

Compositional, physical and chemical modification of polylactide

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Materials

ABSTRACT

Purpose: The purpose of this article was to review some of the modification methods applied to improve mechanical, barrier and/or surface properties of polylactide (PLA).

Design/methodology/approach: The presented modification methods were classified into three groups due to the dominant role of compositional, physical or chemical factor effecting the most PLA properties.

Findings: It was found that incorporation of small amounts of montmorillonite up to 5% leads to formation of a nanocomposite with enhanced tensile strength and improved barrier properties. Corona treatment of pure PLA and PLA contained MMT nanofiller causes a significant decrease in the water contact angle and does not essentially affect the diiodomethane contact angle. This treatment leads to an increase in surface free energy that is much more significant for pure PLA than for PLA containing MMT nanofiller. It was also found that with increasing number up to 1000 of laser pulses of energies 5 mJ/cm² an increase in surface free energy was observed, while the next laser pulses caused decrease of this energy. The determination and comparison of the influence of 3 wt.% of trimethylpropane trimethacrylate (TMPTA) and 3 wt.% of triallyl isocyanurate (TAIC) crosslinking agents on the thermomechanical properties of electron beam irradiated PLA was reported.

Research limitations/implications: A number of various modification methods are widely reported in literature. In this article a review of only such modification methods is presented, which are in line with the newest trends in polymer industry and science.

Practical implications: There are a number of PLA properties, which need to be improved to satisfy specific application conditions. For that reasons researches are leading to find suitable modification methods to improve selected properties of PLA.

Originality/value: This article presents some of modification methods, which are in line with the newest trends in polymer industry and science.

Keywords: Engineering polymers; Nanocomposite; Corona discharge; Laser modification; Electrons irradiation; Reactive extrusion

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1. Introduction

Poly lactide (PLA) is a biodegradable and biocompatible polyester which can be produced from renewable resources [1,2]. Due to new techniques which allow economical production of high molecular weight PLA, this polymer has attracted large attention recently being considered as one of the most promising materials for replacing synthetic polymers [3]. PLA has reasonably good optical, physical, mechanical and barrier properties compared to existing petroleum-based polymers like high density polyethylene (HDPE), polystyrene (PS), polypropylene (PP) and polyethylene terephthalate (PET) (Tab.1). The building block of PLA can exist in optically active D- or L-enantiomers (Fig.1).

Depending on the proportion of the enantiomers, PLA of variable mechanical, barrier and surface properties can be derived. This allows the production of a wide spectrum of PLA grades to match performance requirements [4]. The possibility to process PLA with the use of machinery or processing lines applied to processing common-use polymers, mostly thermoplastics, is an important advantage of this polymer.

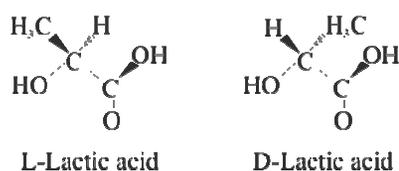


Fig. 1. Lactide acid structure of two different enantiomer forms

Extrusion, injection moulding, casting of films and sheets, thermoforming, foaming and fibre spinning are among the methods utilised for PLA processing [5,6]. The PLA technological waste can be reused to a great extent, which is another significant benefit of this polymer [7].

Independently of PLA advantages, high brittleness, poor heat stability, low impact strength and some surface properties limit some of its applications. To improve these properties, different modification methods like annealing, adding nucleating agents, fibers or nanoparticles were applied. Alternatively, some chemical and physical treatments were also applied to introduce crosslinking between PLA molecules. In order to enhance the material adhesion properties of polymers corona discharge, plasma treatment as well as UV-lamp and laser exposures were applied [8,9].

Table 1. Selected properties of some thermoplastics (“+” – good; “–” - bad) [22]

Property	Polymer:				
	PLA	PE	PS	PP	PET
Biodegradability	+	–	–	–	–
Biocompatibility	+	+	–	–	–
Thermoplasticity	+	+	+	+	+
melting temperature [°C]	145-186	124-136	240	134-174	200-265
glass transition temperature [°C]	53-64	~ -120	~ 100	-18 - -3	69-115
tensile strength [MPa]	28-50	12-44	20-50	19-42	47-90

The aim of this article was to review some of the modification methods applied to improve mechanical, barrier and surface properties of PLA. The presented modification methods were classified into three groups due to the dominant role of compositional, physical or chemical factor effecting the most PLA properties. However, it is important to keep in mind that the modification methods can involve any combination of the three above mentioned types. In the group of compositional modification the influence of silica nanofillers on barrier and mechanical properties of PLA was reported. Some physical modification methods like PLA corona discharge, laser and electron beam irradiation were briefly characterised. Among the chemical methods, peroxide induced cross-linking through the addition of small amount of peroxide during extrusion was discussed. All here presented results are not followed by the detailed description of experimental setup, which can be found in referenced literatures.

