INFLUENCE OF E/P COPOLYMER COMPOSITION ON IMPACT COPOLYMER PROPERTIES
VLIV SLOŽENÍ E/P KOPOLYMERU NA VLASTNOSTI IMPAKT KOPOLYMERU

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E/P copolymer composition evaluation using structural-analytical methods:
NMR, DSC, FTIR, SSA.

Bachelor's thesis is necessary to deliver to a secretary of institute in three copies and in an electronic way to a head of bachelor's thesis. This assignment is enclosure of bachelor's thesis.

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ABSTRACT
Impact E/P copolymer is produced using the gas-phase polymerization, which is catalysed by Ziegler-Natta catalyst. This material, which has excellent mechanical properties, is used in many industries, for example in automotive industry to produce bumpers or instrument panels.

Its properties depend on chemical structure, which was analysed using DSC, SSA, $^{13}$C NMR, ATREF and FTIR. The results were compared with the mechanical properties of the samples – flexural modulus and low-temperature impact strength Charpy.

5 different samples were used for studies, the chosen samples contain different ratio between ethylene and propylene in their copolymer phase. The samples were fractionated using o-xylene extraction to divide the material into crystalline part, composed of crystalline E/P copolymer and PP, and into amorphous phase, formed by E/P rubber. The obtained fractions and the original samples were subsequently analysed using above-mentioned methods.

KEYWORDS
Impact copolymer, fractionation, structural analysis, mechanical properties, amorphous and crystalline phase

KLÍČOVÁ SLOVA
Impakt kopolymer, fracionace, strukturní analýza, mechanické vlastnosti, amorfní a krystalická fáze
DECLARATION

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1 INTRODUCTION

The first manufacture of polypropylene plastics was accomplished in Italy by Montecatini, later fused and renamed to Montedison, in 1957. Less than five years ago, it was discovered, that transition metal catalysts were able to produce crystalline thermoplastic polypropylene. After this discovery, the production was started in the USA and later expanded in the world. 27 years later, there is production of 7 million tons annually in the world. This material has found its using in automotive industry, production of fiber, appliances and as a packaging material because of its good physical proprieties, ease of fabrication and low price.

A rapidly growing innovation of polypropylene was a production of impact copolymers, which are combination of impact resistance, stability and processability with a lower cost than competitive materials. The technology of production was improved. The development of the production was characterized by the use of inert diluent, liquefied monomer and gas-phase. Inert diluent or “slurry” process represents older technology whereas liquefied monomer and gas-phase processes are considered as representatives of newer technologies and are simpler. [7]

As a result of manner of production, usually in reactor synthesized mixture of PP and E/P copolymer, impact copolymers are formed by relatively complicated mixture of more components. Amount and composition of single components influence final properties of the used material.

The studied samples are alloys of polypropylene toughened with an E/P rubber. One of important factor which decides on impact copolymer properties is E/P copolymer composition. The E/P copolymer composition was investigated using some structural analytical methods in this thesis. Experiments were made on model samples with different ratio of monomers, ethylene and propylene, set in a reactor during copolymerization step. The aim of this thesis was experimental verification of methods suitable for studies of impact copolymer structure.

The composition influences chemical and mechanical proprieties of the material. The investigated samples were firstly fractionated using o-xylene extraction, afterwards, the composition of the original sample and the fractions was investigated using structural analysis methods Nuclear magnetic resonance, Fourier transform infrared spectroscopy, Analytical temperature rising elution fractionation, Differential scanning calorimetry and Successive self-nucleation/annealing.
2 THEORETICAL PART

2.1 Ziegler-Natta polymerization of propylene

Ziegler-Natta polymerization, started in the 1950s, is used for the gas-phase polymerization of vinyl monomer. It is possible to prepare a polymer of a specific tacticity, in the case of propylene polymerization an isotactic polypropylene, using this type of catalysis. TiCl₃ or TiCl₄ are usually used as Ziegler-Natta catalyst with an aluminium alkyl as a cocatalyst, mostly Al(C₂H₅)₃. Generally, it is a system of two metal compounds, the metal belongs to the IIIrd group. Later a system of MgCl₂ and Ziegler-Natta catalyst has begun to be used, this system has a high activity and stereospecificity.[17]

MgCl₂ is used as an internal electron donor to increase the catalyst activity, because in the case of the use only the catalyst TiCl₃ with the cocatalyst Al(C₂H₅)₃, the yield is too low.[16,17] Concerning the explanation of the catalyst activity, there exist several theories. Either the high activity is a cause of the destabilization of the titanium-polymer which is bond by withdrawing an electron from the monomer unit. The result of this mechanism is a higher propagation rate constant. The second theory proposes MgCl₂ as a donor of an electron on the more electronegative titanium. The result is a stabilization of the monomer and it is resulting to an acceleration of the monomer insertion and therefore the rate of propagation.[17]

The aluminium alkyl itself as a cocatalyst serves as a Lewis base and it is necessary to add it to the catalyst when a higher stereospecificity is required. [16] This aluminium alkyl represents so called external donor. Concerning the external donor, its function is a retaining of the stereospecificity of the active site. According to Busico’s and Barbé’s theories, the external donor acts as a poisoner of the non-stereospecific sites and promoter of the isospecific sites. The other theory suggested by Soga et al. proposes that the aspecific sites changes to the isospecific sites if the external donor is added to the catalyst and cocatalyst system. [17]

