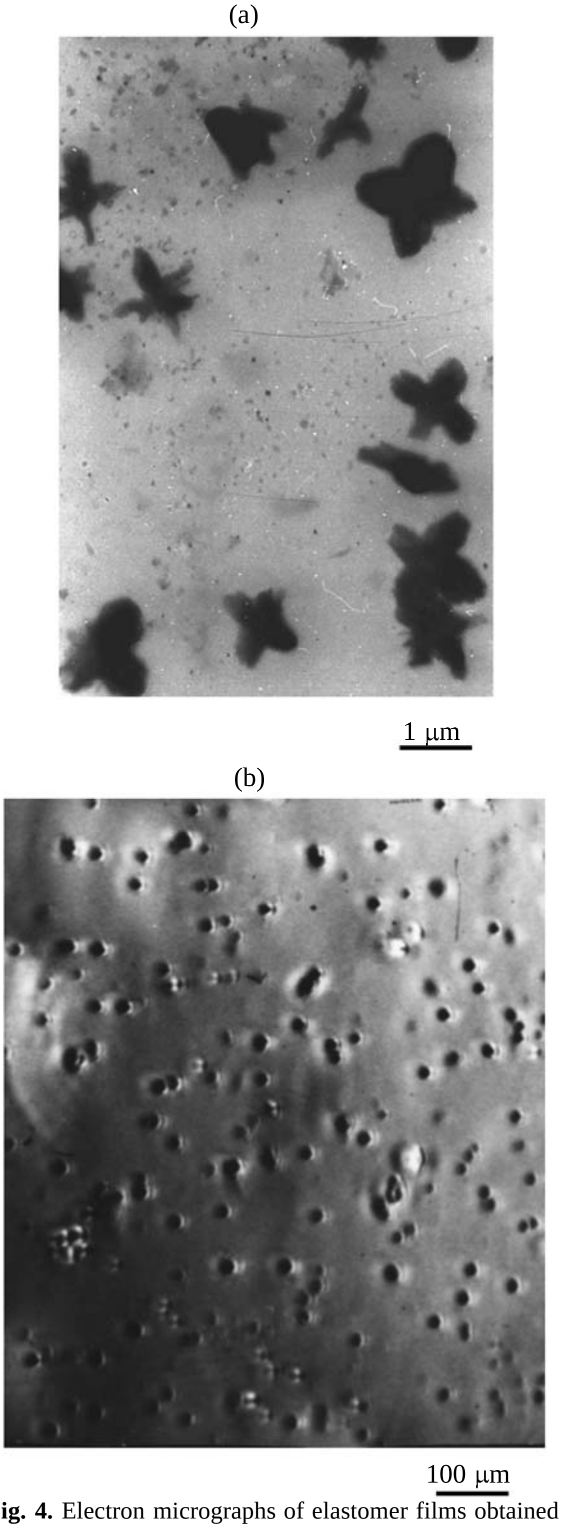


Fig. 4. Electron micrographs of elastomer films obtained from B-160 latex and modified with silver particles. Residual moisture content, %: (a) 15 and (b) 5.

At a low residual moisture content (less than 5%), the colloid formation is limited by the hardening of the polymer matrix; as a result, the diffusion of silver ions becomes slow, and the attainable optical density *D* does not exceed 0.45. The plasmon absorption maximum of the films is observed at 410 nm, suggesting formation of the smaller particles.

At a residual moisture content in the range 5–15%, the forming metal particles have regular spherical shape and are uniformly distributed over the film surface. The average size of the silver particles in B-160 and SKS-65GP films was 35 nm (Fig. 4b). The spectra of the films are characterized by narrow absorption bands (λ_{max} 420–430 nm).

