Microhardness Investigation of Styrene-butyl Methacrylate-methacrylic Acid Copolymer and its Analogous Grafted with Ampicillin

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This paper presents the study of Vickers microhardness performed on a styrene-butyl methacrylate-methylacrylic acid copolymer and the analogous obtained by grafting with ampicilline. The creep properties and the glass transition temperature of the copolymers were investigated.

Keywords: microhardness, styrene-butyl methacrylate-methylacrylic acid copolymer, creep, Tg

The determination of hardness by micropenetration (Vickers microhardness) is an empirical method for assessment of important physical and mechanical properties of polymers and is used quite frequently due to its correlation with other indicators values being possible to calculate the modulus and resistance to deformation, yield, creep and glass transition [1-11]. An important advantage of using microhardness is that measurements are made in very thin polymer films, frequently with a thickness of 10-30 µm, thus requiring small amounts of material [12, 13].

Vickers microhardness comparative study was performed on two copolymers:
- styrene-butyl methacrylate-methylacrylic acid copolymer (S-BMA-MAA) synthesized with composition 40:50:10
- copolymer obtained by polymer-analogous reaction of grafting with ampicilline (S-BMA-MAA-AMP).

The ampicilline grafting copolymer leads to a long-term antibiotic properties used for obtaining of protective varnishes of spaces and furniture used in hospitals and catering units.

S-BMA-MAA copolymer was synthesized by the radical copolymerization in the presence of 2 mol % azo-bis-isobutyronitrile initiator at 80°C for 4 h. The reaction scheme is shown in figure 1. The copolymer was purified by repeated precipitation in hexane. S-BMA-MAA copolymer shows a viscosity from 0.12 to 0.16 (Dl / g) and a glass transition temperature ranging from 55°C to 90°C according to its components blocks.

The copolymer S-BMA-MAA-AMP was obtained by grafting the first copolymer with ampicilline at COOH groups, in dimethylformamide solution at 0°C, in the presence of ethyl chloroformate [14], and the reaction scheme is shown in figure 2. The copolymer S-BMA-MAA-AMP was purified by repeated precipitation in diethyl ether.

Experimental part

Vickers microhardness (H) was measured on films with a thickness of 10-22 µm [13] obtained from the solution casting on a glass substrate to ensure polymer films with a completely smooth surface in order to increase the accuracy of hardness determinations. For a more accurate view of impression printed by Vickers indenter films were lubricated with Ramsey grease [15]. Thus were obtained impressions printed easily measured, as can be seen in figure 3.

Vickers microhardness calculation was performed according to equation (1):

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where:
- Hv - Vickers microhardness, [MPa]
- P - penetration stress, [N]
- d - impression diagonal, [mm].

In order to characterize copolymers more detailed, microhardness study involved varying the stress, time and temperature penetration.

To minimize experimental errors each penetrating determination was repeated several times and the value of diagonal (d) used to calculate microhardness represents an average of the diagonals measured on impression printed.

The strain-hardening coefficients were calculated according to equation (2):

\[ \theta = \frac{\Delta H_v}{\Delta P} \]  

where:
- \( \theta \) - strain-hardening coefficients
- \( \Delta H_v \) - Vickers microhardness variation, [MPa]
- \( \Delta P \) - penetration stress variation, [N]

Results and discussion

The first Vickers microhardness measurements were performed on the S-BMA-MAA copolymer films with thickness of 10 - 22 \( \mu \)m at different penetration stress (fig. 4). Variation of microhardness depending on penetration stress is not uniform, practical showing two slopes of variation, the allure of this diagram being characteristic of micropenetration process. From figure 4 it is found a significant increase of Vickers microhardness in direct correlation with increasing of polymer film thickness.

This phenomenon can be explained if we consider the complex elastic-plastic behaviour of the material subject penetration stress [16-19]. The stress is made by the penetration of spherical indenter head, which subjects the material at compression both vertically and horizontally plane, in the adjacency of the penetration place [20].

\[ H_v = 1.854 \frac{P}{d^2}, \text{[MPa]} \]  

Due to the low penetration time of about 0.1 min [7], it is not ensured the balance of the permanent deformation, and the material shows a small comeback elastic, amplified by the volume of tested copolymer. Thus, the film thickness of 22 \( \mu \)m will present an lower diagonal of impression printed, which leads to the higher microhardness according to the calculating formula.

At low penetration stress, above mentioned phenomenon is difficult to detect, being clearly manifested at higher stress values due to the increasing volume of deformed material.

In order to avoid the influence of the film thickness on microhardness values, in the study was used a relatively constant film with a thickness of 22 \( \mu \)m.

In figure 5 is shown the effect of deformation stress over time (initial, after 1’, 3’, 5’) on the Vickers microhardness of the support S-BMA-MAA copolymer. As it can bee seen, the curves allure of microhardness variation depending on stress is not significantly influenced by the time of penetration. This behaviour indicates that the nature of the morphological changes is not dependent on penetration time, but their magnitude is controlled both by time and stress penetration.

