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S. Belbachir [1,2], F. Zaïri [1], G. Ayoub [1], U. Maschke [3], M. Naït-Abdelaziz [1], J.M. Gloaguen [4], M. Benguediab [2], J.M.Lefebvre [4]

EFFECT OF ULTRAVIOLET IRRADIATION ON THE TENSILE PROPERTIES OF AMORPHOUS POLYLACTIDE FILMS

UTICAJ ULTRALJUBIČASTOG ZRAČENJA NA ZATEZNE KARAKTERISTIKE AMORFNOG FILMA POLILAKTIDA

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Author's address:
[1)] Laboratoire de Mécanique de Lille, 59655 Villeneuve d'Ascq Cedex, France
[2)] Université de Sidi Bel Abbès, Département de Mécanique, 22000 Sidi Bel Abbès, Algeria
[3)] Laboratoire de Chimie Macromoléculaire, 59655 Villeneuve d'Ascq Cedex, France
[4)] Laboratoire de Structure et Propriétés de l'Etat Solide, 59655 Villeneuve d'Ascq Cedex, France

Keywords
- polylactide – poly(lactic acid)
- ultraviolet (UV) irradiation
- molecular weight
- mechanical properties

Ključne reči
- polilaktid – poli(laktična kiselina)
- ultraljubičasto (UV) zračenje
- molekularna težina
- mehaničke karakteristike

Abstract

In this work, the impact of ultraviolet (UV) irradiation on the mechanical behaviour of amorphous biodegradable poly(lactic acid) (PLA) films is analysed. PLA films were submitted to UV irradiation for increasing exposure time. Two kinds of experiments were conducted, chemical and mechanical. The chemical degradation was measured by gel permeation chromatography technique. The PLA films were mechanically investigated by stretching experiments before and after UV exposure. Their mechanical properties were obtained by a video-controlled system. Our purpose is to establish the relationship between macroscopic mechanical response and molecular parameters such as the molecular weight, and external solicitations such as temperature, strain rate and UV irradiation. The interactions between photodegradation and changes in polymer properties are discussed.

Izvod

U radu je analiziran uticaj ultraljubičastog (UV) zračenja na mehaničke karakteristike amorfnog filma biorazgradljive poli(laktične kiseline) (PLA). Film PLA je bio izložen UV zračenju tokom rastućeg vremenskog perioda. Izvedene su dve vrste eksperimenata, hemijsko i mehaničko. Hemijska degradacija je merena hromatografskom tehnikom razlaganja gela. Filmovi PLA su eksperimentalno istraživani zatezanjem (razvlačenjem) pre i posle UV zračenja. Njihove mehaničke karakteristike su dobijene primenom video kontrolisanog sistema. Namena je da se uspostavi zavisnost između makroskopskog mehaničkog odgovora i molekularnih parametara, kao što je molekularna težina, i spoljnjih uticajnih pobuda, kao što je temperatura, brzina deformacije i UV zračenje. Razmatrane su interakcije degradacije svetlošću i promena u karakteristikama polimera.

INTRODUCTION

Considerable efforts are now focused on the degradation of polymers. The research of polymers which degrade in nature is fundamental from an ecological point of view. It is now well established that poly(lactic acid) (PLA) is classified as a biodegradable polymer, /1/. PLA is of great interest since it can exhibit properties close to conventional polymers /2/. This kind of material, derived from renewable resources like corn, is essentially used for food packaging. It is an aliphatic polyester produced from lactic acid. To form a polymer, monomers of lactic acid are linked together. PLA is obtained from the mixture of the lactide monomers with identical and enantiomeric stereocenters (L:L or D:D) and (L:D), respectively. The chemical structure of the repeating unit and its stereoisomers (L and D) are presented in Fig. 1. The PLA is completely amorphous if it contains high quantity of D-isomer, inversely the semi-crystalline PLA contains low amount of D-isomer. In the amorphous polymer, the formed macrochains are completely in disorder. It confers to the polymer its transparency, better mechanical properties and good manufacturing. Many studies reported in the literature, /2-4/, discuss the biodegradation of PLA by micro-organisms or enzymes,

and the resulting effects on its mechanical properties. It is well known that photodegradation alters the mechanical properties of polymers. In the case of PLA only few investigations deal with this subject, /5-8/.

