



# Effects of electron radiation on properties of PLA

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## ABSTRACT

**Purpose:** The aim of the paper was to examine the effects of electron radiation on physicochemical properties of pristine poly(lactic acid) (PLA), or polylactide, and of polylactide containing a selected crosslinking agent.

**Design/methodology/approach:** Samples to be examined were prepared in granulated forms or as moulded pieces and then treated with the high-energy electron radiation (ca. 10 MeV). The methods of gel permeation chromatography (GPC), rheology, Fourier transform infrared (FTIR) spectroscopy, and dynamic mechanical thermal analysis (DMA) were used to determine physicochemical properties of the samples. A humidity sensor was utilised to determine water vapour permeability.

**Findings:** It has been found that PLA undergoes degradation upon the electron radiation. Triallyl isocyanurate (TAIC) when introduced into polylactide causes plasticization of this polymer whereas irradiation of polylactide containing TAIC leads to crosslinking of PLA. Crosslinked PLA exhibits limited plastic flow or no flow at all and an elevated glass transition temperature. Water vapour permeability of a film made of PLA modified this way is much less than that of a film produced from original PLA.

**Research limitations/implications:** Further studies of crosslinked PLA are advisable, especially assessment of the gelation degree, strength of the plasticized material, and biodegradation.

**Practical implications:** Crosslinked PLA may be applied in practical processes, especially in thermoforming in which increased resistance of a material against deformation at elevated temperatures is required.

**Originality/value:** Substantial influence of the electron radiation on properties of PLA was established. The material undergoes significant degradation upon even relatively small radiation doses. In order to crosslink PLA, TAIC in the amount of ca. 3 wt% and the electron radiation doses of up to ca. 60 kGy have to be applied.

**Keywords:** Biodegradable plastics; Polylactide; Crosslinking; Electron radiation

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## MATERIALS

## 1. Introduction

Nowadays, plastics constitute a rapidly developing area of global economy, which is indicated by its growing production equal to ca. 230 mln tones in 2009 [1]. The kind of plastics that have recently become very important at global markets are biodegradable polymers. Considerable progress in technology as well as development of new methods for manufacture of these polymers, the most of which may be processed with commonly used machines, installations, and techniques (extrusion moulding, injection moulding, blow moulding, and thermoforming), significantly contributed to increasing application of the biodegradable polymers. These plastics are being used not only in medicine and tissue engineering but also in manufacturing of everyday items, e.g., packaging for food products. At the same time, better and better availability, lower prices, and beneficial properties of these polymers have initiated in many scientific research institutions a number of studies on syntheses of novel biodegradable materials, which in turn may contribute to further lowering of both product prices and costs associated with environmental protection.

Poly(lactide), or poly(lactic acid) (PLA), is one of important biodegradable polymers, which may become a significant polymer of the 21<sup>st</sup> century [2-8]. It is the most easily available biodegradable polymer produced from renewable resources. Beside many advantages, such as biodegradability, biocompatibility, low energy consumption, and easiness of processing, PLA exhibits also some disadvantages, like mostly brittleness and low tensile strength in the plasticized state. These features limit the scope of applications and possibilities to process this plastic, including thermoforming. Nevertheless, they strongly stimulate development of the methods aiming at improvement of functional qualities of PLA.

PLA (Fig. 1) may exhibit various physicochemical properties that essentially result from the chemical structure of this polymer.

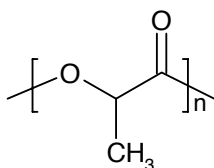


Fig. 1. Structural formula of PLA

The PLA chemical structure significantly depends on the way the technological process (Fig. 2) of polymerisation of a monomer, i.e., lactide (LA), was performed. As a result, different forms of PLA may be obtained. These are as follows:

- L(+)-PLA, where each monomeric unit of a PLA macromolecule shows a specific rotation L;
- D(-)-PLA, where each monomeric unit of a PLA macromolecule shows a specific rotation D;
- L,D PLA, where monomeric units of a PLA macromolecule show both specific rotations (either L or D).