It exist several theories on the Ziegler-Natta polymerization mechanism which can be either monometallic or bimetallic. [17]

After the Cosee theory, which serves for an example of monometallic polymerization, the monomer propene unit is coordinated to the monometallic centre formed by titanium atom in the place of the vacancy and a four-membered ring of titanium is formed. Afterwards, this transition state undergoes the chain migratory insertion and results in the extension of the chain and in the renewal of the vacancy which enables the repeating of the process. [16,17]
The bimetallic mechanism, proposed by Rodriguez and van Looy, which forms the active site such as in the case of TiCl$_4$ or TiCl$_3$ is started with the reduction of the titanium to the lower oxidation state. Then, a cocatalyst alkyl group is bounded to the chloride. The isospecificity is caused through the existence of vacant orbitals in the titanium atoms and this amount of isotacticity is dependent on the position of vacancies in the molecule of the TiCl$_3$ or TiCl$_4$. The monomer propene unit is firstly coordinated to the titanium cation, to the ethyl group which is coordinated to the aluminium cation and to the aluminium cation itself. Secondly, ethyl group is bounded to propene unit and aluminium is coordinated to the propene carbon and whole process is repeated. [17]
2.2 Impact copolymers

Copolymers are polymers formed through copolymerization, the reaction of a mixture of two monomers, which form reciprocally no complexes. The majority of copolymerization reactions are radical reactions. Polymer chain of different sequence of monomers can be formed during the propagation, therefore different types of copolymer are formed. [9] If the monomer units regularly alternate, the final product is called alternating copolymer. Another structural type of copolymer is block copolymer where blocks composed by the same monomer units alternate. Block copolymers are synthesized in two steps. In the first step, a homopolymerization of the monomer units contained in the chain is started, in the second step an excess of another monomer is added to the active reactive mixture. A branched copolymer contains a monomer chain and another monomer branches bound to the chain. Monomer units in a statistical copolymer randomly alternate. [10]

Impact copolymers polypropylenes are usually synthesized in situ in a two-reactor system to get a blend consisting of homopolymer with an ethylene-propylene rubber (EPR). The EPR serves as a toughener for isotactic polypropylene (PP), which is at low temperatures a brittle material without high-impact strength. The rubber-like phase exists as a phase-segregated discrete particle in a continuous matrix of a polypropylene hard phase. These particles are added at 10 – 25 % concentration, which leads to the formation of a discrete phase in the hard phase. These particles, which have a function of toughener, defend crack propagation in the matrix. The energy involved through the crack is dissipating in the matrix material and then the propagation of the crack is inhibited. [1]

The most important mechanical properties which define polymer materials are stiffness, strength, hardness and toughness. These properties are tested using mechanical properties tests divided into static tests, where the material is exposed to slowly changing power, into dynamic tests, where the power changes in shorter time and fatigue tests, where the material is tested during long time under prescribed conditions usually up to the violation of the tested material. Mechanical properties of impact copolymers can be characterised using flexural modulus and Charpy impact strength. Flexural modulus, expressed in MPa, is a result of bend test, this test is important for materials strained by a bend, for example support or roofing. Charpy impact strength is a method used for strength determination of plastics. It determines strength of the material. [29]

2.2.1 Gas-phase process of impact copolymer synthesis

The process of gas-phase polymerization was developed for polymerization of ethylene in the 1960’s. But, this process was delayed for polymerization of propylene because of its economical disadvantage. The yield of propylene gas-phase polymerization by use of transitional metal catalyst was smaller than the yield of polymerization of ethylene because ethylene is more reactive than propylene and contrary to the propylene, in the case of ethylene, there is not a problem with stereospecificity. Firstly, the gas-phase polymerization of propylene was realized in Germany, where an improved catalyst was developed, a catalyst enabling an economical industrial production of homopolymer polypropylene. Additional development of the catalysts enabled in 1970’s the production of impact copolymers using the gas-phase polymerization. [7]

2.2.1.1 Process description

Before the polymerization itself is started, it is necessary to remove an air from the reactor and lead there nitrogen, afterwards the cocatalyst and the catalyst are dosed.

The synthesis itself is made in three steps. In the first step, the liquid propylene is prepolymerized in the aim to yield high polymerization activity and to maintain
the morphology of the catalyst. If the prepolymerization is made depends on the type of catalyst. Then, the prepolymerization is followed by homopolymerization of propylene and in the third step, the propylene is copolymerized with ethylene. The final product is an alloy of PP/EPR with a complicated microstructure. [2]

In the second step, during the homopolymerization of propylene, a porous particle is formed from the homopolymer and inside this particle a copolymerization of propylene with ethylene is. This process causes that the particles are not able to stick to the wall of the reactor, in which the polymerization is accomplished. [2]

One of the industrial in-reactor processes is the gas-phase process INNOVENE. The polypropylene is synthesised in the first reactor, the copolymerization is realised in the second reactor.

![Scheme of the process INNOVENE](source Chemical Market Resources) [18]

During the synthesis, it is necessary to dose hydrogen and nitrogen to the reactor. Brought nitrogen forms an inert atmosphere and the aim of bringing of hydrogen is a transfer of the active centres formed by catalyst system. [17]

### 2.2.2 Impact copolymer composition

The material is composed of homopolymer PP and of E/P copolymer, which forms isolated domains in the hard homopolymer matrix.

