

The Microhardness as an Express Method for Estimation the Depth of Metal Particle Distribution

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Abstract

By measurement of microhardness of silver layer on polyimide films and its reduction after removing the stress, the depth of silver distribution in the polyimide films was calculated. A significant hardening of Kapton 100 HN films was observed especially for cobalt-impregnated materials, which was about 10 μm . The distribution of silver in the film layers was obviously deeper that manifested as entirely lower hardening at microhardness measurement. Because of the initial microhardness of Upilex it was observed strong hardening of the effort, which was led to shallow distribution of metals in the films. For example, Co-metallized films showed 5 μm distribution in the top film layers. Such method could allow precisely and rapidly estimating the distribution of metal particles impregnated in metallized polymeric materials.

Introduction

The development of the whole class of heterocyclic polymers, polyimides particularly, determines the progress in creation of the thermal and radiation stable polymer constructs that are used in airspace apparatus, micro- and radio electronics. Heights of mechanical, dielectric and radiation durability of polyimides (PI) set new tasks on expanding their application range by the way of giving specific physical properties to the materials on their basis. The films on the basis of polyimides characterized by high thermo-plastic and radiate stability are in the most part applied as polymer matrix. At present time the aluminized film blends Kapton (Du Pont, USA) are used in space systems in the low-earth orbit. The aluminized coating is stable to affection of open space factors and to the influence of the atomic oxygen particularly [1]. Due to the high reflectable characteristic in the wide spectral range the silvered polyimide films are the most perspective ones in the field of developing of satellite antennas, telescopes for transmission of information to IR-spectral range of geosta-

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tionary orbits where there is no factor of atomic oxygen [2].

New non-traditional methods of non-traumatizing polyimide metallization (metals: silver, cobalt, nickel) are developed at the Institute of Chemical Sciences in the laboratory of polymer synthesis [3,4]. This enables to avoid expensive technologies and obtain polyimide films with durable and non-removable coatings of both sides of the metal. Crystallinity, homogenous structure and thickness (several microns) of the coating cause its heat and electrical conductivity. Also according to preliminary data the metallized films are condensers with high electric capacity. The formed coatings represent primary mirror surface with high reflection coefficients in visible and IR ranges of spectra (up to 98% relative to silver mirror at normal angle of light incidence). The development of the new technology, modeling of the new metallization parameters including monomers reactivity, investigation of physical and chemical peculiarities of heterogeneous reaction allow to obtain prompt and technically non-complicated the metallized films of different sizes on the basis of industrial polyimides (Kapton, DuPont, USA; Upilex,

Ube Corp. Japan; PM Russia). The development of such novel technology requests new methods for express control of metal distribution in PI films, however it is difficult task due to micron scale of the metal penetration to the polymeric films. The paper is describing an estimation of metal distribution in films by measurement of film microhardness.

Experimental

Metallized polyimide films were prepared at the laboratory of the polymer synthesis at the Institute of Chemical Sciences (ICS) by the method of chemical modification. The silver coatings on the basis layer were obtained by the silver precipitation with chemical reduction of the silver nitrate in the Li-borohydride solution and by the vacuum spraying of silver.

The polyimide film metallization technology developed at the ICS is different from the other described in literature physic – chemical approach to formation of metal phase, that allows to substantially simplify the process and make use of the polyimide films such as Kapton JP[®], HN[®] (Du Pont, USA) Upilex R[®], S[®] (Ube Corp., Japan), PM[®] (Russia). *In situ* carrying out of the chemical reactions in the modified layers make it possible to form metal phase strongly impregnated into polyimide surface.

Non-destructive measurement of microhardness manifests deformability of samples

Ours experimental results may be considered from two points of view. First place it is the definition of certain important exploitation characteristics of presented films or their structure connected with these characteristics. Second they are the experimental bases for modeling for surface layers structure or their forming process. This series of ours experimental results relates to microhardness of experimental films. Measurement of the microhardness according to Vickers consists in determining the average contact pressure developed on the sample surface by a tetrahedral diamond pyramid. The microindentation technique reduces to measuring the size of the indentation remaining on the sample surface upon removal of the loaded indenter. Microhardness is determined by overall deformability of surface layers. In contrast to the different macroscopic mechanical tests the microhardness method permits to disclose the true deformability, which is not camouflaged by the de-

fects influence (scale factor). For example the indentation on such brittle material as inorganic glass is reducible up to 50 percent because of the elastic deformation without the fracture.