The forms L(+)-PLA and D(-)-PLA exhibit high tensile strength ( $\sigma_M = 60-70$  MPa), low tensile strain at break ( $\epsilon_B \cong 3\%$ ),

similar glass transition temperatures ( $T_g \cong 65^\circ\text{C}$ ) and melting points ( $T_m = 160-180^\circ\text{C}$ ), as well as relatively high crystallinity ( $X \leq 60\%$ ) and density ( $d = 1.2-1.3$  g/cm<sup>3</sup>) [4,9].

Physicochemical properties of the L,D PLA form firstly depend on the ratio of the number of monomeric units of the specific rotation L to the number of monomeric units of the specific rotation D. PLA, in which macromolecules are composed of equal numbers of such monomeric units, i.e., racemic PLA, is of inferior mechanical properties, lower  $T_g$  ( $57^\circ\text{C}$ ), and it undergoes degradation more quickly as compared to L(+)-PLA or D(-)-PLA; it is also amorphous. As the racemisation degree increases, i.e., the numbers of the monomeric units L and D become more and more even, the properties of PLA vary significantly [10,11]. That is why the PLA materials are often specified by the contributions of the units L or D. There exist also so-called stereocomplexes of PLA, i.e., blends of L(-)-PLA and D(+)-PLA. They exhibit higher values of  $T_m$  ( $230^\circ\text{C}$ ) but are not easy to obtain and are more expensive than the remaining forms of PLA.

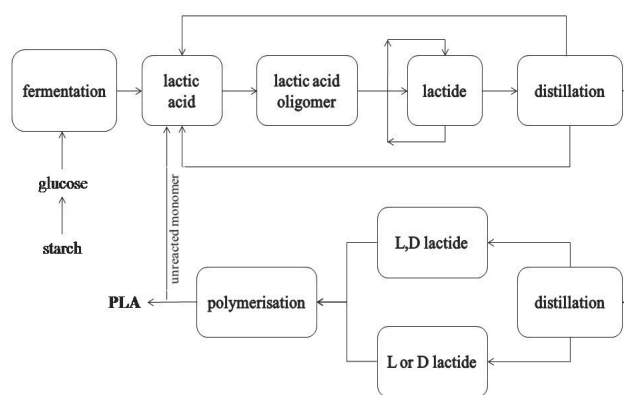


Fig. 2. Scheme of a technological process for manufacture of PLA

Several forms of PLA, designed for various applications, are being manufactured. These forms differ in the fractions of the monomeric units L and D, degree of branching, and average molecular weight. In 1987, the Cargill Corporation (USA), followed some time later by Japanese companies, initiated a project aiming at the development of a technology of manufacturing PLA on a large scale. Now, NatureWorks LLC [12] produces various forms of PLA labelled with a trademark NatureWorks®, e.g., 1000D for lamination, 2000D for extrusion moulding of a thermoformed film, 3000D for injection moulding, 4000D to manufacture a biaxially oriented film, and 6000D to manufacture PLA fibres [12].

Mechanical, thermal, and processing properties of PLA may be modified by making composites or nanocomposites containing some additives, like fillers, nucleants, nanocompounds, or fibres, for which PLA constitutes a matrix. Also, PLA may be blended with other biodegradable polymers of various beneficial properties or be subjected to grafting or copolymerisation in order to improve its properties [13-22].

However, scientific papers or technological reports on radiational modification of properties of biodegradable polymers

are scarce. Few available publications on various methods for the radiation treatment of PLA do not fully explain the process involved. This treatment is most often being performed while using  $\gamma$  radiation or electron radiation [23-25].

The purpose of the present work was to examine the influence of the electron radiation on properties of pristine PLA and of PLA containing various amounts of TAIC. The work included (i) preparation of samples, (ii) irradiation of samples, (iii) assessment of average molecular weight of PLA irradiated with different doses, (iv) rheological measurements, (v) determination of melt flow index (MFI), (vi) FTIR spectra acquisition, (vii) DMA tests, and (viii) water vapour permeability measurements.