#### 2.2.2.1 Homopolymer PP characterization

It is a high crystalline homopolymer PP with high stereoregularity, low-molecular and atactic PP can form part of amorphous phase. This amorphous phase forms an interphase binding the crystalline domains and gives flexibility to the material.
The amorphous phase can be dissolved in xylene. To the contrary, the crystalline part, insoluble in xylene, arranged to the crystals having dimensions in orders of nanometres gives extraordinary impact toughness to the material. [4] The crystallinity is caused by the regular arrangement of the parts of polymer molecules.

The crystallinity itself is one of the fundamental and most important properties of each polymer. The properties of the material such as hardness, modulus, tensile, stiffness and melting point are the consequence of the existence of the crystallinity. The crystalline part is able to the process called crystallization which means a formation of regularly ordered polymer molecules from a molecules existing in a disoriented state. The disoriented state is typical for molecules existing under high temperature, so called melting state when the polymer exists in a liquid state. The exothermic process of the crystallization takes place between glass transition and melting point. [6]

The molecules forming the crystalline part are arranged to lamellas [5] among that the amorphous phase, formed of molecules in disoriented state, exists.

### 2.2.2.2 E/P copolymer characterization

E/P copolymer is composed of amorphous rubber and crystallizable E/P copolymer with longer ethylene and propylene sequences.

The size and the distribution of the dispersed phase (E/P copolymer) is the main factor determining the toughening effect of impact copolymer. The second factor is the interfacial adhesion between the particles of the E/P copolymer and the matrix. The coexistence of the crystalline and of the amorphous phase leads to the macroscopic homogeneity of the blend but this blend is microscopically composed of the separated phase structure. [6]

### 2.2.2.3 Distribution functions

The copolymers are characterised by two distribution functions, the first is broad composition distribution, the second is multimodal composition distribution. The composition distribution of copolymers synthesized using heterogeneous catalysts cannot be theoretically calculated whereas the composition distribution function of a copolymer made over a homogeneous catalyst can be calculated using the following function

$$W(y)dy = \frac{3 \left( \frac{\lambda}{2a_0b_0k} \right)^{\frac{\nu}{2}}}{4 \left[ 1 + \left( \frac{\lambda y^2}{2a_0b_0k} \right)^{\frac{\nu}{2}} \right]}dy$$

(1)

where $\lambda$ represents number-average dispersed phase of growing chains, $a_0$ and $b_0$ represent an average molar copolymer composition and $y = a - a_0 = b_0 - b$ is so called composition deviation parameter $k$ is calculated using the relation

$$k = a_0r_2 \cdot \frac{A}{B} + b_0r_1 \cdot \frac{A}{B}$$

(2)

where $r_1$, $r_2$ are reactivity ratios and $a, b$ represent variable molar copolymer composition.[1]
2.3 Structural analysis methods

2.3.1 $^{13}$C NMR

Nuclear magnetic resonance (NMR) spectroscopy is an analytical technique used for determining chemical structure of the analysed sample. It gives information about the type of hydrogen atoms and about the carbon chain.

It is possible to detect only the nuclei containing spin, it means they have an internal angular momentum. This property belongs to for example $^{13}$C nucleus. The spin orientation in the absence of the external magnetic field is random, but in the case of placing the measured sample into the external magnetic field, the spins are oriented either in parallel or in antiparallel with the vector of the placed external magnetic field.

If so oriented nuclei are exposed to electromagnetic radiation with the frequency of radio waves, the energy is absorbed and the spin is changed. The nuclei change over from their lower energy state to the higher energy state. They are in the resonance with the used radiation, so this method is called nuclear magnetic resonance.

Chemically equivalent nuclei give only one signal, this signal is amplified and detected as a peak.

It is simpler to use $^{13}$C NMR for determining polymer structure because the interpretation of obtained results is easier. This is caused by the fact that in the polymer chain, there are fewer chemically equivalent carbon nuclei than chemically equivalent hydrogen nuclei. So, if $^1$H NMR were used, too much peaks would be obtained and the interpretation would be more complicated. The problem with too low presence of $^{13}$C nuclei were resolved by using of the signal averaging and by using of NMR-spectroscopy with Fourier transformation.

Each nucleus gives resonance at the certain magnetic induction. The location in the spectrum, where the signal is present is called chemical shift. It is expressed in $\delta$ scale as the observed chemical shift in Hz divided by the frequency of the spectrometer in MHz. The chemical shift in the $^{13}$C NMR is influenced by many factors, it depends on the electronegativity of atoms bounded with the atom of carbon and on the hybridization. [14]

The polymer sample must be firstly dissolved in deuterated solvent and after the dissolution, the sample is measured. Measured signal is transformed and obtained as a spectrum. It is possible to obtain detailed information about the amount of each constituent present in the material. [14,15]

2.3.2 FTIR

Fourier Transform Infrared Spectroscopy (FTIR) is a type of Infrared spectroscopy which is an analytical technique belonging to vibrational spectroscopy. Generally, infrared spectroscopy (IR) uses the ability of functional groups, forming the analysed compound, to absorb the passing-through infrared radiation. After this absorption, the functional groups vibrate and evolve a radiation of the certain wavelength, which is detected. The absorbance obeys the Beer-Lambert law, represented by the following equation

$$A = \varepsilon b C$$  \hspace{1cm} (3)

where $A$ represents the absorbance, $\varepsilon$ is the molar absorptivity coefficient, $b$ the path length of the measured sample and $C$ represents the concentration of the determined molecule in the sample.