2. Compositional modification

To improve impact strength and to lower glass transition temperature, PLA is being subjected to modification by blending with other polymers or incorporating various plasticisers, such as poly(ethylene glycol), poly(propylene glycol), poly(propylene oxide), polyoxyethylene, polycaprolactone, oligomers of lactic acid and citrate esters. On the other hand, incorporation of small amounts of montmorillonite (MMT) (up to 5%) leads to formation of a nanocomposite with enhanced tensile strength and improved barrier properties [10,11,12,13]. Proper preparation and modification of MMT and, then, selection of an adequate technique for introducing this component into the PLA matrix, are basic conditions to produce an exfoliated nanocomposite. The methods for MMT modification (exchange of inorganic cations with organic ones [14]) and combining it with the PLA matrix (polymerisation in-situ, solvent technique, or blending with a plasticised polymer [15]) which have been used to date, are still being improved (e.g., in relation to antibacterial properties of the product [16]). This enables preparation of PLA/MMT nanocomposites showing better and better quality and to find new applications for the products [17,18,19].

Żenkiewicz et al. found that MMT in the PLA matrix significantly improves the film barrier properties, because it reduces the transmission of water vapour by more than 40%, of oxygen by almost 40% and of carbon dioxide by up to more than 80% [20,21].

The use of MMT as a component of the films based on the PLA matrix eliminates to a great extent the necessity to apply additional additives reducing the gas transmission. This reduction in permeability is caused mainly by a more parallel ordering of the MMT platelets within the PLA matrix, induced by the film blowing (Fig.2). Thus, the diffusion path of a substance elongates, which improves the barrier properties of the blown films.

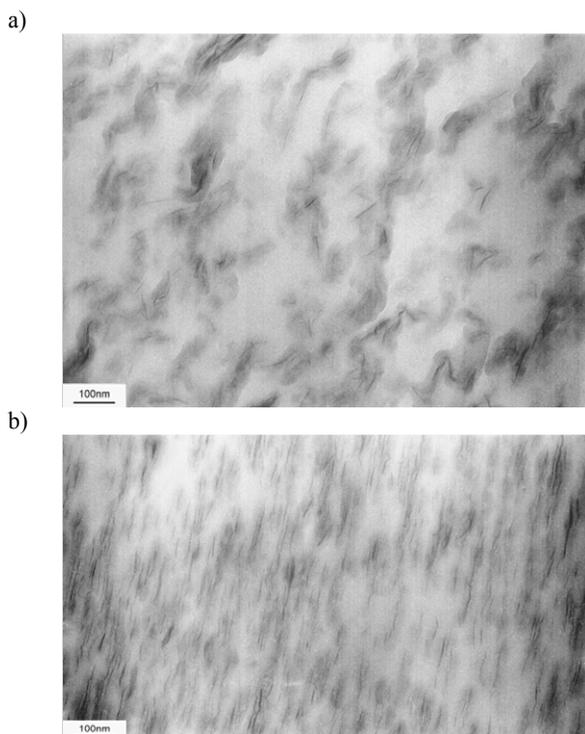


Fig. 2. TEM image of: (a) non-blown PLA/MMT film, (b) blown PLA/MMT film

The presented TEM images suggest that blending MMT with the plasticized PLA using a co-rotating twin-screw extruder with properly designed screws is a good method for producing this way a granulated nanocomposite. Using this nanocomposite for manufacturing and blowing the film uniform arrangement of the MMT platelets within the PLA matrix is achieved. The nanocomposite film prepared in this manner exhibits generally an exfoliated ordered structure with uniformly arranged and oriented MMT platelets.