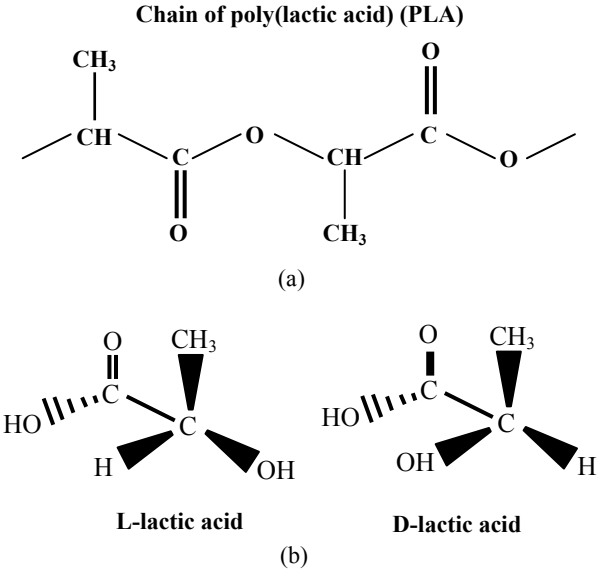

Figure 1. Chemical structure of PLA and its isomers: (a) chain of PLA, (b) the two isomeric forms of lactic acid L and D.
Slika 1. Hemijska struktura PLA i njegovog izomera: (a) PLA lanac, (b) dva izomerička (izomerna) oblika laktične kiseline L i D

In this work, the chemical and mechanical response of amorphous PLA films exposed to UV irradiation is examined.

EXPERIMENTAL

Material

PLA material for performed experiments was provided by Natureworks©. The 200 mm thick PLA layers were obtained by extrusion blowing. Depending on the ratio between D-isomer and L-isomer, PLA can be semi-crystalline or completely amorphous. The provided PLA grade contains 4.3% of D-isomer. Thermal analysis, achieved using a Perkin Elmer differential scanning calorimetry (DSC), showed negligible crystal content (< 1%). Therefore, the provided PLA grade can be considered as almost amorphous. A glass transition temperature of about 59°C was found by DSC. The number average molecular weight, M_n, and the weight average molecular weight, M_w, were evaluated as M_n = 100 250 g/mol and M_w = 198 300 g/mol, respectively. These data were obtained from gel permeation chromatography (GPC).

UV irradiation

PLA films were cut into rectangular shaped samples of dimension 120×190 mm^2. The source of UV irradiation was produced using a device (UV-Minicure©) equipped with an endless belt. The speed of the endless belt was 50 m/min. The dose attaining the PLA film was measured using a spectroradiometer. It was equal to nearly 57 mJ/cm^2 in the wavelength range of 295–400 nm for one pass under UV irradiation. Samples were exposed to UV irradiation for different times and passes. Exposure to UV irradiation was conducted at room temperature without the control of humidity rate.

Molecular weight measurements

The chemical degradation of PLA was revealed by using the variation of molecular weight of the linear polymer. To measure the molecular weight of irradiated and virgin PLA films, the GPC technique was adopted. Solutions of 5 ml of Tetrahydrofuran (THF) containing 50 mg of PLA film were prepared and filtered by using resistant filters with a pore diameter of 0.45 μm (hydrophobic polytetrafluoroethylene PTFE). The equipment was calibrated with polystyrene standards.

Mechanical measurements

The tensile experiments were carried out using an Instron© machine model 5800 connected to a video-controlled system (videotraction©). The local true axial strain rate (in the strain localization zone) was controlled by regulating the cross-head speed, /9/. Figure 2 presents the geometry of the sample used to characterize the mechanical behaviour of PLA films before and after ageing. The PLA films were stretched along their extrusion direction. Influence of the strain rate and temperature on the mechanical response of PLA films was also examined.

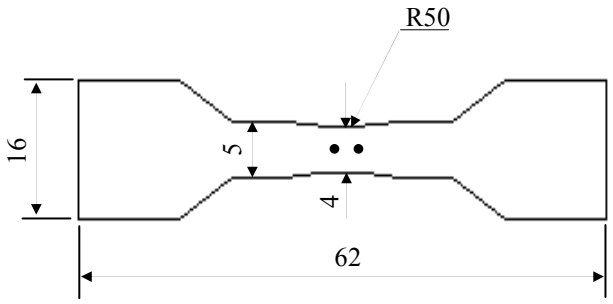

Figure 2. Geometry of tensile sample (dimensions in mm) used for videotraction© tests (the two round markers allow to determine the local true axial strain).
Slika 2. Geometrija uzorka za zatezanje (dimenzije u mm) za ispitivanje postupkom videotraktion© (dva označena kružića omogućavaju da se odredi stvarna lokalna aksijalna deformacija)

