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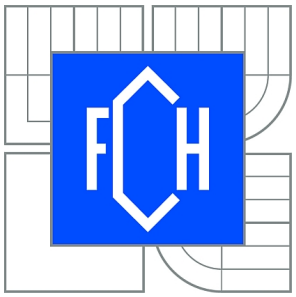

FAKULTA CHEMICKÁ
ÚSTAV CHEMIE MATERIÁLŮ

FACULTY OF CHEMISTRY
INSTITUTE OF MATERIALS SCIENCE

MODIFICATION OF PLA USING REACTIVE EXTRUSION

MODIFIKACE PLA REAKTIVNÍ EXTRUZÍ

DIPLOMOVÁ PRÁCE
MASTER'S THESIS

AUTOR PRÁCE — Bc. JANA MATLÁKOVÁ
AUTHOR

VEDOUCÍ PRÁCE — Mgr. FRANTIŠEK KUČERA, Ph.D.
SUPERVISOR

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Student(ka):	**Bc. Jana Matláková**	
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Zadání diplomové práce:

-literární rešerše současného stavu polymeranalogických reakcí PLA
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-shrnutí výsledků a závěr

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Bc. Jana Matláková	Mgr. František Kučera, Ph.D.	prof. RNDr. Josef Jančář, CSc.
Student(ka)	Vedoucí práce	Ředitel ústavu

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prof. Ing. Jaromír Havlica, DrSc.
Děkan fakulty

ABSTRAKT

Diplomová práce se zabývá roubováním maleinanhydridu a anhydridu kyseliny itakonové na kyselinu poly(mléčnou) (PLA). U modifikované kyseliny poly(mléčné) byla sledována závislost konverze monomerů na různých molárních poměrech monomer/iniciátor při teplotách 180°C a 200°C. Množství naroubovaného monomeru bylo stanovováno acidobazickou titrací a pomocí FT-IR spektroskopií. Vliv stupně naroubování na krystalinitu modifikované PLA byl zjišťován pomocí diferenční kompenzační kalorimetrie, DSC. Degradace PLA byla orientačně pozorována pomocí indexu toku taveniny, MFI.

ABSTRACT

Diploma thesis deals with grafting of maleic anhydride and itaconic anhydride onto the poly(lactic acid) (PLA). The dependence of conversion on the various molar ratios of monomer to initiator was observed on the modified poly(lactic acid) at the temperatures 180 °C and 200 °C. The amount of grafted monomer was determined due to the acido-basic titration and due to the FT-IR spectroscopy. Effect of grafting value on the crystallinity modified PLA was determined by using differential scanning calorimetry, DSC. Degradation of PLA was observed orientation due to the melting flow index, MFI.

KLÍČOVÁ SLOVA

roubování, kyselina polymléčná, maleinanhydrid, anhydrid kyseliny itakonové

KEY WORDS

grafting, poly(lactic acid), maleic anhydride, itaconic anhydride

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DECLARATION

I declare that the diploma thesis has been worked out by myself and that all the quotations from the used literary sources are accurate and complete. The content of diploma thesis is the property of the Faculty of Chemistry of Brno University of Technology and all commercial uses are allowed only if approved by both the supervisor and the dean of the Faculty of Chemistry, BUT.

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CONTENTS

1.INTRODUCTION

In the last century, it happened to the rapid increase of demand for the plastic product and to the replacement of traditional materials (such as metal, ceramic, glass) by plastic. The ceaselessly developing market requires the development of new materials or modification of current, widely applied polymeric materials. Due to the modification the polymer gain the enhanced properties in compered to the virgin one, such as enhanced thermal stability, compatibility, flexibility and rigidity. Modifications can make an insoluble polymer from a soluble on or vice versa.

The growing using of plastic products causes many problems in environment with their disposal. One possibility of these problems solution is utilized polymeric materials from renewable sources such as starch, cellulose, and wood flour, and or the develop biodegradable polymeric materials such as poly(lactic acid) (PLA), poly(ε-caprolactone) and poly(3-hydroxybutyrate).

It isn´t possible to consider that the poly(lactic acid) is a new polymer. In 1845, Théophile-Jules Polouze synthesized poly(lactic acid) by the condensation of lactic acid. In 1932 Wallace Hume Carothers et al. developed new method for lactide polymerization to produce PLA. This method was later patented by DuPont in 1954. Although poly(lactic acid) existed for several decades, its use is limited due to its high cost. Often poly(lactic acid) is utilized in biomedical applications (e.g., biocompatible sutures, implants, biologically active controlled release devices) [1].

A lot of people can have objections that PLA was discovered a long time ago, but opposite is truth. The first mention of its treatment found fifteen years ago. If we look at specialized periodicals, we would find out that almost no articles deal with modification of poly(lactic acid). Therefore it is important to widen possibilities of treatment PLA.

Poly(lactic acid) has similar structure to polypropylene (PP). Polypropylene and PLA has tertiary carbon in their chains. If the polypropylene is modified, the grafting reactions expect on the tertiary carbon atom. This similar behavior will be expected in the case of chemical modification PLA.

In theoretical part this work will be discuss the possibilities of polypropylene modification and current knowledge in poly(lactic acid) grafting. The experimental part of diploma thesis will be focused on the grafting process of maleic anhydride and itaconic anhydride onto the PLA. Effect of grafting conditions will be studied on the conversion, such as reaction temperature, molar ratio of monomer (M) to initiator (I), etc.

2.TEORETICAL PART

2.1. Principle and mechanism of grafting reaction

Grafting copolymers are defined as branched macromolecules which are formed via polymerization reaction in the system containing certain monomer and beforehand added polymer. The monomer is different from the polymer. This process can be accomplished by either "grafting to" or "grafting from" approaches. In the "grafting to" approach reacts functionalized monomer with the backbone polymer, while in the "grafting from" approach is achieved by treating a substrate with initiators followed by polymerization [2], [3], [4].

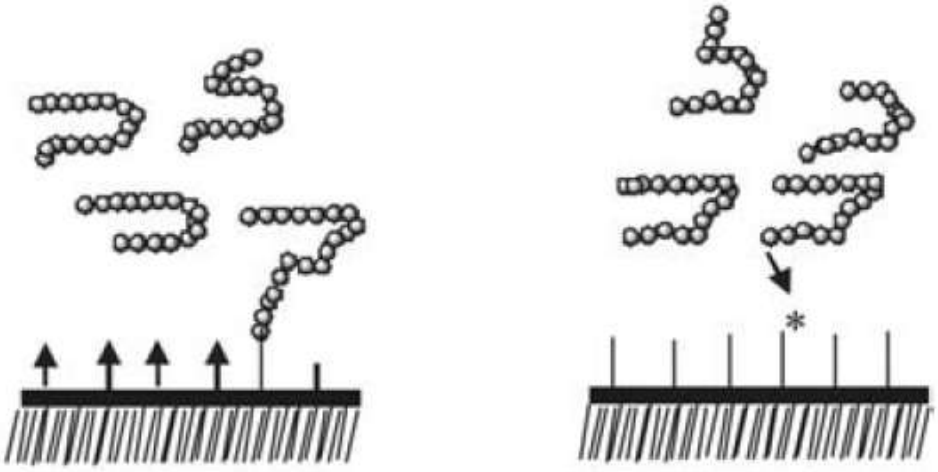


Fig. 1: *Schematic diagram of "grafting to" (left scheme) and "grafting from" [3]*

In consequence of modification of polymer chain the mechanical properties are different from the original polymer. If the grafts are short, most of the mechanical and/or physical properties of the original substrate will be retained. But the chemical properties can be significantly different. The "grafting from" approach is the widely used method for polymer modification. The reaction can be carried out in the heterogeneous as well as homogeneous system. The grafting system contains three types of reactants: polymer, unsaturated monomer and free radical initiator. The important role in grafting reactions plays stabilizers [2], [3], [4].

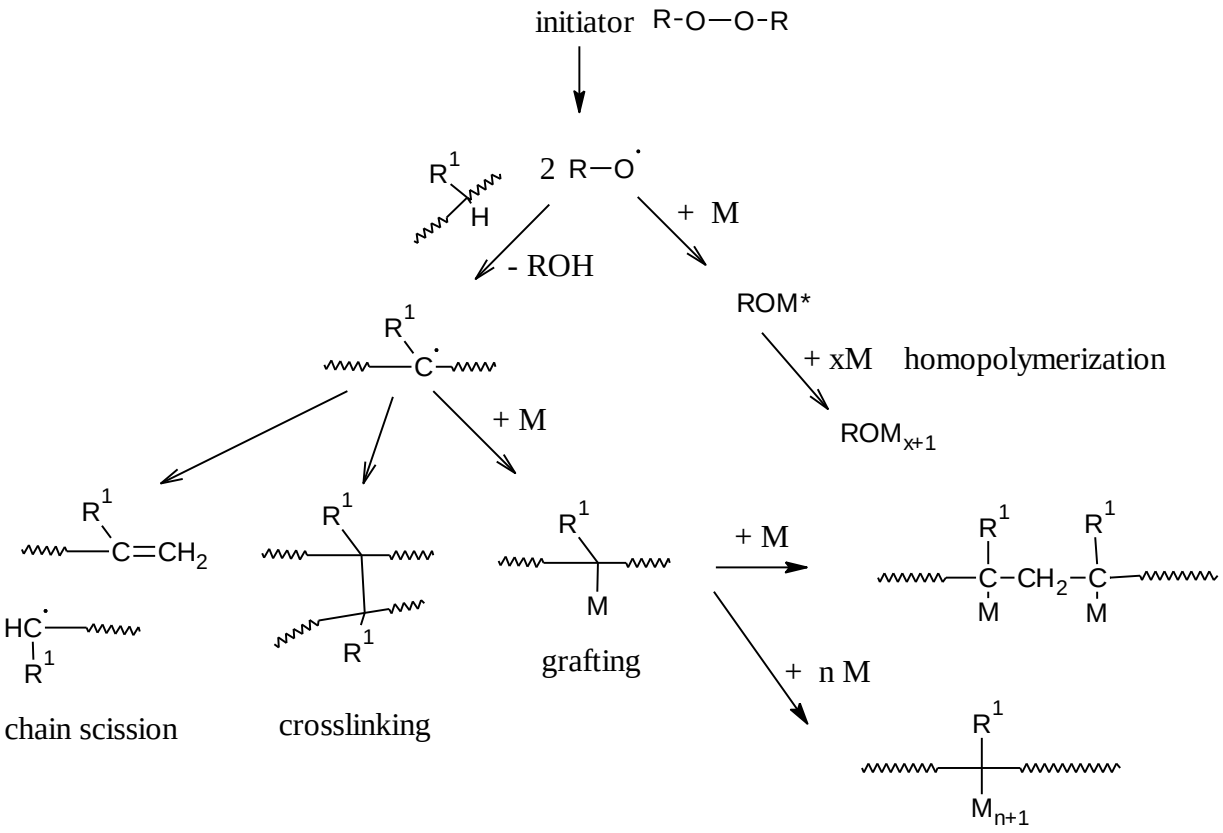


Fig. 2: *Possible reactions in the grafting system*

2.1.1. Initiation reactions

The grafting initiation can be performed by different pathway, such as chemical, radiation, photochemical, plasma-induced and enzymatic process. Chemical means includes two major ways: free radical and ionic. Radical, cationic, and anionic initiators cannot be used indiscriminately, all three types don't convenient for all monomers. Monomers have high selectivity toward the initiator. Some monomers (e.g. acrylates) may not react with cationic initiators, while others (e.g. vinyl ethers) may not react with anionic initiators. Most monomers undergo reaction with a radical initiator, although at varying rates. The radical initiators are widely applied [5], [6].

Radicals are generated by thermal, photochemical or mechanical homolytic cleavage of the labile oxygen–oxygen bond of peroxides at appropriate temperatures (see Fig. 3), or by redox process. The redox initiation can be divided into the two process groups. One group involves either oxidation or reduction of substrate to give radical. The second group involves nonchains reactions, the initiators are used as a catalyst. For example, a copper (I) complex reacts with an alkyl halide to give copper (II) complex and an alkyl radical [2], [3], [6].

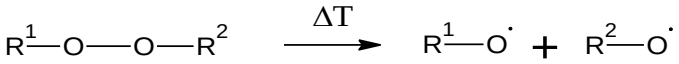


Fig. 3: *General scheme of homolytic cleavage*

The created primary radical abstracts from the polymer the tertiary carbon bonded hydrogen atom to form macroradical.

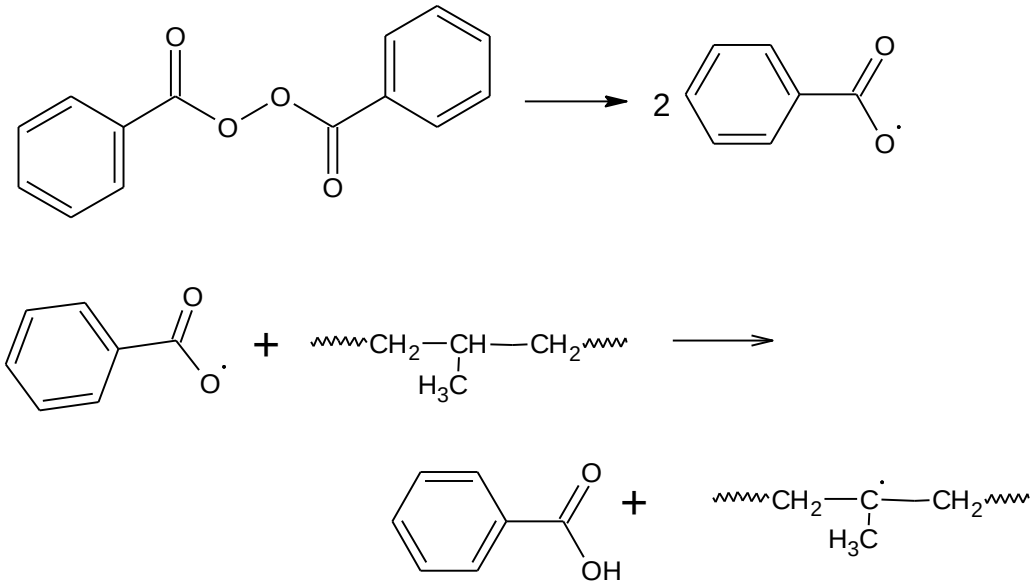


Fig 4:*Homolytic cleavage of dibenzoyl peroxide and formation of PP macroradica*l

2.1.2. Propagation of grafting reaction

The next step in a generating a grafting polymer is the propagation. The formed macroradical react with the selected monomer containing double bonds to formation grafting structure of macroradical. If the branched macroradical reacts with more double bond containing monomer, longer grafts will form. The grafts cause the improvement of its properties. The modified polymers have a lot of industrial applications, including adhesion, painting, coating, etc. [2], [3].

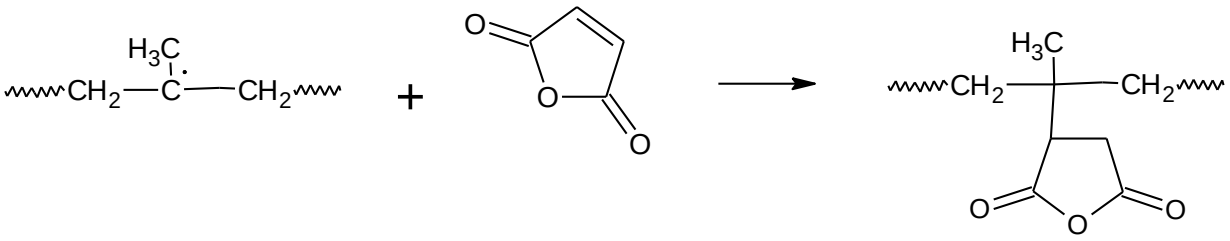


Fig. 5: *Scheme of formation short graft*

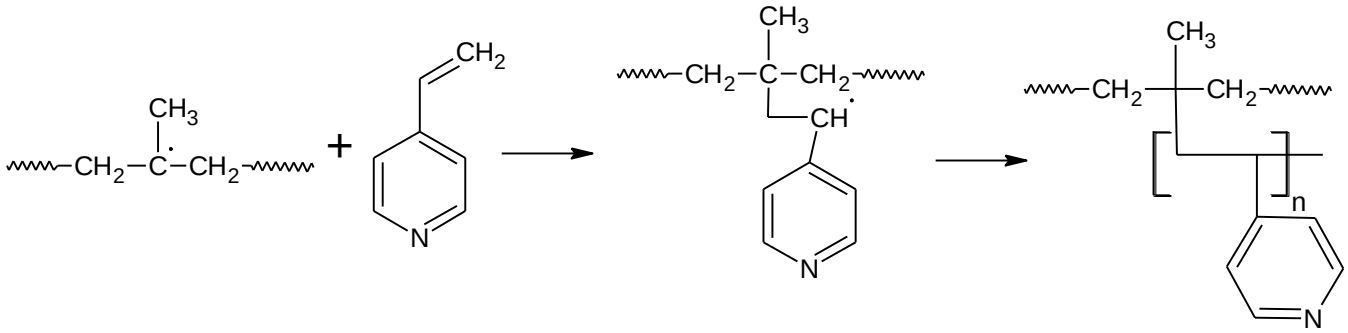


Fig. 6: *General scheme Scheme of grafting reaction of 4-vinylpyridine onto PP (creation of long graft)*

2.1.3. Undesirable reaction in the grafting system

In the grafting system array of reactions can be under way. Beside the desirable grafting reaction there can be unwanted reactions, such as chain scission, branching, crosslinking and monomer homopolymerization.

Chain scission happens when the macroradical breaks up to two smaller fragments thanks macroradical's instability. This reaction causes a reduction of molecular weight and so the polydispersity approaches two. This is characteristic for higher molecular chains. With reduction of molecular weight the melt viscosity decreases (increases value of melt flow index) [2].

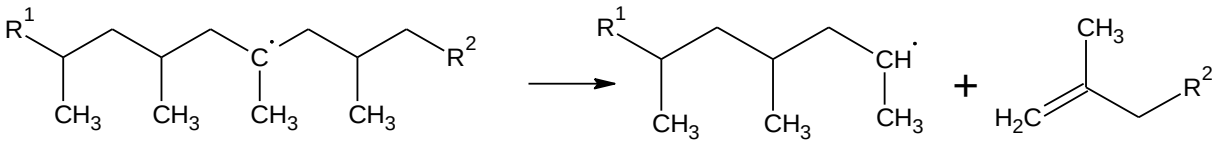


Fig. 7: *Scheme of β-scission of PP*

Long-chain branches are formed when macroradical experiences bimolecular termination by combination. If these branches continue, a three-dimension network will form. With higher molecular weight chains via long-chain branching increases melt strength and improves hardening properties [2], [3].

Crosslinking can sometimes improve properties of the original polymer such as increased service temperature, solvent resistant, flexural modulus, dimension stability. Crosslinking is the association of polymers through a chemical bond. In the most cases, the crosslinking is irreversible. It can be intramolecular or intermolecular [2], [3].

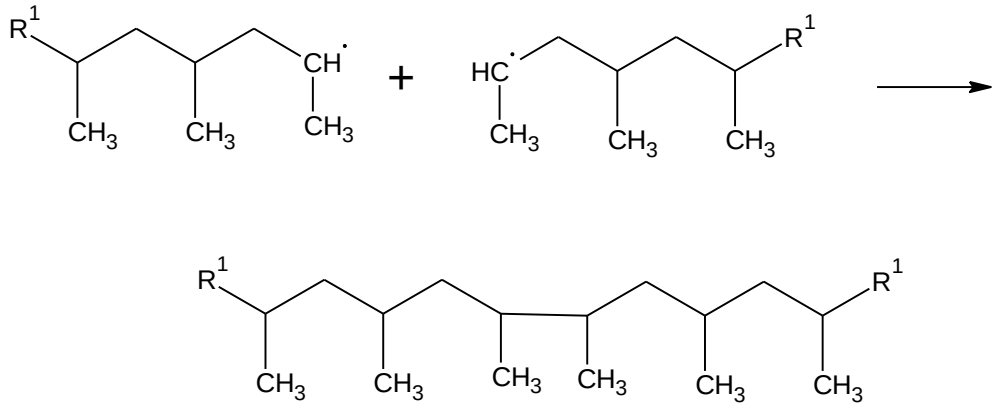


Fig. 8: *Scheme of crosslinking*

2.2. Factors affecting grafting process

2.2.1. Initiators

The nature of initiator influences not only the rate of polymerization but also affects the polymer structure and so possible polymer mechanical properties, too.

The different rates of decomposition of various initiators are caused the differences in theirs and radicals structures. If the structure of the initiator is more bulky, then the rate of decomposition will be greater (the rate constant of decomposition is greater). The differences in the rates of decomposition of various initiators are related in the terms of the initiator half-life $t_{1/2}$ which is defined as the time for the initiator concentration to decrease to one half its original value at a certain temperature and other given conditions. The higher decomposition rate is, the shorter this time is. The rate of decomposition of an organic peroxide may be enhanced when the concentration of peroxide is high, the solvent polar is or substances present in the system are reactive toward the peroxide [2], [3], [4], [5], [6].

Table 1: *Half-lives of chosen peroxides at various temperatures [5]*

	Half-life at (minute-m, hour-h)					
Initiator	50°C	70°C	85°C	100°C	130°C	175°C
Azobisisobutyronitrile	74 h	4.8 h	-	7.2 m	-	-
Benzoyl peroxide	-	7.3 h	1.4 h	20 m	-	-
Acetyl peroxide	158 h	8.1 h	1.1 h	-	-	-
t-Butyl peracetate	-	-	88 h	13 h	18 m	-
Cumyl peroxide	-	-	-	-	1.7 h	-

The other important character of initiator is the initiator efficiency, which can be defined as a fraction of primary radical which abstract hydrogen atoms from the polymer backbone to form corresponding macroradicals. The hydrogen abstracting depends not only on the nature of primary radicals but also on the type of carbon–hydrogen bonds. The abstracting a hydrogen atom from a bulky tertiary alkane is easier than from a less bulky secondary alkane and more reactive than a primary alkane [2], [3], [4], [5], [6].