More uniform and parallel arrangement of the MMT platelets within the PLA matrix and partial straightening of macromolecules of this polymer, induced by the film blowing, caused an increase in longitudinal modulus of elasticity from ca. 2.3 to 3.0 times, in mechanical strength from 1.6 to 2.1 times, and in tensile stress at break from 1.3 to 1.8 times as compared to neat PLA blown film [23]. The important processing condition effecting barrier and mechanical properties of PLA/MMT films was blown moulding ratio defined as a ratio (R) of the blown film sleeve perimeter to the angle head die perimeter. Influence of blown-up ratio on mechanical properties of the studied films as related to those of the non-blown film is presented in Table 2.

Table 2.

Percentage change in Young's modulus (ΔE), tensile strength ($\Delta\sigma_M$) and tensile stress at break ($\Delta\sigma_B$) of PLA/MMT nanocomposite films as compared to neat PLA films processed with different blown-up ratio (R)

R	ΔE , %	$\Delta\sigma_M$, %	$\Delta\sigma_B$, %
2	112	91	69
3	169	163	152
4	317	267	133
5	263	239	122
7	123	139	122

It was found that optimal blown moulding ratio was about 4.

3. Physical modification

Among many others, into the class of physical modifications, corona discharge, laser and electron beam irradiation can be classified. Two first modification methods are applied to modify surface properties, while the third one mostly to improve thermal and mechanical properties. The modification of the surface layer of PLA products is especially vital to medical applications, in which biocompatibility, high affinity, and/or strong adhesion of these materials are particularly necessary. The mentioned features mostly depend on the PLA surface layer properties such as wettability, surface free energy, roughness, as well as kind and magnitude of the electric charge of this layer.

A rapid progress in the design of the equipment intended for the corona treatment enables to apply this method not only to films and plates, but also to tubes, profiled products, and various elements of complex shapes as well as to polymer fibers being a component of plastic composites. This technique is also utilised to initiate and accelerate processes of graft polymerisation occurring on various polymers.

The results of wettability and surface free energy of the corona treated PLA are presented in Figs. 3 and 4.

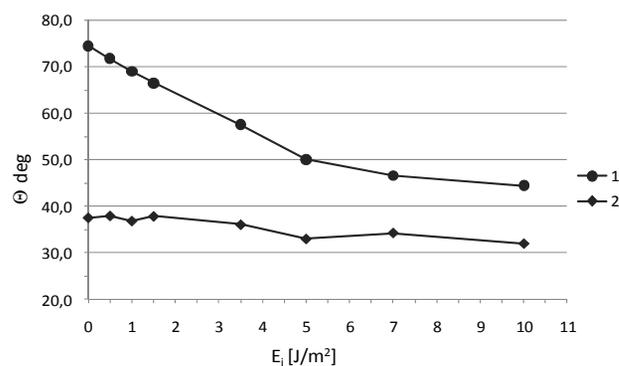


Fig. 3. Influence of the unit energy (E_i) of the corona discharge on the contact angle (Θ) of: (1) - water and (b) - diiodomethane on PLA

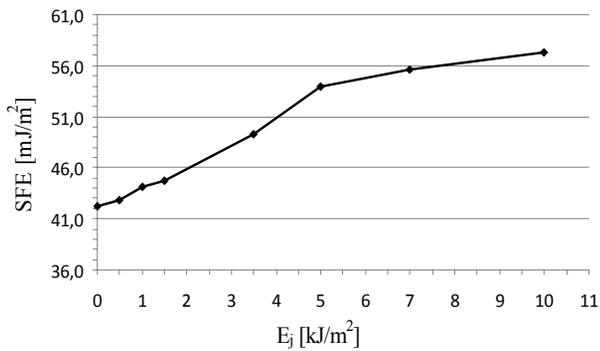


Fig. 4. Surface free energy (SFE) of PLA

It follows from these figures that corona treatment of surface layer of PLA causes a significant decrease in the water contact angle and does not essentially affect the diiodomethane contact angle. The corona treatment leads to an increase in surface free energy that is much more significant for pure PLA than for PLA containing MMT nanofiller [24].