The result is a spectrum, which can be used to determine the amount of the functional group existing in the measured sample and to determine the symmetry of the molecules forming the analysed sample, because the same functional group of other symmetry has its absorption maximum of other wavelength.
Fourier Transform Infrared Spectroscopy is primarily used to analyse organic materials. The spectrum is transformed from the time-domain to the frequency by the use of Fourier transformation.

It exist two half of Fourier-transform pair, one of them is so called intensity falling on the detector $I(\delta)$, it represents the variation of the power density as a function of path length difference and the other half of the pair is the spectral power density $B(\nu)$ showing this variation as a function of wavenumber. These values are given by the following relations

$$I(\delta) = \int_{0}^{\infty} B(\nu) \cos 2\pi \nu \delta \, d\nu$$

and

$$B(\nu) = \int_{0}^{\infty} I(\delta) \cos 2\pi \nu \delta \, d\delta$$

where $\nu$ is a particular wavenumber and $\delta$ represents the path difference. These two equations are interconvertible through the mathematical method called Fourier transformation.

The advantage of FTIR is the reduction of the influence of the noise what leads to the higher and clearer signal. The other advantage of FTIR spectroscopy is a speed of the measurement. The spectrum can be obtained after few milliseconds. [21]

2.3.3 DSC

Differential Scanning Calorimetry (DSC) is one of the most commonly used methods for characterising the thermal properties of polymers.

It is a technique that determines the temperatures and heat flow associated with material transitions as a function of temperature or time. DSC measures the difference between the heat flows to a sample and a reference pan that are exposed to the same temperature program. A heat flow corresponds to a transmitted power that corresponds to an equal change in enthalpy of the sample. When the sample absorbs energy, the enthalpy change is called endothermal, when the sample releases energy the process is called exothermal.

Heat flow is the amount of heat transferred per unit time ($dQ/dt$) – the total quantity of heat transferred $Q$ corresponds to the time integral of the heat flow, $Q$ is expressed in J per unit mass (J/kg or J/g). [27]

$$Q = \int \frac{dQ}{dt} \, dt$$

Change in enthalpy ($\Delta H$) — the quantity of heat absorbed (if $\Delta H$ value is positive) or released (if $\Delta H$ value is negative) by a test specimen undergoing a chemical, physical or a temperature change. It is expressed in J per unit mass (J/kg or J/g). [27]

$$\Delta H = \int_{r_{1}}^{r_{2}} \frac{dH}{dT} \, dT$$

The result of the measurement is a graph of the dependence of heat flow at temperature. It is possible to determine melting temperature, crystallization temperature and enthalpy from this graph. There is a practice to record, for each measurement, a curve in which temperature or time is plotted on the x-axis and heat flow difference on the y-axis [27]
There exist two used types of DSC. The difference between heat flow into both pans is measured either as a function of temperature or as a function of time, while the temperature of the specimens is varying in accordance with a controlled programme. In the case of the power-compensation DSC, this programme keeps the equal temperature of both specimens. In the type of so called heat-flux DSC, the difference in temperature between the test and the reference specimen is proportional to the difference in heat flow.

DSC can be used to determine glass transition, melting and crystallization temperatures, phase transition enthalpy and specific heat, the degree of crystallinity and the thermal and kinetic reaction stability of polymer. The other application of DSC involves measuring the thermal stability of certain products by performing an isothermal (constant temperature) scan over time.

Although DSC is a predominantly qualitative technique it can be used for quantitative analysis too.

Before use, the instrument has to be calibrated so that the signal measured and indicated corresponds to the temperature and energy necessary for standard reference materials which have melting points close to the temperature range used for the material analysis.

This method is used for polymers in any state, glass, semi-crystalline, rubbery or crystalline state, in any form. Samples can be taken from granules, film or sheets or in the form of powder. It is necessary to have a suitably flat surface to ensure good contact with the base of the capsule and then with the oven. The analysed material can contain additives and the analysis can be performed on polymer blends too.

It is necessary to measure a small amount of a sample, around 5 – 10 mg of the sample, because of the thermal proprieties of polymer materials. The polymer sample is heated with reference to the second empty pan, the pans are kept at the same program temperature and the heat flow is measured. If the sample doesn’t show a physical or chemical change, the dependence of heat flow on the time is linear. In the presence of a change related to evolving or consumption of energy, the linearity is disrupted.

It is possible to determine values such as start of the deviation from the basic line, temperature in the inflection point, the highest temperature difference etc.

The result of the measurement is a graph of the dependence of heat flow at temperature. It is possible to determine melting temperature, crystallization temperature and enthalpy from this graph. Each material melts and crystallizes at another temperature, than these values serves to determine the crystalline amount in the measured sample. If the sample is a blend of two polymers or copolymer, two peaks are observed (ref. Fig. 4)
Fig. 4: DSC analysis of a sample containing E/P copolymer and h-PP, crystallization

If the process of crystallization is observed, the crystallization temperature occurs in the minimum of the function because the crystallization is exothermic process on the other hand in the case of melting, the observed melting temperature occurs in the maximum of the function as the endothermic process (ref. Fig. 5)

Fig. 5: DSC analysis of a sample containing E/P copolymer and h-PP, 2nd melting
2.3.4 SSA

Successive self-nucleation annealing (SSA) is a process of segregation of polymer chain leading to the determination of the thickness of lamellas formed by polymer chains. It is necessary to realize, that SSA is the method covering only a crystalline part of polymer material, not amorphous phase.