In grafting system are often used peroxides which have relatively long halflife (in the order of minutes) at normal melt grafting temperature. The initiator concentration has influence on the grafting efficiency. The increase in peroxide concentration increases the grafting degree but this reaction will be concomitant increase of undesirable reactions [2], [3].

2.2.2. Effect of the backbones of polymer and monomer

The backbone polymer can affect kinetics of grafting. Polymer backbone can have influence on the formation of reactive centers on the polymer by the reaction with the initiators and on the reaction of created reactive centers with the monomer. If formed reactive centers are highly reactive toward the monomer, they will readily provide grafting. But if they are unreactive toward the monomer, they won´t provide grafting but crosslinking [3].

Monomers can readily homopolymerize and they can encourage the grafting reaction. But in the system significant amounts of homopolymer will be generated. Monomers can reluctant homopolymerize and they will give short grafts or they can enhance crosslinking [3].

2.2.3. Effect of temperature

Melt free-radical grafting is carried out at higher temperatures compared to the grafting in solution. The most notable influence of temperature is on the rate of organic peroxide decomposition. Peroxide halflife decreases with growing temperature in according with Arrhenius equation [2], [3].

$$k = A \cdot e^{-\frac{E_A}{RT}} \tag{1}$$

Grafting propagation has the reverse reaction (depropagation). With increasing temperature the importance of graft depropagation increases. There is a critical temperature at which the rates of propagation and depropagation are equal. This temperature is called the "ceiling temperature" of grafting, and is denoted T_{cg}. The ceiling temperature T_c corresponds to the free energy change ΔG being zero. Thus

$$\Delta G = \Delta H - T_c \Delta S \tag{2}$$

$$0 = \Delta H - T_c \Delta S \tag{3}$$

$$T_{cg} = \frac{\Delta H}{\Delta S} = \frac{\Delta H}{\Delta S^{\circ} + R\ln[M]} \tag{4}$$

where ΔH and ΔS are enthalpy and entropy of reaction; $\Delta S°$ is the standard entropy and [M] monomer concentration. It means that the ceiling temperature is dependent on the monomer concentration. The higher the monomer concentration, the higher the ceiling temperature [2], [3], [4], [7].

In addition temperature may affect degradation and/or crosslinking. For monomers of which the ceiling temperatures are close to the grafting temperature, the equilibrium will be shifted to grafting, although grafting temperature increase causes growing of grafting rate and polymerization rate [2], [3].

2.2.4. Influence of other factors

Viscosity effects

The viscosity of melt free-radical grafting system can be higher than that of a solution grafting. If the viscosity of medium is high, grafting can be involved due to retardation of various reactive species diffusion [2].

Heterogeneity effects

The grafting system is composed of three types of reactants: monomer, polymer and organic peroxides. Grafting reaction depends on constitute a mixture. If mixture of polymer, monomer and peroxide is homogeneous at molecular scale, the modified polymer will be the most uniform in terms of grafting yield, molecular weight, etc. If the monomer and initiator are completely immiscible with polymer, grafting will occur only at the interface and polymerization will proceed in the aggregates. If the monomer and initiator are partly miscible with polymer, grafting will occur only in the polymeric phase, and polymerization will take place both in the polymeric phase and in the aggregates [2], [7].

2.2.5. Suitable reaction setting

The grafting process can be performed in mixers or screw extruders. The mixers are very often preferred over the screw extruders as a reactor for the study of grafting reactions. But the screw extruders are ideal for continuous processing. Advantage of mixer is exact knowledge of reaction time. It has other useful features:

- ability of mixing highly viscous polymers
- small mixing chamber offers opportunities to modify expensive or exotic chemicals
- easy varying of processing parameters: temperature, mixing time, mixing intensity via the rotation speed of rotors

The increasing screw speed had small influence on the grafting yield. Therefore the grafting is preferred by lower screw speed. It can be considered 180–200 rpm to be high screw speed and 30–60 rpm to low [2].

2.3. Comparison of polypropylene and poly(lactic acid)

Polypropylene and poly(lactic acid) belong to the groups of thermoplastic polymer. But poly(lactic acid) is aliphatic polyesters made from α-hydroxy acids, whereas polypropylene is classified as polyolefin [1], [10].

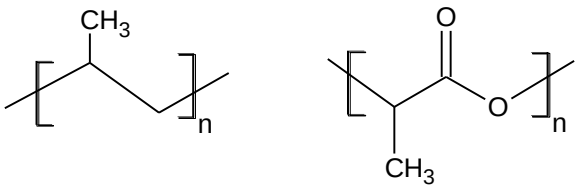


Fig. 9: *Structural formula of PP (left) and PLA*

The high molecular polypropylene is acquired by using Ziegler-Natt catalyst via radical polymeerization. But poly(lactic acid) can be prepared by direct condensation of lactic acid or by the ring-opening polymerization of the lactide dimer. Because of difficulties by preparation the ring-opening polymerization is given preferences to the direct condensation of PLA. Starting material is made by a fermentation process using renewable material (corn, beet). The polymer degrades rapidly in the environment and the by-products have environment friendly. It is possible, that the by-products can be carbon dioxide and water [8], [10].

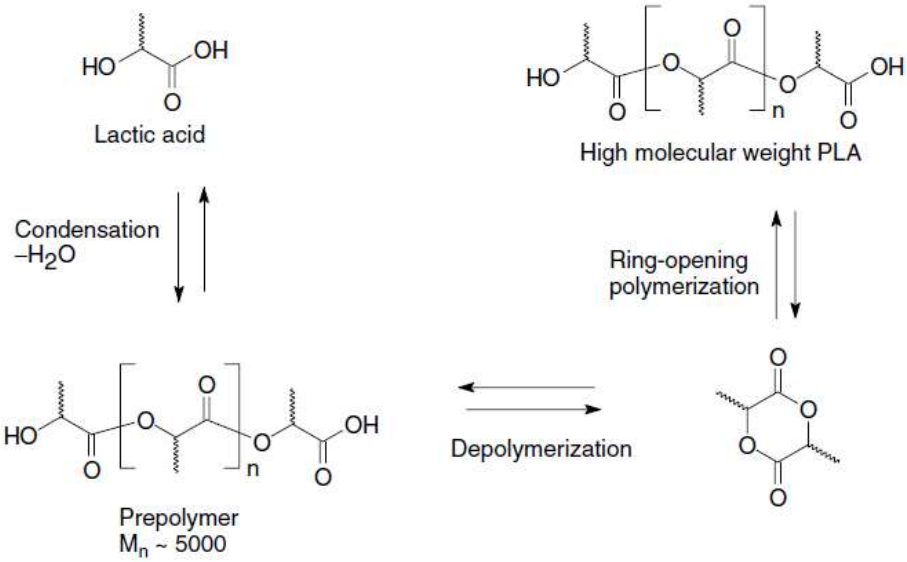


Fig. 10: *Scheme of preparation of PLA via prepolymer and lactide [8]*

Polypropylene can occur as isotactic, synditactic , and atactic stereo-structure depending on the position of the methyl groups. If the methyl groups are in the same plane, then the polypropylene is isotactic. If the methyl groups are alternately above and under the plane, the polypropylene is syndiotactic. The statistic occurring methyl groups are in the case of atactic polypropylene. The mechanical properties depend on the structure of PP [10].

In the dependent on the stereopurity PLA can be semicrystalline or amorphous. L(–)-lactic acid (2-hydroxy propionic acid) is natural and most common form of acid, but D(+)-lactic acid can be produced by microorganisms. D(+)-lactic acid units are incorporated into the L(–

)-lactic acid to optimize the crystallization kinetics for specific fabrications process and applications [1], [8].

Polypropylene is crystalline, hydrophobic. PP has non-polar structure, and good chemical resistance. Polypropylene swells in ketones, hydrocarbons and esters. PP solves in chlorinated and aromatic hydrocarbons at temperatures higher than 90 °C. It is rarely pervious to gases and vapors. It absorbs minimal mineral and vegetal oils. It is resistant to effect of light and higher temperatures [10].

Table 2: *Properties of isotactic, syndiotactic, and atactic polypropylene [10]*

Properties	Isotactic	Syndiotactic	Atactic
Density g/cm^3	0.92–0 .94	0.8–0.91	0.85–0.9
Melting point °C	165	135	–
Solubility in hydrocarbon	insoluble	middle	high
Strength	high	middle	very low

High-molecular-weight poly(lactic acid) is a colorless, glossy. At room temperature is brittle. The amorphous PLA is soluble in the most organic solvents, such as tetrahydrofuran (THF), chlorinated solvents, benzene, acetonitrile, and dioxane. Crystalline PLA is soluble in chlorinated solvents and benzene at elevated temperatures [1], [8], [9].

PLA is stiff, high modulus polymer with mechanical properties comparable to polystyrene. PLA has good mechanical properties, some ones are shown in Table 3 [1], [8], [9].

Table 3: *Selected properties of PLA [1], [8]*

Elastic modulus	3 000–4 000 MPa
Tensile strength	50–70 MPa
Glass transition temperature	around 60–70 °C
Melting point	about 180 °C

Polypropylene is widely used in daily life because of its good mechanical properties and relatively low cost. Its applications have been largely limited due to its hydrophobic properties nevertheless it is applied in automotive components, laboratory equipment, containers of various types, etc. Polypropylene belongs in the group of thermoplastic polymers [10].

PLA may be the polymer with the broadest range of applications because of its ability to be stress crystallized, thermally crystallized, impact modified, filled, and copolymerized. It can be form into transparent films, fibers, or injection molded into preforms for bottles, like PETP. It is excellent for food contact and packaging applications. But the commercial application has been limited by high production costs [1], [8].

Polymer succumbs to the degradation during technologic processing. In the case of polypropylene it is the β-scission, when the long chain falls into two smaller fragments. The breakage entails the reduction of the molecular-weight [10].

The degradation of poly(lactic acid) is based primary on the hydrolysis, followed by bacterial attack on the fragmented residuals. The hydrolysis depends on the temperature, moisture content and on pH. The rate of degradation can be accelerated by acids and bases.

The crystalline phase of PLA hydrolyzes much more slowly than the amorphous one. Above the glass transition temperature is the rate of hydrolysis much greater than below [1], [8].

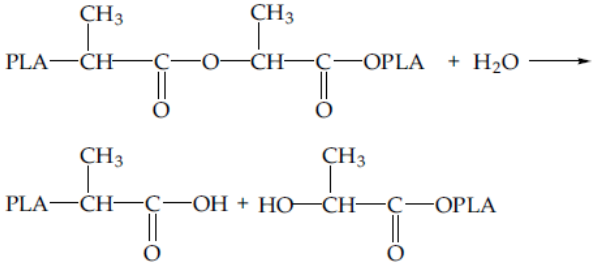


Fig. 11: *Reaction of hydrolysis of PLA [8]*

2.4. Overview of current possibilities of PP modification

Copolymer MAH-*g*-PP can be prepared under solution or melt and in the solid state [11], [12].

The simplest and most used method is the grafting polymerization of maleinanhydride onto polypropylene under melt state. The reactions run in the presence of a radical initiator and in a twin-screw extruder. Lei C. et al. [11] investigated influence of amount of initiator (dicumyl peroxide, DCP) and maleic anhydride onto grafting efficiency. The graft degree first increased and then decreased with the growing amount of DCP and MAH. When an excessive content of DCP was used, the degradation of the PP backbone was induced and so the grafting effect decreased. But the excessive content of MAH caused MAH homopolymerization, because of worse affinity between PP and MAH. Only author Lei C. states that the maleic anhydride is able to homopolymerize. The grafting degree sank too. To enhance of efficiency of grafting was used 1-decene as a second monomer. In compared with styrene 1-decene had better efficiency with less content added, styrene is other possibility of grafting improvement. Styrene and 1-decene inhibited PP degradation.

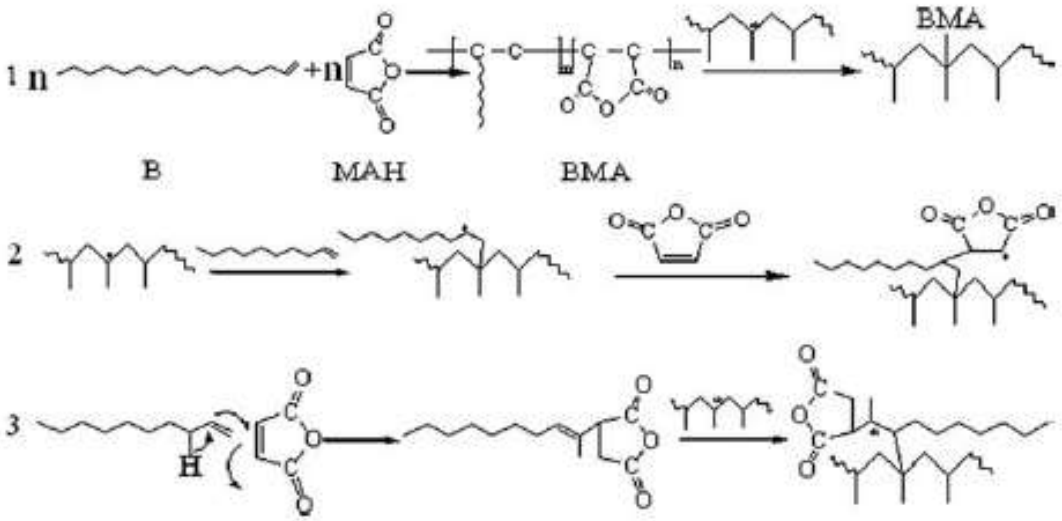


Fig. 12: *Possible mechanisms of MAH melt grafting under the existence of 1-decene [11]*

The other eventuality of the preparation of MAH-g-PP-St copolymer is in the suspension phase. Zheng Y. et al. [12] prepared this copolymer via suspension method. They obtained similar results of dependence graft degree on amount of initiator and monomers as Lei c. et al. [11].

Gartner et al. [13] performed grafting reaction of MAH onto PP in the melt. At first they took model obtained describes relationship between grafting degree and the other independent into the consideration only three factors under the study. The factors were monomer (maleic anhydride) concentration, initiator concentration and the reaction time. They found optimal condition for preparation of MA-*g*-PP: 7.4 % for MA percentage, 1.40 % for initiator percentage, and 900 s for reaction time. These conditions were applied. The experimental value of grafting degree was 1.56 %. The grafting PP they used as a compatibilizer for blends of PP and polyethylene terephthalate.

Yazdani-Pedram et al. [14] functionalized PP in melt by grafting reaction with itaconic acid derivatives, monomethyl itaconate (MMI) and dimethyl itaconate (DMI). The percentage of DMI grafting increased with the increasing quantity of the monomer for a determinate concentration of initiator (2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane, Lupersol 101) up to reach maximal value. This behavior was observed in a case of MMI, too. The thermal analysis showed that the grafting process did not affect the melting temperature of modified PP samples. But it was found that the percentage of crystallinity increased by increasing the percentage of grafting. This rise of crystllinity percentage was attributed to the decrease of molecular weight of modified PP caused β-scission.

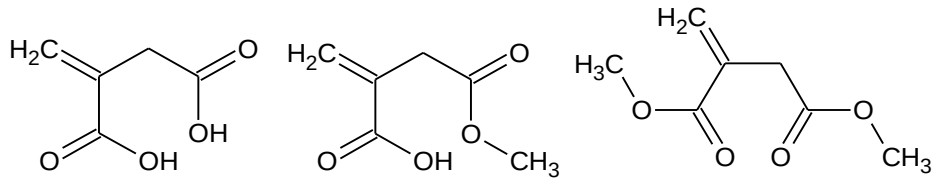


Fig. 13: *Structures of itaconic acid (a), monomethyl itaconate (b) and dimethyl itaconate (c)*

Modified PP is possible to apply as a compatibilizer for PP blends with other polymers or for preparation of composites. Mancada et al. [15] used for PP/clay nanocomposites as a compatibilizer PP grafted itaconic acid (IA). They used montmorillonite, natural and synthetic hectorite as clay. The mechanical properties (tensile modulus and tensile strength) of nanocomposites with montmorillonite were obtained their higher values when modified PP with higher percentage of grafting was used as compatibilizer, compared with values for virgin PP. The nanocomposites with naturel or synthetic hectorite had better mechanical properties when the composites containing compatibilizer having lowest percentage of grafting itaconic acid.

The chemical modification of PP using acrylic acid (AA) has many different methodologies as: ultraviolet irradiation in the presence of benzophenone, etching oxidation, emulsion, suspension process, plasma functionalization, and melt-radical grafting reaction. Amaro et coworkers [16] used reactive extrusion as the traditional and in industrial very applied modification technique. During the reaction the grafting level and molecular weight was

controlled using butyl 3-(2-furanyl)propenoate (BFA) as coagent. The samples were prepared containing BFA and without BFA content. For all samples decreases of molecular weight and polydispersity were observed, but for samples with coagent the decrease was less severe. The grafting level depended on the monomer/peroxide ratio and the presence of BFA. By the constant amount of initiator the grafting level increased with the growing content of AA in absence of BFA. When the coagent was added, only slightly increment of the grafting degree was observed by increasing the AA amount. The graft degree was lower in the sample with BFA compared to sample without BFA by maintain the AA amount constant. The crystallization temperature for all sample had increment with respect to pure PP, indicating the nucleation effect of the grafted AA chains during crystallization. Samples with the highest grafting degree and molecular weight were tested as metal ion adsorption resins. AA-grafted samples accounted a positive stabilization effect toward Al(III) and Zn(II). The highest adsorption efficiency were obtained for Al(III) and Hg(II).

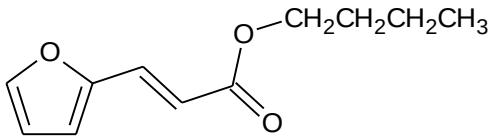


Fig. 14: *Structure of butyl 3-(2-furanyl)propenoate (BFA)*

T. Gang-sheng et al. [17] prepared polypropylene grafted acrylic acid by using supercritical carbon dioxide ($scCO_2$)-assisted solid-state free radical grafting process. When the reaction time was optimized, it was observed graft content of AA and gel percent increased with the increasing reaction time. When the reaction time was 3 hours, the grafting content slowed down slightly, while gel percent increased continuously with growing the reaction time. The CO_2 pressure involved grafting reaction and thus that the gel percent first decreased with increasing CO_2 pressure, reached a minimum and then increased. This reverse progress was possible to see by grafting level of AA, grafting content first increased, reached maximum and then decreased. The values of the CO_2 pressure corresponding minimum gel percent and maximum grafting degree was above 14-15MPa. Reactions were influenced reaction temperature, the higher temperature resulted the smaller gel percent and the higher grafted content. The values of recrystallization temperature, enthalpy of recrystallization and crystallinity after cooling of those PP-*g*-AA samples were significantly higher than those of the blank PP. Crystal morphologies of the blank PP and grafted PP were significantly different. The grafted spherulites had smaller diameter with the increase of AA content compared to bank PP spherulites.

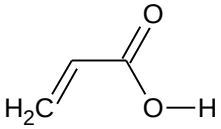


Fig. 15: *Structure of acrylic acid*

The extent of the grafting depends on the reactivity of the monomer toward macroradicals. Polar effects, steric effects, resonance effects and thermodynamic effects are the factors that control monomer reactivity. M. R. Badrossamay et al. [18] had studied graft polymerization of PP with acrylic amide derivates, which were acrylamide (AAM), methacrylamide (MAM), N-*tert*-butylacrylamide (NTAAM) and N-*tert*-butylmethacrylamide (NTMAM). It was found that NTAAM and NTMAM had considerably lower reactivity toward the grafting reaction that AAM and MAM, so grafting yield. Reactivity of monomer depends on structure of both the monomer and the radical. If the macroradical is bulky, it could reduce accessibility of bulky monomers. Thus, larger substituents like NTMAM could have lowest grafting content. The grafting content can be improved by addition of monomer containing double bond of vinyl monemers which react quickly with macroradicals, such styrene. The results shown that in the case of secondary amide monomers instead of increasing contents, the addition of styrene decreased the grafting degree of NTAAM and NTMAM compared to system without styrene.

The aim of Chmela et al. [19] project was the role of water as heat transfer medium and influence of alkyl chain in ester group of a series of methacrylate monomers on the of iPP grafting. The series of methacrylate monomers contained as alkyl groups methyl- (MMA), ethyl- (EMA), butyl- (BMA), ethyl hexyl- (EHMA) and dodecyl (DMA).

