MICROINDENTATION STUDY OF ELECTRON BEAM IRRADIATED POLYAMIDE SAMPLES

GALINA ZAMFIROVA*[a], V. GAYDAROV[a], T. ZAHARESCU[b], and L. G. A. SILVA[c]

[a] *Transport University "T. Kableshkov", 158, Geo Milev Str., 1576-Sofia, Bulgaria,* [b] *Institute for Electrical Engineering, (INCDIE ICPE CA), 313 Splaiul Unirii, P. O. Box 149, Bucharest 030138, Romania,* [c] *Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP) Av. Professor Lineu Prestes 224205508-000 São Paulo, SP.Brazil.*
gzamfirova@mail.bg

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1. Introduction

It has been established that when polymers are irradiated with elementary particles (electrons, neutrons, gamma rays, protons, alpha particles, X-rays or other particles, or their combinations) they inject energy into the material. E-beam radiation is a form of ionizing energy which is characterized generally by its low penetration and high dosage rates[1]. The energy from the electrons absorbed could provoke some molecular or supermolecular changes and as a consequence leads to the structural modification of the irradiated materials. Moreover, the dosage of the radiation and not the dose rate is important in producing the desired improvement.

In polymers such as polyamide, the irradiation produces competing reactions, scission or cleavage and cross linking depending predominately on the dosage of irradiation, but also on the temperature, environment and on other conditions[2,3].

The cleavage reaction, which predominates at low irradiation doses, results in the breakdown of the long polymer chains into shorter ones. The cross-linking reaction, which predominates at high irradiation doses, results in the association of the polymer molecules into a network structure. At intermediate doses there is a mixture of the two reactions. Cleavage normally results in a decrease of tensile strength and modulus of elasticity, whereas cross-linking increases both the tensile strength and the modulus of elasticity. If the dosage is excessive, complete cross-linkage may take place but the samples become brittle. It is desirable the dosage to be such as to enhance the cross-linking without producing brittleness. According to the US Patent 4,015,133 the irradiation dosage should be between $10^4 - 10^{10}$ rads[4].

The study reports on polyamide 6 samples irradiated by an electron beam and the changes in their microhardness parameters provoked by irradiation. The aim is to establish the optimal irradiation dosage regarding the mechanical properties of the material. The supposed structural changes during the radiation are described by the results from the microindentation studies.

2. Experimental

Material

Polyamide 6 (PA 6) samples were supplied by Radici Plastics Ltd. The injection equipment was Battenfeld TM 1000. The thickness of the samples is 2 mm, which guarantees no influence of the subtract hardness. The density is 1.12–1.15 g cm^{-3} and melting point is 215–220 °C.

The preexposure doses were 100, 200, 400 and 600 kGy at a dose rate of 22.4 kGy s^{-1}.

Methods

Vickers microhardness device (mhp –160 at microscope UN–2) was used. The indentor was a regular square diamond pyramid, with top angle 136°. The measurements were provided at room temperature. Loads between 1.25÷ 160 g were used.

The microhardness methods used and characteristics measured were the following:

Mayer's lines are a logarithmic dependence between applied load P and dimension of indentation diagonals d. This dependence comes from Mayer's power law:

$$P = ad^n \quad (1)$$

Respectively in a logarithmic form;

$$lgP = lga + n\ lgd$$

where a and n are physical parameters. Constant a depends on the strength properties and constant n depends on the plastic features of the investigated material. The slope of these lines n is sensitive to non-uniformity of the structure in the depth of the sample. When $n < 2$ or $n > 2$ it means that microhardness decreases or increases, respectively, in the depth of the sample. If $n = 2$ Vickers microhardness is approximately constant along the depth.

Vickers microhardness MHV is a physical value characterizing the local resistance against plastic deformation during penetration. It is connected with the irreversible component of the deformation and is calculated according to the equation:

$$MHV = KP/d^2 \quad (2)$$

where d is the projected diagonal length of the imprint after releasing the indentor and K is a constant, depending on the geometry of the pyramid.