2.3.4.1 Supramolecular structure

Three types of polymer structures are differed.

Amorphous polymer macromolecules are statistically disordered and form macromolecular coil of different volume. Its dimensions change on dependence on conditions such as temperature and presence of some low-molecular substances for example of solvent or plasticizer. Moreover, macromolecular coil dimensions and shape change under mechanical stress at higher temperature. The coils are intertwined if the amorphous polymer is in solid state. Otherwise crystalline polymer can be prepared in its amorphous solid state under suitable conditions such as superfast cooling. [25]

Semi-crystalline polymer macromolecules are folded up, after a segment, the macromolecule turns to an opposite direction, and this macromolecule is partially ordered what corresponds with real solidification conditions. [25] It is possible to differ crystalline and amorphous phases differently distributed in space. This phase distribution is partially dependent on crystalline phase amount. In the case of lower crystalline phase amount, molecular clusters are formed and are surrounded with amorphous phase. The crystalline molecular clusters dimension is about 10 nm. If the crystalline phase amount is higher, crystalline planar shapes called lamellas are formed. Folded crystalline lamellas grow in polycrystalline shape called spherolite, morphological semicrystalline polymer shape. The spherolite growth is realised from one nucleus specifying the crystalline structure of whole spherolite. The space between folded polymer chains is full with amorphous phase. [26]

![Crystalline amorphous structure](image)

Fig. 6: Crystalline amorphous structure, reproduced from [26]
Monocrystals representing crystalline plastics can be prepared only from diluted solutions at suitable conditions mainly at suitable temperature. [25, 26] Crystallization is a spontaneous regular folding of polymer chain in all three directions. Crystal shape is characterised by crystal lattice shape, similar to those of low-molecular crystalline substances. In fact, crystallization is a process of phase transition from liquid to solid state. If the configuration is regular, the chain is flexible, monomer units are symmetrical and intermolecular forces are stronger, the tendency to crystallization is higher.

The crystallization process is composed from nucleation, which means crystalline nuclei formation, and spontaneous growth of crystals. Nucleation is differed into the homogeneous one and the heterogeneous one, realized on a surface of foreign body. Spherolite radius is enlarged linearly with time during the growth of crystals. The growth speed is determined by secondary nucleation on a spherolite surface and contrary to solution crystallization, the growth speed is not associated with diffusion on an interface crystal – melt. The crystalline growth is divided into one-way growth, called fibrillar, two-way growth, printed, and three-way growth, called spherolitic.[26]

2.3.4.2 SSA technique

The SSA method is based on different ability of polymer lamellas to crystallize at variable temperatures according to their length. At first, a polymer material is heated to temperature, which is higher than melting point to eliminate thermal history of a sample. Then, temperature $T_1$ is applied and isothermal crystallization takes place. After that, the sample is cooled down to ambient temperature. The second step starts with heating of the sample to temperature $T_2$, which is lower than $T_1$. The successive steps repeat, until end temperature is achieved. Then, DSC scan is carried out. A scheme of SSA treatment is shown in Fig. 8 below.
Gibbs-Thompson equation is established between the melting temperature and crystal thickness:

\[ \frac{T_{m,i}}{T_m^0} = 1 - \frac{2\sigma_e}{l_i \cdot \Delta H_u} \]  

(8)

where \( T_{m,i}^0 \) represents the equilibrium melting temperature, \( T_{m,i} \) is the melting temperature of each peak, \( \sigma_e \) is the basal surface energy of measured polymer crystals, \( \Delta H_u \) represents the heat of fusion for repeating units and \( l_i \) the segment length between the adjacent branch points.

This equation serves to calculate the length of particular segments:

\[ l_i = \frac{2\sigma_e T_{m,i}^0}{\Delta H_u \left( T_{m,i}^0 - T_{m,1} \right)} \]  

(9)

The amount of the continuous segment is obtained from the value of the normalised heat enthalpy obtained in DSC measurement divided by the relevant segment length. The following equation is used for the calculation of the semi quantitative amount of polymer segments \( Q_i \) of the defined length:

\[ Q_i = \frac{\rho \cdot \Delta H_i}{14.03 \Delta H_u} \cdot \frac{0.2534}{2l_i} \]  

(10)

where \( \Delta H_i \) the heat of fusion for each melting is peak and \( \rho \) represents the density of crystals.

The obtained result of SSA measure is the segment distribution expressed as a dependence of the segment length on a quantity of segment. [13]
2.3.5 Analytical TREF

Temperature Rising Elution Fractionation (TREF) is a technique used to analyse semi-crystalline polymers, more exactly to determine their composition distribution. TREF is based on the principle that components of a polymer blend crystallize at different temperature according to their crystallizability. Analytical TREF gives informations about polymer crystallizability distribution, preparative TREF enables, in addition to that, getting fractionated material for other analytical methods.