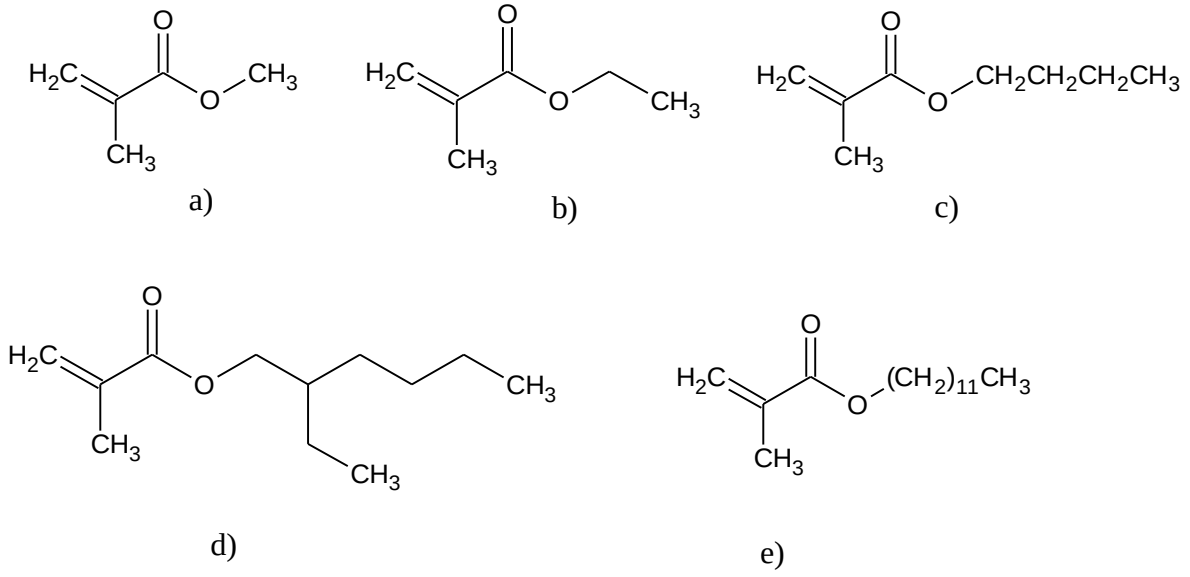


Fig. 16: *Formulas of methyl- (a), ethyl- (b), butyl- (c), ethyl hexyl- (d) and dodecyl methacrylate*

It was found that the grafting efficiency was higher in all cases when reactions carried out in water phase ($NaCl/H_2O$) then without liquid medium. However, grafting performed in the pure water afforded lower efficiency then grafting in NaCl water solution. It was studied effect of the length of alkyl chain. In the series MMA to BMA yield of grafting slightly increased, the samples were prepared with 10 wt% monomer. However, with longer alkyl chain (EHMA and DMA) was grafting yield lower, what is demonstrated in the following Table 4.

Table 4: *Grafting degree and grafting efficiencies of methacrylates [19]*

	Amount of grafted methacrylates (wt %) and grafting efficiencies GE (%)					
Amount of methacrylate in reaction mixture (wt %)	MMA (GE)	EMA (GE)	BMA (GE)	EHMA (GE)	DMA (GE)	DMA Gel content (wt%)
10	5.7 (57.0)	6.8 (68.0)	7.2 (72.0)	3.3 (33.0)	3.7[a] (36.2)[b]	2.0
20	17.3 (86.5)	10.4 (52.0)	10.5 (52.5)	5.5 (27.5)	19.6 [a] (77.0) [b]	21.4
30	22.3 (74.3)	17.0 (56.6)	9.4 (31.3)	13.0 (43.3)	29.5 [a] (64.2) [b]	34.7

[a] total amount of grafted DMA and gel content

[b] the amount of gel content was subtracted for GE calculation

Emma-Louise Burton et al. [20] modified polypropylene by glycidyl methacrylate (GMA) to produce GMA-grafted polypropylene (PP-*g*-GMA). But they explored the effects of adding the reactants (organic peroxide and GMA) in two separate stages. The position and order of the reactant addition were investigated as a possibility to improve graft yields. Two methods of addition were explored: standard (peroxide was added first to the polymer and just then GMA) and reversed (the GMA was added first and initiator after) injection. With the standard injection route, an increase in the grafting of GMA was observed with a decrease in the screw speed (the maximal conversion of the GMA was only 19 %). But the reversed injection is more efficient in the grafting reaction; almost the same degree of the grafting was achieved at the higher screw speed contrary to the standard method. The degree of grafting can be improved using styrene as a comonomer, which was proved.

S. Al-Malaika and E. Eddiyanto in their work [21] have studied the effect of two reactive comonomers, bifunctional one (divinyl benzene, DVB) and a tri-functional one (trimethylolpropane triacrylate, TRIS) on the melt free radical grafting reaction of glycidyl methacrylate (GMA) onto polypropylene (PP). They carried out series of experiments with comonomer DVB or TRIS and without comonomer (convention system). In the presence of DVB the extent of grafting was higher at all temperatures and with all tried initiator then in convention system. Compared to a convention system, the using DVB in the GMA-grafting system required very small concentration of peroxide to achieve high GMA grafting efficiency. The effect of grafting was influenced degradation in PP through chain scission reactions (thanks low concentration of initiator) and formation of poly-GMA. The amount of poly-GMA in the GMA-DVB decreased to insignificant level at all peroxide concentrations, contrary to convention system. Effect of TRIS on the grafting reaction was lower than DVB, but both comonomer systems gave much higher grafting level than in the corresponding system in absence of comonomer.

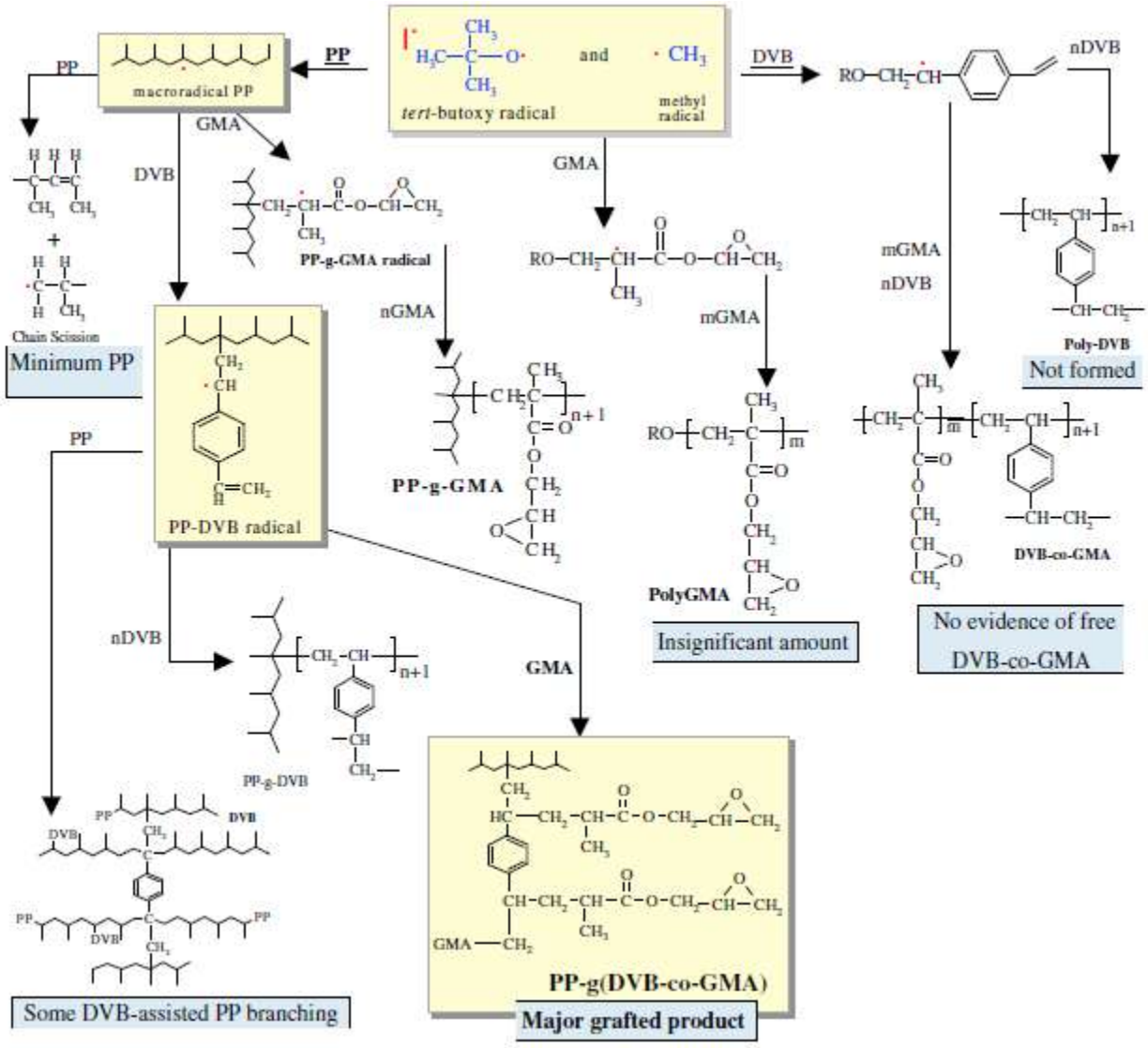


Fig. 17: *Reaction mechanism of melt grafting of GMA on PP in the presence of DVB [21]*

Cheng et al. [22] improved PP by addition of fluorinated methacrylate, 2,3,4,5,5,5-hexafluoro-2,4-bis(trifluoromethyl) pentyl methacrylate (HFPMA), to form fluorinated PP (FPP). The results showed that in the FPP coexisted two types of crystals, α- and β-form. With the increasing of fluorinated methacrylate content decreased the crystallinity and increased relative content of β-form crystal. This has consequence that the contact angles of ethylene and glycol on the FPPs increased with rising in the content of fluorine monomer. The barrier properties were found out on the blow-molding bottles of the PP and FPP. The PP bottle exhibited poor barrier property for acetone and xylene compared to FPP bottles.

This material is very useful in reducing the permeability of organic solvent and thus significant reduction of environment pollution. It can be applied for automotive fuel tanks, vessels for storage of toxic and volatile liquids in the industry [22].

Poly(ethylene glycol) (PEG) has been widely used in materials science and biotechnology due its low toxicity . It has been commonly applied to functionalize to improve hydrophilicity.

In article [23] PP was grafted PEG acrylate. Shi H. et al. used partial pre-irradiated polypropylene as initiator. This method has a lot of advantages compared to conventional

grafting, use of this initiator entails less chain scission side reactions and improvement of biological properties (product becomes non-toxic). Shi H. et al. found that the grafting degree increased with growing dosage of PEG acrylate in the grafting system. Temperature of crystallization of functionalized PP was higher than the neat PP. The temperature increased along the increase of PEG dosage in the product, from 111.8 °C of PP to 118.9 °C. PEG on the PP backbones acted as nucleating agent. The size of crystalline spherulites decreased with the growing of grafting degree of PEG. The hydrophilicity characteristics can be obtained by contact angle measurements. The contact angle value decreased with the higher PEG acrylate content and the polarity increased.

The other possibility of grafting onto PP is 2,4-diamino-6-diallylamino-1,3,5-triazine (NDAM). This copolymer was prepared by Badrossamay et al. [24] , but the aim of this work was comparing of initiators effectivity. They used dicumyl peroxide (DCP) and 2,5-dimethyl-2,5-(*tert*-butylperoxy)hexyne (DTBHY) as initiators. It was found, that the reaction efficiency of the grafting process in the presence of DCP as initiator is almost two times higher than when DTBHY was used as initiator, but the grafting content was higher by DTBHY in comparison to DCP. Higher amount of monomer increased the grafting reaction, while more initiator led to more polymer chain scission and a lower molecular weight of the final product. During the grafting process was more chain scission when DTBHY was used.

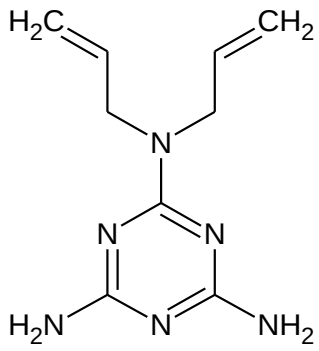


Fig. 18: *Structure of 2,4-diamino-6-diallylamino-1,3,5-triazine*

The other possibility of the grafting on PP is using acrylonitrile (AN) and vinylimidazole (VIm) to form PP-*g*-P(VIm/AN) what is described in the Mostafa's article [25]. The efficiency of grafting process would enhance the using of suitable solvent. The highest grafting degree was achieved in acetone from all tested solvent for grafting of VIm/AN comonomer on the PP fibers whereas the lowest grafting degree was in the case of using of dimethylformamide. The degree of grafting increased as the total irradiation dose (gamma radiation) as well as comonomer concentration increased. The grafting process was affected comonomer composition. It was found that the grafting yield decreased by increasing in the AN content in the comonomer. Reason for it can be it that AN and AN rich copolymers form precipitating homopolymer or copolymer in acetone. The VIm rich grafted PP fibers had higher thermal stability compared to the AN rich grafted PP fibers because PVIm start to decompose at 459 °C but PAN already at 285 °C. The composition of (VIm/AN) graft chains have influence on the removal of Pb, Hg and Cd from their solutions. For all composition affinity towards Cd was very weak but they have considerable affinity towards Pb and Hg.

The affinity increased by increasing the AN content in the chain composition to reach maximum at chain of VIm/AN of composition 50/50 mol %.

Ma L. et al. [26] prepared from PP, m-isopropenyl-α,α-dimethylbenzyl isocyanate (m-TMI) and styrene polymer PP-g-*m*-TMI and PP-g-(St-*m*-TMI). They studied influence cooling rate and composition of grafting PP onto the crystallization behavior. With the growing cooling rate the temperature of crystallization shift to lower values for all samples (PP, PP-g-*m*-TMI, PP-g-(St-*m*-TMI)), because the shorter time for completing of crystallization is. At a given cooling rate the temperature of crystallization apparently increased after grafting *m*-MTI and St onto PP, *m*-MTI reduced the interface free energy of PP nucleation and promoted the crystallization. In the case of the same cooling rate the grafting of *m*-MTI and St could accelerate the crystallization process.

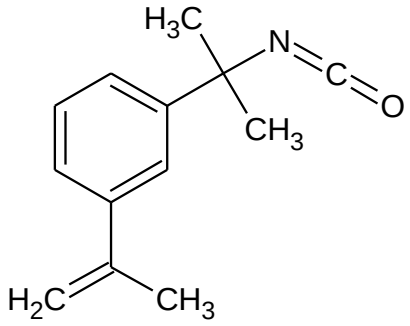


Fig. 19: *Structure of m-isopropenyl-α,α-dimethylbenzyl isocyanate (m-TMI)*

Crosslinking of polyolefins may improve their high temperature properties and extend their applications. Peroxide crosslinking, radiation crosslinking, and silane crosslinking are three main way of crosslinking industrially employed. Peroxide and radiation crosslinking techniques have some disadvantages such as high cost and thickness limitation in radiation crosslinking. In silane crosslinking technique, unsaturated hydrolysable alkysilanes are first grafted and then followed by catalyst crosslinking in the present of trace amount of water [27], [28].

N.C. Liu et al. [27] grafted on isotactic PP two types of silane monomers, methacryloylpropyltrimethoxysilane (VMMS) and vinyltriethoxysilane (VTES) and then they obtained three-dimensional polymers networks. The properties of products were judged in accord with gel percentage. It was found out that VMMS has greater grafting and crosslinking efficiency than VTES. With increasing molar ratio of monomer to initiator, the gel percentages of VMMS crosslinking PP increased rapidly from zero to about 30 wt% at low molar ratios, and the gel percentage increased slowly at higher molar ration of monomer to initiator. In the case of VTES as monomer, at low molar ratio didn't form gel. At higher (then 24 wt%) molar ratio slow increases in gel percentages were observed. With increasing DCP concentration, the gel percentage rose gradually to high level and then no significant increases were observed. They compared influence of initiator type on the gel percentages of crosslinking PP. It was observed that in the case of dibenzoyl peroxide (DBP) gel percentages were higher than DCP at a fixed initiator concentration.

The influence of amount of initiator (DBP) on the grafting reaction studied in the article [28]. They used ethynyl unsaturated silane for modification of polypropylene. With increasing

DBP concentration, the melt flow index (MFI) of the modified PP and the gel percentage changed rapidly until the initiator concentration reached 0.4 wt%. Then the changes were mildly. The changes due to modification of polypropylene were observed on the melt strength. After modification, the melt strength increased by 300 %. But MFI decreased by 83 %. With increasing silane concentration, the MFI and gel percentage of modified PP were changed rapidly and the leveled off. Using azodicarbonamide as blowing agent was made foam from high-melt-strength polypropylene by one-step method.

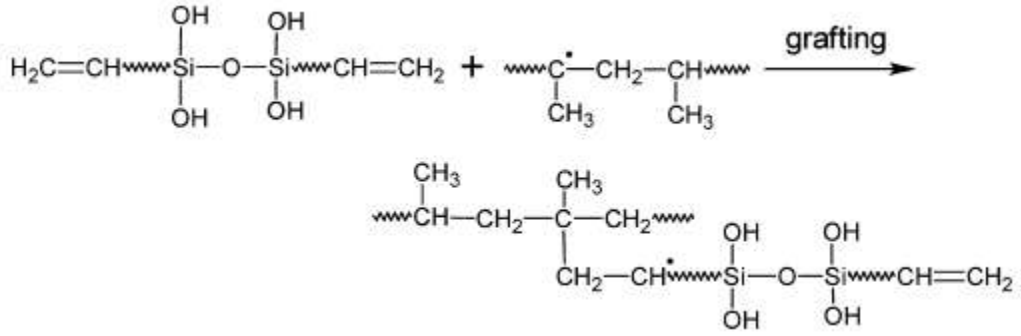


Fig. 20: *Scheme of grafting reaction between the silane condensation and PP macroradical [28]*

2.5. Current situation of grafting onto PLA

Carlson et al. [29] investigated grafting reaction of maleic anhydride onto polylactide taking place in extruder. They ascertained that the extrusion temperature didn't play a large role in the maleation of PLA, two temperatures (180 °C and 200 °C) were studied. When the blend didn't have initiator the reaction had no effect. But the growing initiator concentration resulted increase in the content of MA which was grafted. The addition of initiator (organic peroxide) had negative influence on molecular weight of sample, too. The other analysis showed that the maleated PLA had decomposition temperature from 2 to 7 °C below than virgin PLA. The addition of a small amount of MA onto PLA improved the interfacial adhesion of PLA-based blends and composites.

But David Plackett [30] determined the decomposition temperature of MA-*g*-PLA higher than temperature of pure PLA. He applied different pathway of preparation, via solution. The results showed only minor differences in melting point.

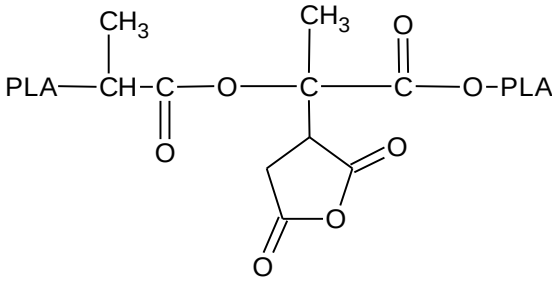


Fig. 21: *Structure of MA-g-PLA [30]*

Wu [31] prepared PLA-*g*-AA, but like this prepared polymer was used to manufacture its composite with sisal fibers. The results of composite observation were compared with results of PLA/sisal fibers composite. At the same sisal fibers content, the PLA/sisal composites had higher melt temperature than the PLA-*g*-AA/sisal fibers composites. The mechanical properties of composites were dependent on sisal fibers content. It was observed that tensile strength at break by PLA-*g*-AA/sisal fibers composite increased with the growing sisal fibers content to the constant value whereas tensile strength at break by PLA/sisal fibers decreased with the growing fibers content. The PLA-*g*-AA/fibers composite exhibited higher water resistance than PLA/sisal composite.

L. Moura et al. [32] prepared grafted copolymer of EVA/PLA using *in situ* polymerization of lactide (LA) in the presence of ethylene vinyl acetate copolymers (EVA). The reaction and copolymer formation led to changes of molecular structures of the polyesters, which promoted changes in melting temperature and crystallinity degree. The branching structure of copolymer caused increase of viscosity value compared to neat PLA. Rheological measurements are very sensitive to molecular changes. This copolymer had slight higher thermal stability contrary to PLA. The addition of biodegradable PLA to EVA promoted an increase in tensile strength, increases of stiffness. But this addition caused a decrease of the elongation at break. Grafted copolymer had better biodegradability. Biodegradation test were carried out in aqueous environment under aerobic condition during 20 days and degradation was characterized by the biochemical oxygen demand method.

The objective of research [33] was synthesis based on the using of a new catalyst magnesium hydride MgH_2 for preparation of poly(vinyl alcohol) (PVA) based-initiator for ring-opening polymerization of lactide. This catalyst was selected because of non-toxicity, magnesium is an environmental metal. This reaction carried out in melt phase and without solvent. The efficiency of reaction dependent on the monomer / PVA ratio, when the ration was smaller the yield was lower. The optimal ratio equal to about 5 gave high yield in graft copolymer. The thermal properties of the PVA-*g*-PLA copolymer were determinate. The value of T_g was observed lower than T_g value of virgin PLA (about 57 °C).

The one of possibility to graft polymer is application of photoinduced grafting process. Gutierrez-Villarreal et coworkers [34] functionalized PLA using assistance of *N*-vinylpyrrolidone (NVP) and as photoinitiator they used benzophenone (BP). The samples were kept constant distance from the UV lamp (source of UV radiation) to the films of 30 cm. The irradiation time was varied to control the degree of polymerization. A control film was prepared following the same procedure without UV irradiation. The irradiation time was up to 10 minutes. The results shown that with the longer time of irradiation of sample the conversion percent (fraction of the weight of total polymer formed including grafted and ungrafted polymer to weight of monomer added), grafting percent (fraction of the weight of grafted polymer after purification from unreacted compounds to the weight of monomer added) and grafting efficiency (fraction of the weight of grafted polymer after purification from unreacted compounds to the weight of total polymer formed including grafted and ungrafted polymer) increased. Within 10 min the conversion percent was 45 %, grafting efficiency 80 % and grafting percentage 36 %. They studied influence of irradiation time on the contact angle. It was found out that contact angle dropt decreased with the growing irradiation time. Pure PLA exhibited a water contact angle of $72° \pm 1°$and after 10 min irradiation $36.6° \pm 1°$. The grafted films were impregnated in a 10 wt % iodine ethanol solution at room temperature for 24h. Forming a reddish-brown color surface indicated

a chemical bonding of iodine onto the grafted PLA films. These modified films were left to work microorganisms. The grafted film inhibited the growth of microorganism, while the virgin sample didn't show this inhibition.

