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INFLUENCE OF POLYMERIZATION CONDITIONS ON THE MICROINDENTATION MECHANICAL PROPERTIES OF POLY(ALLYL(*p*-ALLYLCARBONATE) BENZOATE)

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Abstract. Flat plates of poly(allyl(*p*-allylcarbonate) benzoate) obtained *via* photopolymerization and thermal polymerization have been studied by means of microindentation. The plates were about 3 mm thick. The values of microhardness (*MHV*)/total microhardness (*MHT*) have been determined. Accordingly, structural changes in the plate bulk due to the polymerization method were detected. The plates obtained by photopolymerization possess a superficial layer harder than the inner layers and its thickness is not uniform. Also, microindentention shows that the increase in the polymerization time during thermopolymerization leads to improved elasticity and resistance against plastic deformation. Microindentation data of the plates here studied shows that poor mechanical properties correspond to an unfinished network, while good mechanical properties correspond to a better crosslinked network.

Keywords: microhardness, microindentation, poly(allyl (*p*-allylcarbonate) benzoate), polycarbonate network.

1. Introduction

Hardness is a physico-mechanical characteristic which is defined as a local resistance against penetration of a harder body (indenter). Hardness measurements can be divided into 3 groups (macro-, micro- and nano-) according to the applied load and consequently to the dimensions of the obtained imprints.

– Macrohardness is used to determine quickly the mechanical properties of small samples and usually is applied for routine qualitative control.

– Microhardness is used for studying the relation between mechanical properties and material structure. Its wide application as an investigation method is due not only to the simplicity of the measurements but also to the fact that micro hardness parameters give an idea of the overall picture of the mechanical properties of the material as well as of its structural peculiarities [1-3]. This special position of microhardness amongst the other mechanical properties is a consequence of the physical nature of this characteristic. As microhardness characteristics are sensitive to mechanical properties as well as to polymer morphology, these characteristics could be considered as a link between micro- and macrocharacteristic of the material. Being different from the hardness, microhardness depends on the applied load (10–2000 mN) and respectively on the dimension of the indentation.

– Nanohardnes measurements use new technologies enabling precise control over the applied load and on the indentation depth (Depth Sensing Indentation method) [4, 5]. This method is unique for studies of surface structure and thin coatings.

On the other hand, a lot of work on lineal polycarbonates has been carried out for well known Industries as Bayer, General Electric[6, 7] and a few academic Institutions like Texas State University (St. Marcos), USA Army Research, USA Naval Academy, Mainz University, Siegen University, Messina University, *etc*. However, little information has been reported on poly(aryl carbonate) networks [8]. Polycarbonates are thermoplastic amorphous polymers whose chemical, physical and mechanical properties are in a very good balance. They have very good chemical resistance, impact resistance, toughness, high transparency, good dimensional stability and are usable in a wider temperature range, easy to process, readily recyclable, *etc*. Because of these properties, polycarbonates find many applications and are an object of investigation aiming at additional improving of some properties: by preparing of polymer blends [9, 10]; preparing of nanocomposites [11-14]. An improvement in their properties can also be done by synthesis of novel polycarbonates [6-8]. To improve the thermal stability of PC coordination of metal ions has been tried [15]. However, their low scratch-resistance is a disadvantage. Therefore many efforts directed on improvement of the surface properties by plasma treatment [16], chemical modification [17], ion implantation [18], gamma irradiation [19], and mercury illumination induced an increase of the crosslinking [20]. Hence, the indentation method is an appropriate tool for this type of studies [12, 13, 21].

The aim of this contribution is to find out using microindentation measurements how the conditions of the polymerization process influence the surface properties of the PC samples.

2. Experimental

2.1. Materials and Sample Preparation

Five polycarbonate flat plates having 2–3 mm thickness were analyzed. They are classified into two groups according to the polymerization method.

Group A. Consisting of two flat plates obtained by photopolymerization of allyl(*p*-allylcarbonate) benzoate with Irgacure 184 as photoinitiator (PI). Individual quartz cells filled with the polymerisable mixture were exposed at atmospheric pressure at 308 K, and a distance of 8.4 cm from the UV lamp (Ace-Hanovia medium-pressure quartz mercury vapour arc lamp, 450 W) [1]. Sample A1 was polymerized with 0.3 mol/l of PI and sample A2 with 0.5 mol/l of PI.