## 2. Experimental

### 2.1. Materials

The following materials were used in this work:

- Polylactide (PLA), type 2002D (NatureWorks<sup>®</sup>, USA), characterized by the melt flow index (MFI) equal to 2.7 g/10 min (2.16 kg, 190°C), density  $d = 1.24 \text{ g/cm}^3$ , average molecular weight of ca. 155 500 Da, and content of monomeric units D and L equal to 3.5 and 96.5%, respectively. Its structural formula is shown in Fig. 1.
- Triallyl isocyanurate (TAIC) (Sigma-Aldrich GmbH, Germany), utilised in a liquid state. Its structural formula is shown in Fig. 3.

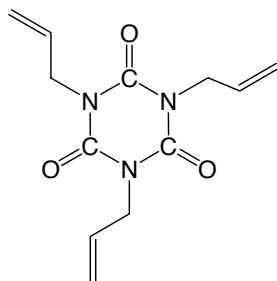


Fig. 3. Structural formula of TAIC

### 2.2. Sample preparation

Granulated samples were obtained using a single-screw extruder, type PlastiCorder PLV 151 (Brabender, Germany), with a screw diameter of 19.5 mm, the length/diameter ratio of 25, and the volume of a plasticizing channel reduced in proportion of 3:1. The device was also equipped with a two-opening die, belt conveyor together with a system of eight cooling fans, granulator, volumetric feeder, and dropper. The zone beneath the hopper was cooled by air blowing. The temperatures of barrel heating zones I, II, and III and of the die of the extruder were set to 180, 190, 190, and 190°C, respectively. The screw rotational speed was constant (100 rpm). The crosslinking agent was dropped into zone I with a rate resulting in the concentrations of 1, 3, or 5% with respect to PLA. Symbols of all the prepared granulated samples are summarized in Table 1.

Table 1.

Symbols of prepared granulated samples

Composition	Radiation dose [kGy]					
	0	10	20	40	60	90
PLA	P0	P1	P2	P4	P6	P9
PLA/TAIC, 99/1	1T0	1T1	1T2	1T4	1T6	1T9
PLA/TAIC, 97/3	3T0	3T1	3T2	3T4	3T6	3T9
PLA/TAIC, 95/5	5T0	5T1	5T2	5T4	5T6	5T9

Using a laboratory injection moulding press type Plus 35 (Battenfeld GmbH, Germany) and the prepared granulated materials, normalized samples were produced in the forms of dumbbells and bars, according to a proper standard [26]. The moulded pieces were designated with the same symbols as those for the granulated materials.

Sample irradiation was carried out with the use of a linear accelerator type LAE 13/9 (Fig. 4), located at the Institute of Nuclear Chemistry and Technology in Warsaw, Poland.

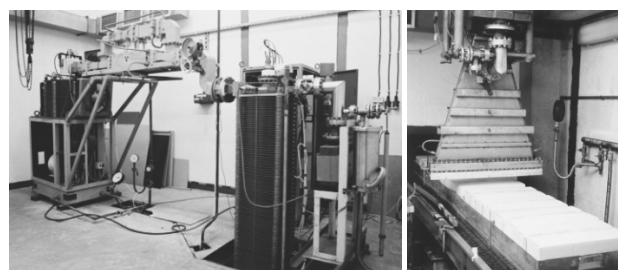


Fig. 4. Electron linear accelerator (on the left: an electron gun and accelerating system; on the right: output window of the accelerator chamber and belt conveyor)

The samples were irradiated with the doses of 10, 20, 40, 60, or 90 kGy. The maximum individual dose was 40 kGy. It was limited by an increase in temperature of the irradiated material, equal to ca. 4-7°C for an individual dose of 10 kGy. Large individual doses cause intensive heating of the material; thus, some additional structural changes may occur. Therefore, several samples were irradiated two or three times, as specified in Table 2.

Table 2.

Doses used for sample irradiation

Total absorbed dose [kGy]	Multiplicity of irradiating dose
10	1×10 kGy
20	1×20 kGy
40	1×40 kGy
60	1×20 kGy + 1×40 kGy
90	1×10 kGy + 2×40 kGy

During the irradiation procedure, all the granulated samples and moulded pieces were placed in aluminium containers in single layers of the thickness of up to 2 mm. The containers were put on the belt conveyor moving at the speed of 0.3-1.2 m/min. The actual speed was related to the radiation dose absorbed by a polymer material being modified.