The works in our laboratory [5,6] have shown that during indentation together with the elastic and actual plastic deformation the original reducible densification occurs too. It is thermodynamic reversible process determined by polymeric chains turning in free volume. During heating the reduction of the indentation can be observed and the relaxation time can be calculated. This deformation process determines the microhardness value. The diffusion processes during metal/polymer surface layer formation are considered to be connected with free volume too it is desirable to analyze these processes in cooperation.

For all presented untreated films depth dependence of microhardness has extreme character (Fig. 1). These results are determined by variation of the load value P from 5 to 20 gram. For the homogenous material the microhardness is constant.

$$H \sim P/D^2,$$

where D - indentation size the value of indenter penetration depth H is proportional to D .

Probably it is necessary to take into account such inhomogeneity of surface layer structure in connection with film modification.

Extreme character microhardness dependence with depth remains for all films after modification (Fig. 2, 3). Because the value of microhardness is essentially less in comparison with such of pure metal, evidently we deal with composite material in which metal particles strengthen the polymer.

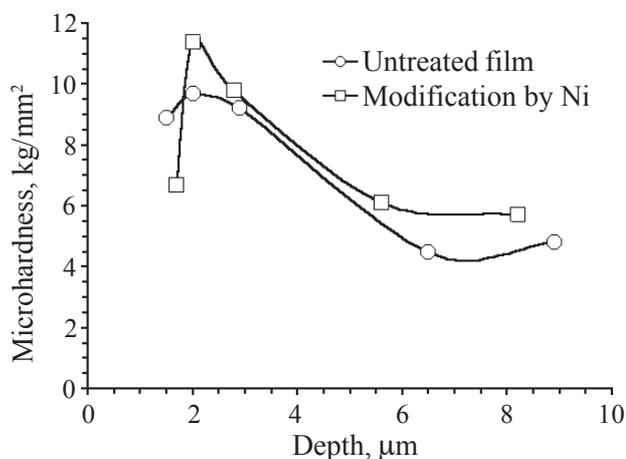


Fig. 1. Dependence of depth on microhardness for metallized Kapton 50 HN films.

Depth dependence of microhardness allows to estimate the depth of metal particle penetration: on this depth two curves (for untreated films and films after modification) coincide together. For Kapton 100 NH significant hardening was observed especially for cobalt (Fig. 2). The depth of metal particle penetration is about 10 micrometer. For another party of samples the depth of silver particle penetration was essentially larger.

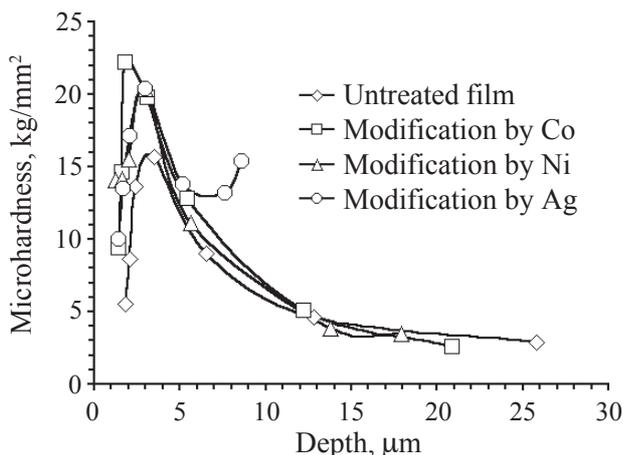


Fig. 2. Dependence of depth on microhardness for metalized Kapton 100 HN films.

Modification in two stages (the replacement cobalt or nickel by silver) gives some decrease of microhardness, but depth dependence is evidently determined by preceding diffusion Co- or Ni-containing compounds. The character of depth dependence of microhardness is essentially different, than in case of one stage modification by silver (Fig. 3).