Total microhardness MHT[5], which is connected with the total deformation, includes elastic, plastic and viscoelastic components. It is given by a similar equation:

$$MHT = KP/D^2 \quad (3)$$

where D is the projected diagonal length of the indentation in the loaded state. Thus defined this value can be considered as a measure for the total penetration resistance of the material.

Microhardness profiles are dependences of the microhardness as a function of the depth of indentation, h, respectively, of the applied load, P.

$$MHV=f(h);\ MHT=f(h);\ MHV=f(P);\ MHT=f(P) \quad (4)$$

It should be noted that if in the depth h MHV, respectively MHT, are determined, this value does not correspond to the real microhardness exactly in this depth. This value includes microhardness properties of all the layers situated between the surface and this depth.

3. Results and discussion

Mayer's lines

Fig. 1 shows the Mayer's lines and n – calculated from their slope parameter. For all samples n value is larger than 2, which shows the general tendency for hardness increasing in the direction perpendicular to the surface. This type of hardness nonuniformity is characteristic for semicrystal polymers because the crystals in the surface layers are not well formed compared with the inner layers as a result of faster cooling during sample preparation. Steric reasons also contribute to this tendency. All irradiated samples have parameter n smaller than that of the initial material, which means the irradiation promotes diminishing of this undesirable tendency.

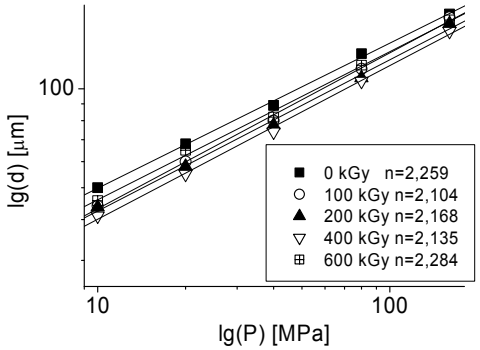

Fig. 1. **Mayer's lines**

Microhardness profiles

Vickers microhardness profiles for all samples are revealed in Fig. 2. These dependencies specify how MHV values change in the direction perpendicular to the surface. As seen the above mentioned hardness increasing in the depth as a tendency is related predominantly to the surface layer (till $h \approx 80$ μm and $P \approx 40$ g), then MHV values remain almost constant. For the nonirradiated sample MHV increases continuously in the whole investigated range of applied loads. Consequently the irradiation favours the structural equalization in the inner layers, but not that in the surface layers.

The straight lines in Fig. 2b connect the MHV values for all samples measured at one and under the same load. Only the data for the sample irradiated with dose 600 kGy do not lie on the linear dependences. That means some drastic changes in the material structure take place in the interval 400–600 kGy.

It is interesting that these lines are almost parallel, except the line at 10 g, revealing that the MHV change with the indentation depth remains the same and does not depend on the applied load.

$$\text{If } P = const \rightarrow \Delta MHV/\Delta h \approx const. \quad (5)$$

Fig. 3 presents the MHT profiles of the initial PA sample and the irradiated samples plotted versus applied

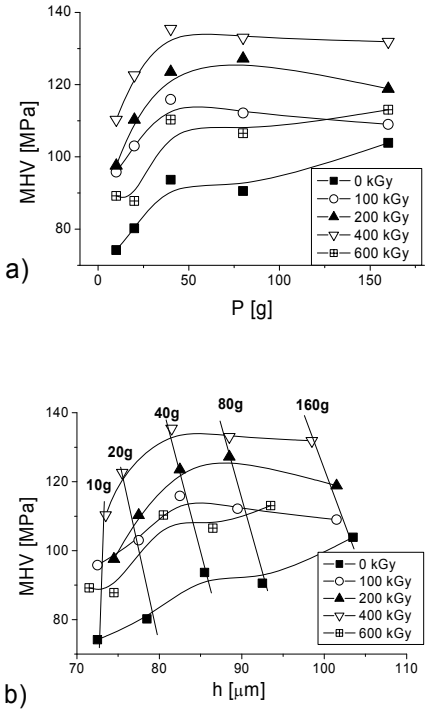

Fig. 2. **MHV profiles for initial sample and for samples irradiated with different dose plotted vs. applied load (a) and *vs.* indentation depth (b)**