Table 1

Plates of group A photocrosslinked at 308 K

Plate	Irradiation time, h	Molarity (mol/l) Irgacure-184	Gel, %
A1	1.25	0.3	89.4
A2	1.5	0.5	90.5

Table 2

Plates of group B. Thermal crosslinking with peroxy-initiator (DSBPDC)

Plate	Polimerization time, h	Polimerization temperature, K	DSBPDC, wt %	Gel, %
B1	6.5	341	6.59	89.6
B2	7	341	6.59	92
B3	8.5	328	4	89.7

Group B. Consisting of three flat plates obtained by thermal polymerization of allyl(*p*-allylcarbonate) benzoate with di-sec-butyl peroxydicarbonate (DSBPDC) as thermal initiator. Sample B1 (6.5 h of polymerization) and B2 (7 h of polymerization) were polymerized with 6.65 wt % of DSBPDC at 341 K. Sample B3 was polymerized with 4 wt % of DSBPDC at 328 K for 8.5 h of polymerization. These poly(allyl(*p*-allylcarbonate) benzoate) plates are transparent, thermoset polycarbonate.

The casting characteristics of the plates are noted in Tables 1 and 2.

2.2. Method of Investigation

Measurements were performed on a microharness tester mhp–160, an extra to the NU-2 microscope. The indenter under the standard loading penetrated the material. For Vickers microhardness the indenter is a regular square pyramid with a top angle of 136°. Penetration direction was perpendicular to the sample surface. Loads of 100, 200, 400, 800 and 1600 mN were used. Loading time was 5 s. The sample was in loaded state for 30 s. Then indenter was extracted from the material and the formed indentation was measured microscopically within 1 μm. Ten measurements for each load were made. All measurements were made at room temperature.

The following microhardness methods and characteristics were used:

2.2.1. Rough determination of the mechanical properties according the indentation shape

The indentation shape gives tentative information about the elastic-plastic properties of the investigated material. Fig. 1 schematically illustrates some possible indentation shape observed on the sample surface after indenter removing.

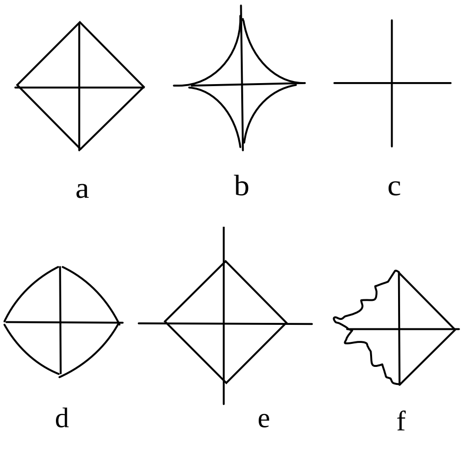


Fig. 1. Different indentation shapes after removing the indenter: plastic materials (a); elastic-plastic materials (b); elastic materials (c); materials with prevalent plastic deformation but without contraction (d) and fragile materials (e, f)

2.2.2. Mayer's lines

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 [2]:

$$P = a \cdot d^n \tag{1}$$

Respectively in logarithmic form:

$$\log P = \log a + n \cdot \log d \tag{2}$$

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

2.2.3. Vickers microhardness (*MHV*)

MHV characterizes the local plastic material resistance against the penetration of the pyramidal indenter and is connected with the irreversible component of deformation, thus characterizes plastic properties of the sample. It is calculated according to the equation:

$$MHV = \frac{kP}{d^2} \tag{3}$$

where *P* is the applied load, *d* is the projected diagonal length of the imprint after the indentor realizing and *k* is a constant depending on the geometry of the pyramid.

Vickers microhardness measurements give possibility to obtain an approximate concept about some mechanical characteristics.

So called Tabors relation – the relation between Vickers microhardness (*MHV*) and yield stress (σ_y) is known from literature [22]:

$$MHV = 3s_y \tag{4}$$

But this relation is valid only for ideal plastic materials. This formula was corrected to be valid for viscoelastic polymers by adding the corrective constant *K*, value of which depends on the type of the material [23]:

$$MHV = 3s_y - K \tag{5}$$

Similarly power relation between MHV and modulus of elasticity, **E**, was established [24-26]:

$$MHV = a \cdot E^b \tag{6}$$

where *a* and *b* are material constants.

