LIGHT INDUCED PHENOMENA IN NEW POLYMERIC THIN FILMS BASED ON AMINOSTYRENE

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Abstract

The light-induced modification of mechanical and optical properties of several aminostyrene-containing polymers has been investigated. The nano- and microindentation techniques were used for determination of mechanical parameters. The variable-energy positron annihilation spectroscopy (slow-positron beam technique) was developed to measure defect depth profiles in the near-surface region. The increase of S-parameter with the increasing of nanohardness and elastic modulus were determined for these materials.

Introduction

Thin polymer films on rigid and flexible substrates have attracted significant attention because of their unique chemical and physical properties as well as their industrial application. For instance, new polymer materials on the base of aminostyrene can be used as information storage media in the photonics, photolithography and holography [1-5]. With the view to facilitate the multiplication of relief optical micro and nano-scale diffraction structures and elements, which were initially recorded on the photoresist layer, the cross-linking layers from copolymers or other compositions, which contained chemically active bonds of 4-aminostyrol: styrene: butylmethacrylate: aminostyrene (ST: BMA: AST) were obtained by us in the Institute of Applied Physics of Moldavian Academy of Sciences. These materials combine the flexibility and easy processing of polymers with hardness of inorganic materials and have been successfully applied on glass, metal and polymeric substrates. In general, these new polymer films are transparent, show a good adhesion, and enhance the scratch and abrasion resistant of a polymeric substrate.

Aminostyrene polymers under action of external factors (ultra-violet irradiation, for example) are exposed to a photochemical transformation leading to deep structural changes [1-7]. As a result the layers become mechanically hard, strong, adhesively stable, undissolving in organic solvents and stable to high temperature. For studying of the mechanical properties of such materials the nano- and micro-indentation techniques were obtained. On the basis of obtained experimental data, physical processes taking place during cross-linking will be revealed, possibilities of polymer media strengthening and obtaining of materials with given properties will be found.

2. Experimental details

2.1. Materials

New polymer materials containing aminostyrene and carbazole were obtained by the method of radical polymerization. All the films had a good transparency and showed a good adhesion to hard (optical glasses) and flexible (transparent poly(ethyleneterephthalate))

substrates. The thickness of the samples ranges from 3 to 35 μm. The layers were exposed to ultra-violet light with incident energy E=10-20 mW/sm^{-2} and also to white light (as a source mercury-quartz lamp PRK-4 with power of 500W was used). The photo-structural transformations were expressed in losing of solubility in organic solvents. Quantitatively, the photo-structural modification is well seen from the spectra of absorption intensity in visible region. The effective elastic modulus and the hardness were determined on the basis of load–displacement data [8]. The reliability of the chosen analytical method was checked using a number of repeats. Information about thermoplastic polymer layers under investigation is presented in Table 1.

Table 1. The characteristics of investigated polymer layers

Sample code	Chemical contents	Composition, (%)
ST:BMA:AST	Styrene:butylmethacrylate: aminostyrene	30:50:20
ST:BMA:AST	Styrene:butylmethacrylate: aminostyrene	40:50:10

2.2. Nano- and micro-indentation tests

Nanoindentation tests were carried out at room temperature using the MTS Systems Nanoindentation II. The Berkovich diamond indenter was used for all the indentations. The maximum force was equal to 500μN and twelve indentations were performed for each sample. The loading and unloading rate was 5 μN/s. The calibration procedure suggested by Oliver and Pharr [8] was used to correct the load frame compliance of the apparatus and the imperfect shape of the indenter tip.

The microhardness measurement were performed at room temperature with a PMT-3 microhardness tester. The hardness in MPa was determined as Hv=1854P/d2, where P is applied load (in mN) and d is the length of the diagonal (in μm). The average value from at least 15 indentation tests was systematically calculated. The maximum scatter typically ranges between 1 and 3% of the hardness value. The variation of hardness as a function of load was performed over the range 98 - 1380 mN.

Optical microscopy (B5 and DMB5 Biological Microscopes) was used for observation of the sample morphology and for the visualization of the final indents.