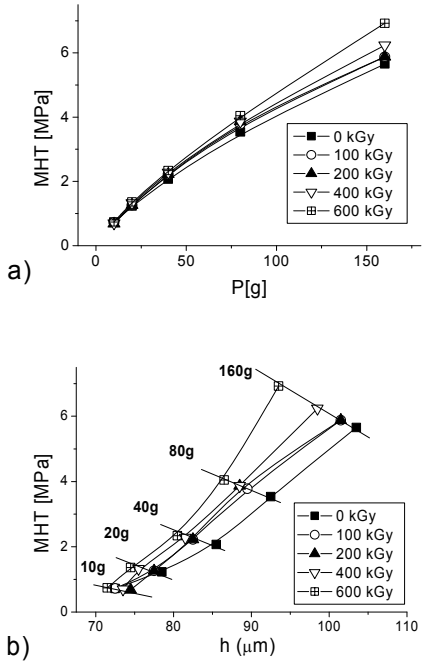

Fig. 3. **MHT profiles for initial sample (□) and for samples irradiated with different doses plotted *vs.* applied load (a) and *vs.* indentation depth (b)**

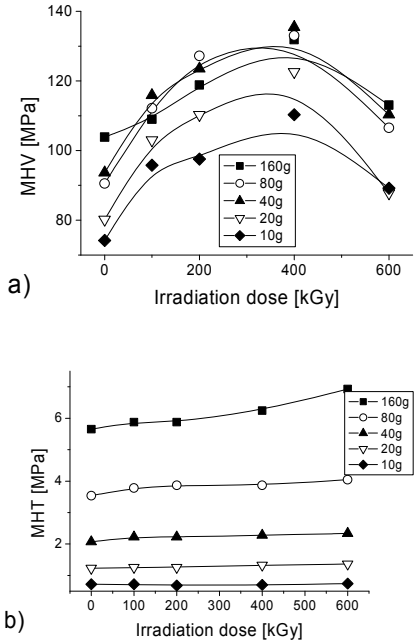

Fig. 4. **Vickers microhardness (a) and Total microhardness (b) *vs.* irradiation dose**

load *P* (Fig. 3a) and versus indentation depth *h* (Fig. 3b). The trend of these curves could be interpreted as follows: Although the total microhardness is a local characteristic, it forms its values not only from the material layers which the indenter penetrates but also from a larger material zone under the indenter, where the material is deformed not only plastically but elastically as well. That is why at bigger applied loads, deeper penetration, respectively, usually the total resistance against penetration increases similar to the resistance increase in the compressed spring – the bigger applied load, the stronger resistance.

The deviation from ideal straight line is due to the presence of the plastic deformation component, but the slope of these dependencies, if approximate to a straight line, could be a rough measure for the elastic properties of the samples. In this case the increasing of the irradiation dose improves the elastic properties.

Influence of the irradiation dose

Comparing Fig. 4a and Fig. 4b, presenting the influence of irradiation dose on Vickers microhardness and total microhardness respectively, it is evident that absorbed energy causes a different effect on these mechanical characteristics. The fast electrons provoke increasing of *MHV* till about 400 kGy and then a decreasing, while *MHT* is almost not sensitive to irradiation dose.

Knowing that Vickers microhardness characterizes plastic resistance against local deformation, for crystal polymers consisting of crystal and amorphous phases, this value could be considered as a constitutive from the inherent contribution of each of the both phases. It is the so called additive law:

$$MHV = f.MHV_c + (1–f)MHV_a, \quad (6)$$

where f is the degree of crystalinity and MHV_c and MHV_a are the inherent Vickers microhardness of the crystal and amorphous areas. But as usual $MHV_a << MHV_c$ and practically could be ignored.

$$MHV = f.MHV_c, \quad (7)$$

So, Vickers microhardness as a measure of plastic resistance against penetration depends predominantly on quantity and quality of the crystals. In this case irradiation influences mainly the crystal phase, respectively, the plastic properties of the material and almost does not influence the elastic ones. As Vickers microhardness is in a power ratio to modulus of elasticity, E ($MHV = aE^b$, a and b are material constants) *MHV* increase roughly signifies a modulus increase also.

