Influence of the Structure of Low MolecularWeight Esters on Poly(lactic acid) in the Plasticization Process - part 1

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Abstract

Polymers derived from renewable sources which are additionally subject to degradation processes are currently an interesting alternative to conventional polymers of petrochemical origin. One of such polymers is poly(lactic acid) (PLA), which can be used in the packaging, textile and also medical industries. Its great advantage is the susceptibility to biodegradation and the non-toxicity of the degradation products. Because of high brittleness and stiffness, the modification of PLA is necessary to improve its plastic deformability, which can expand the new application possibilities. As part of the research work, the modification of PLA by plasticisation was undertaken to improve its plastic deformability properties. The low molecular mass esters from the citrate group and glycerol triacetate were used. The samples extruded from plasticised polymer were characterised using Differential Scanning Calorimetry (DSC) and Gel Permeation Chromatography/Size Exclusion Chromatography (GPC/SEC). The mechanical properties and melt flow rate after modification were determined. The aim of the research was to determine the relationship between the structure of a plasticiser and its ability to reduce the interactions in the polymer chain in order to develop an optimal polymer-plasticiser arrangement. Based on this research, there was no relationship between the efficiency of the plasticisation process and the increasing molecular mass of the plasticiser. The additional chemical (acetyl) group in the plasticiser also does not increase the efficiency of the PLA plasticisation process. In the next steps of the research, functional forms will be produced, i.e. fibers, films, and fittings from the selected polymer-plasticiser systems.

Keywords

polylactic acid, plasticisation, GPC/SEC, citrate, glycerol triacetate.

1. Introduction

In recent years, there has been an increase in the use of plastics in various branches of life. Many of the products based on plastics are disposable or have a short-term usage, which means that they generate the largest proportion of waste. An alternative to the traditional plastics may be biodegradable polymers, usually obtained from biodegradable raw materials. Among the biodegradable polymers, the largest group are aliphatic polyesters, the most common of which is poly(lactic acid) (PLA).

PLA is one of the most extensively studied biodegradable and renewable aliphatic polyesters. PLA has exhibited great potential in packing, textile and leading medicine applications, such as biocompatible or bioabsorbable materials and medical devices [1, 2], because of its generally recognised safety [3]. However, widespread PLA applications are hampered by its indigenous drawbacks, such as relatively high cost, low heat distortion temperature, and inherent brittleness. Progress in the technology of producing PLA has reduced its price, but it is still more expensive than polymers obtained from petrochemical raw materials on a mass scale, such as polyethylene, polypropylene and polystyrene. Amorphous PLA is a polymer whose glass transition temperature (T_g) is in the range of 55-60°C, which makes it stiff and brittle at room temperature, with a modulus of elasticity of 3.0-3.5 GPa. The crystallinity of PLA slightly increases the value of the elastic modulus, deteriorating its already small ability of plastic deformation [4]. The low crystallinity of PLA seriously limits its applications. Therefore, research is being carried out to compose PLA with other polymers acting as plasticisers. In the literature, there have been many attempts to mix PLA with other chemical compounds in order to lower the melt viscosity, increase ductility and improve processing properties [5-16]. The presence of a plasticiser in crystallisable polymers influences the processes of crystallisation and melting, lowering not only the T_g but also (to a lesser extent) the melting point of the polymer crystals (T_m).

There are many theories describing the mechanism of the influence of plasticisers on polymers, but none are exhaustive. Therefore, it is important to get familiar with them to better understand the plasticisation process.