RESULTS AND DISCUSSION

Effects of temperature and strain rate

In general, the mechanical behaviour of polymers is sensitive to temperature and strain rate variation. As an example, Fig. 3 presents true stress-strain curves obtained under different strain rates at room temperature (about 25°C) and at a temperature of 50°C. The strain rate and temperature dependence of the yield stress is clearly pointed out. At room temperature, the stress-strain response is characterized by a stress drop after yield (strain softening) followed by a plateau. At this temperature the PLA films exhibit a brittle behaviour. Indeed, failure occurs at a strain of about 25%. It is characterized by the formation of macrocracks that lead to failure. At 50°C the polymer is more ductile and its strain at break increases up to ~150%. At small strains the PLA films show a strain softening phenomenon, but at large strains a very rapid strain harden-

ing response is highlighted. The macroscopic behaviour is characterized by the formation and development of a neck.

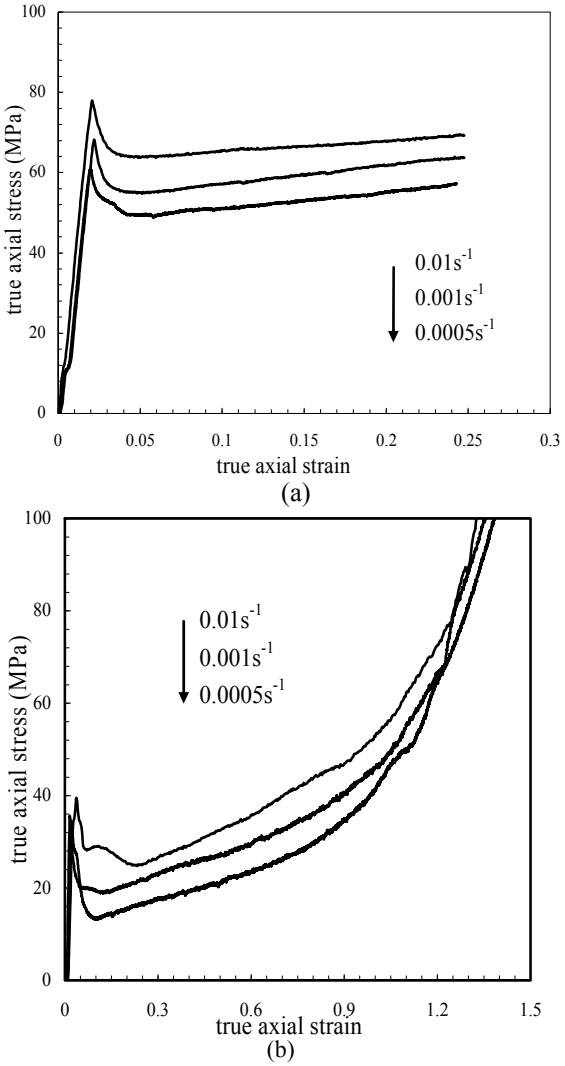

Figure 3. Stress-strain curves under different strain rates: (a) at 25°C; (b) at 50°C.
Slika 3. Krive napon–deformacija pri različitim brzinama deformacija: (a) na 25°C; (b) na 50°C

A stress-whitening phenomenon was observed during stretching. This can be attributed to craze formation, /10/.

Further investigations are presently in progress from a morphological point of view.

The temperature plays an important role on the failure properties. Figure 4 shows the local strain at break as a function of temperature in the range from 25 to 50°C: it increases markedly with the stretching temperature.

These experiments were conducted in order to choose the appropriate conditions for the study of PLA film ageing by UV irradiation. All measurements on the effect of UV irradiation on PLA were conducted using a strain rate of 0.001 s^{-1} and at a temperature of 50°C.

Effects of UV irradiation

The effects of UV irradiation on modifications of PLA properties from a chemical point of view were investigated by using the average molecular weights of the polymer as indicators of the photodegradation. They were determined by GPC. The experimental results are given in Table 1.