Lasers enable to perform precise changes in the properties of small fragments of surfaces of complex shapes [25,26]. The ultraviolet laser radiation can change the surface geometrical structure and initiate chemical reactions that cause formation of polar functional groups within the surface layer of the material to be modified [27,28,29]. Compared to UV exposure, high energy nanosecond UV-laser irradiations will cause a significant higher density of radicals. Due to time-dependant diffusion process in the surface layer, the radicals cannot be completely saturated by reaction with oxygen and therefore other recombination processes become more important [30]. The physicochemical phenomena associated with laser induced alterations are still not fully understood and are continually a subject of intensive studies [31,32,33]. The results of wettability and surface free energy of PLA irradiated with different number of ArF excimer laser pulses of energies 5 mJ/cm² are presented in Figs. 5 and 6, respectively.

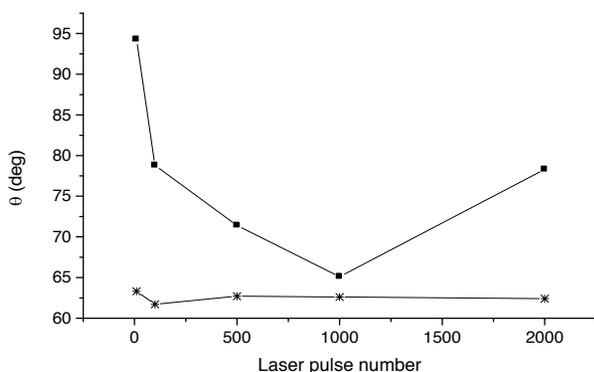


Fig. 5. Contact angle of PLA irradiated with different number of laser pulses and measured by the use of water (■-) and diiodomethane (-x-)

It was found that with increasing number up to 1000 of laser pulses of energies 5 mJ/cm² an increase in surface free energy was observed, while the next laser pulses caused decrease of surface energy.

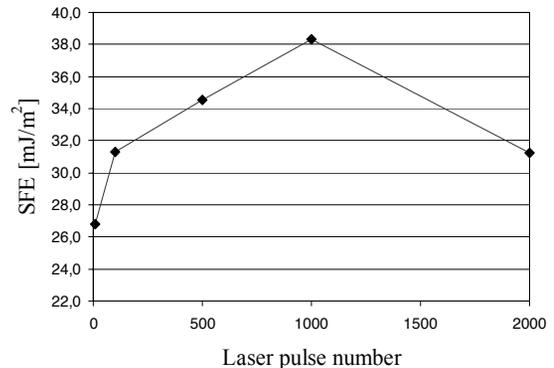


Fig. 6. Surface free energy (SFE) of PLA versus laser pulse number

To improve heat stability and mechanical properties high energy electron irradiation can be applied to introduce crosslinking between PLA molecules. In general, the crosslinking and degradation processes are simultaneously occurring in amorphous regions of polymers as an effect of electron irradiation. To favour crosslinking over degradation processes, some crosslinking agents are added into polymers. The determination and comparison of the influence of 3 wt.% of trimethylpropane trimethacrylate (TMPTA) and 3 wt.% of triallyl isocyanurate (TAIC) crosslinking agents on the thermomechanical properties of electron beam irradiated PLA was reported previously [34].

TMPTA and TAIC introduced to PLA caused a decrease in glass transition temperature from 61.4 to 61.0 and to 59.0 for PLA/TMPTA and PLA/TAIC, respectively (Fig.7a-c). It shows that TAIC act as plasticizer more significantly than TMPTA. This difference can be attributed to better miscibility of TAIC than TMPTA molecules in PLA phase. TMPTA and TAIC introduced to PLA caused an increase in cold-crystallization enthalpy, which rose from 3.3 to 18.3 and to 7.5 J for PLA/TMPTA and PLA/TAIC, respectively (Fig.7a-c). Significantly higher increase in cold-crystallization enthalpy of PLA/TMPTA than of PLA/TAIC can indicate on better nucleating ability of TMPTA than TAIC molecules. It can be concluded that PLA blended with TMPTA formed more heterophase system than PLA blended with TAIC because heterophase nucleating agents have commonly better nucleating ability.

The cold-crystallization enthalpy of PLA/TMPTA increased with increase of radiation dose (Fig.8a,b). This can be attributed probably to radiation induced degradation of PLA chains which could rearrange more easily. Two different melting peaks arise at temperature of 145.7 and 151.2°C for PLA/TMPTA irradiated at 100 kGy (Fig.8b).