The relation between microhardness amd the modulus of elasticity has a physical reason because both depend on the material structure and the corresponding intramolecular and intermolecular interactions.

2.2.4. Total microhardness (*MHT*)

The so called total microhardness [27-29] is very important, because it gives rather different information about the material structure and its mechanical properties. So, in many investigations the dimensions of the indentation diagonals at loaded state (*D*), and the microhardness calculated from it are more important. *MHT* is defined by the analogy to Vickers microhardness:

$$MHT = \frac{kP}{D^2} \tag{7}$$

Some Russian authors name it "un-restored" microhardness [30]. Thus defined *MHT* value can be considered as a measure for the local total material resistance against penetration and is related to the total deformation, including elastic, plastic and viscoelastic components.

2.2.5. Microhardness profiles

Microhardness profiles are dependences of the Vickers microhardness and total microhardness as a function of the applied load (*P*), respectively on the penetration depth (*h*):

$$MHV = f(P);\quad MHV = f(h);$$
$$MHT = f(P);\quad MHT = f(h) \tag{8}$$

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

3.1. Rough Determination of the Mechanical Properties According to the Indentation Shape

The microphotographs of the imprints for group A (samples A1 and A2 at load $P = 1600$ mN) are shown in Figs. 2 and 3 and that of the group B in Fig. 4 (B1, B2 and B3 at load $P = 800$ mN).

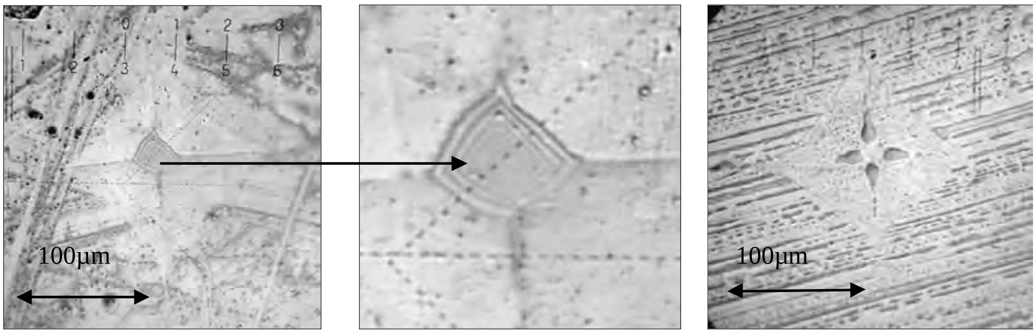
According to the indentation shape all samples exhibit indentation type "elastic-plastic". The dimension and the shape of the restored indentation after indenter extracting do not change during the time, *i.e.* viscoelastic relaxation is negligible and will not be taken into account in the studied indentation experiment.

Similarly, when keeping down the indenter at constant load it does not go deeper. That means the viscoelastic deformation component is negligibly small.

3.1.1. Group A

The microphotographs show sometimes small droplets situated at the edge (Fig. 2, sample A2,) or at the bottom of the pyramidal imprint (Fig. 2, sample A1). If magnifying bottom of the imprint on image A1 (A1m) many concentric lines can be seen on it, which is typical of light interference. That is to say, at the bottom of the imprint there is a liquid which could be the unreacted monomer.

Another peculiarity, which occurs on many images, for example in the imprint of sample A1, loaded with 800 mN, is that the imprint seems to be divided horizontally in two parts: the small pyramid with smooth surface of the side and the grand truncated pyramid with porous surface (Fig. 3). This effect has been observed more frequently in bigger imprints. That means that there is a superficial layer structure of which is different from that of the inside. Moreover, the relation between the dimensions of the small and big truncated pyramids at identical imprints is not equal, what means the sample's structure is not uniform in the depth. The dimensions of the one side of the square imprints are emphasized by dashed lines in Fig. 3. So, the indentation shapes of photocrosslinked plates show that the chemical structure of the network is inhomogeneous, because the reactivity of the photoinitiator decreases along the pathway of the UV light, in a similar behaviour the double bond of allyl(*p*-allylcarbonate) benzoate reacts less and less towards the inner part of the plates. So, the concentric lines and drops on the imprints of plate A1, and plate A2 are possibly the unreacted liquid monomer.