The fractionation is made in the column, where the diluted sample is injected, heated to the initial temperature and then cooled. During the cooling, certain fraction crystallizes. Crystallized fractions of the material are obtained from the column at the followed heating period. TREF apparatus is composed of solvent reservoir, from which the solvent flows through the pump, providing a constant flow of solvent during the elution. Sample is dosed to the column placed in the oven, where the fractionation of the sample itself runs. The fractions are detected by the infrared detector and the detected signal is processed. The result of the TREF analysis is a fractogram containing several peaks depending on the number of the fractions, created as a dependence on the growing temperature. [19,20]

![Scheme of TREF elution apparatus](image)

Fig. 9: Scheme of TREF elution apparatus, reproduced from [19]
3 EXPERIMENTAL PART

3.1 Model samples

The investigated samples were five different samples of impact copolymer, named K1148, K1159, K1139, K1147 and K1127. They were synthesized in 50-liters reactor. Polymer powder with process stabilizers was homogenized in a single-screw extruder and granulated. The stabilization system was composed of 0.03% Irganox 1010, 0.03% Irgafos 168, 0.03% Sandostab P-EPQ, 0.02% DHT-4A (hydrotalcite) and 0.1% NaBz.

The homopolymer matrix is equal in all samples. The amount of E/P copolymer is equal in all samples, but in the samples, there are differences in composition of E/P copolymer, which means ratio of ethylene and propylene. The difference in composition of E/P copolymer is expressed as RCC2 value, which means the content of ethylene monomer units in E/P copolymer. RCC2 is measured using $^{13}$C NMR and FTIR. $^{13}$C NMR gives information about sequence length distribution in the analysed samples and about sequence constitution, however results obtained from FTIR measurement is expressed only as wt% of RCC2 and as wt% of ethylene units in impact copolymer (see Tab. 3). Mechanical properties of the analysed samples are strongly different especially in the low-temperature Charpy impact strength and Flexural modulus grows progressively (see Tab.1 below).

The model samples were fractionated using the o-xylene extraction into two fractions and subsequently evaluated using below mentioned analytical methods to determine the composition and structure of E/P copolymer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FM(MPa)</th>
<th>Charpy impact strength(kJ/m²), -20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1127</td>
<td>662</td>
<td>3,8</td>
</tr>
<tr>
<td>K1159</td>
<td>728</td>
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<td>8,3</td>
</tr>
<tr>
<td>K1139</td>
<td>796</td>
<td>9,8</td>
</tr>
<tr>
<td>K1148</td>
<td>826</td>
<td>3,6</td>
</tr>
</tbody>
</table>

3.2 Fractionation

The o-xylene extraction was used as the method of fractionation. This method is based on the international standard ISO 6427: 1982 (E), Annex B. The result of this fractionation was the sample separated into soluble fraction in o-xylene, so called XS, and into insoluble fraction in o-xylene, so called XI. The sample intended to fractionation is further called the original sample.

3.2.1 Method of o-xylene fractionation

The amount of 0,5 g of the sample intended to fractionation was placed into Erlenmeyer flask containing 100 ml of 98% o-xylene and refluxed under 144,4 °C in nitrogen atmosphere for 30 minutes. The solution was cooled 1 hour in thermostat under the temperature of 23 °C. The precipitated gel was filtered from the solution into evaporating pan, the filtrate formed by the in xylene soluble fraction was evaporated and the gel containing the insoluble fraction in o-xylene was reextracted. The filtrate was evaporated from the pan and the almost dry pan was placed into a vacuum oven at 105 °C and at a pressure less than 1 kPa for 2 hours. After, the pan was cooled to the laboratory temperature and weighed. The xylene extract percent was calculated using following equation:
\[ XS (\text{wt } \%) = 100 \left[ B \frac{E - F}{D} \cdot (B + C) \right] \cdot \frac{H}{C(G - H)} \]  

(11)

Where \( B \) is the weight of xylene, \( C \) represents weight of sample, \( D \) aliquot which is to be centrifuged, \( E \) tube with the aliquot before centrifuging, \( F \) tube with the aliquot after centrifuging, \( G \) filtrate for evaporation and \( H \) residue after evaporation. The weights were appointed in grams.

Obtained fractions were stored under low temperature, approximately under 4 °C.

Fig. 10: Photo of the used extraction apparatus

3.3 Methods of EVALUATION

3.3.1 DSC

The fraction XS and XI was analysed, 3 measurements of each sample were done, DSC analysis of each basic sample was made too. It was used a calorimeter DSC Q100 made by TA Instruments for the analysis. The calorimeter is calibrated on indium, the measurement was made in nitrogen atmosphere. The measurement was made using the norm EN ISO 11357-1 called Plastics – Differential scanning calorimetry.

7,5 mg of the sample was weighed and placed into the measurement aluminium pan. The initial temperature of XS fractions was -20 °C, of XI fractions 40 °C and of the basic samples 50 °C. The temperature growth was ended after reaching 200 °C. The samples were held at 200 °C 10 min without difference, if the original sample or fractions were measured. Afterwards, the sample was cooled and after cooling, the low temperature was held during 3 min in the case of fractions and 1 min in the case of original samples. The heating rate was equal to the cooling rate, their value was 10 °C/min. The volumetric flow rate of nitrogen was 50 ml/min.
The low initial temperature of XS fractions analysis was chosen because of the presence of amorphous phase, in which phase transitions take place under lower temperature than phase transitions of crystalline phase.

The first melting was done to eliminate the thermal history, the peaks obtained during crystallization and second melting were evaluated.