The tensile strength of the elastomer films containing silver ions as a function of the amount of $AgNO_3$ introduced passes through a maximum (Fig. 5). As the $AgNO_3$ concentration is increased to 0.05 M, the polymer strength increases relative to the unmodified sample owing to donor–acceptor interaction of silver ions with lone electron pairs of the C=O groups of the adjacent polymer chains ($\text{–ROC=O}^{\delta-}\rightarrow\text{Ag}\leftarrow\text{O}^{\delta-}\text{=COR–}$). At the Ag^+ concentrations exceeding 0.05 M, the strength decreases because of partial coagulation of the latex, accompanied by formation of polymer particle agglomerates (polymer crumb); as a result, defects arise in the film structure. Irradiation of both Ag^+-modified and unmodified B-160 latex films enhances their strength compared to the nonirradiated films (Fig. 6). The highest strength is attained upon irradiation for 100 min; longer irradiation affects the strength insignificantly. Irradiation of the silver-modified films increases the strength by a factor of 1.5. As compared to the irradiated unmodified polymer, the strength increases by a factor of 1.2. We believe that this is caused both by photochemical cross-linking of the polymer itself (this is confirmed by an increase in the content of C–C bonds detected in the X-ray photoelectron spectra) and by the polymer "cross-linking" via metal nanoparticles. The coordination-unsaturated surface metal atoms of the nanoparticles interact with the oxygen atoms of the carbonyl groups of the B-160 latex. An increase in the number of particles in the course of irradiation results in an increase in the number of $Ag_n^0\leftarrow(\text{C=COR–})_m$ bonds involving them. Upon irradiation for more than 60 min, the photooxidation processes disturbing the polymer surface layer start to compete with the cross-linking. Also, high concentrations of particles in the polymer disturb its intrinsic structure. As a result, irradiation for more than 100 min does not noticeably affect the polymer strength.

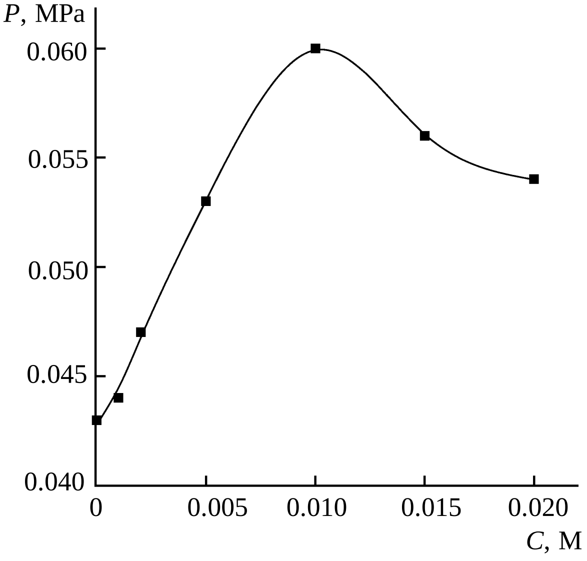


Fig. 5. Tensile strength of an elastomer film obtained from B-160 latex as a function of the concentration of $AgNO_3$ introduced.

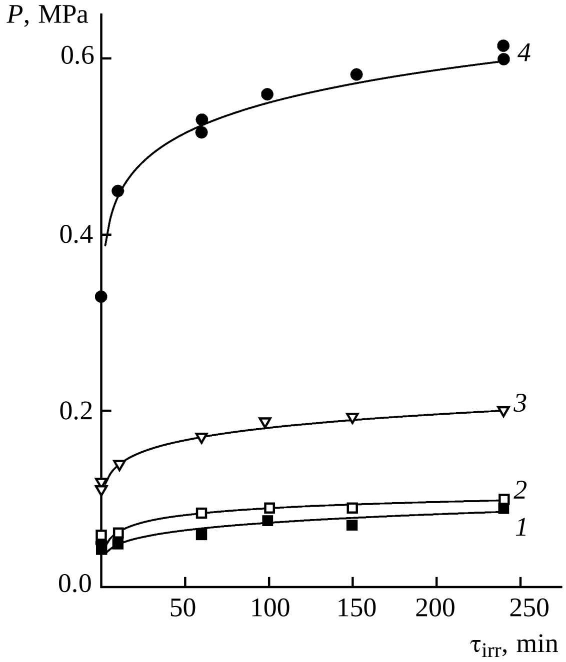


Fig. 6. Tensile strength of elastomer films as a function of the irradiation time: (*1*) unmodified B-160 latex film, (*2*) B-160 latex film modified with silver nanoparticles, (*3*) unmodified SKS-65GP latex film, and (*4*) SKS-65GP latex film modified with silver nanoparticles.

A specific feature of SKS-65GP films is that their strength increases in the course of irradiation for 240 min. Irradiation of the silver-modified films enhances their strength by a factor of 2. As compared to the irradiated unmodified polymer, the strength increases by a factor of 3.