As mentioned in the introduction many authors prove that at small doses the scission processes prevail and crosslinking dominates at higher doses. It has been established for PE, and probably it is true for polyamides also, that Vickers microhardness is sensitive to molecular weight only for relatively short macromolecules ($M_\eta < 10^5$). For larger molecules this parameter does not influence

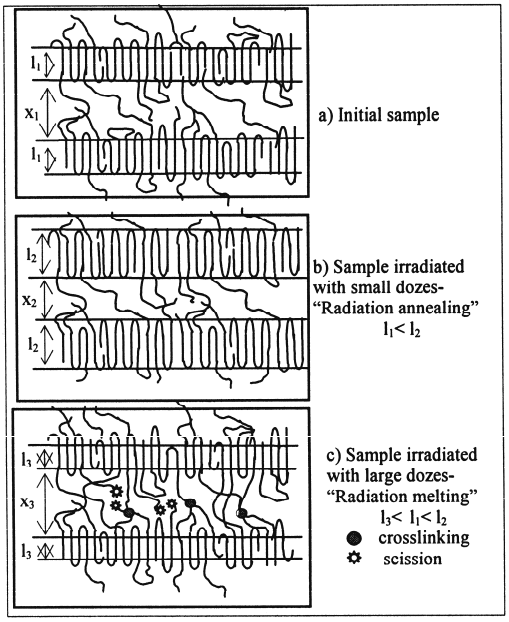

Fig. 5. **Scheme of supermolecular structure of the initial sample (a) and the supposed structural changes during irradiation annealing (b) and radiation melting (c);** l – lamella thickness, x – interlamella distance

MHV values. Crosslinking on principle takes place in the amorphous zones increasing resistance against elastic deformation, but in our case of microindentation measurement this effect is not remarkable. So, all chemical changes provoked by irradiation do not have direct influence on the micromechanical properties, but changes in the supermolecular structure, especially in the crystal phase, cause the changes in the micromechanical behavior.

We suppose that the small quantity of the irradiation contributes to so called "irradiation annealing"[6]. It consists in decreasing the lamella defects and interlamella stresses. Also a little enlarging of the lamella thickness and improving the lamella surface take place on account of the molecule ends or molecule loops.

When irradiation doses are high the structural changes are related to the so called "radiation melting"[6]. It consists in pushing some defects or mayhems in the crystal lamella to its surface. Most probably it is due to the transport of energy by excitons along the macromolecules and in this way the lamella surface becomes more defective, hence lamella thickness decreases a little. Destructions and crosslinkings occur simultaneously predominately in disordered zones. Fig. 5 shows the scheme of the supposed structural changes.

4. Conclusions

Irradiation of polyamide 6 with an electron beam influences the mechanical properties in the following way:

- Till about 400 kGy resistance against local plastic deformation increases, the module of elasticity increases, respectively. This is due to changes in the crystal phase known as a "radiation annealing". At higher doses Vickers microhardness and modul of elasticity decrease because of so called "radiation melting".
- Total microhardness does not change during the irradiation.
- Microhardness profiles demonstrate nonuniformity in sample structure. Surface layers are softer than the inner ones. Irradiation prevents the undesirable tendencies and leads to structural equalization in the inner layers, but not of the surface ones.

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G. Zamfirova[a], V. Gaydarov[a], T. Zaharescu[b], and L. G. A. Silva[c] (*[a] Transport University "T. Kableshkov", Sofia, Bulgaria, [b] Institute for Electrical Engineering, Bucharest, Romania, [c] Instituto de Pesquisas Energéticas e Nucleares São Paulo, SP. Brazil.):* **Microindentation Study of Electron Beam Irradiated Polyamide Samples**

The study reports on PA samples irradiated by an electron beam and the changes in their microhardness parameters provoked by irradiation. It has been established that total microhardness is not sensitive to irradiation dose, while Vickers microhardness passes through a maximum for samples irradiated with dose of 400 kGy. That means that irradiation affects predominantly the crystal phase. The crystal structure passes through the so called "irradiation annealing", followed by "irradiation melting".