Poly(ethylene-octene) copolymer is a thermoplastic polyolefin elastomer (TPO) and is widely employed as a toughening agent in numerous polymer blending system. But these systems are immiscible by the high polarity difference between polymers components. C.-H. Ho et al. [35] prepared TPO-*g*-PLA as a compatibilizing agent for PLA/TPO blends. First had to be functionalized TPO by using the maleic anhydride. Afterwards the functionalized TPO reacted with PLA in the presence of 4-methylaminopyridine (DMAP). It was found that the graft reaction exhibited high reactivity at high temperature and DMAP concentration. But the rate of degradation PLA increased with the reaction temperature and growing amount of used DMAP. They investigated the influence of prepared TPO-*g*-PLA in TPO/PLA blends on the mechanical properties. The results shown, that the tensile strength and the tensile modulus remained without enhancement. Nevertheless, the tensile toughness and elongation at break increased with the concentration of the compatibilizers, but decreased when 5 wt% of TPO-*g*-PLA copolymer was used. It was found that the TPO-PLA copolymers with longer PLA chains accounted higher efficiency in the compatibilization of the TPO/PLA blends.

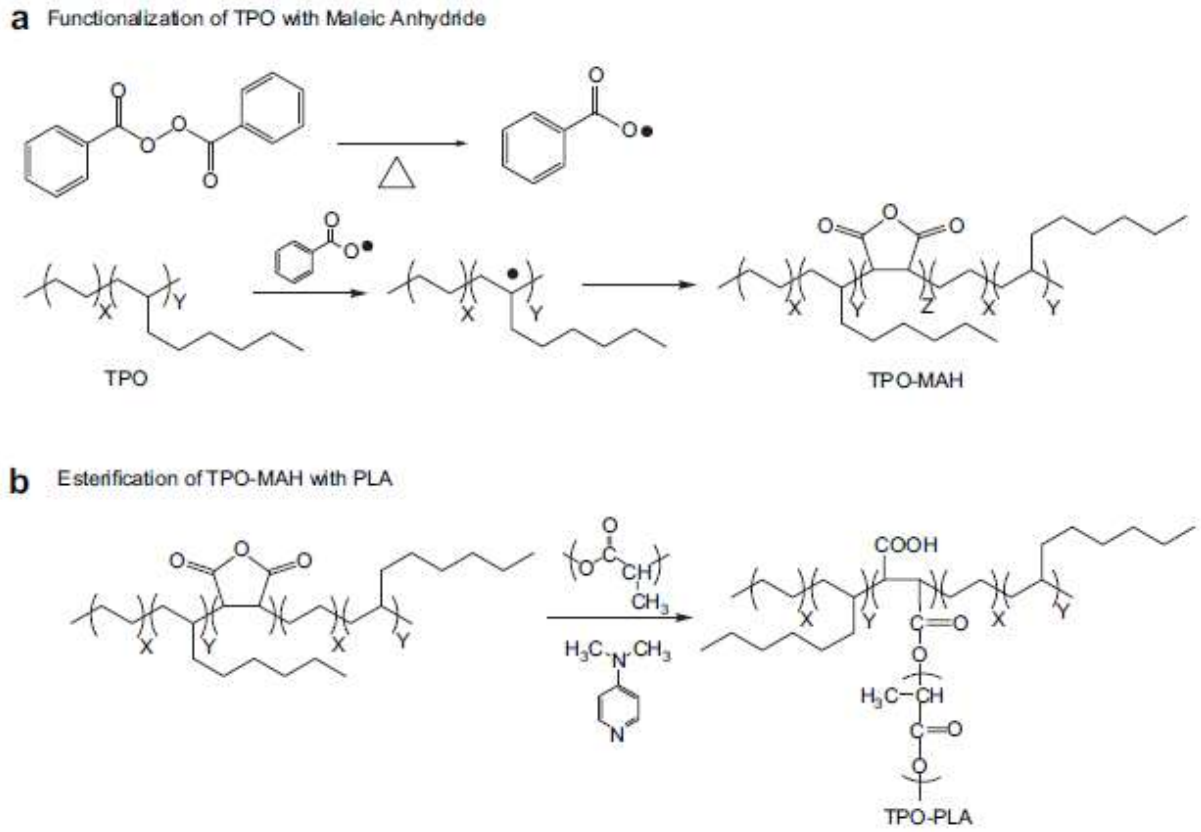


Fig. 22: *Synthesis scheme of TPO-PLA copolymer [35]*

The mechanical properties of polymer can be enhanced due to using of the toughening component in the system. As the toughening component is possible to employ styrene–ethylene–butylene–styrene block (SEBS) copolymer, which exhibits balanced elasticity, good processibility and thermal stability. The aim of article [36] was developed to prepare SEBS-*g*-polylactic acid (SEBS-*g*-PLA) copolymers in solvothermal process. The grafting reaction vessel contained chloroform as a solvent and benzoyl peroxide as an initiator. The test results

shown that the mechanical properties of SEBS-*g*-PLA of under various grafting degree were improved compared to pure SEBS. For example, more than 200 % elongation at break and about 200 % tensile strength through incorporation of 16 % graft degree of SEBS-*g*-PLA, compared to those of SEBS. The grafting degree of copolymer increased with the increase of reaction temperature to achieve maximal value at 120 °C and afterwards the grafting degree decreased sharply when the temperature was higher than 120 °C to reach a constant value when the temperature was up to 140 °C. The graft degree was dependent on the reaction time, concentration of initiator and PLA content, too. The grafting level of SEBS-*g*-PLA was rather low within 3h, and then it rapidly increased with an extended reaction time up to 5 h and then slightly decreased. The GD increased with the growing amount of initiator up to 0.5 g/30 ml and then it slightly decreased. The same behavior was in the case of PLA content, the maximal graft degree was obtained when the PLA content was 2.0 g/30 ml.

R. Ouhib et al. [37] produced amylose-*g*-PLA copolymer (A-*g*-PLA). The process of the preparation was composed through three steps: partial silylation of the hydroxyl groups on amylose chain, ring-opening polymerization of lactide initiated from all remaining hydroxyl groups on partially silylated amylose and silylether deprotection under mild conditions. They compared different silylating agents and their combinations. From all possibilities was selected N,O-bis-(trimethylsilyl)acetamide as optimal silylating agent. During the polymerization the stannous octoate was used to reduce the extent of the transesterifications. The other option to restrict transesterification probability was stopped deliberately before complete conversion of lactide. It was essential to control temperature. The ideal temperature was below 120 °C. The deprotection of silylated copolymers had been realized due to the hydrolysis of the silylether groups.

For environmentally friendly plastics can be used starch as low cost and renewable filler but native starch have to be modified to obtain thermoplastic starch (TPS). Water, glycerol and methanamide are often used modifiers. To improve the interfacial adhesion of components in blends can be applied glycidyl methacrylate grafted poly(ethylene octane) (GPOE). This was aim of the article [38]. With the growing GPOE content (from 0 to 15 wt%) the elongation at break of blends dramatically rose. When 10 wt% GPOE was used in blends, the elongation at break grew more obviously in comparison with that in non-GPOE blends. But with adding GPOE and with growing content of TPS the tensile strength decreased. The elongation at break of blends with various TPS content increased first and then decreased sharply. The highest elongation was in blends with 10 wt% TPS and 10 wt% GPOE. Because of the plasticization effect of TPS and GPOE the glass transition temperature T_g of all PLA blends was lower than that of pure PLA. With the increasing TPS content the T_g decreased to approach the T_g of GPOE. Melting temperature T_m and ΔH_m continuously dropped with growing TPS content, but in T_m and ΔH_m were no changes with growth of GPOE content. Q. Shi et al. [38] found out that the PLA blends with GPOE had higher biodegradation rates compared with the PLA blends without GPOE. The decomposition temperature of PLA with increasing thermoplastic starch content first increased and then decreased.

2.6. Aim of diploma thesis

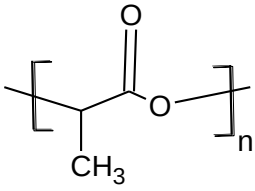
Aim of diploma thesis is chemical modification of poly(lactic acid). In the experimental part the theoretical knowledge of grafting various monomers onto polymer will be verified. The grafting process will be run in presence of peroxide as initiator and maleic anhydride or itaconic anhydride as monomers at selected temperatures. The treated PLA will be characterized using chosen analytic method. Primarily the monomer conversion will be determined. But the thermal properties will be studied, likewise.

3. EXPERIMENTAL PART

3.1. Chemicals

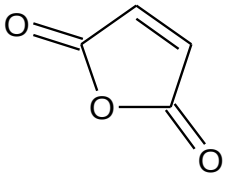
Polymer - Poly(lactic acid)

- Producer: Futtero, Belgium
- MFI: 18.2±0.1 g·10 min^{-1}
- CAS: 33135-50-1



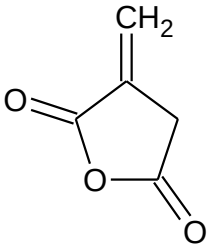
Monomer A – maleic anhydride

- Producer: Sigma Aldrich
- M_r = 98.06
- CAS: 108-31-6



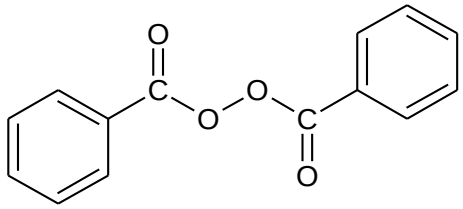
Monomer B – itaconic anhydride

- Producer: ZhongShun&Tech, China
- M_r = 112.085
- Purity ≈ 97 %
- CAS: 2170-03-8



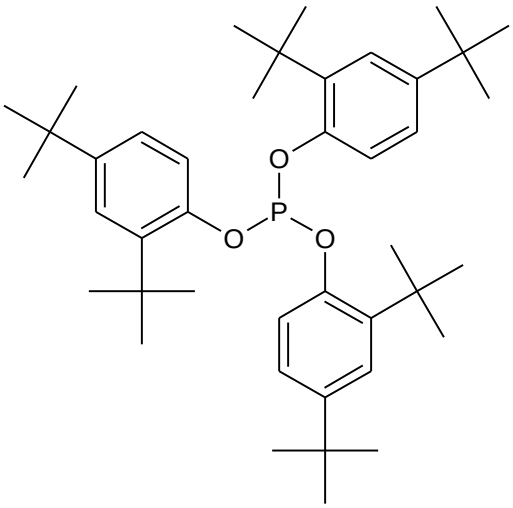
Initiator – dibenzoyl peroxide

- Producer: Fluka
- M_r = 242.23
- Purity ≈ 97 %
- Half-life for temperature 180 °C: 0.9 s
- Half-life for temperature 200 °C: 0.23 s
- CAS: 94-26-0



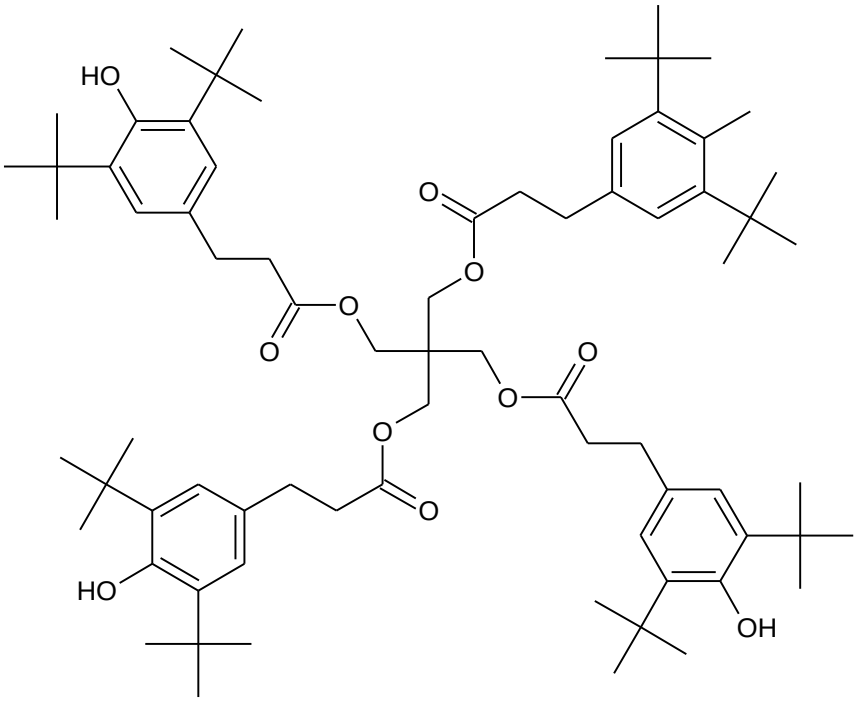
Stabilizer – Kingfos 168

- Producer: Kingyorker
- CAS: 31570-04-4



Stabilizer – Kingnox 1010

- Producer: Kingyorker
- CAS: 6683-19-8



Other chemicals:

chemicals	Producer	M [g·mol^{-1}]
1,2-Dichlorbenzene	Sigma-Aldrich	147.01
1,2-Dichlorethane	Lachema, a.s.	98.96
1,4-Dioxane	Lachema, a.s.	88.11
Benzene	Lach-ner, s.r.o.	78.12
Butyraldehyde	Sigma-Aldrich	72.11
Chloroform	Lach-ner, s.r.o.	119.38
Ethanol	Lihovar Kojetín	46.07
Ethyl methyl ketone (pure)	Lach-ner, s.r.o	72.11
Ethyleneglycol	Lachema, a.s.	62.07
Gaseous argon	Siad S.p.A.	39.95
Gaseous nitrogen	Siad S.p.A.	28.01
Hexane	Lachema, a.s.	86.16
Isopropylalcohole	Lach-ner, s.r.o.	60.10
N,N-dimethylformamide	Lachema, a.s.	73.10
Potassium hydroxide	Lach-ner, s.r.o	56.11
Potassium phthalate monobasic	Sigma-Aldrich	204.22
Propane-1,2-diol	Lach-ner, s.r.o.	76.10
Tetrachloroethylene	Lach-ner, s.r.o	165.83
Tetrahydrofuran	Lach-ner, s.r.o	72.11
Toluene	Lach-ner, s.r.o	92.14
Vinyl acetate	Sigma-Aldrich	86.09
Xylene pure (mixture of isomers)	Lach-ner, s.r.o	106.12

3.2. Instruments and software

Mixer Brabender Duisburg; Brabender, GER; Volume of reaction chamber 25 ml
Ceast modular melt flow 7024000; Ceast, ITA
Differential Scanning Calorimeter; TA Instruments
Software Universal Analysis 2000 4.7.02 TA Instruments
Infrared Spectrometer Nicolet iS 10; Thermo Scientific
Software Omnic 8.0.342; Thermo Fisher Scientific
Vacuum drier Vacucell 111 standard (MBT); Merci, s.r.o., ČR; 20–200 °C
Hydraulic press Fontijne LPB 300; Fontijne, NL; max. pressure 300 kN

3.3. Methods of samples preparation

3.3.1. Method of stabilization

The stabilization was carried out in chamber of mixer at 180 °C. PLA was dried 6 hours at 60 °C before application. The screw speed of mixer was 30 rpm. The polymer melt was formed in chamber mixer during 2 minutes. The stabilization was finished at time 6 minutes. The specimens were token out after expiration 10 minutes from polymer addition into the chamber. The treated poly(lactic acid) were kept in LDPE bags.

Kingnox 1010 and Kingfos 168 were used as stabilizers. The concentration of stabilizers was 0.1 wt% and 0.5 wt%. The optimal stabilizing agent was appraised on the basis of melt flow index (MFI) results.

3.3.2. Method of sample preparations for initiator concentration optimalization

The samples preparations performed in chamber of mixer at 180 °C. PLA was dried 6 hours at 60 °C before application. Then PLA was stored in inert (argon) atmosphere. Reaction chamber was purged using nitrogen before modification. The screw speed of mixer was 30 rpm. The reaction system was purged with nitrogen during the reaction. The polymer melt was formed in the chamber mixer during 2 minutes and then the stabilizers were added. The monomer was mixed one minute after addition of stabilizer. Initiator was mixed into the reaction system in the time 4 minutes from start of grafting. The reactions were finished at time 6 minutes. The specimens were token out after expiration 10 minutes from addition of polymer into the chamber. The treated poly(lactic acid) were stored in LDPE bags.

Maleic anhydride was utilized as a monomer. The concentration of monomer was constant, 0.5 %. The optimal concentration of initiator was found.

3.3.3. Method of sample preparation for reaction time optimization

The modification reactions were carried out in chamber of mixer at 180 °C. PLA was dried 6 hours at 60 °C before application. Then PLA was stored in inert (argon) atmosphere. Reaction chamber was purged using nitrogen before modification. The screw speed of mixer was 30 rpm. The reaction system was purged with nitrogen during the reaction. The PLA melt was formed during 2 minutes and then the stabilizers were added. The monomer was added one minute after mix of stabilizer. Initiator was mixed into the reaction system in the time 4 minutes from start of grafting. The reactions were performed in the range for 1 minute to 10 minutes. Time of reaction was a 1 minutes longer. The specimen was token out after expiration 14 minutes from polymer addition into the chamber. The treated poly(lactic acid) were stored in LDPE bags.

The concentration of maleic anhydride was 0.5 %. The optimal initiator concentration was determined in previous point.

3.3.4. Preparation of sample with different ratio of n(M)/n(I)

The grafting reactions carried out in chamber of mixer at 180 °C and 200 °. Initially, PLA was dried 6 hours at 60 °C before application. Then PLA was stored in inert (argon) atmosphere. Reaction chamber was purged using nitrogen before modification. The screw speed of mixer was 30 rpm. The reaction system was purged with nitrogen during the

reaction. The PLA melt was created in mixer chamber during 2 minutes and then the stabilizers were added. The monomer was put into one minute after addition of stabilizer. Initiator was mixed into the reaction system in the time 4 minutes from start of grafting. The reactions were for time 6 minutes. The specimens were token out after expiration 10 minutes from addition of polymer into the chamber. The treated poly(lactic acid) were stored in LDPE bags.

Concentrations of monomers were chosen 0.25 %, 0.5%, 0.75%, and 1 %. The initiator concentration was found out in previous point.

3.3.5. Separation of unreacted monomer

Separation of unreacted monomer was based on the dissolve prepared sample in appropriate solvent and then the polymer was precipitated in given precipitating agent. Therefore it was necessary to choose suitable solvent and precipitating agent. The dissolution was under was boiling solvent by using reflux condenser. The experimental determined solubility is in Table 5.

Table 5: *Solubility of PLA in selected solvents, where 1 is insoluble and 5 is very good soluble*

Solvent	**Scale of solubility**				
	1	2	3	4	5
1,2-Dichlorethan			×	×	
1,2-Dichlorobenzene					×
1,4-Dioxan	×	×			
Benzene	×				
Butyraldehyde	×				
Chloroform			×		
Ethanol	×				
Ethyl methyl ketone	×				
Ethylene glycol	×				
Hexane	×				
Isopropylalcohole	×				
N,N-dimethylformamide					×
Propane-1,2-diol	×				
Tetrachloroethylene		×			
Tetrahydrofuran				×	
Toluene	×				
Vinyl acetate		×			
Xylene	×				

1,2-dichlorobenzene was selected as a suitable solvent and ethanol as precipitating agent on the basis the experimental measurement.

Amount of 3-4 g of sample was dissolved in 20 ml boiling solvent. When the polymer was completely dissolved only then the polymer was precipitated into 100 ml ethanol, washed with ethanol and finally the sample was filtered using the Büchner funnel. The obtained polymer was dried first 3 hours at 50 °C and besides dried 6 hours at 60 °C in vacuum drier.

3.3.6. Preparation of films for infra-red spectroscopy (FTIR)

Polymeric films were prepared in chamber of hydraulic press Fontijne heated up 200 °C. Amount of 0.2 g precipitated polymer was let plastification on the PTFE plate during 4 minutes. Then the film was pressed between the hot plates during 1 minute and then followed cooling. The samples were stored in LDPE bags in desiccator with silica gel to prevent absorption of humidity.

3.4. Characterization of grafted PLA

3.4.1. Determination of melt flow index (MFI)

Melt flow index (MFI) is defined as a mass of polymer flowing through the defined capillary of jet in ten minutes. Polymer is in melt phase. The speed of mass flow of melt is described in equation:

$$\dot{m} = v \cdot S \cdot \varphi \tag{5}$$

where ρ is density of polymer melt, v is its flow speed and S is the profile of flow.

In accord with values of melting flow index we are able to guess the approximate molecular weight and polymer processibility.

For determination these conditions were applied: temperature 210 °C, weight 2.16 kg and charge of sample was 5-6 g. The samples were heated for 4 minutes before own measurement.

3.4.2. Acido-basic detection of monomers conversion

For determination of monomer conversion was used acido-basic titrations. On the analytic balance was weighed roughly 0.5 g of precipitated sample. This amount of grafted sample was dissolved in 20 ml appropriate boiling solvent under back condenser. The hot solution was let to cool at laboratory temperature. Then the solution was titrated by ethanolic solution of potassium hydroxide. As an indicator was utilized phenolphthalein, which colour change from uncoloured to pink has in the range of pH 8.2–10 [39].