### 2.3. Methodology of research

The assessment of average molecular weight was made by the method of the gel permeation chromatography (GPC), using a LabAlliance gel chromatograph and Jordi Gel DVB Mixed Bed chromatography column (10×250 mm). A refractive detector of the detection temperature of 35°C and chloroform as the eluent were utilised. The chromatograph was calibrated using polystyrene as a reference material. Filtrates obtained due to dissolution of granulated samples in chloroform within 48 h were examined.

Rheological tests were performed with the use of a Haake Rotovisco RT20 rotational rheometer operating in an oscillation mode and utilising a plate/plate measuring system. The measurements were carried out at 165°C over the frequency range of 0.01-40 Hz. The examined samples in the form of moulded pieces were prepared by hot pressing of a granulated material, using a hydraulic press. During the rheological tests, changes in both viscosity ( $\eta$ ) and modulus of elasticity ( $G'$ ) were recorded.

Determination of the melt flow index (MFI) was carried out according to a relevant standard [27] with a capillary plastometer type LMI 4003 (Dynisco, Germany). The measurements were made at 190°C under the piston loading of 2.16 kg.

Examinations of an upper layer of the moulded pieces were performed by the FTIR spectroscopy, using a Nicolet iS10 instrument (Thermo Scientific, USA). The technique of attenuated total reflectance (ATR) was applied over the wavenumber range of 4000-400  $\text{cm}^{-1}$ . Averages of 16 spectra (scans) were accepted as final results.

The DMA tests were executed by a dynamic thermo-mechanical analyzer type Q800 (TA Instruments, USA). One-point bending of a 15  $\mu\text{m}$  amplitude and 1 Hz frequency was applied over the temperature range of 25-200°C at the heating ramp of 3°C/min [28,29].

The assessment of water vapour permeability was carried out according to a proper standard [30], with the use of an L80-5000 instrument (PBI-Dansensor, Denmark). The tests were performed by using a humidity sensor, at a constant temperature of 38°C and relative humidity of 90%. Samples in the form of a circular film fragment with a 50 mm radius and ca. 100  $\mu\text{m}$  thickness were utilised. The samples were conditioned prior to the tests by being held at 23±1°C for 24 h and at a relative humidity of 50±5%.

## 3. Results

### 3.1. Average molecular weight

The GPC results revealed a significant influence of the electron radiation on samples P (pristine PLA). As found, the number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) clearly decrease upon the radiation (Table 3). The number-average molecular weight of PLA diminishes upon the maximum dose (90 kGy) by ca. 74% and the weight-average molecular weight, by ca. 57%. The polydispersion degree ( $PD = M_w/M_n$ ) does not essentially vary, except a substantial increase upon the maximum dose, indicating a larger dispersion of PLA macromolecule sizes. The electron radiation

causes cracking of chemical bonds in the PLA macromolecules, due to which various radicals appear (Fig. 5). Thus, degradation of PLA occurs upon the radiation.

Table 3.

Average molecular weights ( $M_n$  and  $M_w$ ) and polydispersion degrees ( $PD$ ) for individual P samples

Sample	$M_n$ [Da]	$M_w$ [Da]	$PD$
P0	155500	360600	2.32
P1	114300	262900	2.30
P2	85700	198100	2.31
P4	61300	168900	2.76
P6	49700	136500	2.75
P9	40700	155800	3.83

The radical (a) forms due to dehydrogenation occurring at a secondary carbon atom in a PLA macromolecule. The radicals (b) and (c) occur as a result of cracking of a C-C bond present in a monomeric unit of PLA. Formation of the radicals (d) and (e) is less probable because they can occur after cracking of a C-O bond present in the main chain of a PLA macromolecule. Radicals of the (a) type are the most stable and most prevalent among the radicals forming in PLA upon ionising radiation [31-33].

