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

UTICAJ ULTRALJUBILJASTOG ZRAČENJA NA ZATEZNE KARAKTERISTIKE AMORFNOG FILMA POLILAKTIDA

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

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.

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/. 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.

Keywords
• polylaktid – poli(laktična kiselina)
• ultraljubičasto (UV) zračenje
• molekularna težina
• mehaničke karakteristike

Izvod
U radu je analiziran uticaj ultraljubičastog (UV) zračenja na mehaničke karakteristike amorfog filma biorazgradljive poli(laktične kiseline) (PLA). Film PLA je bio izložen UV zračenju tokom rastućeg vremenskog perioda. Izvedene su dve vrste eksperimenata, hemijski i mehanički. 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 izmedju makroskopskog mehaničkog odgovora i molekularnih parametara, kao što je molekularna težina, i spoljnih uticajnih pobuda, kao što je temperatura, brzina deformacije i UV zračenje. Razmatrane su interakcije degradacije svetlosću i promena u karakteristikama polimera.
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/.

![Chemical structure of PLA and its isomers: (a) chain of PLA, (b) the two isomeric forms of lactic acid L and D.](image)

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 $M_n = 100250$ g/mol and $M_w = 198300$ g/mol, respectively. These data were obtained from gel permeation chromatography (GPC).

**UV irradiation**

PLA films were cut into rectangular shaped samples of dimension $120 \times 190$ mm$^2$. The source of UV irradiation was 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.

![Geometry of tensile sample (dimensions in mm) used for videotraction© tests (the two round markers allow to determine the local true axial strain).](image)

**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-
The macroscopic behaviour is characterized by the formation and development of a neck.

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

\[
\text{Table 1. Gel permeation chromatography (GPC) results: Influence of UV irradiation on chemical properties of PLA films.}
\]

<table>
<thead>
<tr>
<th>Irradiation dose (mJ/cm²)</th>
<th>Average molecular weight</th>
<th>The number</th>
<th>The weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M_n )</td>
<td>( M_w )</td>
<td>( g/mol )</td>
</tr>
<tr>
<td>0</td>
<td>100 250</td>
<td>198 300</td>
<td></td>
</tr>
<tr>
<td>3420</td>
<td>64 150</td>
<td>148 150</td>
<td></td>
</tr>
<tr>
<td>3990</td>
<td>65 550</td>
<td>148 800</td>
<td></td>
</tr>
<tr>
<td>5130</td>
<td>61 800</td>
<td>138 900</td>
<td></td>
</tr>
<tr>
<td>9120</td>
<td>58 150</td>
<td>131 150</td>
<td></td>
</tr>
</tbody>
</table>

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/cm² 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 photooxidation 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.
The degree of chain scission per macromolecule can be expressed by the following formula:

\[ S = \frac{M_n}{M_n^0} - 1 \]  

(1)

where \( M_n \) and \( M_n^0 \) 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.

Table 2: Influence of UV irradiation on mechanical properties of PLA films at 50°C.

<table>
<thead>
<tr>
<th>Irradiation dose (mJ/cm²)</th>
<th>Elasticity modulus (MPa)</th>
<th>Yield stress (MPa)</th>
<th>Parameters at break</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3884</td>
<td>35.5</td>
<td>165</td>
<td>1.54</td>
</tr>
<tr>
<td>1995</td>
<td>3257</td>
<td>29.5</td>
<td>121.5</td>
<td>1.43</td>
</tr>
<tr>
<td>2850</td>
<td>2689</td>
<td>22</td>
<td>100.5</td>
<td>1.37</td>
</tr>
<tr>
<td>3420</td>
<td>2411</td>
<td>22</td>
<td>87</td>
<td>1.32</td>
</tr>
<tr>
<td>5700</td>
<td>1142</td>
<td>18</td>
<td>72</td>
<td>1.28</td>
</tr>
<tr>
<td>9120</td>
<td>1011</td>
<td>10</td>
<td>66</td>
<td>1.27</td>
</tr>
</tbody>
</table>

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:

\[ q = q_\infty - \frac{C}{M_n} \]  

(2)

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

Table 3 presents the values of \( C \) and \( q_\infty \) 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.
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.

### Table 3. Values of parameters $C$ and $q_\infty$ of Flory law.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$C$</th>
<th>$q_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elasticity modulus</td>
<td>$4 \times 10^7$ MPa g/mol</td>
<td>7878.7 MPa</td>
</tr>
<tr>
<td>Yield stress</td>
<td>$3 \times 10^6$ MPa g/mol</td>
<td>66.8 MPa</td>
</tr>
<tr>
<td>Parameters at break</td>
<td>Stress</td>
<td>$10^7$ MPa g/mol</td>
</tr>
<tr>
<td>at break</td>
<td>Strain</td>
<td>$3.5 \times 10^4$ g/mol</td>
</tr>
</tbody>
</table>

**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.

### REFERENCES