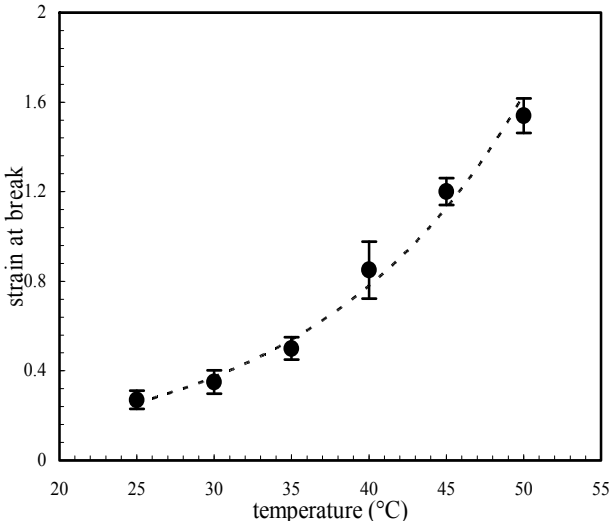

Figure 4. Strain at break as a function of temperature for a strain rate of 0.001 s^{-1}.
Slika 4. Deformacija pri lomu u funkciji temperature za brzinu deformacije 0.001 s^{-1}

Table 1. Gel permeation chromatography (GPC) results: Influence of UV irradiation on chemical properties of PLA films.
Tabela 1. Rezultati hromatografije prodiranja gela (GPC): uticaj UV zračenja na hemijske karakteristike PLA filmova

Irradiation dose	Average molecular weight	
	The number	The weight
	M_n	M_w
mJ/cm^2	g/mol	g/mol
0	100 250	198 300
3420	64 150	148 150
3990	65 550	148 800
5130	61 800	138 900
9120	58 150	131 150

One can see that both weight and number average molecular weights (M_w and M_n, respectively) decrease upon increasing UV dose. Here performed investigation showed that after a dose submission of 9120 mJ/cm^2 the number average molecular weight M_n drops to half the original value for the virgin PLA film (from M_n = 100 250 g/mol to M_n = 58 150 g/mol). Based on these experimental findings, one can conclude that chain scission is the predominant degradation mechanism in this case. The high energy of UV irradiation contributes to the activation of many reactions in the polymer. It is directly related to the experimental conditions (temperature, humidity, intensity of UV irradiation, wavelength of irradiation, history of manufacturing procedure and storage of polymer, but also many others) /8, 11, 12/. The behaviour of PLA films exposed to UV irradiation can be explained by different mechanisms including photo-oxidation and chain scission by photodecomposition of virgin PLA. According to literature, /5, 8/, it seems that PLA can be photodecomposed following the Norrish II mechanism, as recalled in Fig. 5.

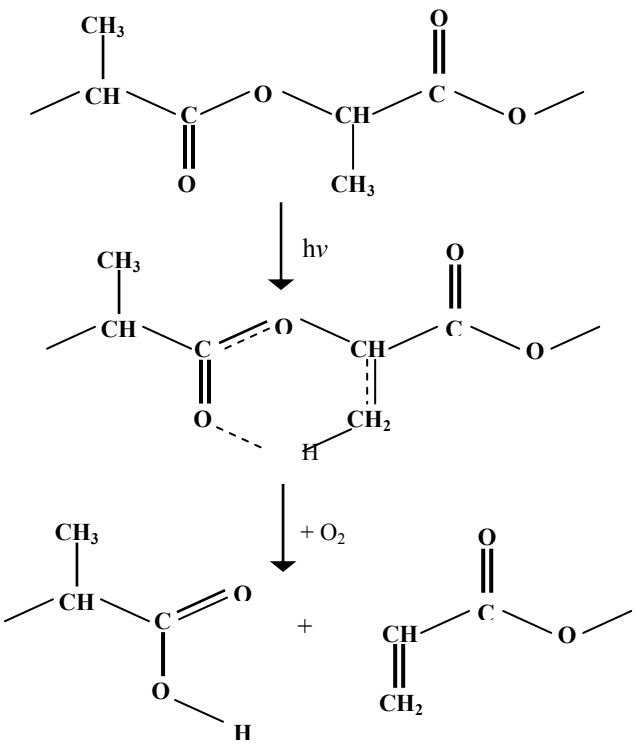

Figure 5. Photodegradation of PLA via Norrish II mechanism.
Slika 5. Degradacija PLA zbog svetlosti mehanizmom Noriš II

The degree of chain scission per macromolecule can be expressed by the following formula:

$$S = \frac{M_{n0}}{M_n} - 1 \tag{1}$$

where M_{n0} and M_n are the number average molecular weights before and after degradation, respectively.