2.3. Variable-energy positron annihilation spectroscopy

The variable-energy positron annihilation spectroscopy (slow-positron beam technique) was developed to measure defect depth profiles in the near-surface region. The positron beam system is made using a 0,5 GBqβ^+ source of ^{22}Na assembled in transmission with 5μm single-crystalline tungsten moderator. The beam transport is realized by solenoid. The diameter of the beam is 5mm. The beam intensity is 1x10^5 e$^+$/s. The samples were mounted in an ultrahigh vacuum (UHV) chamber. The gamma-annihilation spectrum was recorded with a high-purity Ge detector having an energy resolution of 1.5 keV, full width at half maximum (FWHM) at 514 keV. The data were acquired with digitally stabilized multichannel-analyzer system (ORTEC 919). The Doppler broadening of the 511 keV γ-ray peak was measured at room temperature as a function of incident positron energy in the range from 0.1 to 40 keV, counts were collected in the 511 keV annihilation line at each incident energy.

3. Results

3.1. Elastic modulus, nano- and micro-hardness for as-grown polymers

Nanoindentation testing can be used as a qualitative tool for investigating polymer film uniformity. The nanohardness and elastic modulus for as-grown polymer layers, determined by the method of Oliver and Pharr [8], are presented in Table 2.

Table 2. Nanohardness (h) and elastic modulus (E) for as-grown aminostyrene containing polymer layers

Sample code	Chemical composition, %	E, GPa	h, GPa
ST:BMA:AST	30:50:20	3,81826±0,01862	0,14587±0,00163
ST:BMA:AST	40:50:10	3,61249±1,06804	0,11274±0,0426

As we can see from Table 2 the nanohardness depends on chemical composition and thickness more significantly than the elastic modules. Taking into account the reference values of H and E for this type materials [13], a good agreement with these values was obtained.

The dependence of microhardness (H) on load (P) for AST:ST:BMA – (10:40:50, mol.%) is shown in Fig. 1.

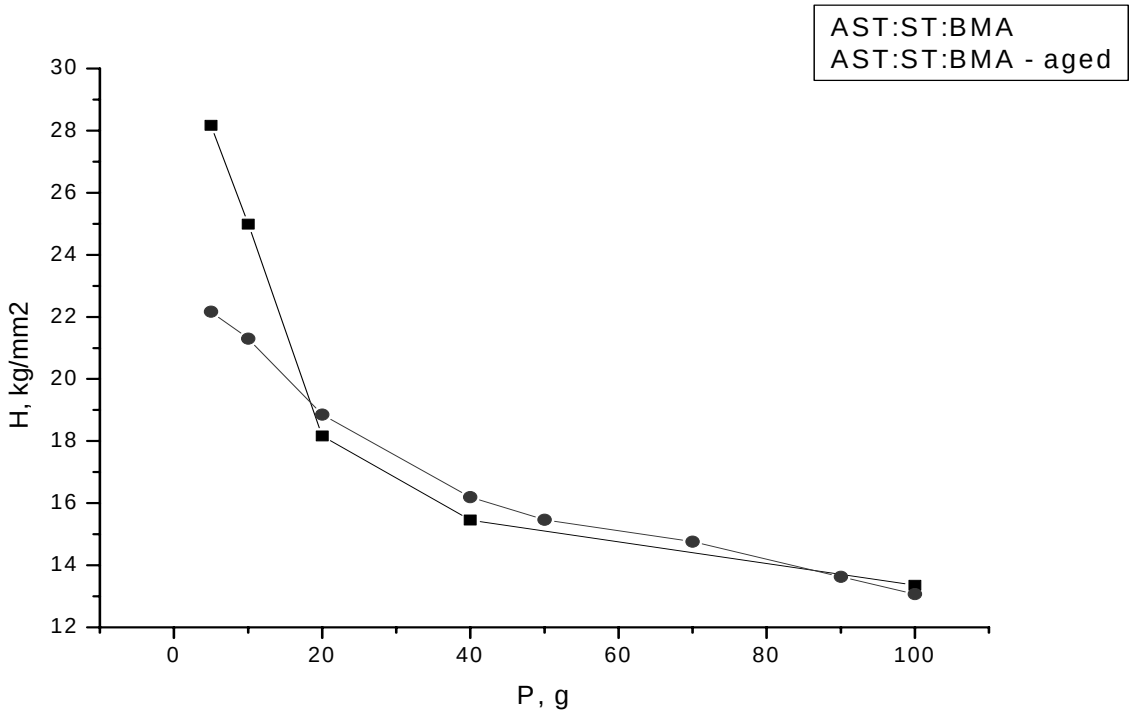

Fig. 1. Effect of the applied load on the measured hardness of the AST:ST:BMA – (40:50:10, mol.%) for fresh samples (■) and the ones aged during 4 months (●).