A1 A1m A2

Fig. 2. Light microscopy images of the imprint for sample A1 and A2 after loading with 1600 mN. The images A1m is the fragment of the image of A1 at higher magnification

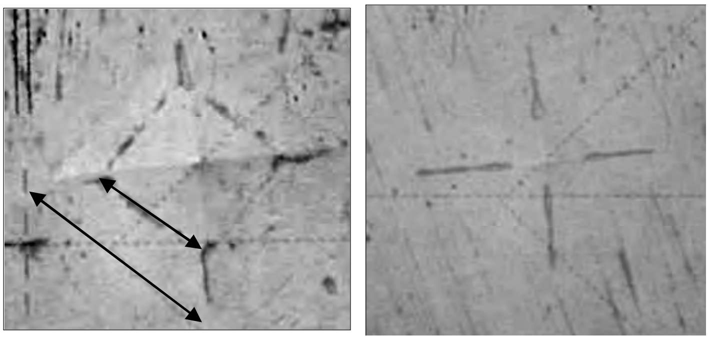
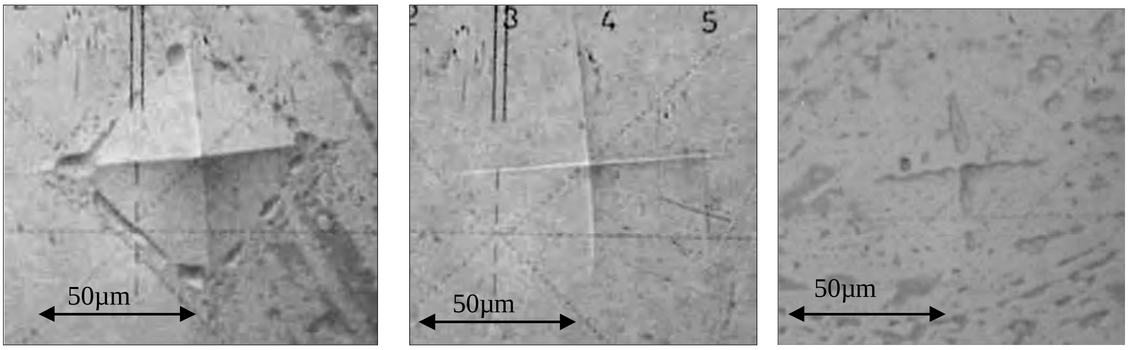


Fig. 3. The imprints made on sample A1 (load 800 mN) at different places of the surface



B1 **B2** **B3**

Fig. 4. Light microscopy images of the imprint for samples B1, B2 and B3 after loading with 800 mN

3.1.2. Group B

The imprints in the sample polymerized for 6.5 h (B1) are well visible squares. The imprints keep their square form even at a small load. That means the plastic properties are prevailing in this material.

The imprints in the sample polymerized for 7 h (B2) are not well-defined. Only diagonals of the imprints could be seen. This is typical of a material with elastic-plastic properties but with prevailing elasticity.

The imprints in the sample polymerized for 8.5 h (B3) are much smaller and almost invisible. The imprint diagonals could be guessed on the small groves filled with a liquid. That means the material has typical elastic properties.

3.2. Mayer's Lines

Fig. 5 plots the Mayer's lines. The parameter *n* obtained from the lines slope is presented. The parameters *n* for the both samples A are very close and their value is < 2, hence the microhardness slightly decreases in the depth, *i.e.* the surface layers are harder than the inner ones.

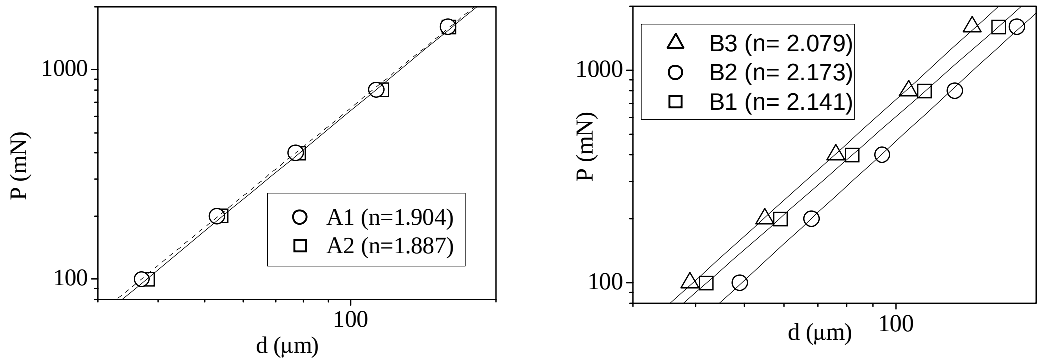
All samples from group B have $n > 2$, *i.e.* the microhardness slightly increases in the direction perpendicular to the sample surface.