As shown in Figure 1, there are three classical theories. The lubricity theory says that the plasticiser reduces the friction between the polymer molecules. The plasticiser molecules perform the function of a lubricant by reducing internal resistance to the sliding of polymer chains. [17,18]. The gel theory, first formulated by Doolittle, extends the lubricity theory [19, 20], and according to this theory, the polymer is formed by a tri-dimensional structure which is maintained by loose links between macromolecules along the polymer chains. The gel theory says the plasticiser reduces the number of these points by breaking some junctions between active centres on the polymer at attachment
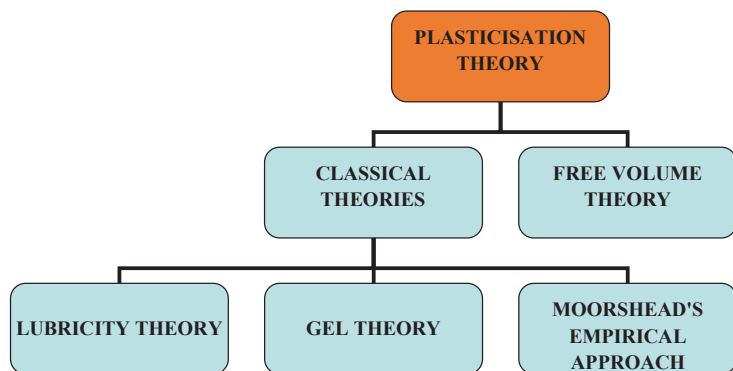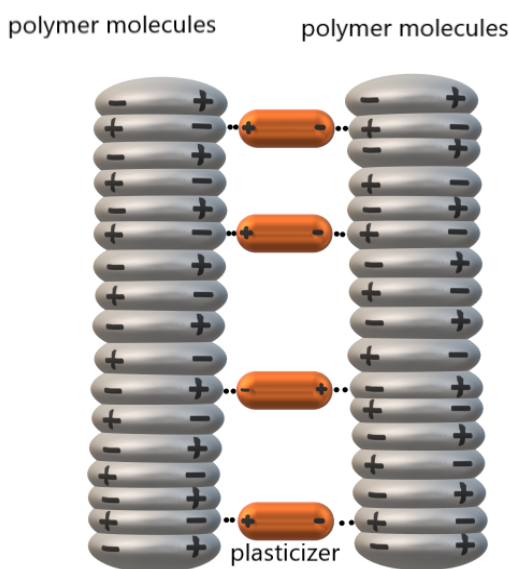
Fig. 1. Theories of plasticization
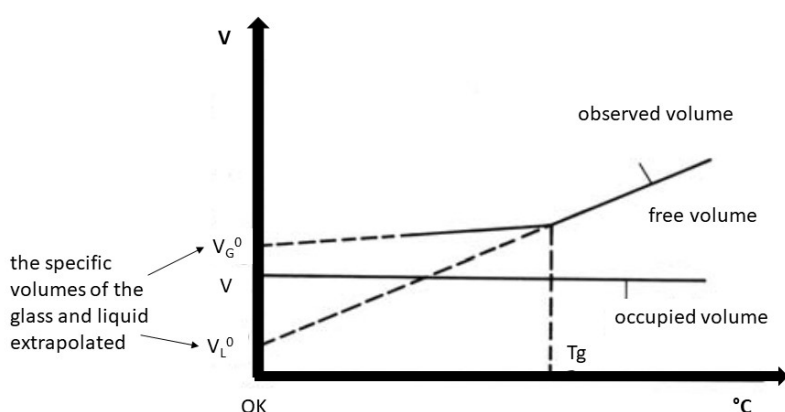

Fig. 2. Mechanism of plasticiser's action

Fig. 3. Free volume theory [22, 23]

points, allowing the polymer to be deformed without breaking. There are solvation-desolvation and aggregation-disaggregation equilibria between molecules of the polymer and plasticiser.

Plasticizer molecules swell the gel and facilitate the movement of polymer molecules, thus imparting flexibility. The lubricity and gel theories agree that plasticisers penetrate the structure of the polymer, separating chains and thus reducing intermolecular forces between them [18]. Moorshead's empirical approach was an attempt to enrich the above theories with information on why some polymers can be plasticised so efficiently while others cannot, why some chemicals are good plasticisers, and why some structures in plasticisers confer such interesting properties. This theory shows how many factors are important: sufficiently long polymer chains, and optimal crosslinked and crystalline polymer. The structure of the plasticiser molecule as a whole has a profound effect on the properties of the plasticised compound. Polar groups are essential for good compatibility and non-polar groups provide high flexibility in plasticised compounds. Both types of groups are necessary to achieve compatibility and flexibility (Figure 2). This theory suggests that the branched chain in the aliphatic plasticiser is equivalent to a shorter molecule. It also shows the relationship between the higher molecular weight of the plasticiser and the lower plasticising effect [18, 21].

Nowadays, the free volume theory extends the above ideas. According to this theory in the structure of the polymer there occurs a free internal volume, which allows for movement of the polymer chain. The polymer acquires flexibility due to this mobility. For plasticised polymers, the theory attempted to explain the decrease in the glass transition temperature with the plasticiser content. According to Figure 3, the amount of free volume in the polymer increases sharply at the glass transition temperature T_g.