It appeared that hardness of the samples is clearly load-dependent. The measured hardness decreases with an increase in the test load. It is noteworthy that most metals and ceramics exhibit such a load dependent hardness, which is usually referred as indentation size

effect (ISE). The origin of the ISE remains unclear even though several explanations have been proposed (low resolution of the objective lens, intrinsic structural factors of the material, hardening during indentation, indentation elastic recovery) [9]. Since the plastic strain contribution decreases with a decrease in the indent volume, a decrease in hardness with an increase of the diagonal d for the lower test loads is observed. It is also necessary to note that the changes of H take place only on the surface of samples, in the volume of samples (at $P \leq 20$ g the H values are close and at $P \sim 90$g practically equal). On the basis of the obtained data it is possible to make a conclusion about high quality of our polymer materials.

3.2. Influence of the UV-irradiation on nano-parameters of aminostyrene-containing polymer materials and the effect of storage time at room temperature

It is known that the action of solar-like light on aminostyrene-containing polymer induces the formation of radicals, the emission of volatile molecules and cross-linking. The latter is responsible for the formation of three-dimensionally-connected rigid network, thereby enhancing the material strength. The observations of irradiation influence on nanomechanical parameters of investigated aminostyrene containing polymer materials are shown in Fig. 2. In order to assess whether aminostyrene content mainly determines the mechanical properties of aminostyrene layers under UV irradiation the series of ST:BMA:AST with varying AST (10% and 20%) were made.

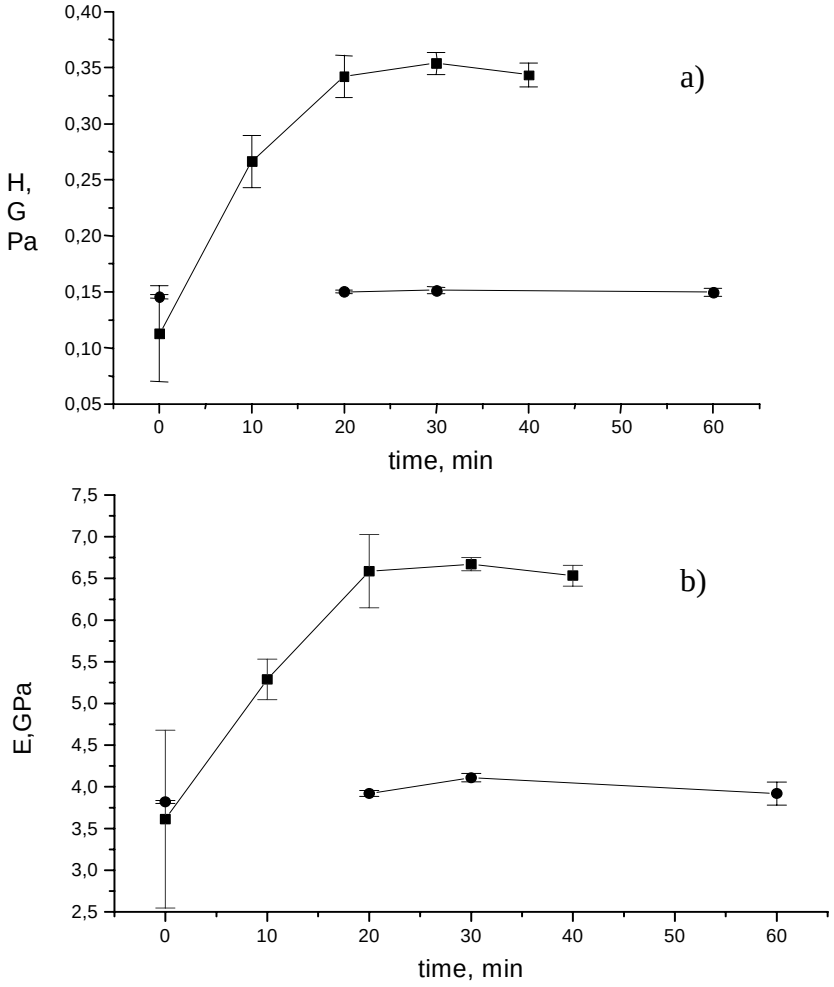

Fig. 2. The hardness (H) (a) and effective elastic modulus (E) (b) versus time of irradiation:
■ for ST:BMA:AST (40%:50%:10%) (layers I) and
• for ST:BMA:AST (30%:50%:20%) (layers II).