The dependence of heat flow on temperature difference was obtained in the graphic form. The melting point, alternatively the crystallization point of each compound was read as a maximum of the peak just as the enthalpy representing the peak area.

The original measured data had to be transformed in the PC program called PeakFit v.4 produced by Jandel. The aim of this transformation was obtaining the results what are on the same base-line in order to compare them.

![DSC graph](image)

Fig.11: Description of DSC graph evaluation

### 3.3.2 SSA

The SSA analysis was made on all five original samples and on their XI fractions, XS fractions were not measured. The warmed bath is calibrated on a higher initial measuring temperature than the melting point of amorphous phase is, then it is impossible to measure. Three measures of each sample were done.

It was necessary to make basic DSC analysis to determine the initial temperature for SSA fractionation, which is found as a heel of DSC peak.

Concerning the original samples, it was first necessary to press thin films to be able to cut out small pieces of them and close the pieces into aluminium pans. It was weighed about 10 mg of the sample. It was necessary to assure that the weighed samples would not leak out.

So prepared samples were placed into a glass tube, evacuated and sealed up into a glass tube and placed to the thermostat of brand name JULABO HE filled with silicon oil. The measure was made under nitrogen atmosphere. The thermostat was heated to a higher temperature than is the initial temperature of the measurement because of the elimination of the thermal history. After, the thermostat was cooled and reheated to the initial step.
temperature \( t_r \) corresponding to 180 °C. This temperature was maintained 2 hours, followed by 60 min of cooling to laboratory temperature. Then, the temperature was risen to a new step temperature 3 °C lower and the whole cycle was repeated until the step temperature 70 °C was reached.

The through SSA fractioned sample was measured on DSC, at a certain temperature crystals have been crystallized, crystal thickness is in direct dependence on inhomogeneities and defects in the polymer chain. The heating and cooling rate was 10 °C/min, the maximal temperature was 210 °C. The results were obtained from the first melting.

The basic DSC data were normalised and adapted in MS Excel. Base-line was arranged through calculation in MS Excel. The result was more detailed thermal than the analysis obtained by DSC alone.

The calculation with ethylene unit was used for E/P copolymer. It was realised using the equations (9) and (10) for calculation of segment length and quantity of segment.

### 3.3.3 NMR

The aim of \(^{13}\)C NMR analysis was obtaining the information about the detailed structure of the samples and the composition of the measured samples. The measure was made on all original samples and on all their fractions.

It was used 210 to 250 mg and this amount was dissolved in a solution mixture composed of 2 ml of 1,2,4-trichlorobenzene and 0.5 ml of deuterated benzene. The dissolution was made under 130 – 140 °C in cells, of the diameter of 10 mm, used for NMR measurement. If the sample is not stabilized, the mixture of 0.15% CaSt a 0.5% Irganox B225 is used for stabilization. The following solution homogenization is made under nitrogen atmosphere during 6 hours.

The \(^{13}\)C NMR measurement was done under 125 MHz, using pulse of 77°, repetition time, which is a time delay between pulses, was set on 15 s, the measurement was made less than 125 °C. Waltz was used as a decoupling. Decoupling means a pulse sequence and it serves in NMR analysis for elimination of signal fusion by hydrogen. Sweep width was 60 ppm, time domain which is related with resolution was set on 64 k. 500 scans were made to sufficient assurance of an optimal ration signal to noise.

Observed measured signal integrals were used for other calculations. The Markovian statistics of 1\(^{st}\) order was used for calculated molar fraction, this calculated result was compared with experimentally observed molar fraction, the observed results were used for standard deviation calculation based on a principle of least square method.

The obtained results were processed as a distribution of propylene and ethylene in sequences and as dyads and triads molar distribution. Dyad means a couple of two different monomer units, triad is a definition of three different monomer units.

### 3.3.4 FTIR

The aim of FTIR analysis was the determination of the concentration of ethylene in the samples. Transmission spectra of polymer films were measured, the thickness of the pressed films was 0.1 – 0.3 mm. The spectrometer FTIR Nicolet Nexus was used, the resolution was set on 2 cm\(^{-1}\), 32 scans were accumulated. In the ethylene sequence area there are bands 720 and 730 cm\(^{-1}\) what represent longer CH\(_2\) chain and the band 735 cm\(^{-1}\) what represents the sequence -(CH\(_2\))\(_n\) in the PEP sequence.

The concentration was calculated using Lambeert-Beer law. Using a calibration equation made of standards containing 5 up to 20 wt% of ethylene, the ethylene content in the samples was estimated. Measured ethylene sequences area, situated between 758 and 682 cm\(^{-1}\), was divided by the reference area situated between the wavenumbers
4490 cm\(^{-1}\) and 3950 cm\(^{-1}\). Reference area is proportional to film thickness, vibrations of groups CH, CH\(_2\) and CH\(_3\) are situated there.

The concentration is calculated using the following equation:

\[
\frac{A_{\text{ethylenseq}}}{A_{\text{ref}}} = \frac{E_{\text{ethylenseq}}}{E_{\text{ref}}} \cdot \frac{c_E}{c_{E,P}}
\]

(12)

where \(A_{\text{ethylenseq}}\) represents the measured absorbance at 758-682 cm\(^{-1}\), \(A_{\text{ref}}\) the absorbance between 4490 cm\(^{-1}\) and 3950 cm\(^{-1}\), the ratio \(E_{\text{ethylenseq}} / E_{\text{ref}}\) is constant, \(c_E\) represents the concentration of ethylene sequences and \(c_{E,P}\) represents the concentration of ethylene and propylene which spectrum occurs between 4490 cm\(^{-1}\) and 3950 cm\(^{-1}\).