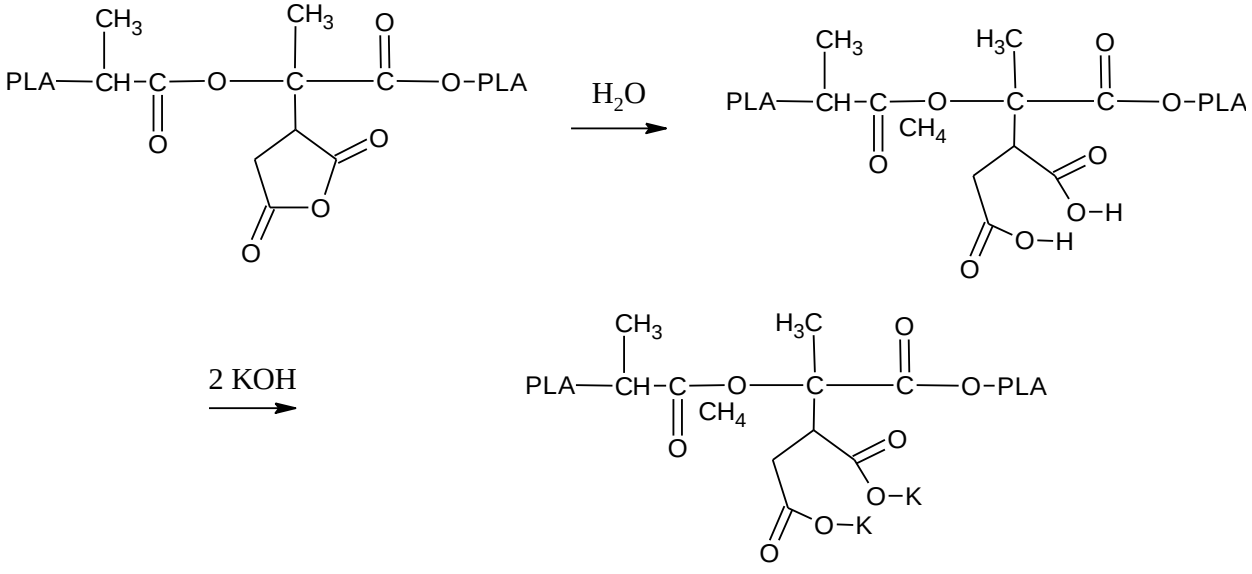


Fig. 23: *Scheme of reaction during titration of MAH-g-PLA*

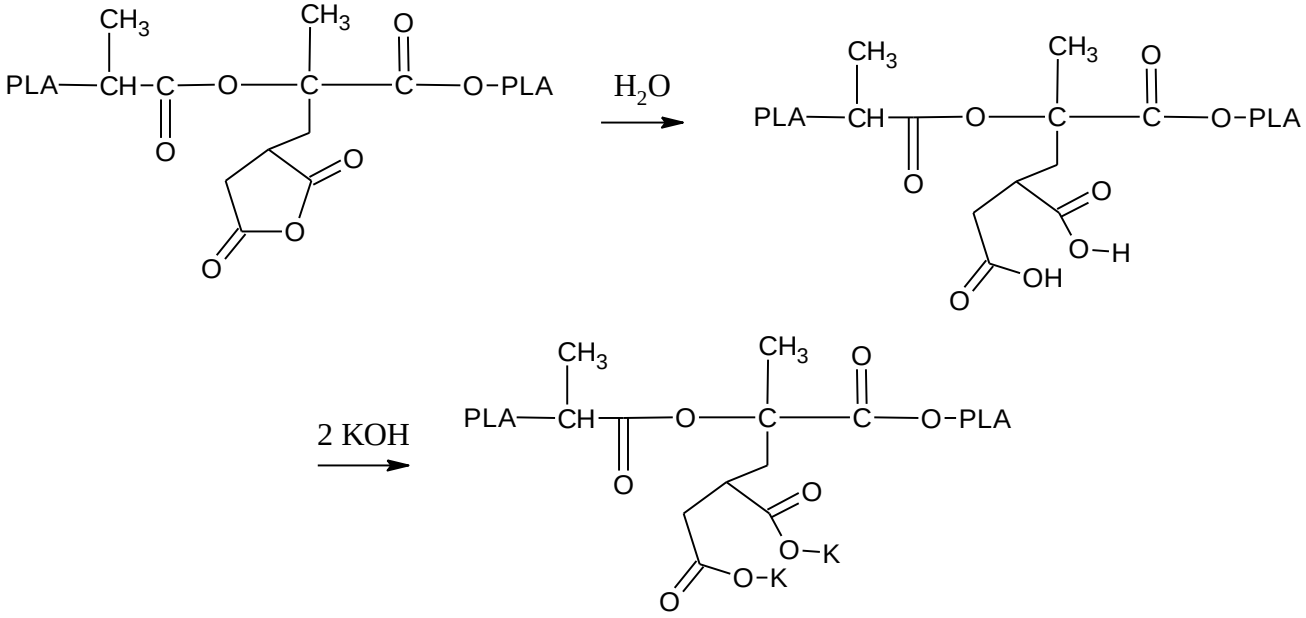


Fig. 24: *Scheme of reaction during titration of IAH-g-PLA*

The accurate concentration of potassium hydroxide solution was determined by the titration of potassium phthalate monobasic solution in water. As an indicator was utilized phenolphthalein.

The monomer conversion (α) was calculated by following Eq. (6):

$$\alpha = \frac{n_{\exp}}{n_{teor}} \tag{6}$$

where n_{exp} is amount of substance determined experimentally and n_{teor} is theoretical amount of substance.

3.4.3. Infrared spectroscopy (FTIR)

The modified PLA specimens were characterized using FT-IR spectroscopy. IR spectroscopy information was obtained on an Infrared spectrometer Nicolet iS 10. The IR spectra were taken in the interval from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} and 128 scans were performed for each specimen.

3.4.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry is thermal method for characterization of polymers. This method is based on measurement changes of absorbed or emitted heat energy. Thermal properties all samples were measured using TA Instruments differential scanning calorimeter.

The sample weighted around 10 mg. The sample was twice heated under nitrogen protection (flow rate was 70 ml/min). The rate of heating was 10 °C/min in the range from 40 °C to 200 °C. Only second heating was used for analysis, the first heating could be influenced by thermal history of sample.

4. RESULTS AND DISCUSSION

4.1. Determination of stabilizers concentration

Stabilization of polymer is used to prevent the various effects, such as chain scission, statistical recombination or cross-linking. A lot of stabilizers are available on the market, but the stabilizers have various function and efficiency. Therefore it is necessary to find the most suitable one with required properties. It was studied stabilizing effect of two most frequently common used stabilizers: Kingfos 168 and Kingnox 1010. The stabilization of PLA was carried out in a melt at 180 °C. The effectiveness of stabilizers was appraised by the measuring of MFI. The conditions of MFI measurement were applied: temperature 210 °C, weight 2.16 kg and charge of sample was 5-6 g. The samples were heated for 4 minutes before own measurement. The MFI values of both stabilizers at various concentration and combination are shown in Table 6.

Table 6: *Value of MFI for stabilized PLA*

PLA sample	Kingnox 1010 [wt%]	Kingfos 168 [wt%]	MFI [g/10 min]
1	0.1	-	27.7
2	0.5	-	21.8
3	-	0.1	28.5
4	-	0.5	25.6
5	0.1	0.1	11.3
6	0.5	0.5	13.3
7	-	-	15.2
8	-	-	16.6

The combination of stabilizers Kingnox 1010 and Kingfos 168 (concentration 0.1 wt%) was picked as sufficient for stabilization of PLA. The higher concentration could counteract the required grafting reaction on the PLA chain. The individual stabilizers didn't have so effect as their combination. Detailed study of PLA stabilization was not the aim of this work, however the stabilizers could influence the grafting process.

4.2. Influence of initiator concentration on the MAH conversion

Before the samples of PLA will be treated, it is necessary to determinate the optimum initiator concentration. If the concentration were too low, the reaction wouldn't carry out in desired yield. But on the others hand, if the initiator concentration were too high, the unwanted reaction would carry out, such as chain scission or decomposition. But we cannot forget that the polymer chains are protected from the generation of undesirable reaction by low molecular stabilizers in the most case. The present of stabilizers in the grafting system decreases the initiator efficiency. Therefore it is essential to find out the optimal initiator concentration for each concentration of stabilizers.

The amount of grafted monomer is usually around 0.5 wt% in commercial sold modified polymers, therefore the concentration of MAH was chosen 0.5 wt% for determination of optimal DBP concentration. The concentration of MAH was constant, whereas the concentration of DPB grew up. The lowest initiator concentration was in molar ratio

of monomer (M) to initiator (I) n(M)/n(I) = 1/0.2 and the highest chosen concentration in n(M)/n(I) = 1/0.8. The samples with higher initiator concentration were prepared twice for the better reproducibility's sake. The preparation of samples was carried out at 180 °C.

Table 7: *Composition of MAH grafted samples prepared for DBP concentration determination*

Sample	m(PLA) [g]	w(M) [%]	m(M) [g]	n(M) [$\cdot 10^3$ mol]	w(DBP) [%]	m(DBP) [g]	n (DBP) [$\cdot 10^3$ mol]	n(M)/n(I)
GM102	20.0	0.5	0.1	1.02	0.25	0.05	0.26	1/0.2
GM104	20.0	0.5	0.1	1.02	0.50	0.10	0.41	1/0.4
GM106	20.0	0.5	0.1	1.02	0.75	0.15	0.62	1/0.6
GM108	20.0	0.5	0.1	1.02	1.00	0.20	0.83	1/0.8

The concentration ratio of monomer to initiator c(M)/c(I) will be used instead of n(M)/n(I). The relation between c(M)/c(I) and n(M)/n(I) is following:

$$c = \frac{n}{V} \tag{7}$$

$$\frac{c(M)}{c(I)} = \frac{n(M)}{V} : \frac{n(I)}{V} = \frac{n(M)}{n(I)} \tag{8}$$

$$\frac{c(M)}{c(I)} = \frac{n(M)}{n(I)} \tag{9}$$

where V is volume of mixture. The volume of mixture is in all cases constant.

The MAH conversion in precipitated samples was determined by acido-basic titration. The calculated values of MAH conversion are shown in Table 8, furthermore the weight of samples used for titration, the theoretical and experimental determined amount of MAH in the sample are mentioned in the table. The results of MAH conversion were graphed in Fig. 25.

It was found out that the MAH conversion grew up with increasing DPB concentration, as shown in Fig. 25. It was selected the initiator concentration with MAH conversion higher than 0.5. The MAH conversion increase with the growth of DBO concentration, but on the other side the values of MFI increase also. The much high MFI indicates that polymer yields to the degradation and that this modified polymer is not suitable for industrial processing.

Table 8: *Calculated values of conversion for samples containing constant MAH concentration and various DBP concentrations*

Sample	c(M)/c(I)	m(PLA-*g*-MAH) [g]	$n(MAH)_{teor}$ [$\cdot 10^5$ mol]	$n(MAH)_{exp}$ [$\cdot 10^5$ mol]	α(MAH)
GM102	1/0.2	0.3978	2.03	0.51	0.25
		0.5028	2.56	0.72	0.28
		0.5028	2.56	0.75	0.29
GM104	1/0.4	0.5086	2.59	0.97	0.37
		0.5028	2.56	0.97	0.38
		0.4948	2.52	1.04	0.41
GM106	1/0.6	0.4994	2.55	1.23	0.48
		0.5017	2.56	1.35	0.53
		0.5052	2.58	1.09	0.42
		0.5000	2.55	1.36	0.53
		0.5000	2.55	0.85	0.33
GM108	1/0.8	0.4990	2.54	1.56	0.61
		0.4500	2.30	1.69	0.74
		0.5000	2.55	1.39	0.54
		0.5000	2.55	1.31	0.52

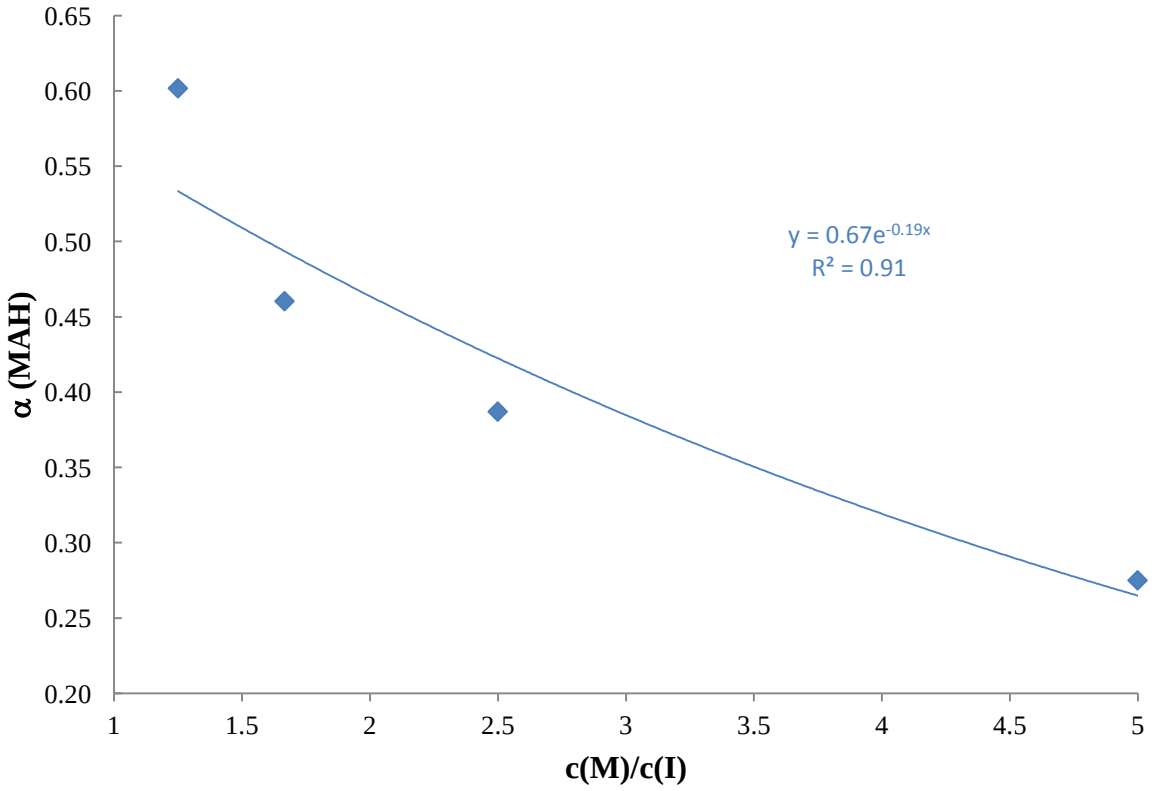


Fig. 25: *Dependence of conversion on the various ratio c(M)/c(I) for samples containing 0.5 wt% maleic anhydride*

4.3. Influence of the reaction time on the MAH conversion

The reaction time has important effect on the conversion. The conversion increases with the growing reaction time to reach maximum value and then the values are approximately constant. The reaction time depends on the chosen initiator and its half-time ($\tau_{1/2}$). The ideal reaction time should be equal to $10 \cdot \tau_{1/2}$. The DBP has half-lifetime 0.9 s at 180°C and 0.23 s at 200 °C.

The samples were prepared with the 0.5 wt% content of MAH and concentration of DBP, which was determined in previous point. The used amount of DBP was 1 wt%. Time of reaction was measured after that the initiator was added into the system. The reaction time ranged from 60 s to 600 s at 180 °C. The grafting degree was found out by acido-basic titration from precipitated samples likewise.

But in this case the conditions of sample preparation were set so that the initial growth of conversion wasn´t detected. It wasn't possible to move out the sample from reaction chamber a few seconds after addition of DBP. For determination of initial conversion growth it would be good to try different method of sample preparation, for example grafting reaction in solution.

Measured data (in Table 9 and in Fig. 26) shown that the greatest conversion of MAH occurred, when the reaction time was 6 minutes. This reaction time was applied for following modification of poly(lactic acid). The conversion value ranged from 0.34 to 0.59.

Table 9: *Data of MAH conversion time dependence at reaction temperature 180 °C*

Reaction time [s]	m(PLA-*g*-MAH) [g]	$n(MAH)_{teor}$ [$\cdot 10^5$ mol]	$n(MAH)_{exp}$ [$\cdot 10^5$ mol]	α(MAH)
60	0.4999	2.55	0.86	0.34
	0.5004	2.55	0.88	0.35
	0.5005	2.55	0.86	0.34
120	0.4998	2.55	1.09	0.43
	0.5001	2.55	1.13	0.44
	0.5007	2.55	1.13	0.44
180	0.5004	2.55	0.97	0.38
	0.5006	2.55	0.97	0.38
	0.5000	2.55	0.95	0.37
240	0.5000	2.55	1.02	0.40
	0.5004	2.55	1.02	0.40
300	0.5003	2.55	0.88	0.35
	0.5004	2.55	1.04	0.41
	0.5000	2.55	1.04	0.41
360	0.5004	2.55	1.50	0.59
	0.5005	2.55	1.00	0.39
	0.5004	2.55	1.07	0.42
420	0.5000	2.55	1.20	0.47
	0.5001	2.55	1.15	0.45
480	0.5000	2.55	1.01	0.40
	0.4999	2.55	0.97	0.38
540	0.5005	2.55	1.24	0.49
	0.4999	2.55	0.92	0.36
	0.5000	2.55	0.99	0.39
600	0.5006	2.55	1.13	0.44
	0.5005	2.55	1.06	0.42

If we would examine the relation between grafting time and monomer conversion in initial stage of grafting reaction better, the process could be carried out in solution. The procedure would be following: the reactants (PLA and monomer) will dissolve in hot suitable solvent (1,2-dichlorobenzene) under back condenser during continual stirring. When the dissolution will be complete, then the fixed amount of initiator can be added. After initiator addition the samples will be taken out at regular intervals (around 5–10 s). The samples will be then precipitated and dried. The monomer conversion will be determined via acid-basic titration. Grafting in solution wasn't aim of diploma thesis, therefore the time influence of MAH conversion until time 60 s wasn't determined.

The suggested method is useful for research into dependence of monomer conversion on the reaction time, but the conditions of solution method are different from these which were used in this work.

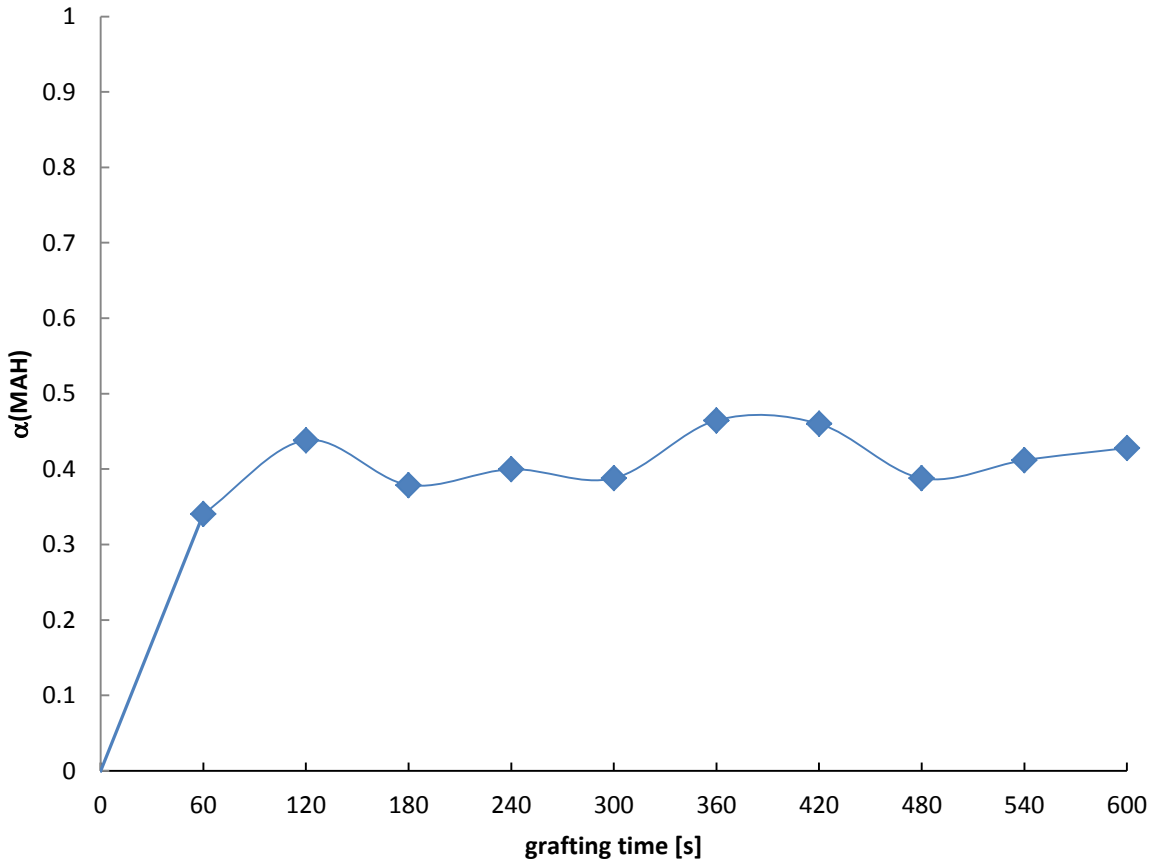


Fig. 26: *Influence of reaction time on the MAH conversion at 180 °C*

4.4. Influence of temperature and monomer concentration on the monomer conversion

As it was mentioned in theoretical part of work, the monomer conversion depends on the many factors, such initiator concentration, temperature of reaction, concentration of monomer or reaction time. The main influence of temperature is on the decomposition of initiator. With the increasing temperature the half-time of initiator decreases and the rate of grafting reaction will be faster. The temperate affects the molecular weight of graft like this that the molecular weight decreased with growing grafting temperature.