A comparison of the layers shows that the irradiation time increase corresponds to H and E increase in E and H by a factor of 3 and 1,8 respectively only for the first group materials (ST:BMA:AST (40%:50%:10%)). In the case of the second group (ST:BMA:AST (30%:50%:20%)) practically independence on irradiation time was observed. The change of matrix has significant effect on the effective elastic modulus and hardness of aminostyrene coatings.

The ageing represents a process of spontaneous changing of polymer compound properties (strength, hardness, etc.) running at their storage. The influence of ageing on the nanomechanical parameters of aminostyrene compounds was studied for ST:BMA:AST materials on a hard substrate. The materials were kept during one month at room temperature. The result of these investigations is given in Fig. 3.

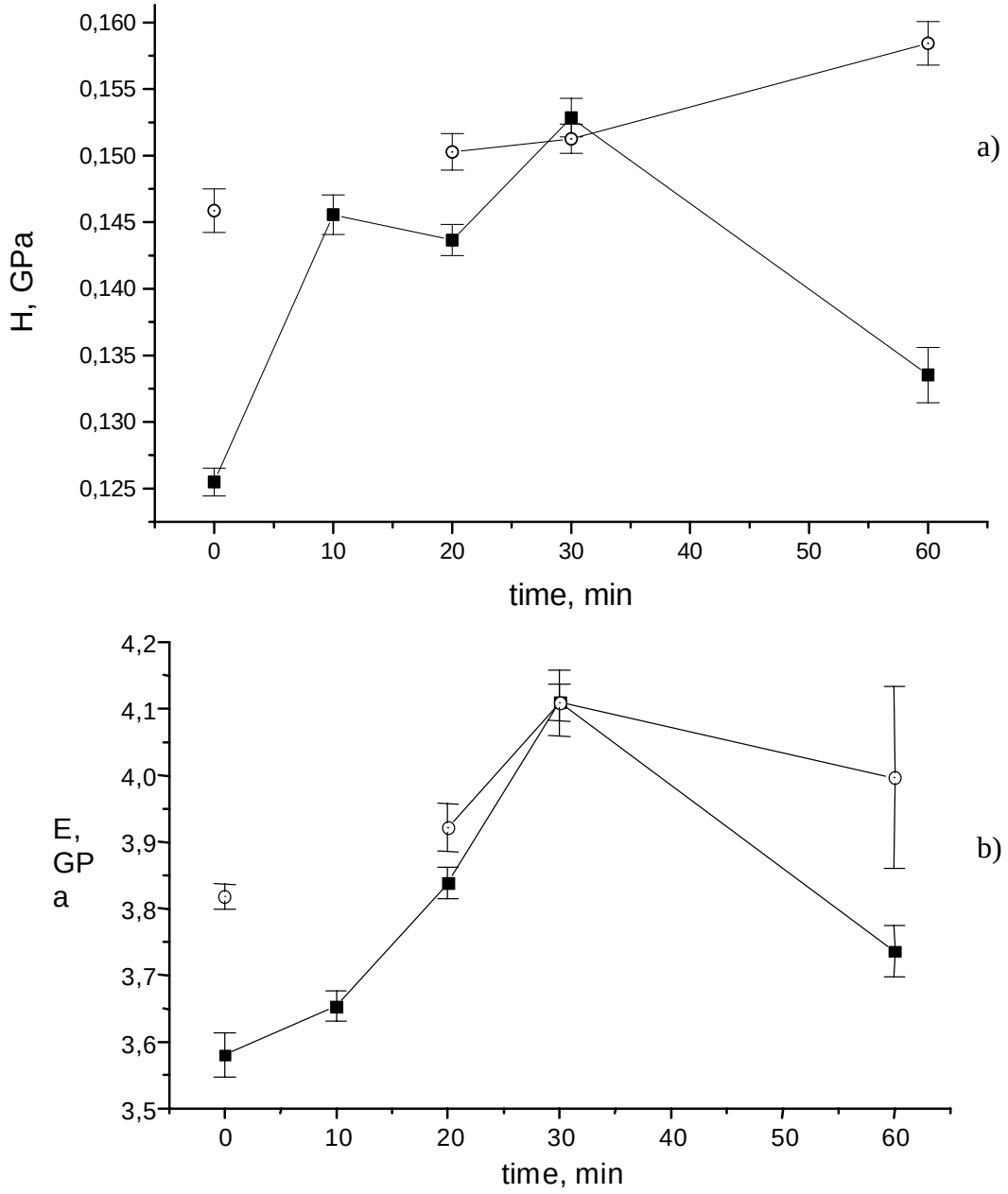

Fig. 3. The hardness (a) and elastic modulus (b) versus of irradiation time for fresh ST:BMA:AST layers (○) and the ones aged during two months (■).

The H and E values for fresh and aged ST:BMA:AST samples do not practically change in the case of maximal hardening (the irradiation time is equal to 30 min.). The obtained result represents a considerable interest. The processes of