Free volume can come from three possibilties. The first is the motions of the chain ends of the polymer. The second possibility is the presence of the side chains in the structure; however, by itself the main chain of the polymer can be responsible for free internal volume. The motions and, therefore, the free volume of a polymer system may be increased in a variety of ways. According to this theory, increasing the number of end groups (low molar mass) or the length of the side chains may affect the motions. The increase in the possibility

Property	Value	Method
Specific gravity, g/cm³	1.24	ASTM D792
Relative viscosity	3.1	CD Internal Viscotek Method
Melt index (210°C), g/10 min	15-30	ASTM D1238
Glass transition temperature, °C	55-60	ASTM D3417
Crystalline melt temperature, °C	160-170	ASTM D3418

Table 1. Properties of 6201D PLA according to manufacturer's data

of main chain movement by the inclusion of segments of low steric hindrance and low intermolecular attraction also has an effect and brings about internal plasticisation. Raising the temperature can increase the motions. The introduction of lower molecular mass compounds, for example plasticisers, can cause an increase in the motion elements of the polymer structure. It implies not only the addition of molecules with T_g lower than that of the polymer itself, but also the relatively small plasticiser molecules add a large free volume to the system and increase the number of end groups [18, 23]. In fact, the explanation is much more complicated. This theory does not consider, for example, the phenomenon of anti-plasticisation, viscosity, elastic modulus, and many other properties [24]. Therefore, for each type of polymer and its application, an appropriate plasticiser should be selected to achieve the proper change in plastic properties.

The study aimed to modify poly(lactic acid) in the plasticisation process with the use of low molecular weight ester compounds from the citrate group and glycerol triacetate, as well as to investigate the influence of the PLA plasticisation process on its chemical, physical and mechanical properties. Also, the authors wanted to determine the relationship between the chemical structure of the plasticiser and its impact on polymer chains. The following plasticisers were used to modify PLA: glycerol triacetate, triethyl citrate, acetyl-triethyl citrate, tributyl citrate, and acetyl-tributyl citrate. The compounds used differed in molecular weight and structure and had additional acetyl groups in their structure. The samples extruded from plasticised polymer were characterised using various measuring techniques. The thermal properties were determined by DSC. The mechanical properties, including Young's modulus after modification, were examined using a tensile tester. Moreover, the melt flow rate (MFR) of the regranulate and molecular parameters, i.e. the average molar mass and molar mass distribution, were determined using GPC/SEC.

2. Materials and Methods

2.1. Materials

Poly(D,L-lactide) 6201D polymer from Nature Works® LLC (USA) was used in the research (Table 1). This biopolymer had been certified for food packaging pursuant to section 201(s) of the Federal, Drug, and Cosmetic Act, and Parts 182, 184, and 186 of the Food Additive Regulations.

The plasticising process was carried out by mechanical mixing of polymer containing the low molar mass esters (10% wt.) in a melted state in an extruder (Zamak Mercator, Poland) equipped with a twin-screw. The process was conducted using a single-orifice forming head in the temperature range of of the extruder of 150–220°C, at a screws speed of 150 rpm. and torque in the range of 3–4 Nm. The extruded filament was immersed in a water bath at 35°C and then cut into pellets. Then the pellets (regranulate) were dried in two stages, initially at an ambient temperature of approx. 23°C and then in a vacuum dryer (Binder, Germany) at 35°C for 48 hours under reduced pressure (20 hPa), which resulted in the effective removal of water. The commercial substances used for the plasticisation process are presented in Table 2.

2.2. Methods

Thermal Analysis was carried out by means of *Differential Scanning Calorimetry (DSC)*. The analysis was performed at a heating/cooling rate of 20°C/min in a temperature range of -60÷200°C using Diamond apparatus (Perkin Elmer, Germany).

Melt Flow Rate (MFR) estimation was determined using an LMI 4003 plastometer (DYNISCO Polymer Test, USA). The measurement was carried out on the basis of own measurement procedure at 180°C with the use of a spinneret with a 0.5 mm capillary. The filament obtained by a plastometer was further used to estimate mechanical properties.

Molar Mass Distribution and Polydispersity *of* polymers were determined by the GPC/SEC method using Agilent Series apparatus (Agilent Technologies, USA) equipped with a refractometric detector (Optilab, Wyatt Technology, USA) and Astra software (Wyatt Technology, USA). The tests were performed using one PLgel Mixed-C 300 mm chromatographic column (Agilent Technologies, USA) at an eluent ($CHCl_3$) flow rate of 0.7 cm³/min. The average molar weights were determined using the universal calibration technique and the following values of K and a constants in the Mark-Houwink-Sakurada equation: a=0.794 & K=0.0049 for polystyrene (PS) [25], and a=0.759 & K=0.0153 for PLA [26].