Table 10: *Concentration of components used for determination of influence various c(M)/c(I) on the MAH conversion level*

Sample	m(PLA) [g]	w(M) [%]	m(M) [g]	n(M) [·10^3 mol]	w(DBP) [%]	m(DBP) [g]	n (DBP) [·10^3 mol]	n(M)/n(I)
GM104	20.0	1.00	0.20	2.04	1.00	0.20	0.83	1/0.40
GM105	20.0	0.75	0.15	1.53	1.00	0.20	0.83	1/0.53
GM108	20.0	0.50	0.10	1.02	1.00	0.20	0.83	1/0.80
GM116	20.0	0.25	0.05	0.51	1.00	0.20	0.83	1/1.60

Treatment of PLA occurred at constant concentration of initiator, but the concentrations of monomer were various. The DBP concentration was determined previously, but these concentrations of monomers were chosen: 0.25 %, 0.5 %, 0.75 %, and 1 %. MAH and itaconic anhydride (IAH) were utilized as monomers. The grafting reactions were carried out at 180 °C and 200 °C. The monomer conversion in precipitated samples was determined using the acido-basic titration.

The amount of grafted monomer was determined by the acido-basic titration. The calculated values of MAH onto the PLA are shown in Table 11–12.

Table 11: *Effect of various MAH concentrations on monomer conversion at 180°C*

Sample	c(M)/c(I)	m(PLA-*g*-MAH) [g]	$n(MAH)_{teor}$ [$\cdot 10^5$ mol]	$n(MAH)_{exp}$ [$\cdot 10^5$ mol]	α(MAH)
180-GM104	1/0.40	0.4999	5.10	1.53	0.30
		0.5009	5.11	1.48	0.29
		0.5005	5.10	1.27	0.25
180-GM105	1/0.53	0.5003	3.83	1.24	0.32
		0.5003	3.83	1.14	0.30
180-GM108	1/0.80	0.4999	2.55	1.05	0.41
		0.5005	2.55	1.53	0.60
		0.5001	2.55	1.31	0.52
180-GM116	1/1.60	0.5000	1.28	0.85	0.67
		0.5001	1.28	0.95	0.74

Table 12: *Effect of various MAH concentrations on monomer conversion at 200°C*

Sample	c(M)/c(I)	m(PLA-*g*-MAH) [g]	$n(MAH)_{teor}$ [$\cdot 10^5$ mol]	$n(MAH)_{exp}$ [$\cdot 10^5$ mol]	α(MAH)
200-GM104	1/0.40	0.5004	5.10	1.03	0.20
		0.5006	5.10	1.30	0.25
		0.5000	5.10	0.96	0.19
200-GM105	1/0.53	0.5004	3.83	1.22	0.32
		0.5005	3.83	1.05	0.28
		0.5008	3.83	0.83	0.22
200-GM108	1/0.80	0.5000	2.55	1.15	0.45
		0.5004	2.55	1.35	0.53
		0.4999	2.55	0.98	0.39
200-GM116	1/1.60	0.5005	1.28	1.05	0.83
		0.4999	1.27	1.03	0.81

Measured data (see Table 11–12) shown that with increasing MAH concentration the MAH conversion decreased. The maximal conversion ranged around 0.8 when c(M)/c(I) was 1/1.6. The minimum of MAH conversion was found out when the concentration of MAH was much higher than initiator concentration (the c(M)/c(I) was 1/0.4).

Although the fact that the half time of DPB decomposition is 0.9 s for temperature 180 °C and 0.23 s for temperature 200 °C effect of reaction temperature on the conversion wasn't

noticeable, as shown Fig. 27. The MAH conversion was approximately same. In most concentrations the values of conversion were similar or lightly higher, when the samples were treated at 180 °C. Only when the MAH concentration was the lowest, the noticeable difference was observable. The PLA treated at 200 °C had higher MAH conversion then the sample modified at 180 °C.

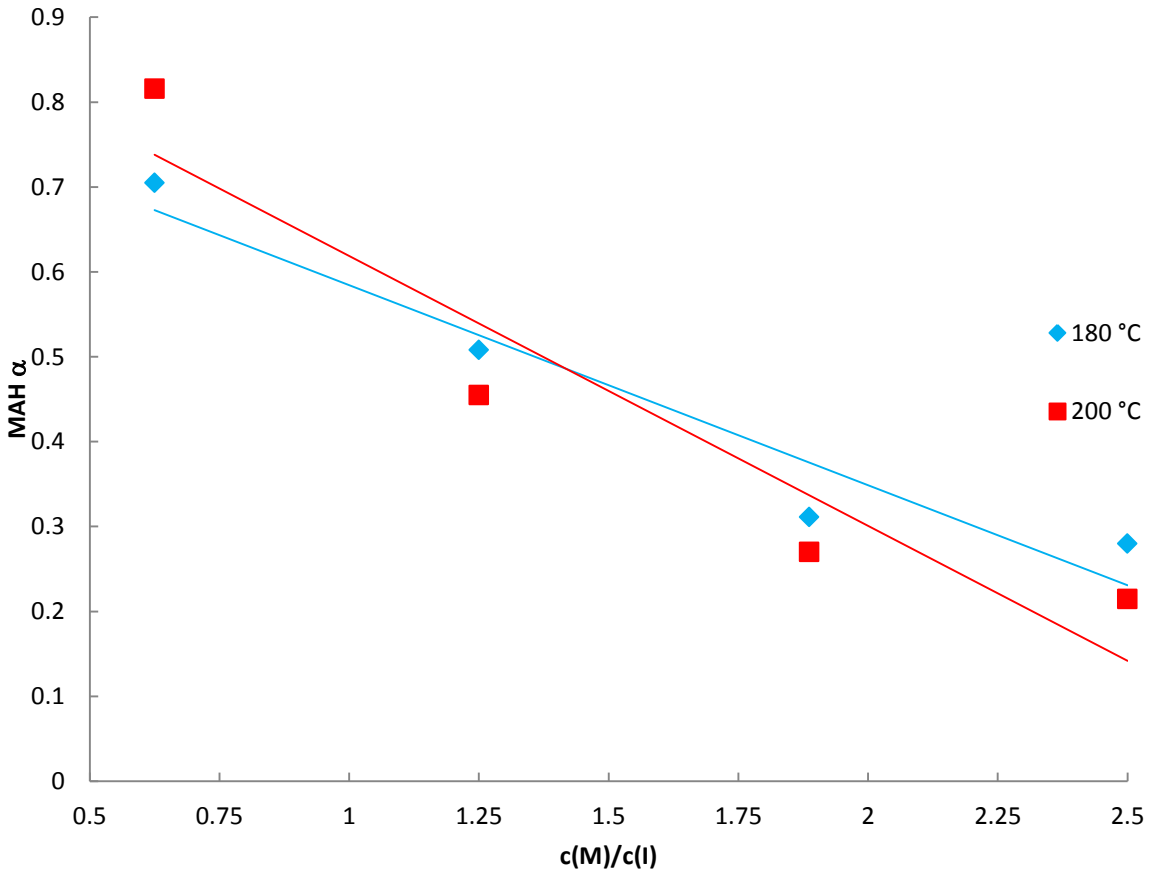


Fig. 27: *Temperature dependence of MAH conversion on the molar ratio monomer/initiator.*

Table 13: *Composition of samples used for determination of influence various c(M)/c(I) on the IAH conversion level*

Sample	m(PLA) [g]	w(M) [%]	m(M) [g]	n(M) [·10^3 mol]	w(DBP) [%]	m(DBP) [g]	n (DBP) [·10^3 mol]	n(M)/n(I)
GI104	20.0	1.00	0.20	0.45	0.85	0.17	0.71	1/0.40
GI105	20.0	0.75	0.15	0.89	0.85	0.17	0.71	1/0.53
GI108	20.0	0.50	0.10	1.34	0.85	0.17	0.71	1/0.80
GI116	20.0	0.25	0.05	1.78	0.85	0.17	0.71	1/1.60

Table 14: *The observed IAH conversion at various IAH concentrations at 180 °C*

Sample	c(M)/c(I)	$m_{IAH\text{-}g\text{-}PLA}$ [g]	$n(IAH)_{teor}$ [$\cdot 10^5$ mol]	$n(IAH)_{exp}$ [$\cdot 10^5$ mol]	α(IAH)
180-GI104	1/0.4	0.5003	4.46	0.97	0.22
		0.5007	4.47	0.93	0.21
		0.4996	4.46	1.02	0.23
180-GI105	1/0.53	0.5000	3.35	0.88	0.26
		0.5005	3.35	1.15	0.35
		0.5005	3.35	1.00	0.30
180-GI108	1/0.8	0.5004	2.23	0.85	0.38
		0.5001	2.23	0.87	0.39
		0.5002	2.23	1.02	0.46
180-G116	1/1.6	0.5008	1.12	0.74	0.66
		0.4998	1.12	0.80	0.72

Table 15: *Dependence of IAH conversion on the initial IAH concentration at 200°C*

Sample	c(M)/c(I)	m(IAH-*g*-PLA) [g]	$n(IAH)_{teor}$ [$\cdot 10^5$ mol]	$n(IAH)_{exp}$ [$\cdot 10^5$ mol]	α(IAH)
200-GI104	1/0.4	0.4999	4.46	1.16	0.26
		0.5000	4.46	1.14	0.26
		0.5003	4.46	1.11	0.25
200-GI105	1/0.53	0.4999	3.35	1.16	0.35
		0.5000	3.35	1.09	0.33
		0.5003	3.35	1.14	0.34
200-GI108	1/0.8	0.5002	2.23	1.03	0.46
		0.5003	2.23	0.96	0.43
		0.4999	2.23	0.97	0.44
200-GI116	1/1.6	0.5004	1.12	0.89	0.80
		0.5000	1.12	0.99	0.88
		0.5005	1.12	0.88	0.79

The obtained IAH conversion values are shown in Table 14–15. The values of IAH conversion decreased with growing IAH concentration. But the IAH conversion was slightly higher at the samples modified at 200 °C, as shown in Fig. 28. But IAH gave similar dependence of monomer conversion on the monomer concentration, monomer conversion decreased with growing initial concentration.

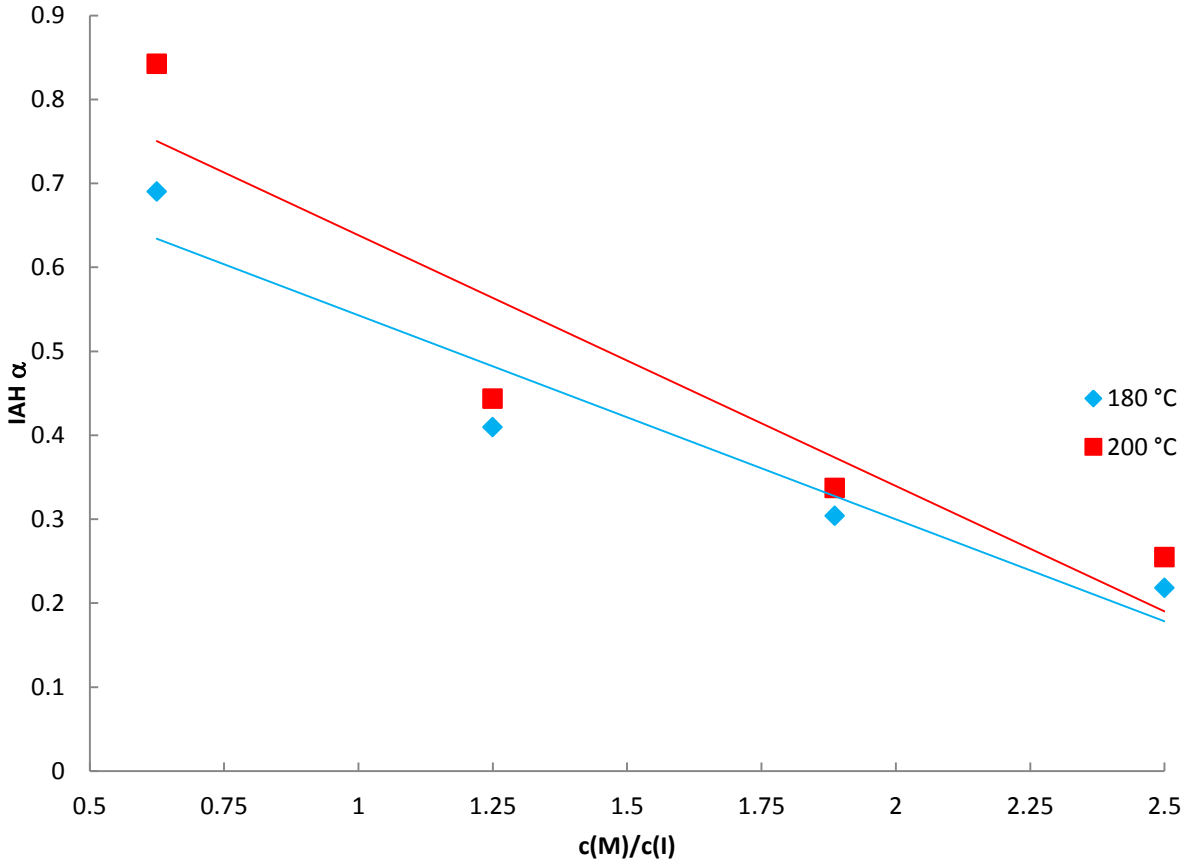


Fig. 28: *Conversion of IAH at various reaction temperatures*

If we compared the conversion of MAH and IAH, we found that conversions are similar. The dependences of monomer conversion on the molar ratio had the same directions of the line, as shown in Fig. 29. But the conversions dependences were only shifted about 0.03. If the PLA will be modified with IAH and MAH at the same concentration of initiator and monomers, MAH conversion will be higher 0.03 in compared with IAH conversion.

The copolymerization parameter of MAH is equal 0.00. This means that the probability of homopolymerization is equal 0. If the results of IAH conversion were compared with MAH results, we found out that both IAH and MAH showed similar grafting behavior. It was concluded that the IAH didn't homopolymerize at selected temperatures. This statement was supported by IAH ceiling temperature (90°C) [40].

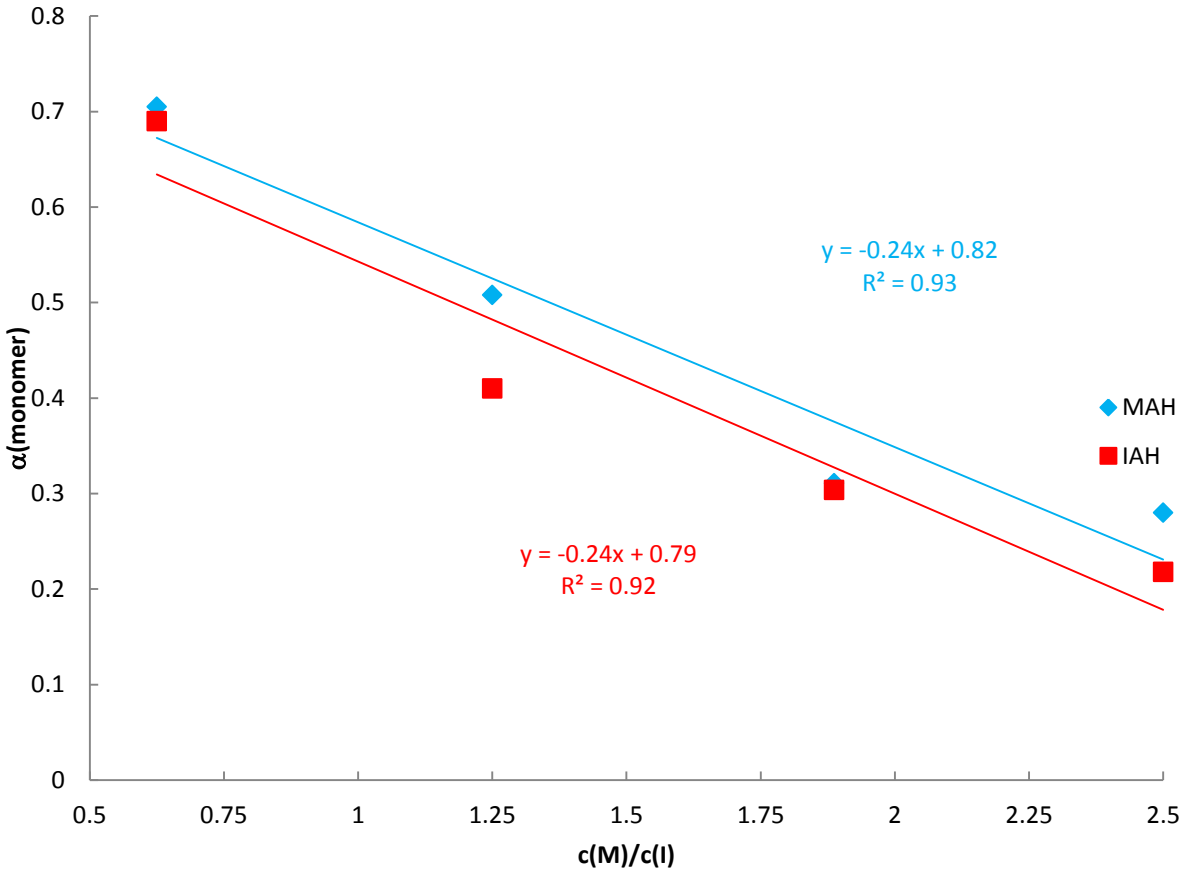
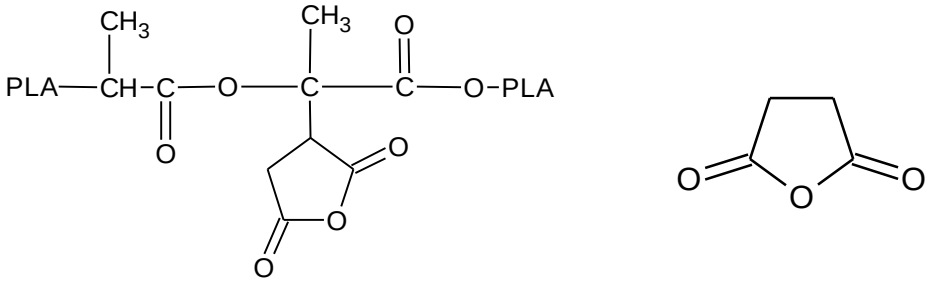


Fig. 29: *Monomer effect onto conversion at 180°C*

4.5. Attempt on qualitative and quantitative analysis using FT-IR spectroscopy

Spectra were taken over the interval of wavenumbers ranging from 400 to 4000 cm^{-1}. The PLA obtain a lot of characteristic peaks in the whole extent of measurement. The one of the most intensive peaks was observed at 1770 cm^{-1}. This peak is possible to attribute to the stretching vibration of carbonyl (C=O) in ester bond of polyesters chain. The peaks located around 2900 cm^{-1} were attributed to the symmetric and asymmetric stretching vibration of methyl groups (CH_3). The peak located at 2880 cm^{-1} belonged to the CH group. The peaks situated around 1100–1300 were the stretching vibration of C-O-C groups.



a) b)

Fig. 30: *Scheme of PLA modified MAH (a) and succinic anhydride (b) structure*

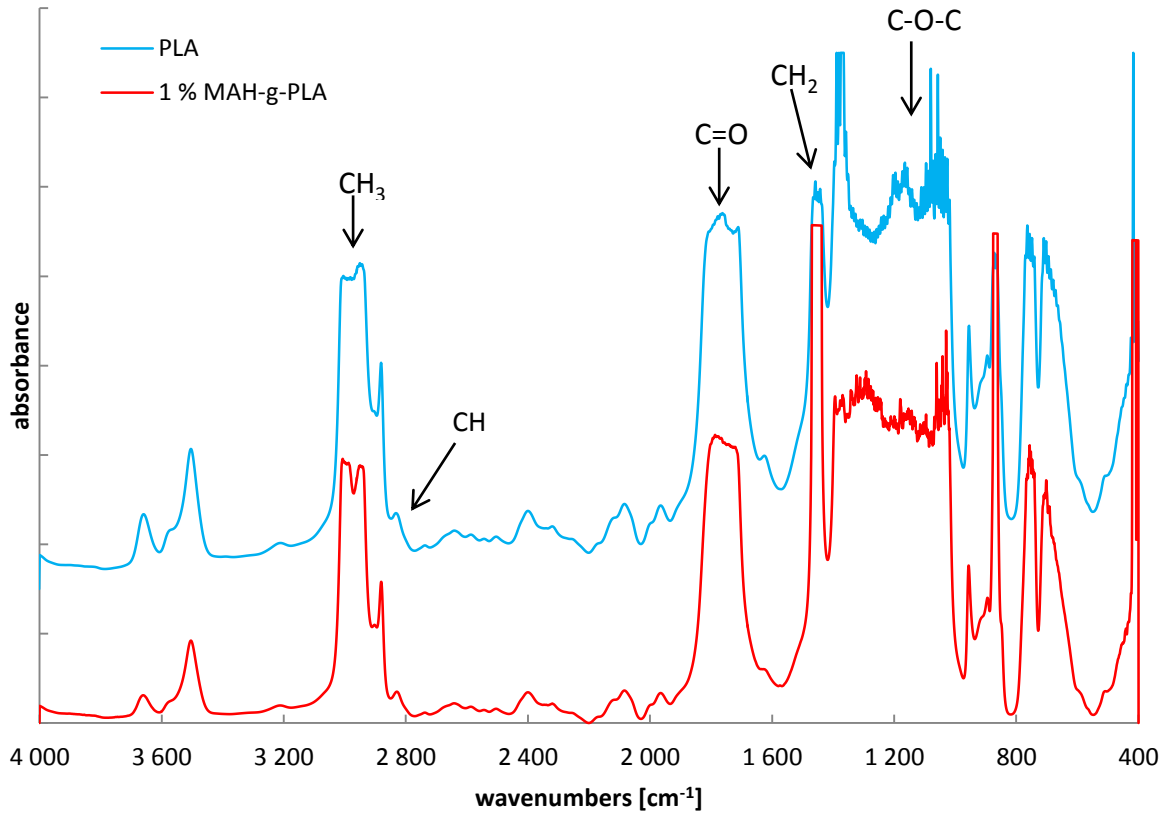


Fig. 31: *Comparison of PLA and MAH-g-PLA IR spectra*

The Fig. 30 shows that the grafted MAH in MAH-*g*-PLA has similar structure with the succinic anhydride. The grafted MAH and succinic anhydride contain the C-O-C group, C=O group and CH_2 groups, whereas CH_2 group doesn't include in the initial MAH structure. The presence of CH_2 group in the grafted MAH and the absence this group in PLA chain could be used for quantitative determination of grafted MAH amount by FTIR spectroscopy. The typical peaks for PLA, MAH and succinic anhydride were found in the IR spectrum library [41], [42] and these peaks were assigned to groups in the polymer structure using IR tables [43], these peaks are mentioned in Table 16–18. The CH_2 group presence in succinic anhydride is given peak located at 1419 cm^{-1}. But CH_2 group of grafted MAH should be located around 1419 cm^{-1} because this peak will be shifted as results of π-electron density.