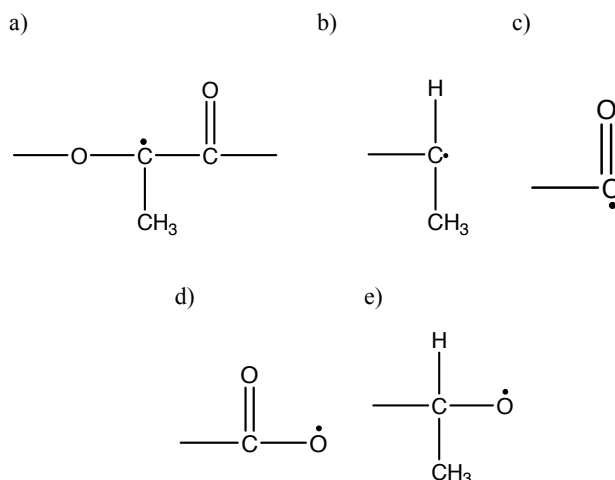


Fig. 5. Structural formulae of various radicals formed in PLA upon electron radiation (see text)

The discussed structures may then (i) undergo mutual recombination, (ii) undergo recombination with a low molecular weight radical, (c) cause transfer of a radical from a polymeric chain to a molecule of initiator, monomer, or solvent, (d) undergo disproportionation or exchange. Thus, the electron radiation may initiate formation of new chemical compounds, including oligomers and polymers of physicochemical properties differing from those of PLA. The GPC results indicate that oligomeric derivatives of lactic acid form most probably.

### 3.2. Rheology

The rheological tests confirm that PLA degradation occurs upon the electron radiation (Figs. 6 and 7). The test results are shown in the form of surface diagrams, obtained with the use of a computer program STATISTICA 8. Fig. 6 shows that PLA viscosity significantly decreases as the radiation dose increases. This quantity diminishes also when the oscillation frequency of the rheometer rises, which is associated with the growth of both shearing forces and temperature. As follows from the figure, major changes in the viscosity occur already at small doses (10 or 20 kGy) and low frequencies (up to 10 Hz). This indicates a substantial susceptibility of the examined material to degradation upon the electron radiation and shearing forces.

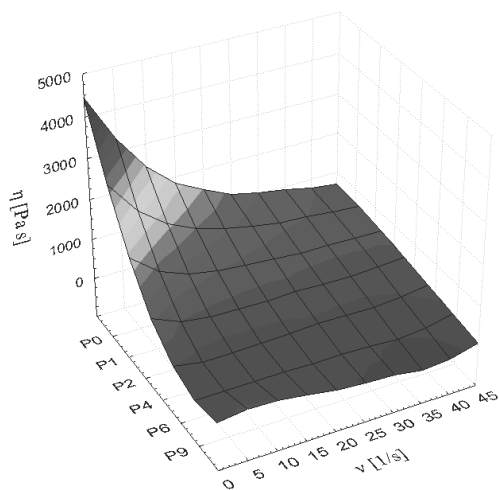


Fig. 6. Viscosity ( $\eta$ ) of individual P samples vs. rheometer oscillation frequency ( $\nu$ )

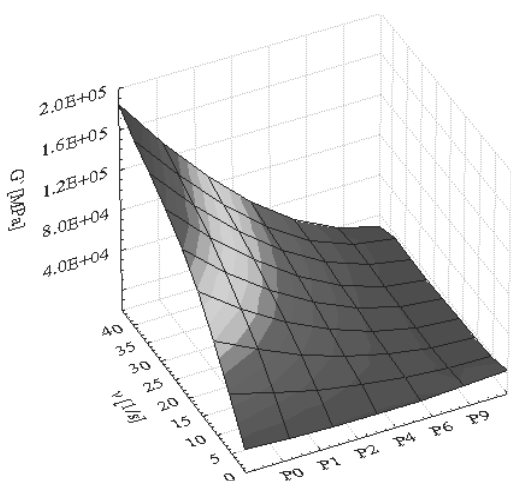


Fig. 7. Modulus of elasticity ( $G'$ ) of individual P samples in plasticized state vs. rheometer oscillation frequency ( $\nu$ )

Strong degrading effect of the electron radiation on PLA is also reflected in Fig. 7 that shows changes in modulus of elasticity ( $G'$ ) of PLA in plasticized state.