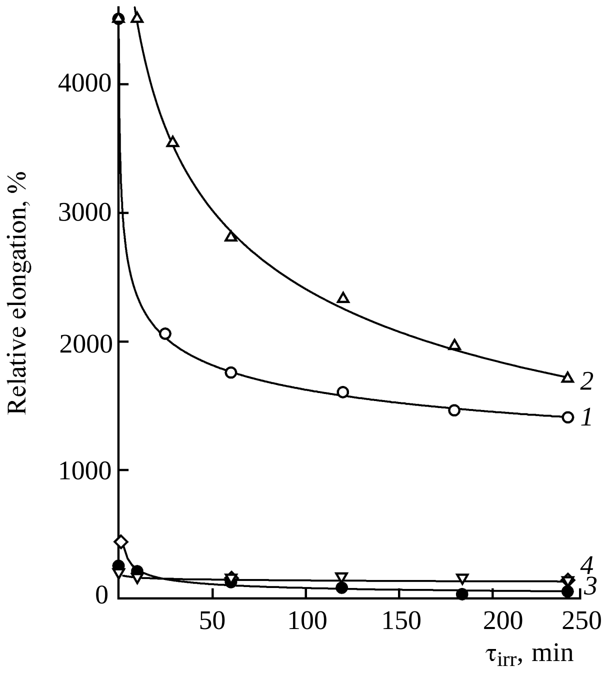


Fig. 7. Relative elongation of elastomer films as a function of the irradiation time: (*1*) unmodified B-160 latex film, (*2*) B-160 latex film modified with silver nanoparticles, (*3*) unmodified SKS-65GP latex film, and (*4*) SKS-65GP latex film modified with silver nanoparticles.

The B-160 films with incorporated nanoparticles are more elastic than the straight polymer (Fig. 7). Upon irradiation for 240 min, the elongation of Ag-modified films reaches 1700%, and that of unmodified films, 1400%. The increased elasticity is due to a contribution of the M_n^0–C=COR– interaction. In the unmodified polymer, the formation of rigid C–C chains in the course of irradiation decreases the strength and, as a consequence, the elasticity of the films. It is interesting that the elongations of the irradiated silver-modified SKS-65GP films virtually coincide with those of the nonirradiated analogs, which is due to the nonpolar nature of the polymer chains and the occurrence of strong dispersion interactions in the film bulk. This fact is responsible for the higher strength of SKS-65GP films compared to butyl acrylate films.

Thus, we developed a procedure for photochemical modification of butyl acrylate and butadiene–styrene latex films with silver nanoparticles and analyzed in detail the structural changes that accompany the reduction of silver ions in the polymer films in the course of UV irradiation. We found that the size of silver nanoparticles is determined by the residual moisture content in the films and varies in the range from 35 nm to 2 µm. The modification of the elastomer films with silver nanoparticles increases the tensile strength and relative elongation compared to the unmodified samples.

EXPERIMENTAL

To prepare silver nanoparticles, we used analytically pure grade $AgNO_3$ solutions. As polymeric matrices we used B-160 poly(butyl acrylate) latex and SKS-65GP poly(butadiene–styrene) latex. To prepare silver nanoparticles in the presence of a latex, 2×10^{-4}–2×10^{-2} M $AgNO_3$ solutions were mixed with a latex in the volume ratio latex : $AgNO_3$ = 4 : 1. Films were prepared by application of the solution onto quartz glass by the method of surface renewal and were dried in the dark to constant weight, after which the films were irradiated for 6 h with a monochromatic UV light (λ_{exc} 254 nm, luminous flux intensity 4.8×10^{16} quanta cm^{-2} s^{-1}. The film thickness was 0.4 mm. The formation of silver nanostructures was monitored spectrophotometrically (SF-2000) by the appearance of the characteristic absorption at 200–700 nm. The particle distribution in the bulk of the latex dispersion was studied by electron microscopy on a Hitachi HU-11 transmission electron microscope. Histograms were constructed for samples consisting of 700 silver particles. X-ray photoelectron spectra were recorded on a Kratos Analytical AXIS-Ultra electron spectrometer with excitation by monochromatic AlK_α radiation (1486.6 eV). The spectra were processed using the Kratos Analytical software. The atomic concentrations were determined from the areas of the photoelectron peaks, taking into account the spectrometer transmission function after the background subtraction (by Shirley's method or linear) and using the corresponding sensitivity factors (ionization cross sections). The tensile strength and relative elongation were measured with an RMI-5 tensile-testing machine.

ACKNOWLEDGMENTS

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