Mechanical Properties were determined using an Instron 5544 Tensile Tester (Norwood, MA, USA) according to the PN-EN ISO 139:2006 standard. The following parameters were estimated at 20 ± 2°C and relative humidity RH 65±4 %:
- - breaking tenacity according to PN-EN ISO 2062:2010 method A
- - elongation at break according to PN-EN ISO 2062:2010 method A
- - initial tensile modulus according to PN-P-04669:1984

The filaments formed of regranulates obtained during the MFR analysis were used for mechanical tests.
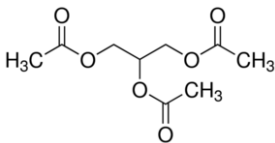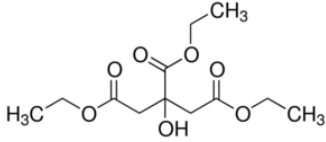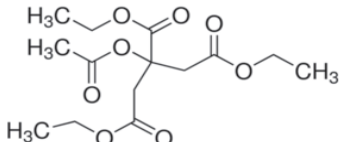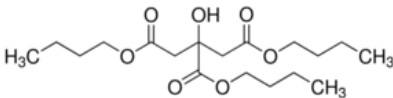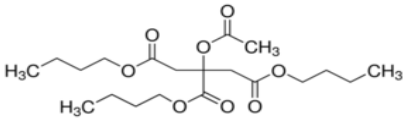
Plasticiser	Producer	M_w, g/mol	Structure
Glycerol triacetate (TAC)	ThermoFisher Scientific, Germany	218	
Triethyl citrate (TEC)	Gentham, UK	276	
Acetyl triethyl citrate (Ac-TEC)	TCI, Japan	318	
Tributyl citrate (TBC)	Acros, USA	360	
Acetyl tributyl citrate (Ac-TBC)	Merck, Germany	402	

Table 2. Substances used in the PLA plasticisation process

Sample indication:
base PLA; unmodified polymer
TAC: PLA with 10% wt. of glycerol triacetate
TEC: PLA with 10% wt. of triethyl citrate
Ac-TEC: PLA with 10% wt. of acetyl triethyl citrate
TBC: PLA with 10% wt. of tributyl citrate
Ac-TBC: PLA with 10% wt. of acetyl tributyl citrate

Spectral Analysis was carried out by Fourier Transform Infrared Spectroscopy - Attenuated Total Reflectance (FTIR-ATR). The analysis was performed in the range 4000-400 cm^{-1} using a Nicolet iS50 Spectrometer (Thermo Scientific, USA) and ATR attachment equipped with a diamond crystal. The accuracy of wavenumber reading for characteristic bands was ± 1cm^{-1} and the number of scans for baseline and spectrum collection was 32.

3. Results and Discussion

3.1. Characteristics of modified regranulates

For the base PLA and PLA regranulates containing 10 wt.% of the plasticiser, thermal analysis was performed (DSC). The results are presented in Table 3 and Figure 4.

As a result of the modification of PLA with low molecular mass plasticisers, the glass transition temperature was reduced by approx. 20°C. The additional acetyl group in the citrates did not significantly reduce the T_g value. A single glass transition was observed for all modified samples because only one T_g value was determined, which provided the good miscibility of polymer and plasticisers. For all plasticised samples, the cold crystallisation temperature was moved to the lower temperature and the cold crystallisation enthalpy (ΔH_{cc}) was changed. After plasticisation, a double transition to the plastic state was determined (two T_m values). A slight decrease in these values was observed, which was a result of the presence of plasticisers, and they influenced the melting process of the polymer.

The samples after plasticisation were subjected to rheological analysis, the results of which are presented in Figure 5. The MFR value for all the modified granules increased significantly.

3.2. GPC/SEC analysis

GPC/SEC analysis was performed to determine the molar parameters after the modification of PLA. The average molar mass (M_w) is presented in Figure 6 and the molar mass distribution (MMD) in Figure 7.