3.3. Microhardness Profiles

3.3.1. Microhardness profiles of the samples from group A

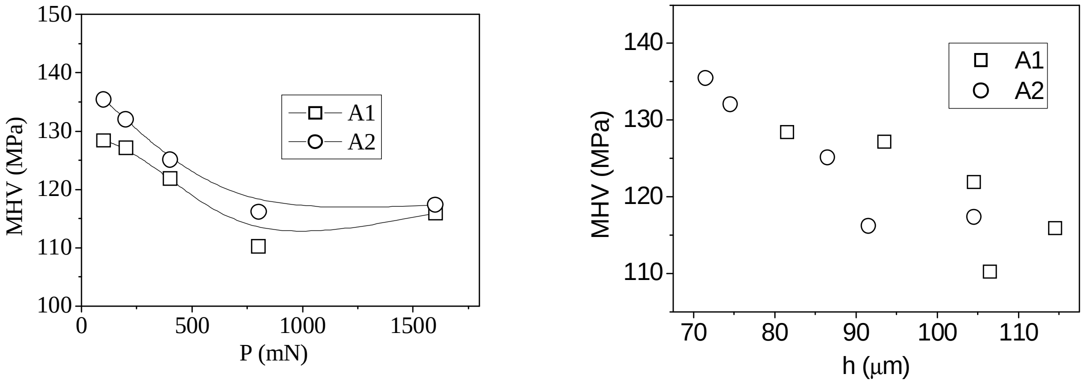
– Vickers microhardness profiles

The values of the Vickers microhardness as a function of the applied load and as a function of the indentation depth are plotted in Figs. 6a and 6b, respectively. Sample A2, polymerized with more amount of photoinitiator, is harder than sample A1. Taking into account the above mentioned relations between *MHV* and *E* and between *MHV* and σ_y, it could be concluded that sample A2 possesses higher modulus of elasticity and greater yield stress. This affirmation is only qualitative because using only this indentation test the constant *K*, *a* and *b* could not be determined and these mechanical properties could not be exactly calculated.



a) b)

Fig. 5. Mayer's lines for the sample from group A (a) and group B (b)



a) b)

Fig. 6. Vickers microhardness as a function of the applied load *P* (a) and indentation depth *h* (b)

The *MHV* profiles show that *MHV* decreases in the depth, as was also indicated by the parameter *n* of Mayer's lines. But from these profiles it is clearly seen that MHV decreasing is not uniform. When the load increases up to 800 mN, that corresponds to indentation depth about 100–105 μm, the microhardness decreases and afterwards does not change. That means that around this depth there is some difference in the material structure. So, these measurements confirm the microscopically observed difference in the bottom and the upper part of the imprint. Perhaps it is due to the different influence of the UV-light on the rate, degree or mechanism of polymerization in the superficial and in the inner polymer layers.

<u>– Total microhardness profiles</u>

Profiles of the total microhardness *MHT* are plotted in Fig. 7a as a function of the applied load and in Fig. 7b as a function of the indentation depth. *MHT* increases in the depth, which is a typical trend for this characteristic and resulting from its physical nature. *MHT* includes not only resistance against plastic deformation, but also resistance against elastic deformation. This effect is similar to the resistance of the compressed spring – the more the compression the bigger the resistance. Sample A2 possesses higher values for *MHT* than sample A1, *i.e.* sample A2 is more resistant against plastic deformation, as well as against total deformation. The change in this characteristic is also not uniform in the depth. The trend of the curves of total microhardness profiles changes in the depth around 85–90 μm for sample A2 and around 100–105 μm for sample A1.