Cold-crystallization enthalpies of PLA/TAIC samples significantly decrease with increase of radiation dose (Fig.8c,d). These results indicate that crosslinking network was formed in amorphous phase, which in effect could not crystallize.

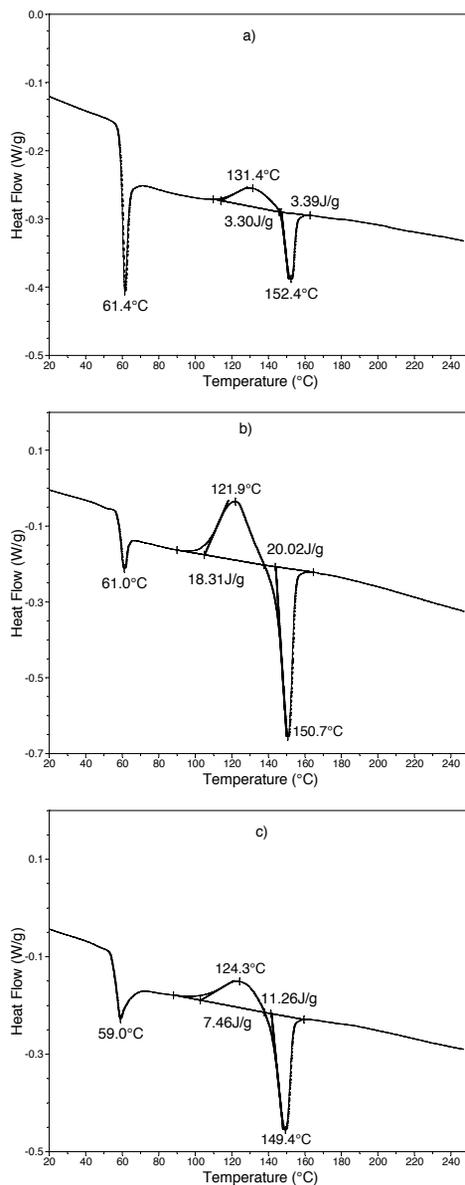


Fig. 7. DSC thermograms recorded during the first heating at the rate of 10 °C/min of: a) PLA sample, b) PLA/TMPTA sample, c) PLA/TAIC sample

It was also found that TMPTA favours degradation over crosslinking reactions, contrary to the TAIC, which favours formation of crosslinking network of amorphous PLA phase. This originated in better miscibility of PLA with TAIC than with TMPTA. Better resistance of PLA/TAIC samples to degradation process can arise from protective action of aromatic rings included in the molecules of TAIC. Irradiation has not considerably effected viscoelastic properties of PLA/TMPTA and PLA/TAIC samples at room temperature. However, tensile and impact strength of PLA/TMPTA samples were decreased