For the plasticised samples a slight reduction in the molar mass of about 5% was observed. For GPC analysis, this change is within the permissible measurement error for this method. The result of the regranulation process was a slight degradation of PLA during processing at high temperatures. In the MMD curve, no significant differences were observed in the distribution of
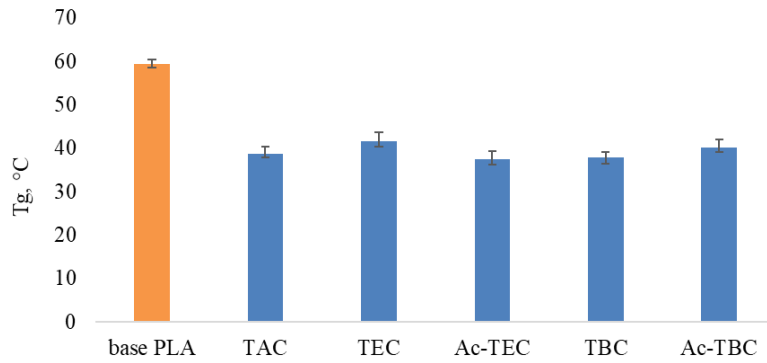
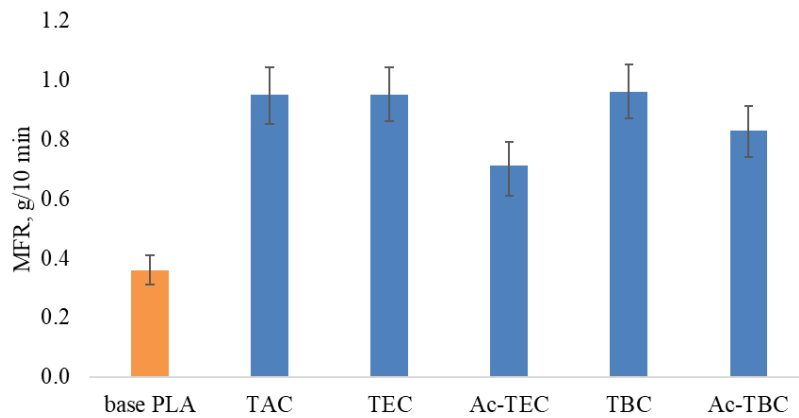Fig. 4. Glass transition temperature after the second heating

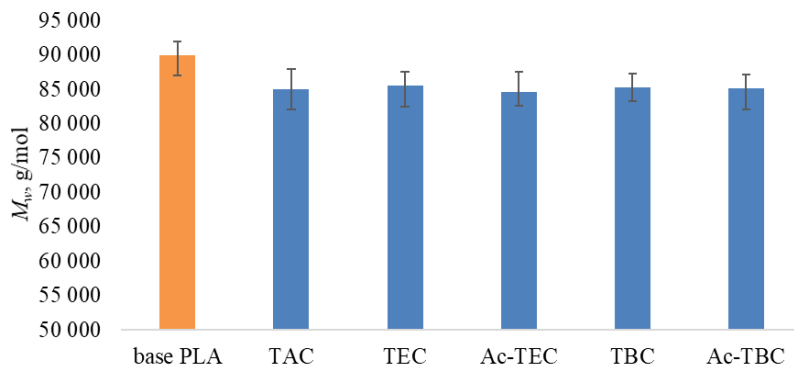Fig. 5. MFR values of the base and plasticised PLA

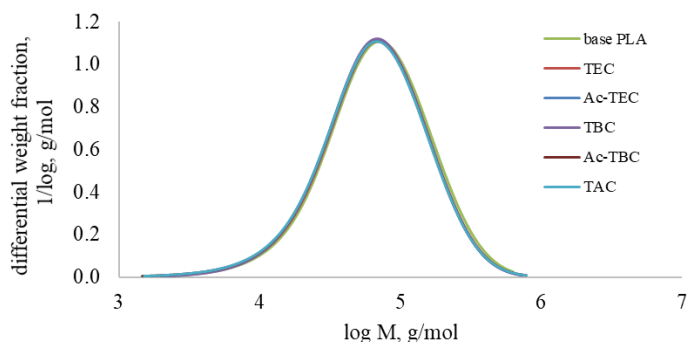Fig. 6. Molar mass (M_w) estimated using RI detector

Fig. 7. Molar mass distribution curves

molar masses after the modification process. Modification with low molecular mass substances did not change the value of M_w or the distribution of molar masses (MMD), which proves the molecular stability of the polymer-plasticizer system.

3.3. Mechanical analysis

For the plasticized samples in the form of filaments (0.5 mm diameter), mechanical testing was performed, the results of which are presented in Figures 8-10.