It follows from Fig. 7 that the modulus of elasticity ( $G'$ ) decreases as the radiation dose increases, the changes being larger at higher frequencies. This suggests worsening of elastic properties of PLA modified by irradiation. However, the modulus increases with the rising oscillation frequency, especially for the non-modified sample or samples irradiated with doses up to 20 kGy. For doses above 20 kGy, changes in the modulus are relatively small, which may result from substantial degradation of PLA and major variations in viscosity of individual samples do not occur any more.

Significant degradation of PLA upon the electron radiation has been confirmed by our other studies, including, e.g., melt flow index measurements, static tensile strength tests, and impact strength tests [34,35].

The investigation results show that PLA deteriorates upon the electron radiation, mainly because macromolecules become shorter, the molecular weight decreases, and mechanical properties worsen. In order to limit the degradation of PLA and improve some properties of it, introduction of additional components into this polymer is necessary. TAIC (Fig. 8) is one of such possible additives. It is a multifunctional, low molecular weight compound containing three allyl groups in a molecule. These groups ( $-\text{CH}_2-\text{CH}=\text{CH}_2$ ) decompose into pairs of free radicals (Fig. 8), when the compound absorbs energy quanta of the electron radiation. One of these radicals may recombine with a hydrogen atom detached from PLA whereas the other, with the radical created at the secondary carbon atom of a PLA macromolecule. This way, a cross-linkage between PLA chains is formed through a TAIC molecule. As a result, two or three allyl groups of TAIC combine with two or three macromolecules of PLA [36].

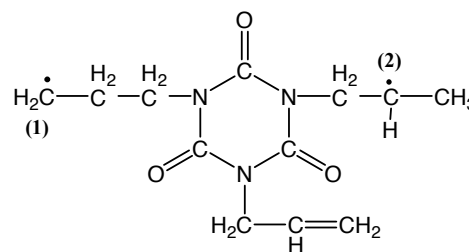


Fig. 8. Possible sites of radical formation in a TAIC molecule

The combined effect of the electron radiation and TAIC may cause crosslinking of PLA, the result of which should depend on the applied radiation dose and used amount of the crosslinking agent, i.e., amount of TAIC.

### 3.3. Melt flow index

Results of the MFI measurements are presented in Figs. 9 and 10. It follows from Fig. 9 that PLA undergoes degradation upon the electron radiation. As the radiation dose rises, MFI of P samples strongly increases, e.g., by 440% for sample P1 and by 6733% for sample P9, with respect to sample P0.

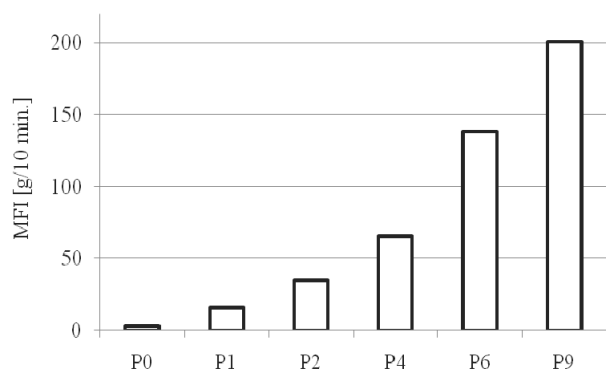


Fig. 9. Melt flow index for individual P samples

PLA samples containing various amounts of TAIC (1, 3, or 5 wt%) exhibit increased, with respect to pristine PLA, values of MFI, which evidences the plasticizing effect of this component. The larger the content of TAIC, the greater the value of MFI, which increases maximum by ca. 630%, as observed for sample 5T0 (Fig. 10).