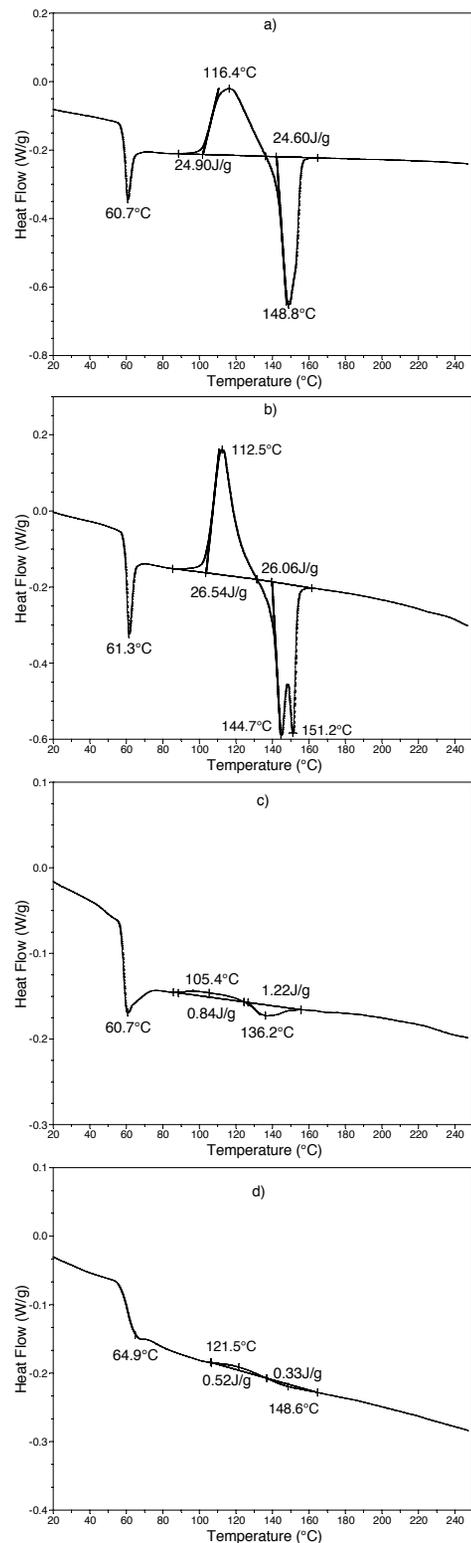


Fig. 8. DSC thermograms a) PLA/TMPTA sample irradiated at 40 kGy, b) PLA/TMPTA sample irradiated at 100 kGy, c) PLA/TAIC sample irradiated at 40 kGy, d) PLA/TAIC irradiated at 100 kGy

with increase of radiation doses (Fig.9), while an improvement of these properties was observed for PLA/TAIC samples (Tab.3).

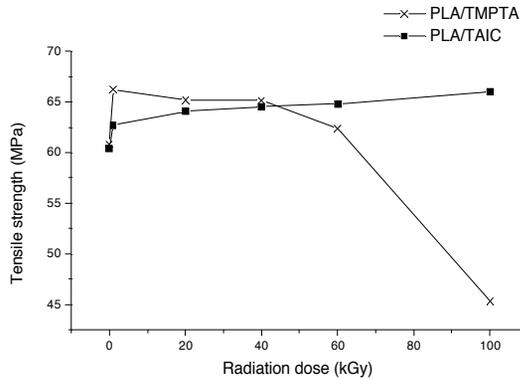


Fig. 9. Tensile strength of PLA/TMPTA and PLA/TAIC samples as a function of radiation dose

Table 3. Impact strength of PLA/TMPTA and PLA/TAIC samples irradiated at different radiation doses.

Radiation dose [kGy]	Impact strength [kJ/m ²]	
	PLA/TMPTA	PLA/TAIC
0	2.73 ± 0.01	2.60 ± 0.05
10	2.35 ± 0.20	2.77 ± 0.02
20	1.96 ± 0.17	2.78 ± 0.01
40	1.55 ± 0.02	2.81 ± 0.02
60	1.45 ± 0.02	2.86 ± 0.03
100	1.41 ± 0.01	2.78 ± 0.02

4. Chemical modification

Among the chemical methods, peroxide induced cross-linking is the simple one, which has been widely applied through the addition of small amount of peroxide during extrusion. By reactive extrusion peroxides decompose forming free radicals. These radicals present in polymer matrix can promote chain scission, branching, cross-linking or any combination of the three. These reactions will influence physical properties such as melt viscosity, crystallinity, glass transition temperature, melting temperature, tensile and impact strengths.

Sodegard et al. [35] investigated peroxide-induced crosslinking of PLA using different peroxide agents at a constant weight ratio of 5%. They found that dialkyl peroxides having no carbonyl groups, such as dicumyl peroxide (DCP) degraded PLA, while hydroperoxides and peroxides with carbonyl group stabilized the polymer. Takamura et al. [36] were also examining

PLA crosslinked with various type of peroxides under constant mole ratio. They found that DCP is decomposing on cumyloxy radicals, part of which is further decomposing on methyl and acetophenone radicals. They also found that longer extrusion time favour crosslinking over degradation reactions of PLA blended with DCP.

We were also determining the influence of small amount of DCP (up to 1%) on thermal and mechanical properties of PLA. It followed from this research that primary free radical formation originated in thermal dissociation of DCP on cumyloxy radicals, which reacted with PLA forming hydroxycumyl and PLA radicals. In effect, PLA radicals reacted and formed crosslinked structure. It was also found that DCP decomposed leading to formation of acetophenone (Fig.10). PLA structure also degraded because reduction in carbonyl and ether groups was observed.