For the modified filaments with 10% wt. of glycerol triacetate (TAC), triethyl citrate (TEC), acetyl triethyl citrate (Ac-TEC), tributyl citrate (TBC) and acetyl tributyl citrate (Ac-TBC), the small change in the breaking tenacity was approx. 5-9%, and for Ac-TBC the decrease in tenacity was approx. 19% (Figure 8). Based on the results, the elongation at break increased significantly for all modified samples (Figure 9). For PLA plasticized with triethyl, tributyl and acetyl tributyl citrate, the elongation increase was 130%, 150% and 140%, respectively. The increase in the breaking elongation shows the influence of the plasticizers on the polymer chains i.e. reducing the intermolecular interactions in the polymer. Young's modulus, which is the coefficient of proportionality between the normal stress and the elongation, is presented in Figure 10. The lower modules Y values after modification were determined, except for the sample with acetyl-triethyl citrate (Ac-TEC). The lowest values of approx. 172 cN/tex were recorded for the sample modified with tributyl citrate (TBC) and its acetylated form (a decrease of approx. 30%). The modification of PLA with triethyl citrate and glycerol triacetate also reduced the value of Young's modulus. The modified samples were more flexible and easily subjected to stretching (deformation), which was also confirmed by the significantly increased values of the elongation at break.

Sample	Thermal analysis					
	T_g, °C	ΔC_p, J/gK	T_{cc}, °C	ΔH_{cc}, J/g	T_m, °C	ΔH_m, J/g
base PLA	60.0	0.50	123.9	42.1	165.9	42.2
Plasticiser	Plasticised PLA					
TAC	38.8	0.51	100.8	35.2	150.0 **161.9**	35.3
TEC	41.7	0.52	104.2	35.1	153.0 **164.4**	35.3
Ac-TEC	37.5	0.50	101.6	34.3	149.8 **162.1**	34.4
TBC	37.8	0.49	93.0	34.6	148.9 **163.7**	34.8
Ac-TBC	40.1	0.52	96.0	35.0	151.0 **164.1**	35.0

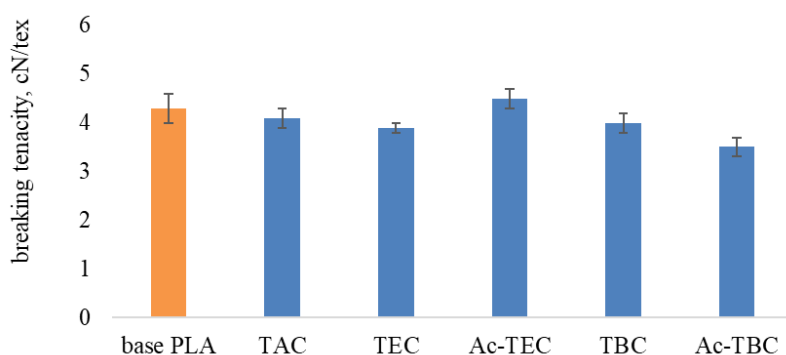*Table 3. Thermal parameters obtained during the second heating*

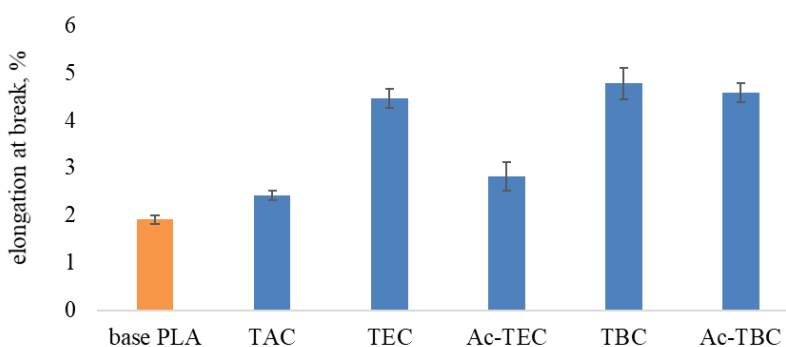*Fig. 8. Breaking tenacity of the base and plasticized PLA*

Fig. 9. Elongation at break of the base and plasticized PLA

3.4. Spectral Analysis

For plasticized PLA and plasticizers (TAC, TEC, Ac-TEC, TBC and Ac-TBC) structural analysis was performed using the FTIR-ATR technique. The results are presented in Figures 11 and 12.