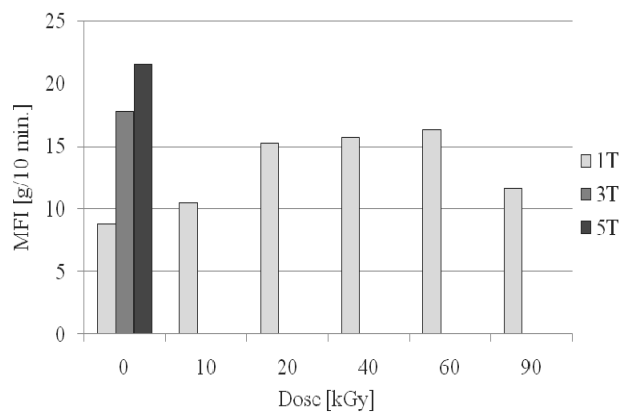


Fig. 10. Melt flow index for individual T samples

For samples containing 1 wt% of TAIC, the increase in MFI with the rising radiation dose is smaller in relation to the P samples. This suggests that two processes, crosslinking and degradation, occur simultaneously. Irradiated sample 1T still exhibits greater MFI as compared to sample P0, indicating that degradation occurs in this material. At the same time, the increase in MFI is not as high as in the case of irradiated P samples, which demonstrates that some crosslinking occurs in sample 1T. Introduction of 3 wt% of TAIC and irradiation cause a significant decrease in MFI. The dose as low as 10 kGy reduces MFI by 98% (sample 3T1, Fig. 10). When the dose is above 20 kGy, the material cannot be extruded through a plastometer die, which evidences considerable crosslinking of PLA. The 5-wt% content of TAIC and irradiation cause similar effects as in the case of the 3-wt% content of TAIC. Thus, 3 wt% of TAIC is sufficient to achieve radiational crosslinking of PLA.

### 3.4. Decay of double bonds of the crosslinking agent

Figs. 11 and 12 present some FTIR data for the studied samples. The spectra of samples 3T (Fig. 11) include (at  $\lambda = 1645 \text{ cm}^{-1}$ ) a band additional in relation to the spectra of samples P. It is attributed to a vinyl group and its intensity decreases as the electron radiation dose increases.

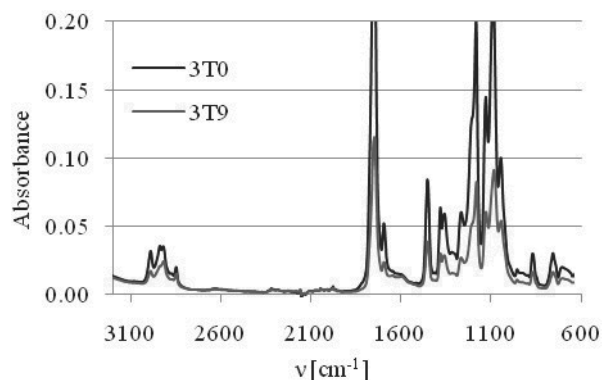
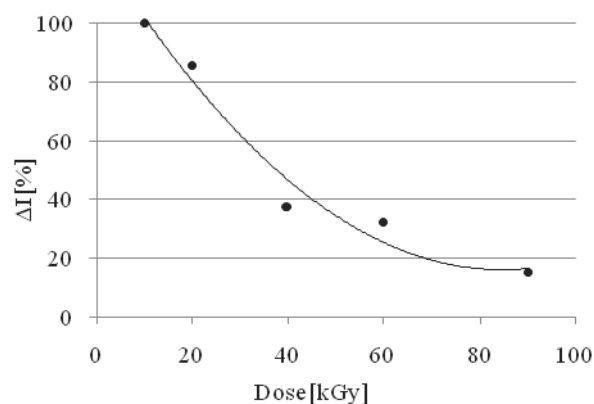


Fig. 11. FTIR spectra of samples 3T0 and 3T9

Fig. 12 illustrates decay of the number of the C=C bonds of the TAIC allyl groups.

Fig. 12. Relative change ( $\Delta I$ ) in absorption band intensity of the vinyl group ( $\lambda = 1645 \text{ cm}^{-1}$ ) for individual samples 3T

The double bond decay, reflected by a decrease in the absorption band intensity of the vinyl group, indicates formation of radicals in TAIC molecules, which participate in creating cross-linkages between PLA chains.

### 3.5. Glass transition temperature

Results from the DMA method show that PLA containing 3 wt% of TAIC exhibits a lower glass transition temperature ( $T_g$ ) as compared to non-modified PLA (Fig. 13). It means that TAIC is a good plasticizer of PLA. As Fig. 13 shows,  $T_g$  of samples

containing TAIC increases with the rising radiation dose. The maximum value of  $T_g$  is already observed for the dose of 60 kGy. Larger doses do not practically affect that value.  $T_g$  of pristine PLA (samples P) slowly diminishes as the radiation dose increases, which confirms growing degradation of PLA.