The grafted MAH amount could be determined via different method. The first one will be based on the comparison peaks area of C=O group in virgin and in treated material, but the thickness of samples muss be same. The various thickness of sample should be involved negative the results. The amount of grafted MAH will be determined by difference between the peaks at 1770 $cm^{-1}$of modified and pure PLA. The peaks area should be increased with growing grafted MAH amount. The second method is based on the comparison of intensity characteristic peaks. The peaks belonging to the CH_3 group (2997 cm^{-1}; 2947 cm^{-1}) and CH_2 (1419 cm^{-1}) peaks were chosen for determination of grafting MAH amount. The grafted MAH amount will be defined by: $\frac{I(CH_2)}{I(CH_3)} = f(MAH)$. The thickness of sample films muss be same, too.

Table 16: *IR peak band assignment for semicrystalline and amorphous PLA [41], [42]*

Semicrystalline PLA		Amorphous PLA		Assignment
IR ν[cm^{-1}]	Intensity	IR ν[cm^{-1}]	Intensity	
2997	M	2997	M	$\nu_{as}CH_3$
2947	M	2947	M	$\nu_{s}CH_3$
2882	W	2882	w	$\nu_{s}CH$
1760	VS	1760	VS	ν(C=O)
1452	S	1452	S	$\delta_{as}CH_3$
1348, 1388	S	1385	S	$\delta_{as}CH_3$
1215	VS	1211	VS	ν_{as}C-O-C
1185	VS	1185	VS	ν_{as}C-O-C
1130	S	1130	S	$r_{as}CH_3$
1090	VS	1090	VS	ν_{s}C-O-C
1045	S	1045	S	ν C-CH_3

The intensity of each band is classified as VS (very strong), S (strong), M (medium), w (weak), s (symmetrical), and as (asymmetrical)

Table 17: *Characteristic IR peaks of maleic anhydride spectrum [41], [42]*

IR ν [cm^{-1}]	Intensity	Assignment
3118	M	ν_{as}(=CH–)
1852	S	ν_{s}(C=O)
1779	S	ν_{s}(C=O)
1240	VS	ν_{as}C-O-C
1058	VS	ν_{s}C-O-C

The intensity of each band is classified as VS (very strong), S (strong), M (medium), w (weak), s (symmetrical), and as (asymmetrical)

Table 18: *Characteristic IR peaks of succinic anhydride spectrum [41], [42]*

IR ν [cm^{-1}]	Intensity	Assignment
1862	S	ν_{s}(C=O)
1785	S	ν_{s}(C=O)
1419	M	$\delta(CH_2)$
1279	VS	ν_{as}C-O-C
1211	VS	ν_{as}C-O-C
1052	VS	ν_{s}C-O-C

The intensity of each band is classified as VS (very strong), S (strong), M (medium), w (weak), s (symmetrical), and as (asymmetrical)

4.6. Influence of grafting on the β-scission of PLA chain observed using MFI

Melting flow index is widely used for appraisal polymer processibility in industry. The index determines the material viscosity and approximate molecular weight. If the value of index is higher, this means that the material has lower viscosity and flows easier. The higher value of MFI can indicate that the polymer has lower molecular weight. The molecular weight can change during modification by influence of undesirable reaction. This method is useful for preliminary observation of degradation during processing. And MFI helps to qualify incoming materials and to help anticipate changes in the process. If the polymer is modified, the values of MFI increases with the increase of monomer content, the initiator concentration.

The higher values of MFI could be caused with amount of unreacted MAH, as shown in Table 19. It was observed that the MFI grew with increasing MAH concentration. The similar behavior was possible to watch in the case of samples containing IAH as monomer (Table 20). The unreacted monomer could function as internal lubricant or plastificator. The effect of unreacted monomer as lubricant or plastificator can be limited by separation of ungrafted monomer. The separation of unreacted monomer is based on the precipitation of sample. The MFI of precipitated will have substantially lower value, which was proved by H. Postulkova in her bachelor thesis [44].

Table 19: *Melting flow index of MAH-g-PLA measured at 210 °C and by weight 2.16 kg*

Sample	c(M)/c(I)	MFI of samples prepared at [g/10 min]	
		180 °C	200 °C
GM104	1/0.40	25.3 ± 1.3	16.7 ± 0.8
GM105	1/0.53	23.2 ± 1.4	16.6 ± 0.9
GM108	1/0.80	19.8 ± 1.3	17.9 ± 1.0
GM116	1/1.60	18.4 ± 1.1	17.3 ± 1.3

Melt flow index can be used for preliminary appraisal if the undesirable reactions occur in the grafting system, such as degradation. The measured MFI shown that the effect of stabilizers was sufficient and degradation of PLA chain didn't occur.

Table 20: *MFI of samples PLA modified with IAH measured at 210 °C and by weight 2.16 kg*

Sample	c(M)/c(I)	MFI of samples prepared at temperature [g/10 min]	
		180 °C	200 °C
GM104	1/0.40	13.6 ± 0.7	14.9 ± 0.9
GM105	1/0.53	14.4 ± 0.8	13.8 ± 0.7
GM108	1/0.80	14.2 ± 0.8	13.4 ± 0.9
GM116	1/1.60	12.3 ± 0.6	13.3 ± 0.7

4.7. Effect of grafting yield on the thermal properties observed using DSC

In general, the most of polymer is combination of crystalline and amorphous (without arrangement) structures. These polymers are called semi-crystalline and have different crystallinity content. The crystallinity content can be influenced by modification of polymer chain. The crystallinity content decreased with increasing grafting level. Differential scanning calorimetry was used for appraisal of changes glass transition temperatures (T_g) and crystallinity. As the temperature is above the T_g, the material becomes more rubbery. The knowledge of T_g is essential for many applications.

The thermal history of samples affected the values of first heating during DSC measurements. Therefore the second heating was employed for comparison of changes, the thermal history was eliminated and the values belonged to the properties of material.

The crystallinity content (w_c) was calculated according to the following equation:

$$w_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \cdot 100\,\% \qquad (10)$$

where ΔH_m and ΔH_{cc} are the melting and the cold crystallization enthalpies, and ΔH_m^0 is melting enthalpy for 100 % crystallic polymer. In the case PLA, the value of ΔH_m^0 is 93.6 $J \cdot g^{-1}$ [1].

The glass transition temperature of modified PLA with MAH and IAH was lower than the temperature of virgin PLA. With increasing content of monomer (MAH and IAH) for every sample the temperature decreased, but the change in the T_g wasn´t so noticeable. The T_g decrease ranged from 1 °C to 2 °C, particular T_g are mentioned in Table 21–24.

Table 21: *Values of T_g and T_m modified PLA with MAH at 180 °C obtained from DSC curves*

Content of MAH [%]	T_g [°C]	T_m [°C]	ΔH_{cc} [$J \cdot g^{-1}$]	ΔH_m [$J \cdot g^{-1}$]	w_c [%]
0.0	60.1	152.7	-	0.2175	0.23
0.25	59.5	152	20.80	22.18	1.47
0.5	59.4	152.5	19.22	21.47	2.40
0.75	59.1	153.2	17.92	18.03	0.12
1	58.6	145.2	20.47	20.79	0.34

Table 22: *Values of T_g and T_m modified PLA with MAH at 200 °C obtained from DSC curves*

Content of MAH [%]	T_g [°C]	T_m [°C]	ΔH_{cc} [$J \cdot g^{-1}$]	ΔH_m [$J \cdot g^{-1}$]	w_c [%]
0.0	60.1	152.7	-	0.2175	0.23
0.25	59.7	152.3	19.73	20.28	0.59
0.5	59.5	151.7	22.42	22.91	0.52
0.75	59.5	151.2	22.72	22.80	0.09
1	59.5	152.1	18.67	19.87	1.28

Table 23: *Thermal properties of PLA modified with IAH at 180°C measured using DSC*

Content of IAH [%]	T_g [°C]	T_m [°C]	ΔH_{cc} [J·g^{-1}]	ΔH_m [J·g^{-1}]	w_c [%]
0	60.1	152.7	-	0.2175	0.23
0.25	59.6	152.5	16.59	17.15	0.60
0.5	59.6	152	20.07	20.42	0.37
0.75	59.5	153.1	17.65	18.03	0.41
1	58.9	152.8	13.24	13.75	0.55

Table 24: *Thermal properties of PLA modified with IAH at 200°C measured using DSC*

Content of IAH [%]	T_g [°C]	T_m [°C]	ΔH_{cc} [J·g^{-1}]	ΔH_m [J·g^{-1}]	w_c [%]
0.00	60.1	152.7	-	0.2175	0.23
0.25	59.9	152.3	18.7	19.94	1.33
0.5	59.6	152.2	18.17	19.01	0.90
0.75	59.4	151.9	17.19	18.39	1.28
1	59.5	152.5	15.87	16.77	0.96

Considerable exothermic peak was observed in DSC curves (Fig. 32–35). This peak belonged to the cold crystallization, which it is special manner of crystallization, when crystalline structure arises during heating of sample. The cold crystallization continued directly to melting without interstage. Cold crystallization enthalpy was compared with melting enthalpy and it was found out, that the grafted PLA is amorphous material. The amount of crystallic phase was minimal as it was supported with calculation of crystallinity content (values are shown in Table 21–24). Maximal content of crystalline phase was 2.4 %.

The melting temperatures of PLA were in the most case lower in comparison with virgin poly(lactic acid). Maximal difference between original PLA and treated PLA reached 7 °C.

Significant difference between maleic anhydride and itaconic anhydride modified poly(lactic acid) wasn't observed. The values of glass transition and melting temperature were approximately same.

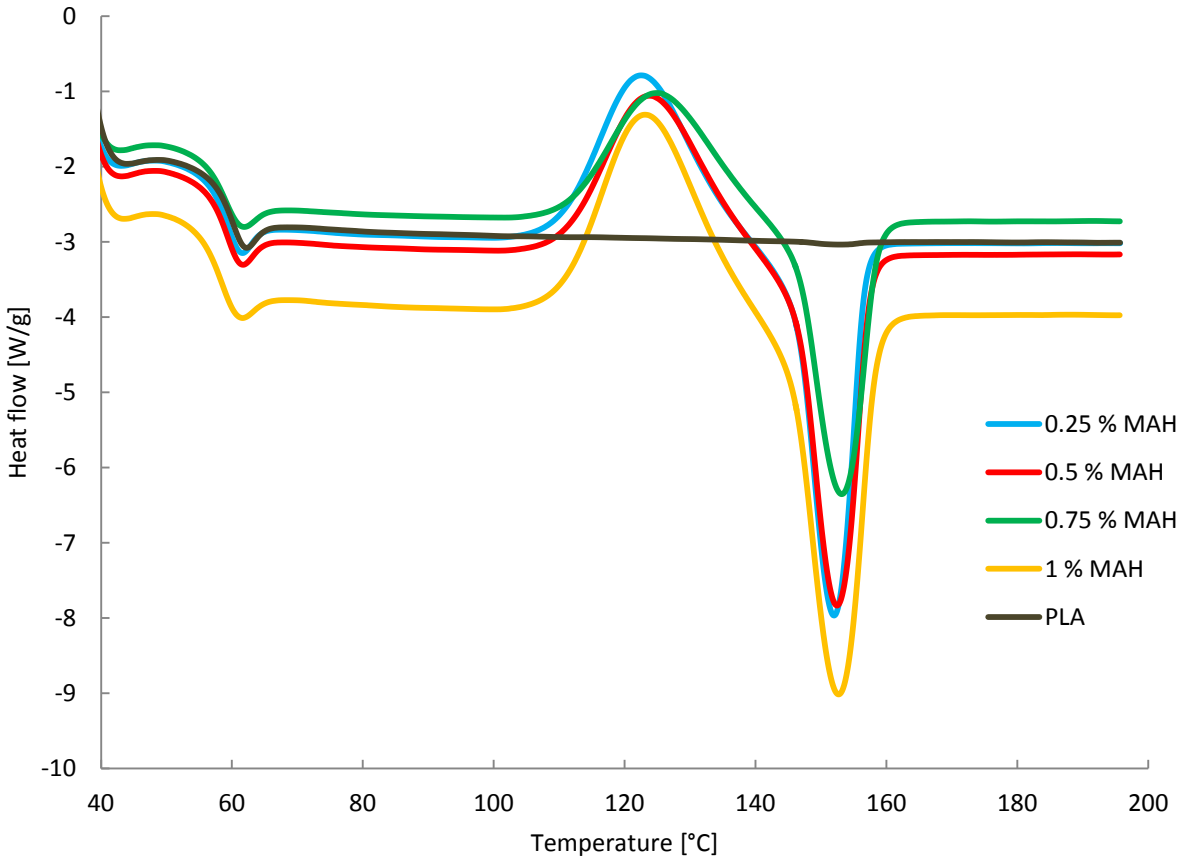


Fig. 32: *DSC curves of modified PLA with various MAH concentrations at 180 °C*

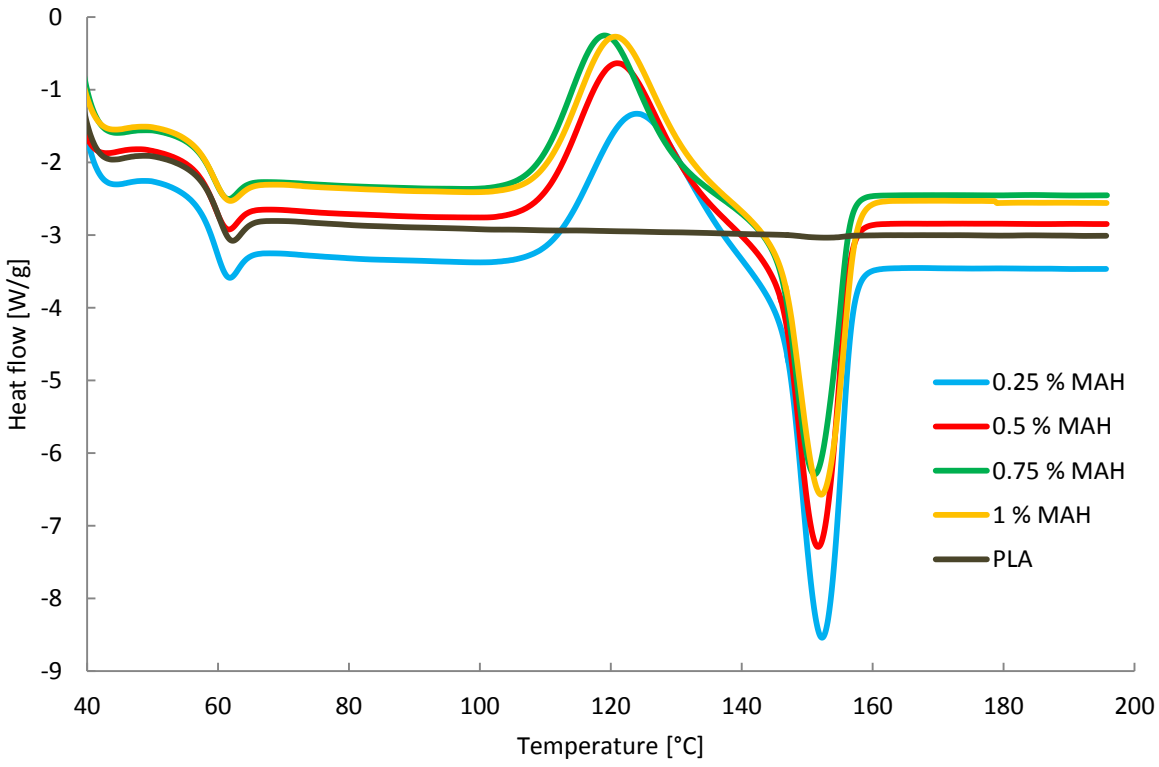


Fig. 33: *DSC curves of PLA-g-MAH prepared at 200 °C*

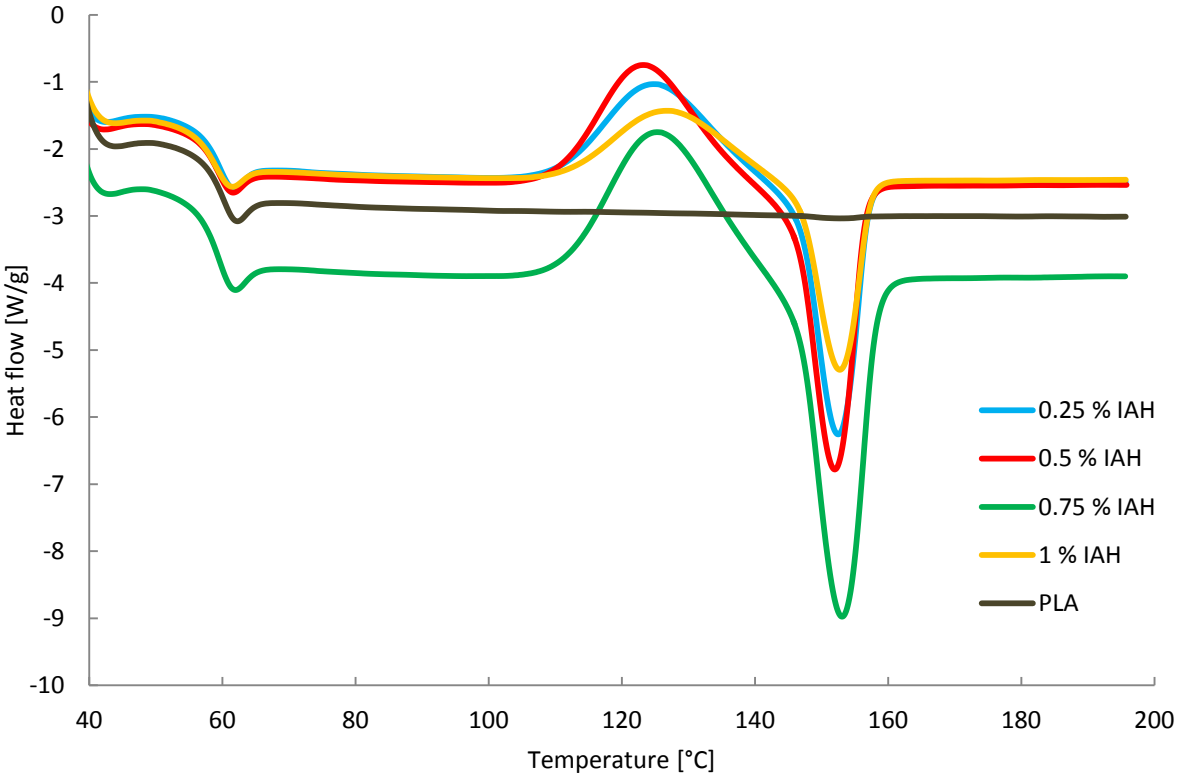


Fig. 34: *DSC curves of PLA modified with various IAH concentration at 180 °C*

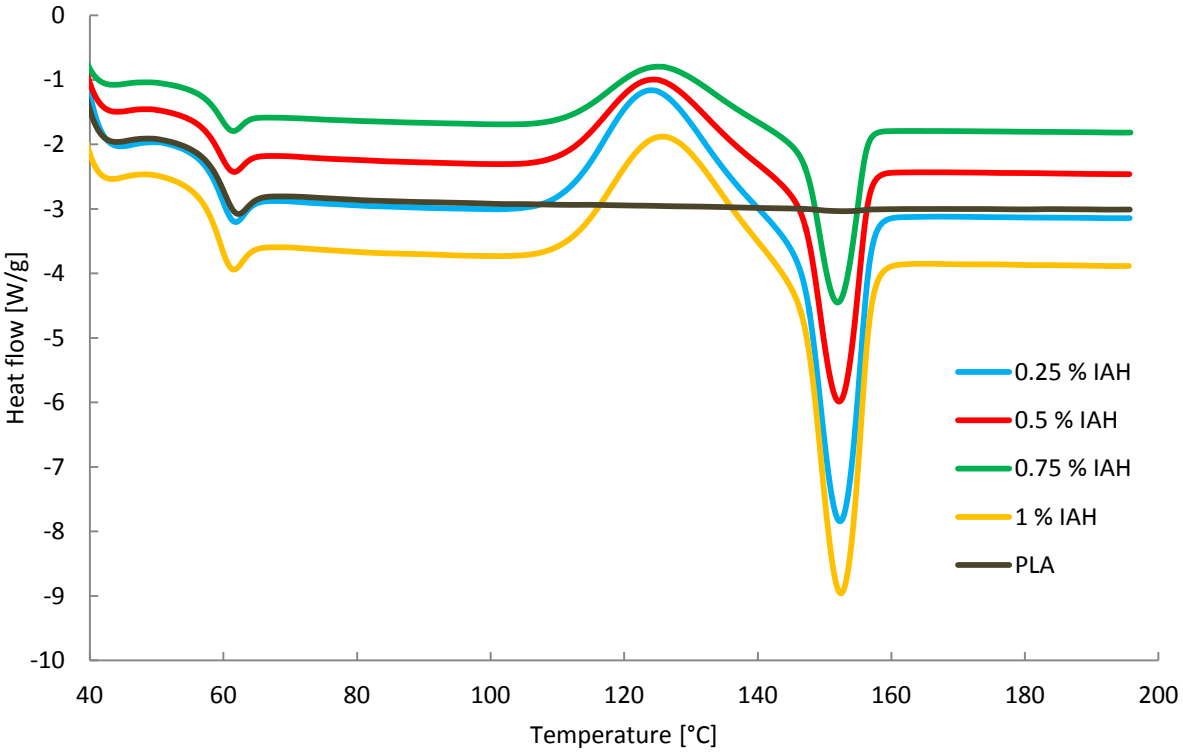


Fig. 35: *DSC curves of PLA modified with various IAH concentration at 200 °C*

4.8. Optimization of reaction parameters of MAH-g-PLA and IAH-g-PLA preparation

The monomer conversion and MFI are the important criterions in industrial production. T. Arvai [45] solved optimization of PP-g-IAH production in his bachelor's thesis. The solution is based on the fixing maxima of relation between ratio of monomer conversion to MFI and mass fraction of initiator to monomer.