As a result of the modification of PLA with plasticizers, structural changes in the FTIR-ATR spectrum in the high wavenumber region of 3100-2800cm^{-1} were observed (Figure 11A). In this region, citrates peaks were visible (Figure 12A) as a result of the plasticizers' presence. Maiza et al observed that with an increasing content of citrate, the intensity of the peaks at 1453 cm^{-1}, 2992 cm^{-1}, 2944 cm^{-1} and 2881 cm^{-1} respectively, corresponding to PLA, decreased until disappearance [27]. With an increasing concentration of the citrates, the plasticizers' peaks overlapped the PLA's peaks rather than decreased. Singh et al. also observed changes but only in the high wavenumber region (3100-2800cm^{-1}) in the FTIR-ATR spectrum of PLA-TEC [28]. Gálvez et al. observed that a couple of bands around 2995cm^{-1} and 2950cm^{-1} (corresponding to C-H aliphatic symmetric and asymmetric stretching vibrations) increase with the amount of Ac-TBC. They also concluded that a rise in the intensity of the carbonyl stretching band (1750 cm^{-1}) appeared because of the Ac-TBC and PLA interactions [29]. In this research a rise in the intensity was also observed in the region characteristic for the –C=O ester carbonyl group (Figure 11-B) In the FTIR-ATR technique, which is a surface analysis, it is difficult to propound such conclusions. Unfortunately, literature on this topic is scarce. This problem shall be covered in future studies on that topic. In the region 1800-600cm^{-1}, some changes were observed. The FTIR-ATR spectrum of the base PLA showed a low intensity of the band at 950 cm^{-1} and high one after modification (Figure 11-B). This can be assigned to the coupling of the C-C backbone stretching with the CH$_3$ rocking mode as well as to sensitivity to the chain conformation of PLA α crystals (band 923 cm^{-1}) [30-32]. But in this region a signal from the plasticizers was also observed, therefore this band is inappropriate in this case. Instead, the bands at 868 cm^{-1} (the amorphous phase) and 756 cm^{-1} (the crystalline phase in the PLA) can be used [28, 33-35]. The amorphous phase is more accessible to
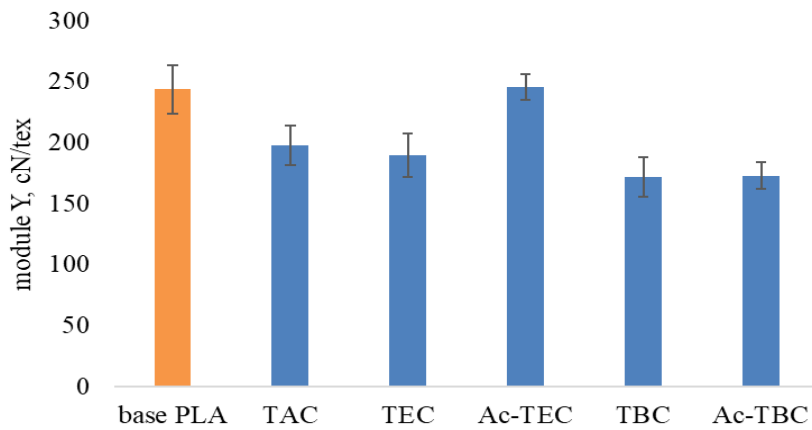
Fig. 10. Young's modulus of the base and plasticized PLA

plasticizers, therefore higher intensity of the band (869cm^{-1}) was seen (Figure 11-B). In the medium region of 1500-1000 cm^{-1} many bands from the plasticizer were observed, and interpretation in this region was difficult.