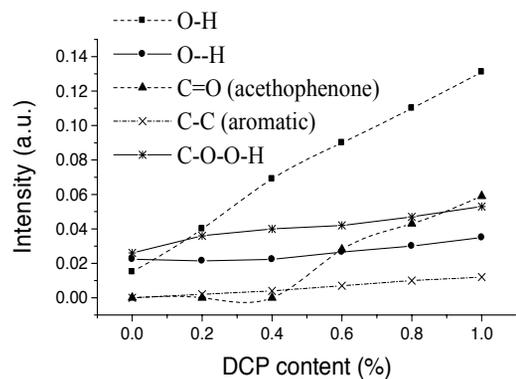


Fig. 10. Effect of DCP content on intensities of individual FTIR bands referred to respective functional group (functional groups are marked on the figure; free and bonded H atoms were marked as O-H and O--H, respectively)

The analysis of gel content (X_z) and swelling degree (X_s) showed that addition of DCP caused crosslinking of PLA as well as an increase in the degree of swelling (Fig.11).

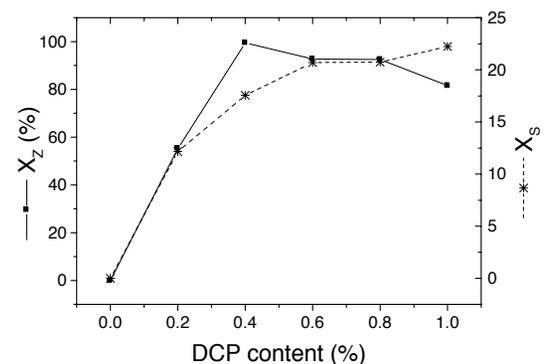


Fig. 11. Gel fraction (X_z) and degree of swelling (X_s) of PLA mixed with different amount of DCP

The gel fraction of PLA significantly increased to 93% with increasing DCP content up to 0.4%. However, further increase of DCP caused a slight decrease in gel fraction to 82%. The higher the DCP concentration, the larger the number of primary radicals produced, therefore a higher crosslinking density was obtained. However, higher than 0.4% DCP concentration is undesired for crosslinking because radicals produced of DCP degrade PLA structure. Study on the degree of swelling of PLA in chloroform indicated that X_S was increasing with increasing DCP content. These results seem to be in contradiction with X_Z results. However, an increase in X_S values indicate that crosslinking can simultaneously be accompanied by the formation of the low molecular weight decomposition and degradation products, which were washed out by chloroform, and thus caused the increase in X_S .

Dynamic mechanical analysis (DMA) showed that addition of DCP caused PLA to plasticize as well as to be crosslinked. With increasing DCP content an increase in tensile strength while decrease in impact strength was observed (Fig. 12).

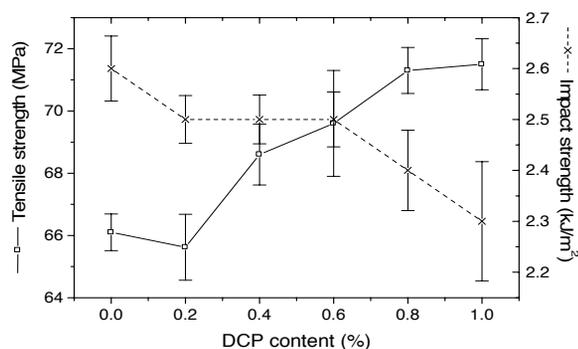


Fig. 12. Tensile and impact strength of PLA mixed with different amount of DCP

Tensile strength increased with increasing DCP content from 66.1 to 72 MPa, while impact strength decrease from 2.6 to 1.5 kJ/m². The slight increase in tensile strength was caused by crosslinking. The decrease of impact strength is most likely to be a combined results of PLA degradation and the formation of gaseous degradation products in the polymer matrix leading to formation of voids.

5. Conclusions

PLA has many advantages as compared to petroleum-based thermoplastics mostly because is biodegradable under conditions of industrial composting and can be produced from vegetables (e.g. starch obtained from various plants), which enable to save fossils, first of all crude oil. Nevertheless, there are a number of PLA properties, like brittleness, impact strength, heat stability, permeability of some gases, which need to be improved to satisfy specific application conditions. The research works are leading to find suitable modification methods to improve these properties and number of various modification methods are widely reported

in literature. However, the purpose of this article was to review only such modification methods, which are in line with the newest trends in polymer industry and science. The presented methods were classified into three groups of compositional, physical and chemical modifications. In practice, many modification methods consist in various combinations between these three types.

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