ageing are considerably retarded at maximal hardening. This result is also proved by the fact that nanoindentation technique can be used to accurately estimate the hardness and the elastic modulus of cross-linked layers on the basis of load-displacement data, originally proposed by Oliver and Pharr [12].

3.3. The light influence on the microhardness

The Fig. 4 shows the influence of UV-light on micro-parameter (H) for aminostyrene-containing polymer layers ST:BMA:AST (30%:50%:20%).

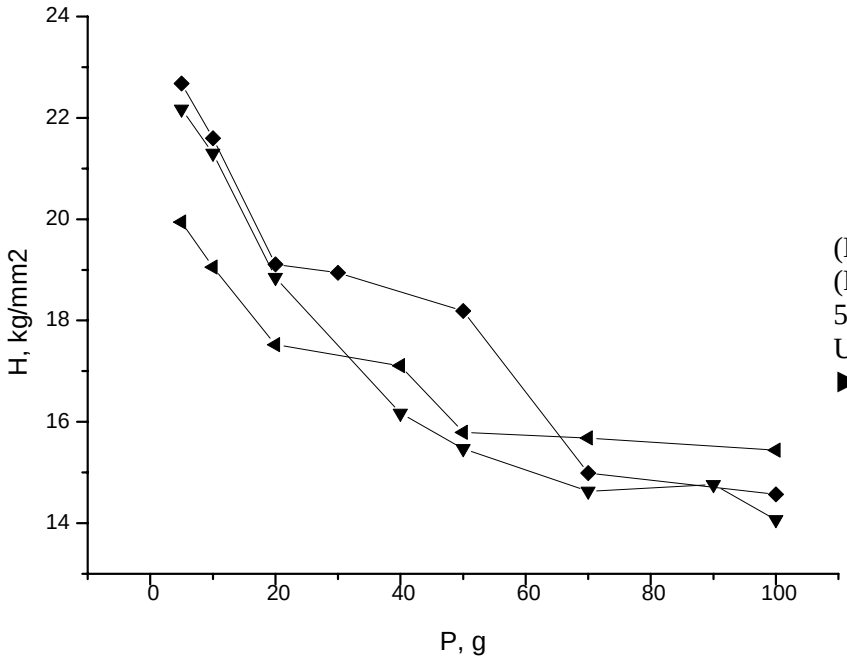

Fig. 4. Micro-hardness (H) values versus applied load (P) for ST:BMA:AST (30% : 50% :20%) at different time of UV-irradiation, min (▲ - 20; ► - 30; ■ - 40).

As we can see from Fig. 4, the influence of UV irradiation on the H is not significant. This result is in a good agreement with the data obtained for this type materials by the nanoindentation technique.

3.4. The positron measurement for ST:BMA:AST polymer materials

Various experimental methods based on positron annihilation have evolved into important tools for researching the structure and properties of condensed matter [15]. In particular, positron techniques are useful for the characterization of defects in solids [16] and for the investigation of solid surfaces [17, 18].