3.3.2. Microhardness profiles of the samples from group B

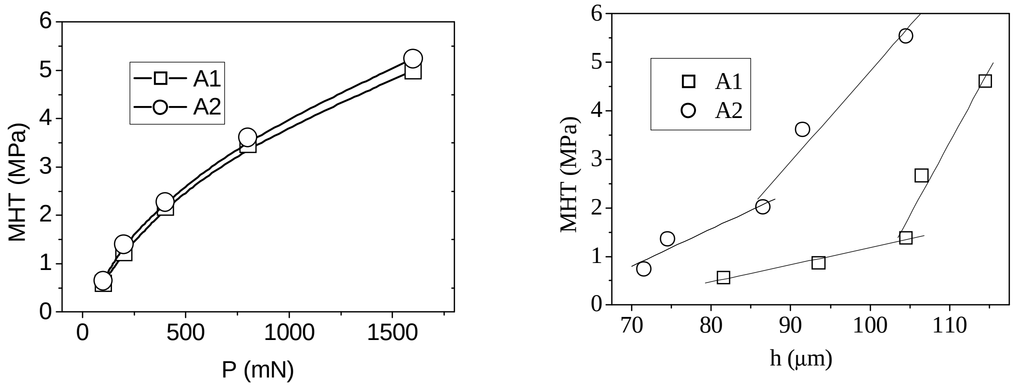
<u>– Vickers microhardness profiles</u>

The *MHV* profiles for all samples of this group show that *MHV* increases in the depth (Fig. 8). In contrast to the samples polymerized by photoinitiator (group A), where the *MHV* decreases not uniformly in the depth, here the *MHV* increases monotonically. This trend of the *MHV* profile is habitual for crystal polymers because usually their crystal structure in the superficial layers is less perfect. Since *MHV* is very sensitive to the type, quantity and quality of the crystal phase, lamella dimensions, *etc.*, *MHV* changes for crystal polymers are often interpreted by changes in the crystal phase. However, in the case of polycarbonates, which are amorphous polymers the smaller surface hardness could be as result of less compact packing of the macromolecules because of faster cooling of the superficial layers. V. P. Privalko *et al.* have established that isothermally treated sample exhibits higher microhardness. This result is attributed to the overlap of a network of ultramicrocrystals on the original entanglement network in the untreated PC sample [31]. This effect is another possible explanation of the higher microhardness in the inner layers.

Sample B1 possesses the smallest *MHV*, followed by sample B2 and B3, *i.e.* the larger the time of polymerization, the bigger the resistance against plastic deformation. But this approach to results explanation in any cases could not be quite correct because of the different elasticity of the samples to which Vickers hardness is not sensitive. Especially, sample B3 is very elastic, as seen from the photos of its imprints while sample B1 is quite plastic. Therefore this method is not appropriate for measurements of elastic materials. In the case of elastic-plastic materials with a prevailing elastic deformation component *MHT* measurements are more reliable because the *MHT* value includes the resistance against all deformation components (elastic, plastic, viscoelastic) caused during the penetration.

<u>– Total microhardness profiles</u>

In Fig. 9 the dependences of *MHT* are plotted *vs.* indentation depth. The strongest resistance against the penetration exhibits sample B3, followed by samples B2 and B1. All dependences increase in the depth, which is natural for this characteristic, but the slope of curve B3 is the steepest and the slope of the B1 is the smallest. It means that sample B3 is the most elastic and sample B1 – the least elastic one from this group. Thereby the measurement of *MHT* profiles confirms the initial assumption made by the indentation shape.



a) b)

Fig. 7. Total microhardness as a function of the applied load *P* (a) and indentation depth *h* (b)