The optimization curves for IAH-*g*-PLA are shown in Fig. 36. It was seen that dependencies didn't achieve maximum. The monomer conversion increased with growing initiator concentration but the MFI only fluctuated around certain MFI value. Fluctuation of MFI values attributed to the good effects of stabilizers. Therefore the dependence of ratio of monomer conversion to MFI on concentration fraction of initiator to monomer had increasing character. The same behavior was observed in the case of MAH-*g*-PLA likewise.

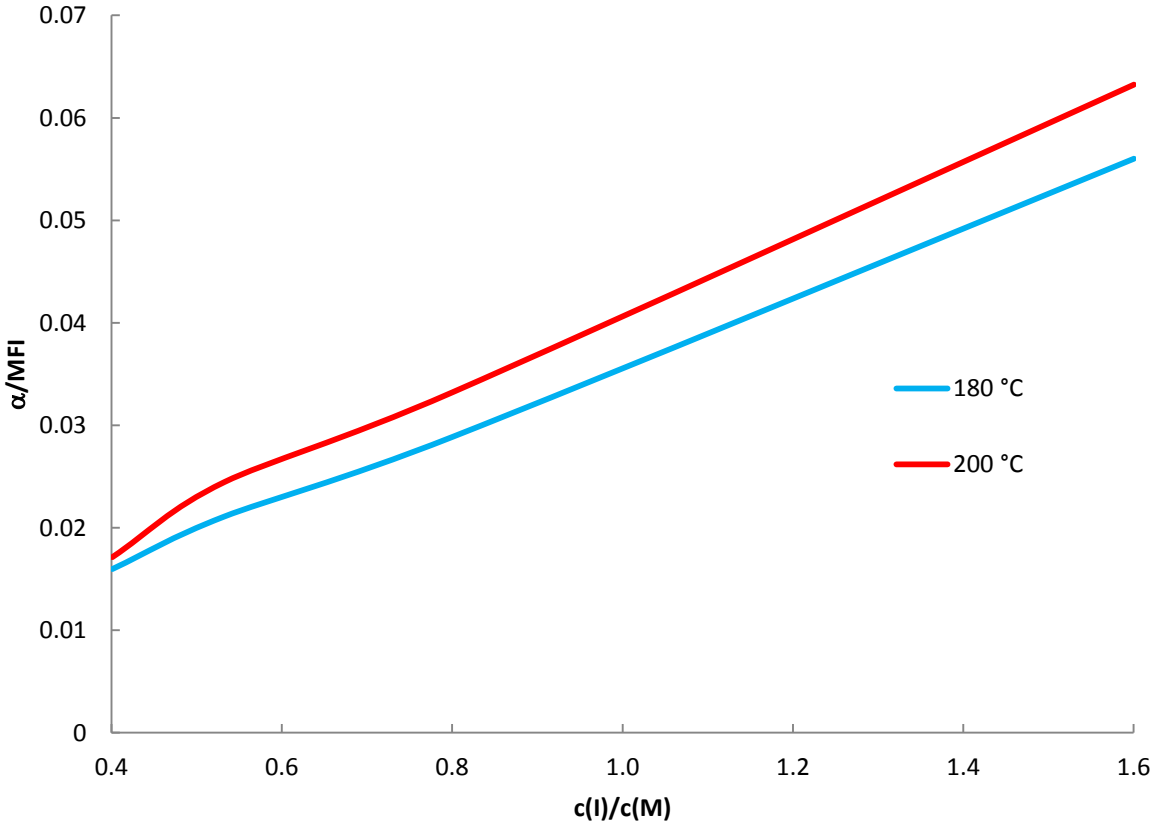


Fig. 36: *Graphical illustration of relation between ratio of IAH conversion to MFI and c(I)/c(M)*

5. CONCLUSION

This diploma thesis deals with chemical modification of PLA using MAH and IAH. In the theoretical part the principles of grafting reaction were discussed at first. Afterward the current possibilities of grafting on the PP and PLA were summarized.

In experimental part the theoretical knowledge of grafting reaction were verified. It was found that the monomer conversion decreased with increasing monomer concentration at constant DBP concentration. The reaction temperature involved the rate of grafting but not monomer conversion. The monomer conversion of samples modified at 180 °C was approximately same with the conversion of samples treated at 200 °C. Homopolymerization of MAH didn't occur in grafting reaction. The results of IAH were similar to the MAH results. It was concluded, on the basis of similarity of MAH and IAH conversion, that IAH didn't form the homopolymer at selected temperatures. This conclusion was verified subsequently in literary sources. The methods of grafted MAH amount determination were suggested by FTIR spectroscopy.

Influence of grafting yield on the β-scission was observed using MFI. The MFI increased with growing monomer concentration. The unreacted monomer could function as internal lubricant or plastificator. MFI can be used for preliminary degradation investigation. The degradation didn't occur in the processing on the basis of MFI results. The stabilization of PLA was sufficient.

It was investigated by DSC that the original PLA contained minimal content of crystalline phase, although the authors in literary sources mentioned that the crystalline content can be around 35 %. The values of T_g decreased with amount of monomers, but the changes in T_g wasn't so noticeable. The treated PLA contained lower amount of crystallic phase, which it was supported with calculation of crystallinity.

The relation between ratio of monomer conversion to MFI and concentration fraction of DBP to monomer showed that monomer conversion increased with the growing initiator concentration but the values MFI were approximately equal. The selected method of stabilization PLA reached excellent results.

The experimental part of this diploma thesis resulted in the new material which can be utilized as compatibilizer for PLA blends with other polymers, e.g. PE and PP.

6. REFFERENCES

[1] AURAS, R., LIM, L.-T., SELKE, S. E.M., TSUJI, H.: *Poly(lactic acid): Synthesis, structures, properties, processing, and application.* New Jersey: John Wiley & Sons, Inc., 2010. 528 p. ISBN 978-0-470-29366-9

[2] AL-MALAIKA, S.: *Reactive modifiers for polymers*. 1st ed. London: Kluwer Academic Publishers, 1997. 420 p. ISBN 07-514-0265-6

[3] BHATTACHARYA, A., RAWLINS, J. W., RAY, P.: *Polymer Grafting and Crosslinking*. New Jersey: John Wiley & Sons, Inc., 2009. 341 p. ISBN 978-0-470-40465-2

[4] RADO, Rudolf: *Premenné reakcie polymérov budené peroxidmi*. Bratislava: Alfa, 1970. 212 p.

[5] ODIAN, George: *Principles of polymerization*. 4th ed. New Jersey: John Wiley & Sons, Inc., 2004. 812 p. ISBN: 0-471-27400-3

[6] MATYJASZEWSKI, K., DAVID, T. P.: *Handbook of Radical Polymerization*. New Jersey: John Wiley & Sons, Inc., 2002. 936 p. ISBN: 0-471-39274-x

[7] LAZÁR, M., BLECHA, T., RYCHLÝ, J.: *Chemické reakcie polymérov*. Bratislava: Alfa, 1987. 248 p.

[8] MOHANTY, Amar K; MISRA, Manjusri; DRZAL, Lawrence T. *Natural fibers, biopolymers, and biocomposites*. Boca Raton : Taylor & Francis, 2005. 875 s. ISBN 08-493-1741-X.

[9] HARTMANN, M. H.: *Biopolymers from Renewable Resources*. Berlin: Springer-Verlag, 1998. 417 p. ISBN: 3-540-63567-x

[10] MLEZIVA, Josef, ŠŇUPÁREK, Jaromír. *Polymery – výroba, struktura, vlastnosti a použití.* 2nd ed. Praha: Sobotáles, 2000, 537 p

[11] LEI, C., LI, S., CHEN, D., WU, B., HUANG W.: Melt Grafting of Maleic Anhydride onto Polypropylene with 1-Decene as a Second Monomer. *Journal of Applied Polymer Science*. 2011, vol. 119, p. 102-110

[12] ZHENG, Y., ZHAO, S., CHENG, L.: Synthesis and reaction kinetics model of suspension phase grafting polypropylene with dual monomers. *Polym. Bull.* 2010, vol. 64, p. 771-782

[13] GARTNER, C., SUÁREZ, M., LÓPEZ, B. L.: Grafting of Maleic Anhydride on Polypropylene and Its Effect on Blending with Poly(ethylene terephthalate). *Polymer Engineering and science*. 2008, p. 1910-1916

[14] YAZDANI-PEDRAM, M., VEGA, H., QUIJIDA, R.: Melt functionalization of polypropylene with methyl esters of itaconic acid. *Polymer*. 2001, vol. 42, p. 4751-4758

[15] MONCADA, E., QUIJADA, R., LIEBERWIRTH, I., YAZDANI-PEDRAM, M.: Use of PP grafted with Itaconic Acid as a New Compatibilizer for PP/Clay Nanocomposites. *Macromolecular Chemistry and Physics.* 2006, vol. 207, p. 1376-1386

[16] AMARO, L. P., RIVAS, B. L., COIAI, S., PASSAGLIA, E., AUGIER, S., CIARDELLI, F.: Grafting of Polypropylene and Its Potential Use as Metal Ion Adsorption resin. *Journal of Applied Polymer Science*. 2009, vol. 113, p. 290-298

[17] GANG-SHENG, T., TAO, L., LING, Z., LI-XIA, H., WEI-KANG, Y.: Supercritical carbon dioxide-assisted preparation of polypropylene grafted acrylic acid with high grafted content and small gel percent. *The Journal of Supercritical Fluids*. 2009, vol. 48, p. 261-268

[18] BADROSSAMAY, M. R., SUN, G.: Acyclic halamine polypropylene polymer: Effect of monomer structure on grafting efficiency, stability and biocidal activities. *Reactive and Functional Polymers*. 2008, vol. 68, p. 1636-1645

[19] CHMELA, Š., FIEDLEROVÁ, A., JANIGOVÁ, I., NOVÁK, I., BORSING, E.: Grafting of iPP Powder with Methacrylate Monomers in Water Medium. *Journal of Applied Polymer Science*. 2011, vol. 119, p. 2750-2758

[20] BURTON, E.-L., WOODHEAD, M., COATES, P., GOUGH, T.: Reactive Grafting of Glycidyl Methacrylate onto Polypropylene. *Journal of Applied Polymer Science*. 2010, vol. 117, p. 2707-2714

[21] AL-MALAIKA, S., EDDIYANTO, E.: Reactive processing of polymers: Effect of bifunctional and tri-functional comonomers on melt grafting of glycicyl methacrylate onto polypropylene. *Polymer Degradation and Stability*. 2010, vol. 95, p. 353-362

[22] CHENG, S., WEN, D.: Fluorinated Polypropylene Barrier Materials: Preparation and Characterization. *Journal of Applied Polymer Science*. 2010, vol. 116, p. 2793-2801

[23] SHI, H., SHI, D., YIN, L., LUAN, S., YIN, J., STAGNARO, P.: Preparation of PP-g-PEG by using partial pre-irradiated polypropylene as initiator and its properties. *Polym. Bull*. 2010, vol. 65, p. 929-940

[24] BADROSSAMAY, M. R., SUN, G.: A study of radical copolymerization on polypropylene during extrusion using two peroxide initiators. *Polym Int*. 2010, vol. 59, p. 155-161; www.soci.org

[25] MOSTAFA, T. B.: Chemical Modification of Polypropylene Fibers Grafted Vinyl Imidazole/Acrylonitrile Copolymer Prepared By Gamma Radiation and Its Possible Use for the Removal of Some Heavy Metal Ions. *Journal of Applied Polymer Science*. 2009, vol. 111, p. 11-18

[26] MA, L., LI, L., GUO, C.: Influence of m-isopropenyl-α,α-dimethylbenzyl isocyanate and styrene on non-isothermal crystallization behavior of polypropylene. *J Therm Anal Calorim*. 2010, vol. 101, p. 1101-1109

[27] LIU, N. C., YAO, G. P., HUANG., H.: Influences of grafting formulations and processing conditions on properties of silane grafted moisture crosslinked polypropylenes. *Polymer*. 2000, vol. 41, p. 4537-4542

[28] SONG, G., YANG, S., YANG, C., SHE, X.: Foaming polypropylene prepared by a novel one-step silane-grafting and crosslinking method. *J Porous Mater*. 2006, vol. 16, p. 297-301

[29] CARLSON, D., NIE, L., NARAYAN, R., DUBOIS, P.: Maleation of Polylactide (PLA) by Reactive Extrusion. *Journal of Applied Polymer Science*. 1999, vol. 72, p. 477-485

[30] PLACKETT, D.: Maleated Polylactide as an Interfacial Compatibilizer. *Journal of Polymers and the Enviroment*. 2004, vol. 12, p. 131-138

[31] WU, C.-S.: Preparation, Characterization, and Biodegradability od Renewable resource-Based Composites from Recycled Polylactide Bioplastic and Sisal Fibers. *Journal of Applied Polymer Science*. 2012, vol. 123, p. 347-455

[32] MOURA, I., NOGUEIRA, R., BOUNOR-LEGARE, V., MACHADO, A. V.: Biobased grafted polyesters prepared by *in situ* ring-opening polymerization. *Reactive and Functional Polymers*. 2011, vol. 71, p. 694-703

[33] GUERROUANI, N., MAS, F., SCHUÉ, F.: Synthesis of Poly(vinyl alcohol)-*graft*-poly(ε-caprolactone) and poly(vinyl alcohol)-*graft*-poly(lactide) in Melt with Magnesium Hydride as Catalyst. *Journal of Applied Polymer Science*. 2009, vol. 113, p. 1188-1197

[34] GUTIERREZ-VILLARREAL, M. H., ULLOA-HINOJOSA, M. G., GAONA-LOZANO, J. G.: Surface Functionalization of Poly(lactic acid) Film by UV-Photografting of *N*-Vinylpyrrolidone. *Journal of Applied Polymer Science*. 2008, vol. 110, p. 163-169

[35] HO, C.-H., WANG, C.-H., LIN C.-I, LEE, Y.-D.: Synthesis and characterization of TPO-PLA copolymer and its behavior as compatibilizer for PLA/TPO blends. *Polymer*. 2008, vol. 49, p. 390-3910

[36] QI, R., LUO, M., HUANG, M.: Synthesis of Styrene–Ethylene–Butylene–Styrene Triblock Copolymer-*g*-Polylactic acid copolymer and Its Potential Application as a Toughener for Polylactic acid. *Journal of Applied Polymer science*. 2011, vol. 120, p. 2699-2706

[37] OUHIB, R., RENAULT, B., MOUAZIZ, H., NOUVEL, C., DELLACHERIE, E., SIX, J.-L.: Biodegradable amylose-*g*-PLA glycopolymers from renewable resources. *Carbohydrate Polymers*. 2009, vol. 77, p. 32-40

[38] SHI, Q., CHEN, C., GAO, L., JIAO, L., XU, H., GUO, W.: Physical and degradation properties of Binary or ternary blends composed of poly (lactic acid), thermoplastic starch and GMA grafted POE. *Polymer Degradation and Stability*. 2011, vol. 96, p. 175-182

[39] Lachner.com [online]. 2011 [cit. 2011-04-12]. *Fenolftalein.* Dostupné z WWW: http://www.lach-ner.com/fenolftalein-indikator-100-gr/d-70902/

[40] VERBEEK, C. J. R., HANIPAH, S. H.: Grafting Itaconic Acid onto Polyethylene Using Extrusion. *Journal of Applied Polymer Science.* 2010, vol. 116, p. 3118-3126

[41] POUCHERT, Charles J. *The Aldrich Library of FT-IR Spectra*: *Edition I. Volume 2*. 1st Ed. Milwaukee: Aldrich Chemical Company Inc., 1985, 1567 s.

[42] POUCHERT, Charles J. *The Aldrich Library of FT-IR Spectra*: *Edition I. Volume 1*. 1st Ed. Milwaukee: Aldrich Chemical Company Inc., 1985, 1392 s.

[43] BOEHM, Stanislav a Svatava SMRČKOVÁ - VOLTROVÁ. *Strukturní analýza organických sloučenin*. 1. vyd. Praha: VŠCHT, 1995, 152 s. ISBN 80-7080-235-9.

[44] POŠTULKOVÁ, H. *Roubování polypropylenu deriváty kyseliny itakonové*. Brno: Vysoké učení technické v Brně, Fakulta chemická, 2012. 48 s. Vedoucí bakalářské práce Mgr. František Kučera, Ph.D..

[45] ARVAI, T. *Technologická optimalizace čtvrtprovozní výroby PP-g-IAH*. Brno: Vysoké učení technické v Brně, Fakulta chemická, 2011. 40s. Vedoucí bakalářské práce Mgr. František Kučera, Ph.D..

7. LIST OF USED SYMBOLS AND ABBREVIATIONS

[M]	Monomer concentration
A	Amylose
AA	Acrylic acid
AAM	Acrylamide
AN	Acrylonitrile
as	Asymmetrical
BMA	Butyl methacrylate
BP	Benzophenone
c	Concentration
DCP	Dicumyl peroxide
DMA	Dodecyl methacrylate
DMAP	4-Dimethylaminopyridine
DMI	Dimethyl itaconate
DSC	Differential scanning calorimetry
DTBHY	2,5-Dimethyl-2,5-(*tert*-butylperoxy)hexyne
DVB	Divinyl benzene
EHMA	2-Ethyl hexyl methacrylate
EMA	Ethyl methacrylate
EVA	Ethylene vinyl acetate
FPP	Fluorinated polypropylene
FT-IR	Infrared spectroscopy
GD	Graft degree
GMA	Glycidyl methacrylate
GPOE	Glycidyl methacrylate grafted poly (ethylene octane)
HFPMA	2,3,4,5,5,5-Hexafluoro-2,4-bis (trifluoromethyl) pentyl methacrylate
I	Initiator
IA	Itaconic acid
IAH	Itaconic anhydride
LA	Lactide
M	Medium
MAH	Maleic anhydride
MAM	Methacrylamide
MFI	Melt flow index
MMA	Methyl methacrylate
MMI	Monomethyl itaconate
m-TMI	m-Isopropenyl-α,α-dimethylbenzyl isocyanate
NDAM	2,4-Diamino-6-diallylamino-1,3,5-triazine
n_{exp}	Experiment determined amount of substance
NTAAM	N-*tert*-butylarcylamide
n_{teor}	Theoretical amount of substance
NTMAM	N-*tert*-butylmethacrylamide
NVP	*N*-vinylpyrrolidone
PEG	Poly(ethylene glycol)
PLA	Polylactide; polylactic acid

PLA	Poly(vinyl alcohol)
PP	Polypropylene
S	Strong
s	Symmetrical
$scCO_2$	Supercritical carbon dioxide
SEBS	Styrene–ethylene–butylene–styrene block copolymer
St	Styrene
T_{cg}	Ceiling temperature of grafting
T_g	Glass transition temperature
T_m	Melting temperature
TOP	Thermoplastic polyolefin
TPS	Thermoplastic starch
TRIS	Trimethylolpropane triacrylate
VIm	Vinylimidazole
VMMS	Methacryloylpropyltrimethoxysilane
VS	Very strong
VTES	Vinyltriethoxysilane
w	Weak
w_c	Crystallinity content
wt%	Percentage by weight
BFA	Butyl 3-(2-furanyl)propenoate
ΔH	Enthalpy
ΔH_{cc}	Cold crystallization enthalpy
ΔH_m	Melting enthalpy
ΔS	Entropy
$\Delta S°$	Standard entropy
α	Conversion of monomer after grafting