The different positron techniques are based on the analysis of annihilation radiation. They can be classified into two principal groups, which are distinguished by the positron sensitivity to the electron density (positron lifetime measurement) and to the electron momentum distribution in the sample (Doppler-broadening spectroscopy and angular correlation of annihilation radiation). For aminostyrene polymer thermoplastic layer investigations the slow-positron-beam technique was applied. The S(E) positron depth scan measurements for ST:BMA:AST films are given in Fig.5.

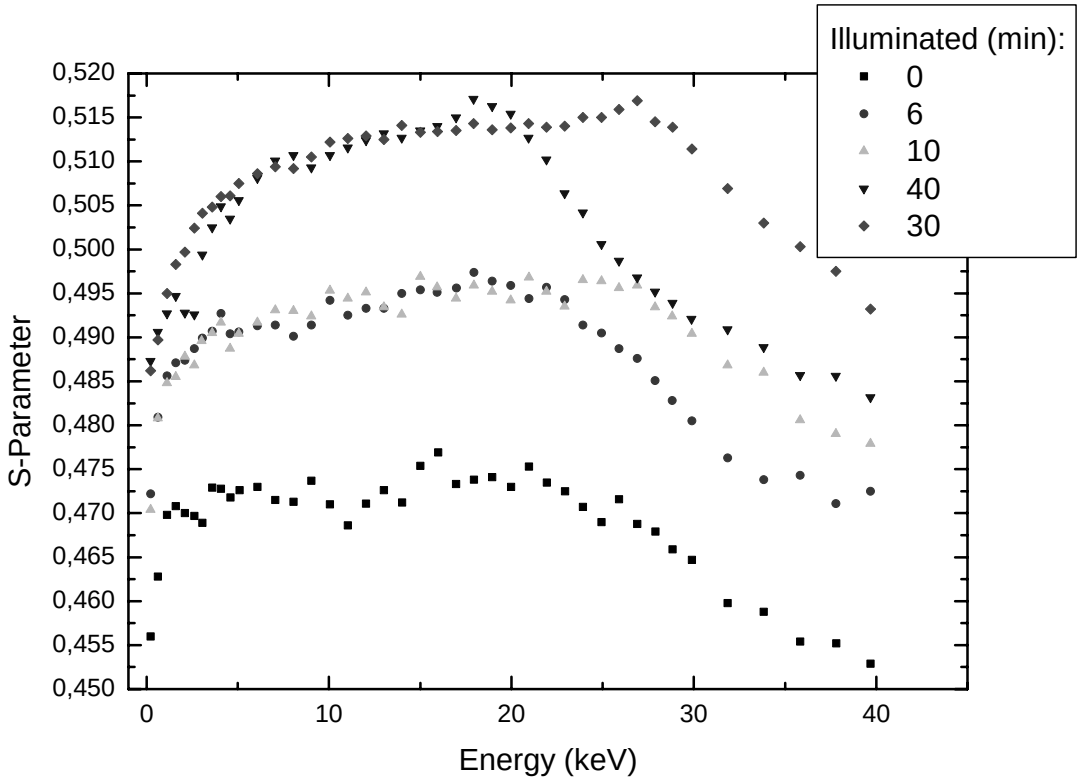

Fig. 5. Result of positron annihilation Doppler Broadening measurement for STA:BMA:AST films at different irradiation time.

The maximum positron energy was 40 keV. The increase of S-parameter with the increase of H and E takes place for these materials (Fig. 5). This high S-parameter is caused by the occurrence of open-volume defects. The increase of curves in the energy range up to about 5keV is due to a low surface S parameter. Positrons implanted into a small depth are able to diffuse back to the surface.

The resulting S-parameter is a superposition of the S-parameters of the surface state, of the defects. In the case of high defect concentration, the positron diffusion length becomes smaller. This leads to a rise of the S-parameter.

Conclusions

1. A set of aminostyrene- containing polymer materials before and after cross-linking process by nano- and microindentation techniques have been investigated.
2. The conditions for improvement of mechanical properties by different types of treatment have been established.
3. Load and depth sensing indentation has proved to be a powerful tool for an accurate estimation of mechanical properties of cross-linked aminostyrene layers on hard and soft substrates.
4. The positron measurements for STA: BMA: AST films were carried out additionally. The correlation between S-parameter and increase of nanohardness and elastic modulus takes place.

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