Although there is a dispersion of microhardness values [13, 21, 22]) it can be observed, that especially at high penetration stress, the decrease of microhardness in direct correlation with the penetration time, due to the advanced increase of the copolymer deformation, emphase the practical two-stages of variation.

The material deformation are due both to modification of the free volume and the change of molecular and to supramolecular morphology of copolymer [1, 4, 23]. In the first step, the greater slope can be explained by the fact that at small penetration stress, the free volume variation occurs at impression printed polymer, allowing elastic deformation with a higher component, which leads
to a lower final impression, thus resulting a fast growth of microhardness. In the second stage, the higher penetration stress makes that the major weight of modification to be owed to the plastic non-reversible deformation of the polymer, as a result of molecular and supramolecular morphological changes. Thus, the impression printed size is maintained at higher values leading to a smaller increase of microhardness.

For a clearer evidence of the creep effect, in figure 6 is presented the variation of the parameter $d_2$ (as a measure of creep deformation values) depending on the penetration time. With all the irregular variation of determinations, however can be identified maxim peaks values that allow an extra creep measurement [24].

The strain-hardening coefficients ($\theta$) calculated according to equation (2) for the two-stages of creep variation are presented in table 1.

From the data presented in table 1 it can be seen that at first step of the microhardness variation depending on the time of penetration, strain-hardening coefficients ($\theta_1$) raise with increasing of penetration time, while at the second stage, their value ($\theta_2$) show no significant variation, being in the limit of experimental errors. The strain-hardening coefficients from the first step show a higher twice value compared to the $\theta$ coefficients from the second stage. This variation of strain-hardening coefficients reflects the morphological changes of copolymers subject to the time penetration stress. In the first step of the material penetrating, the deformation of the copolymer is higher mainly due to easier modification of the free volume (higher $\theta$ coefficient). In the second step, the change of free volume is less intense and the material is becoming more consolidated, and the main contribution at share hardening is due to morphological changes of the copolymer with a lower participation at the total deformation (lower $\theta$ coefficient) [25, 26].

In order to determine the glassy transition ($T_g$) of the copolymers it was studied the microhardness variation depending on the temperature of penetration tests. In order to minimize the data dispersion, the determinations were performed on several films with a thickness in the range 10 to 22 $\mu$m and the heating-cooling cycles were repeated several times. However high relative dispersion penetration values are revealed when it was determined microhardness correlation - $T_g$. This phenomenon was mentioned by other researcher's [4, 21].

In figures 7 and 8 is shown microhardness dependency of both copolymers with temperature and it can be observed, a significant variation due to its intense change of the free volume of polymers [4, 27, 28].

In the case of S-BMA-MAA copolymer (fig. 7), the variation of microhardness with temperature at penetration stress of 0.02 N is more difficult to appreciate, but in correlation with the values obtained from determinations under load of 0.05 N can be determined that $T_g = 57^\circ$ C.

The allure curves of the microhardness dependence versus testing temperature of (S-BMA-MAA-AMP) copolymer obviously differ from those of the (S-BMA-MAA) copolymer indicating that the presence of ampicilline groups grafted onto the polymer chain leads to significant changes in the morphology of the copolymer. However, the (S-BMA-MAA-AMP) copolymer (fig. 8) effectively exhibits the same glass transition temperature of 57$^\circ$ C.

The DSC determinations carried out at a heating rate of 20$^\circ$/min confirmed $T_g = 57^\circ$ C for tested copolymers.

Conclusions
The Vickers microhardness characterization method of copolymers has highlighted elastic-plastic behaviour of the copolymers, attested by creep determinations.

The presence of the ampicilline group grafted onto polymer chain, made a change in the morphology of the copolymer evidenced by microhardness / temperature diagrams, but does not significantly influence the glass transition.

References
5. STAMM M., Polymer Surface and Interface, Springer Verlag, Berlin, 2008
10. KUSY R.P., WHITLEY J.Q., KALACHANDRA S., Polymer 42 (6), 2001, p. 2585
12. CRAWFORD R.J., “Microhardness testing of plastics”, in Polymer Testing, (3) 1, 1982, p. 37
14. GIOHEA P., ROBU S., PRISACARI V., FILIP V., SPURCAIU B., IANCU L., GRIGORESCU R. M., Mat Plast. 51 (1) 2014, p.94
15. BARTENEV G.M., ZELENEV Yu. V., Visshaia Shkola (Moldova), 1983, p. 94
22. GULJ VE., KULESNEV V.N., Visshaia Shkola. M.1972, p. 320
24. BOYARSKAYA YU.S., GRABCO D.Z., KATS M.S., Microhardness, Chisinau, 1996, p. 294
28. LOPEZ J., Polymer Testing, 12 (6), 1993, p. 437

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