Figure 6 gives the evolution of S in PLA chain versus emitted dose. The number of scissions begins to increase linearly with increasing dose, then, from a certain dose value, the scission rate levels off.

The mechanical behaviour of photodegraded PLA was examined at 50°C, a temperature close to the glass transition temperature. Note that the glass transition temperature may decrease upon UV irradiation, /7, 11/. From the experimental stress-strain curves, the following parameters were obtained: elasticity modulus, yield stress, stress and strain at the break. All mechanical properties of films subjected to UV irradiation for increasing exposure times are presented in Table 2.

A marked decrease of elastic modulus and yield stress is observed. When the PLA films are submitted to UV exposure, their capacity to develop plastic deformation is noticeably reduced. Indeed, a drop in stress and strain at break after photodegradation can be observed. It may be postulated that the process of chain scission strongly influences both stages of craze nucleation and growth, thus inducing fracture of stretched PLA films at an early stage of deformation. It is still however not straightforward to derive a clearcut explanation of how the mechanical properties of photodegraded PLA films depend on chemical degradation and related polymer physical structure evolution.

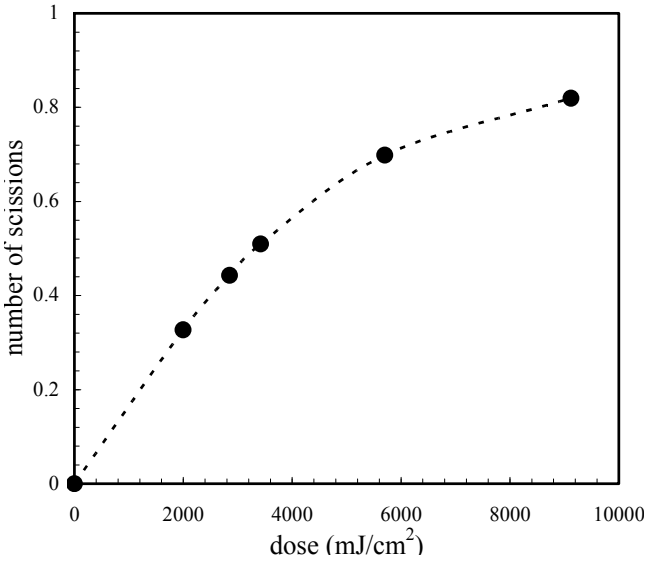

Figure 6. Number of scissions as a function of emitted dose.
Slika 6. Broj odsečaka u zavisnosti od emitovane doze

Table 2. Influence of UV irradiation on mechanical properties of PLA films at 50°C.
Tabela 2. Uticaj UV zračenja na mehaničke karakteristike PLA filma na 50°C

Irradiation dose	Elasticity modulus	Yield stress	Parameters at break	
			Stress	Strain
	E	σ_Y	σ_m	δ
mJ/cm^2	MPa	MPa	MPa	%
0	3884	35.5	165	1.54
1995	3257	29.5	121.5	1.43
2850	2689	22	100.5	1.37
3420	2411	22	87	1.32
5700	1142	18	72	1.28
9120	1011	10	66	1.27

Considering the average molecular weight as a pertinent parameter of the photodegradation, a relationship between the macroscopic mechanical properties and the photodegradation parameter M_n may be established by means of a typical Flory law:

$$q = q_\infty - \frac{C}{M_n} \tag{2}$$

where q is the mechanical property of concern, C is a material parameter and q_∞ represents the q value of an hypothetical sample with an infinite molecular weight.

Table 3 presents the values of C and q_∞ for the elastic modulus, the yield stress, the stress and strain at break. These mechanical properties are plotted as a function of the photodegradation parameter in Figures 7 and 8.

Respecting the stretching behaviour of the photodegraded polymer, many parameters may be operative at the molecular level. Decrease in the local entanglement density relating to chain scission is a primary one, but the presence of small molecules as byproducts of chain scission may not be excluded, with the consequence of plastification effect.