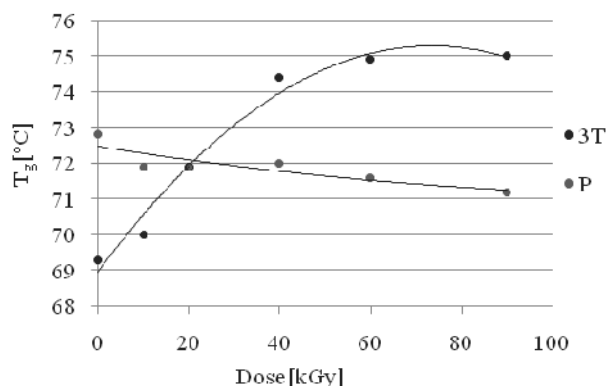


Fig. 13. Glass transition temperatures ( $T_g$ ) for individual samples P and 3T

### 3.6. Water vapour permeability

Modification of PLA properties by irradiation is being used for practical applications. Products made of PLA containing TAIC and modified by irradiation exhibit improved functional qualities, e.g., superior barrier property (lower water vapour permeability) in relation to non-modified products. This is confirmed by the results of water vapour permeability measurements, presented in Fig. 14.

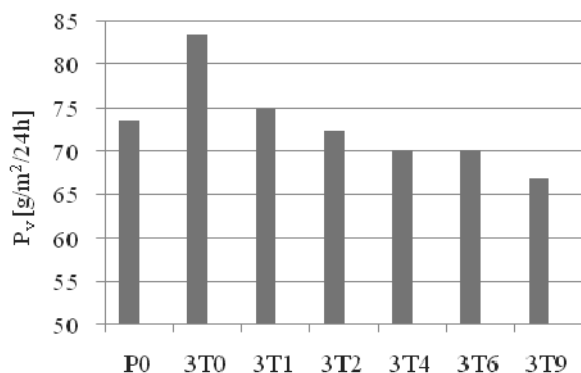


Fig. 14. Rates of water vapour transmission ( $P_v$ ) through films made of modified PLA

As follows from the figure, water vapour permeability of the film produced from non-irradiated PLA and containing 3 wt% of TAIC is greater than that of the film made of original PLA. It may be associated with a plasticizing effect of TAIC introduction and, thus, easier diffusion of water molecules through the 3T0 film. The 3T1 film exhibits slightly greater permeability as well. Presumably, the plasticizing effect in this sample due to TAIC

prevails over the crosslinking effect due to irradiation. For doses above 10 kGy, the water vapour permeability gradually decreases because of growing crosslinking of PLA.

## 4. Conclusions

- Polylactide (PLA) belongs to a group of the best recognised biodegradable polymers. New ways of manufacture and improvement of properties of PLA cause rapid lowering of price and better availability of this polymer. However, in spite of many beneficial properties, this plastic exhibits some disadvantages that preclude it from or limit its application in many areas. As a consequence, PLA properties have to be modified by physical and/or chemical methods.
- Crosslinking is one of these methods, which can especially be advantageous when PLA is meant to be applied in manufacture of rigid films designed for thermoforming or of products of increased thermal resistance, being used at elevated temperatures.
- Crosslinking of polylactide is a novel issue, which is evidenced by a small number of publications on this subject. The existing reports on the PLA crosslinking are fragmentary. This implicates necessity to perform suitable research and technological work.
- The electron radiation itself causes no crosslinking of PLA. Instead, degradation and worsening of both processing properties and functional qualities of the polymer occur.
- In order to crosslink PLA by the electron radiation, introduction of a crosslinking agent to the polymer is required. Such agent has to be a multifunctional, low molecular weight compound.
- Triallyl isocyanurate is one of the effective crosslinking agents. Introduction of this compound to PLA followed by treatment with the electron radiation yields plastic of improved physicochemical properties and functional qualities.

## Acknowledgements

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