For Upilex 25 F film the plot is similar. All microhardness changes finish at the depth of 5 mi-

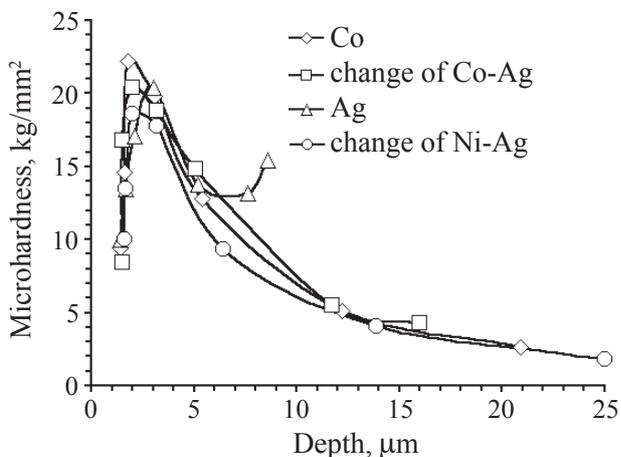


Fig. 3. Dependence of depth on microhardness for metalized Kapton 100 HN films.

rometer. At the same time Upilex 25 F film is more hard and elastic and the microhardness of original and modified films is essentially larger, than one for Kapton films (Fig. 4). However for this solid film the diffusion during modification probably initiates the structure loosening and microhardness reduction.

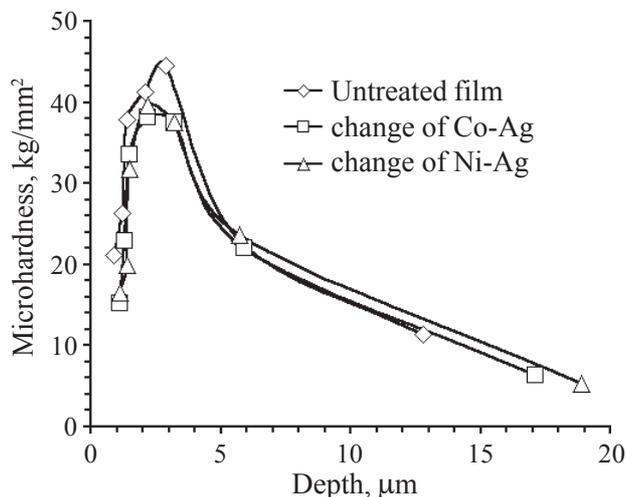


Fig. 4. Dependence of depth on microhardness for metalized Upilex 25F films.

Ours experimental results were received only at loading, which are too small for the crack formation in indentation corners. Value of the microhardness characterizes the damageable of films surface too because the deposition of indentation is a model of the damage from grains. The developed method has showed itself as a good candidate for express-analysis of metal penetration to films and their distribution there.

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References

1. Malay K. Ghosh, K.L. Mittal (eds.), Wet chemical modification of polyimide surfaces: chemistry and application. in *Polyimides. Fundamental and Applications*. 1996, p. 630.
2. Stoakley D. M., Clair A.K.S. Synthesis and characterization of self-metallizing palladium-doped polyimide films. *Polym. Prepr.* 37(1):541 (1996).
3. A. Zainullina, S. Kudaikulova, G. Boiko, B. Zhubanov, M.J.M. Abadie. One step synthesis of

- alicyclic polyimides. Part 1. Investigation of effect of amides of carboxylic acids on polyimide formation in protolytic medium. *Sci. Israel – Technol. Adv.* 2(3-4): 1-9(2000).
4. A. Zainullina, S. Kudaikulova, G. Boiko, B. Zhubanov, Ya. Vygodskii, M.J.M. Abadie, One step synthesis of alicyclic polyimides. Part 2. Kinetics of the process in the presence of amides. *Sci. Israel – Technol. Adv.* 2(3-4): 10-19(2000).
 5. I.V. Razumovskaja, L.L. Muhina, G.M. Bartenev, About the mechanism of inorganic glass deformation during the microindentation. *Reports of USSR Academy of Science.* 1973, V. 213, No 4, pp. 822-825.
 6. V.A. Gorin, L.L. Muhina, I.V. Razumovskaja. The influence of the electrophysical factors on the some polyolefin microplasticity which formed during plastic flow under high pressure. *Reports of Russian Academy of Science,* 1998, V. 358, No 4, pp. 502-505.

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