Table 3. Values of parameters C and q_∞ of Flory law.
Tabela 3. Vrednosti parametara C i q_∞ za zakon Flori

Parameters		C	q_∞
Elasticity modulus		$4\ 10^8$ MPa.g/mol	7878.7 MPa
Yield stress		$3\ 10^6$ MPa.g/mol	66.8 MPa
Parameters	Stress	10^7 MPa.g/mol	285.2 MPa
at break	Strain	$3.5\ 10^4$ g/mol	1.88 MPa

Regarding the latter point, it may have a strong influence on the yield stress and elasticity modulus values since the mechanical tests are performed in the vicinity of the glass transition temperature. Regarding the crazing process, local cavitation may be eased, in favour of craze nucleation. It is worth noting that the small strain parameters are more markedly affected than the ultimate properties, thus inferring that the global entanglement network is not primarily concerned, in agreement with the molecular weight distribution data.

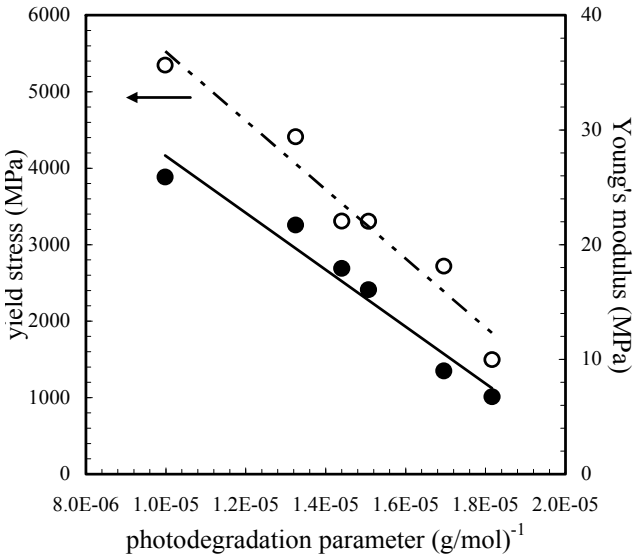

Figure 7. Young's modulus and yield stress as a function of the photodegradation parameter (symbols: experiment; lines: Flory law).
Slika 7. Modul elastičnosti i napon tečenja u funkciji parametra degradacije svetlošću (simboli: eksperiment; linije zakon Flori)

CONCLUSION

In this work, the chemo-mechanical behaviour of amorphous PLA films exposed to UV irradiation was investigated. Experimental results demonstrate that GPC technique and video-controlled tensile testing measurements are useful methods for investigating changes in chemical and mechanical properties of PLA caused by UV irradiation. The decrease of the length of molecules by chain scission during photodegradation yields a reduction in average molecular weights of PLA. This is accompanied by the deterioration of mechanical properties, such as elasticity modulus, yield stress and properties at fracture (break).

A complex interplay of local chain scission, local entanglement density evolution and plastification may be evoked in order to account for the observed behaviours. Ongoing work is focused at elucidating their respective roles in the photodegradation process.

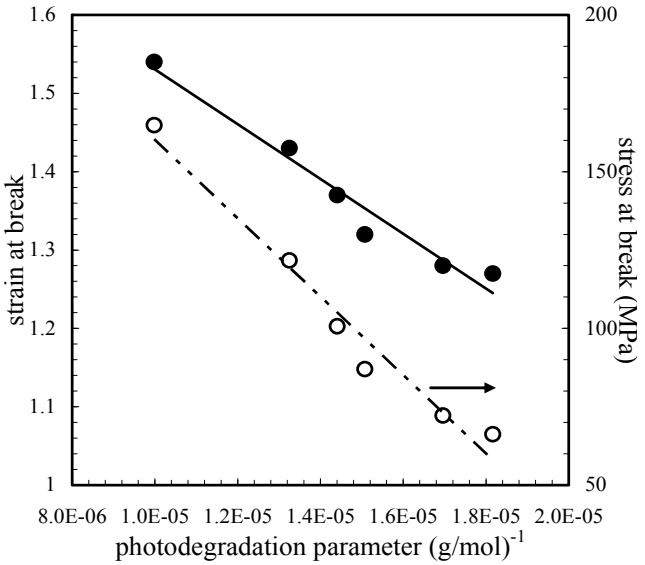

Figure 8. Stress and strain at break as a function of photodegradation parameter (symbols: experimental data, lines: Flory law).
Slika 8. Napon i deformacija pri lomu u funkciji parametra degradacije svetlošću (oznake: eksperiment, linije: zakon Flori)

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