4. Conclusion

For all modified samples the MFR shifted towards higher values compared to the base polymer. Also, the T_g value in the second heating shifted towards lower values by approx. 20°C according
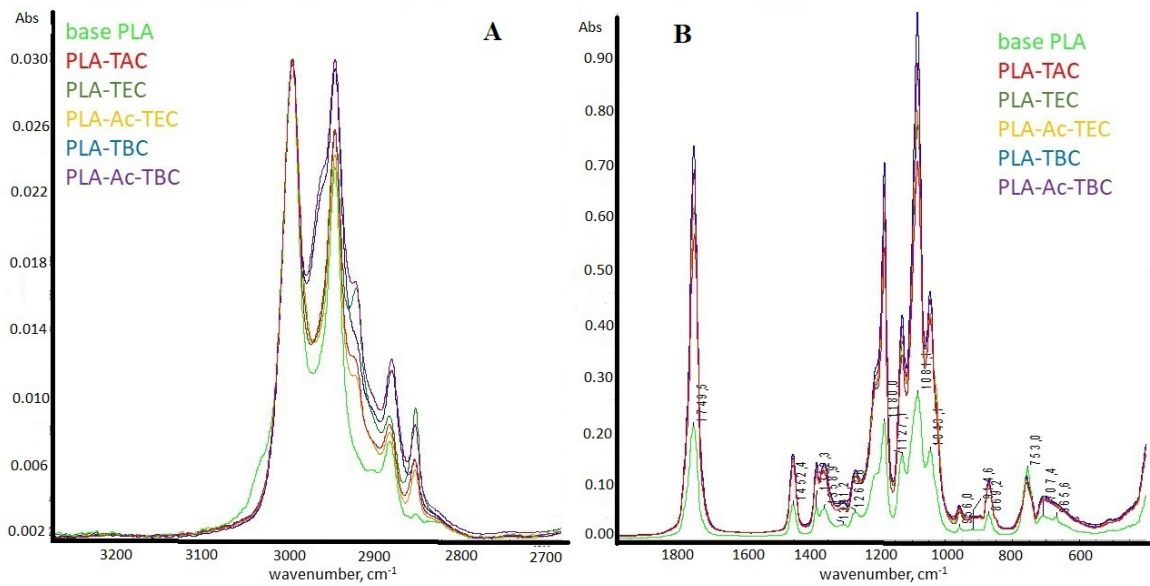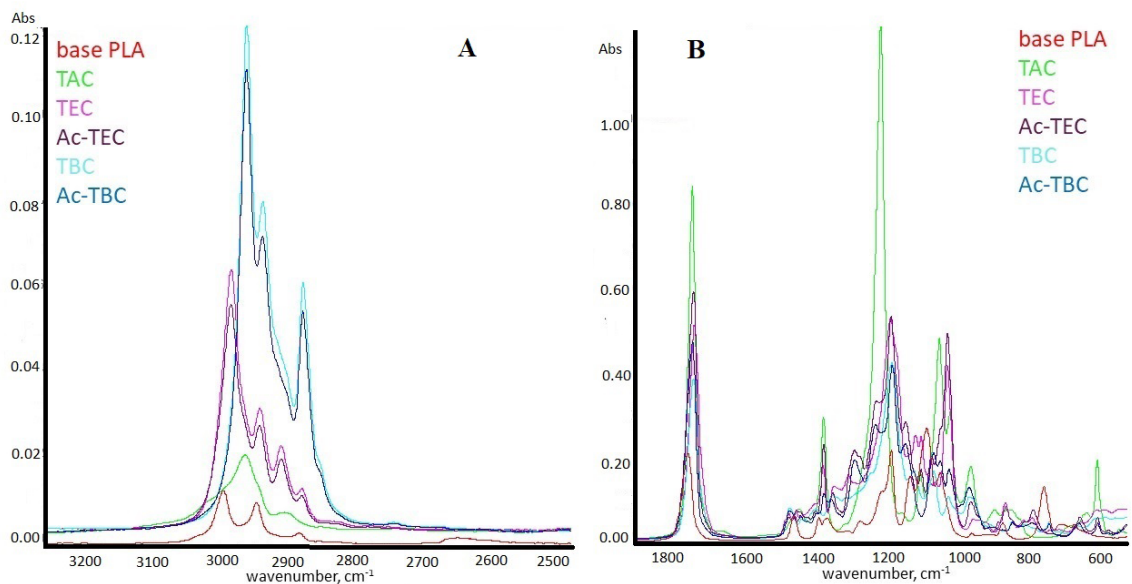

Fig. 11. FTIR-ATR spectra for plasticized PLA

Fig. 12. FTIR-ATR spectra for plasticizers

to the free volume theory. A single glass transition temperature for all modified PLA was observed, which proves the good miscibility of the components of the compositions prepared. For all samples, no polymer degradation was observed and the MFR value increased twice concerning the base PLA sample. This proved that the compounds (LME) significantly influenced the polymer macromolecules. The additional acetyl group in the citrates (Ac-TEC and Ac-TBC) did not cause a significant impact on the value of MFR and T_g. The additional group did not significantly reduce the intermolecular interactions in the polymer chains despite the larger molecule than in the non-acetylated form.

The most favorable mechanical properties were obtained for triethyl citrate and tributyl citrate, i.e. a significant increase in the elongation at break and a significant decrease in Young's modulus, which proves a reduction in intermolecular interactions in the polymer chains. The research conducted confirmed that the addition of low molecular mass esters reduced the interactions in the polymer chain, as follows from the free volume theory of plasticization. The compounds used showed a similar effect, no relationship was observed between the chemical structure of the plasticizers and their effect on the polymer.

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