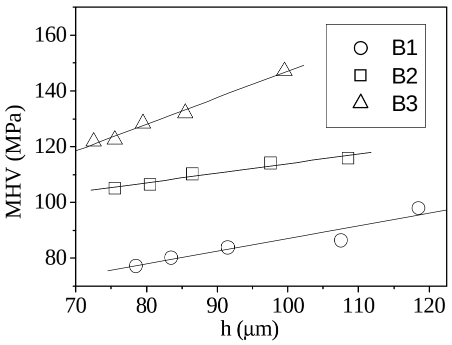


Fig. 8. Vickers microhardness plotted *vs.* indentation depth *h*

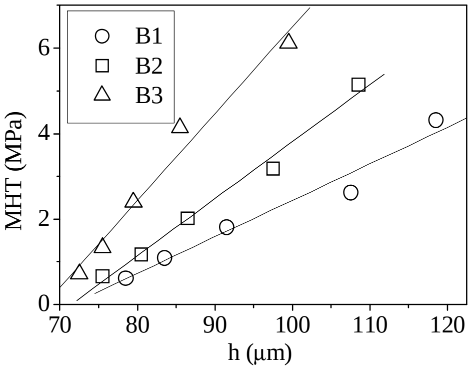
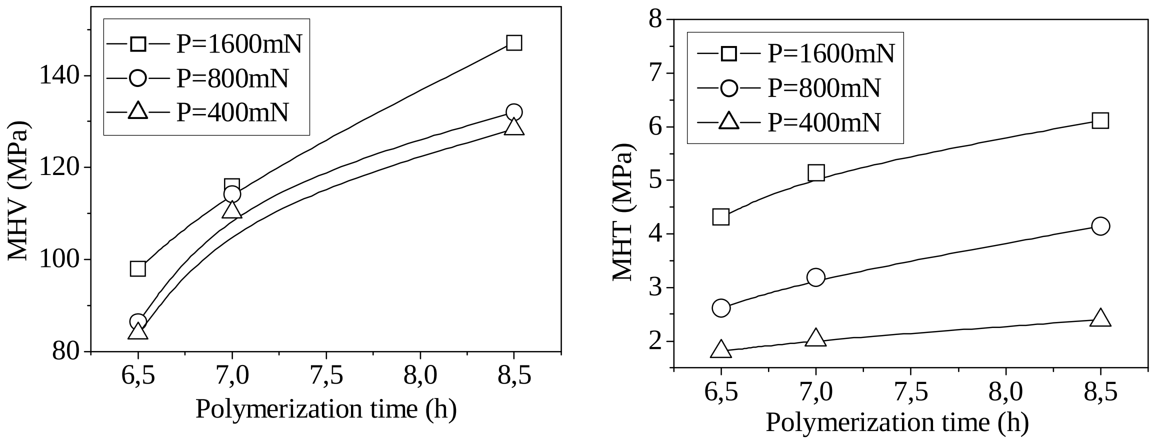


Fig. 9. Total microhardness plotted *vs.* indentation depth *h*



a) b)

Fig. 10. Dependences of *MHV* (a) and *MHT* (b) as a function of the polymerization time

Fig. 10 shows the dependences of *MHV* (a) and *MHT* (b) as a function of the polymerization time. At longer polymerization time the density of the crosslinking increases. As a consequence the resistance to plastic deformation improves, as well as the resistance to total deformation. Knowing the relation between *MHV* yield stress and modulus of elasticity, respectively, it is evident that with the increase of the polymerization time these mechanical characteristics also are improved.

4. Conclusions

It has been shown that microhardness testing is an appropriate technique to determine the mechanical properties and to relate such properties with the microstructure of the poly(allyl(*p*-allylcarbonate) benzoate) networks created by two different methods of crosslinking: photopolymerization and thermal crosslinking.

1. Plates of poly(allyl(*p*-allylcarbonate) benzoate) obtained *via* photopolymerization at different times of polymerization are not uniform in the depth. They possess a superficial layer harder than the inner layers and its thickness is not uniform.
2. Plates obtained *via* thermopolymerization at different polymerization times are more uniform. The increasing time of polymerization leads to the increase in the elasticity, resistance against penetration, modulus of elasticity, and yield stress of the material or as a whole its mechanical properties are improved due to the fact that thermal crosslinking is more complete at longer polymerization time.

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ВПЛИВ УМОВ ПОЛІМЕРИЗАЦІЇ НА МІКРОІНДЕНТУВАННЯ ПОЛІ(АЛІЛ(*p*-АЛІЛКАРБОНАТ) БЕНЗОАТУ)

Анотація. *Методом мікроіндентування досліджено плоскі пластини полі(аліл(р-алілкарбонату) бензоату) товщиною біля 3 мм, отримані за допомогою фотополімеризації і термічної полімеризації. Визначено значення мікротвердості до загальної мікротвердості. Відповідно, були виявлені структурні зміни в пластинах в залежності від методу полімеризації. Пластини, отримані фотополімеризацією, мають твердіший поверхневий шар порівняно з внутрішніми шарами і його товщина не є рівномірною. За допомогою мікроіндентування показано, що збільшення часу полімеризації при термополімеризації приводить до поліпшення еластичності та опору до пластичної деформації. Доведено, що недостатні механічні властивості відповідають незавершеній сітці, а непогані – сітці, яка краще зшита.*

Ключові слова: *мікротвердість, мікроіндентування, полі(аліл(р-алілкарбонат) бензоат), полікарбонатна сітка.*