Fig. 12: Example of FTIR spectrum of an impact copolymer sample

### 3.3.5 Viscosity measurement

Polymer viscosity is depended on concentration and molecular weight. Viscosity of more concentrated solutions is higher than viscosity of more diluted solutions. Moreover, the viscosity measurement enables to understand the phase morphology and rheological behaviour of the polymer. [24]

The viscosity measurement is defined by standard EN ISO 1628-3, where are determined conditions of reduced viscosity, known as a viscosity number, measurement and conditions of internal viscosity measurement. This standard is related to polypropylene, polyethylene and their copolymers. After this standard, the diluted solutions at 135 °C are measured and the measurement could be influenced by additives.
The solution of the sample equal to exactly 0,001 mol·dm$^{-3}$ was prepared. 22 - 27 mg of the sample was weighed and diluted in 1,2,4-trichlorobenzene containing 0,05 wt% of stabilizer Santonox at 150 °C under mixing. After 2 hours, it was possible to measure. Firstly, the flowing of the unadulterated solvent was measured twice to determine zero time $t_0$. The used viscosimeter acc. to Ubbelohde was emptied and dried. Afterwards, it was filled with a solution containing the diluted sample. Each solution was measured twice and two solutions were prepared from each sample. After the solution measure, $t_0$ was measured again.

The two measures of one solution can differ in maximally 0,2 s.

The intrinsic viscosity was calculated using the following relations:

$$I = \frac{t - t_0}{t_0 \cdot c}$$  \hspace{1cm} (13)

and $$[\eta] = \frac{I}{1 + k \cdot c \cdot I}$$  \hspace{1cm} (14)

where $I$ determines reduced viscosity, $c$ the concentration of the measured solution, $\eta$ determines intrinsic viscosity and $k$ is a coefficient depended on the concentration of polymer and its structure.

The unit of IV value is mg·L$^{-1}$. [28]

3.3.6 ATREF

Analytical TREF was used to prove that no amorphous phase is present in crystalline XI fraction. The analysis was made on five XI fractions of the samples.

The 0,02% solution of the sample in 1,3,5-trichlorobenzene was prepared and 2,0 ml of this solution was injected to SS column 300×10 (ID) mm containing inert support. The initial temperature was 140 °C, the sample was cooled at rate of 6 °C per hour. Afterwards it was heated from 20 °C to 140 °C at rate of 2 °C per minute. The mobile phase flow was 1 ml·min$^{-1}$. The record of the concentration in dependence on the elution temperature was obtained for each measured sample. The base line was determined after the analysis of proper solvent without polymer sample.

The ATREF analysis result was a graph containing normalised infrared response on dependence on temperature growth. The composition of the analysed sample is determined from the obtained graph shape. It is possible to differ amorphous phase from the crystalline-one or from the semicrystalline phase.
4 RESULTS AND DISCUSSIONS

4.1 Original samples

Examined samples contain the same h-PP matrix and the content of E/P copolymer is equal what is visible in RC value, what was calculated from polymerization data (see Tab. 4). The random copolymer (RC) is the whole amount of E/P copolymer which is synthesized in the 2nd reactor. The samples are different in their composition characterised by RCC2 value between 27.1 and 69.8 wt% what was determined using $^{13}$C NMR analysis and FTIR. The RCC2 value represents the amount of ethylene in E/P copolymer and this value is obtained by polymerization conditions. The content of ethylene in impact copolymer was determined using FTIR analysis and is represented as C2 value (see Tab.3). FTIR measurement was evaluated only in the case of original samples, because the measurement of XI fractions does not correspond to standards of measurement (see Fig. 31 and Fig. 32). In the case of XS fractions, the evaluation of FTIR measurement could not be done because the concentration of XS fractions was out of calibration.

![FTIR spectrum of the sample K 1139 in the form of higher absorbance of infrared radiation at certain wavenumbers – XI fraction](image-url)
Fig. 9b: FTIR spectrum of the sample K 1139 in the form of higher absorbance of infrared radiation at certain wavenumbers – original sample

Further information about composition was obtained from $^{13}$C NMR analysis (see Tab.2). The $^{13}$C NMR and FTIR analysis results are identical, but there are small differences. $^{13}$C NMR analysis gives RCC2(E) value too, which represents the content of ethylene in E/P copolymer and in h-PE, formed during polymerization. The h-PE content in the sample is given by the value in Tab. 2.

The h-PP value, obtained by the calculation from $^{13}$C NMR measurement, does not correspond to the content of h-PP matrix in the sample which value is from mass balance of polymerization 63 – 65 %. It is caused by data processing using the Markovian statistic of 1st order and this model considers as E/P copolymer only molecules with the certain propylene sequence length. If the propylene sequence length is longer, this sequence is considered as h-PP. This is evident in Tab. 2 and Fig. 15, where it is visible that the amount of h-PP in the samples grows with descending RCC2 value. The similar situation is in h-PE content in the samples, where the statistical model considers ethylene sequence of the certain length as h-PE. Then, the inverse dependence is observable, where the PE content in the samples grows with RCC2. The samples are ordered with the growing amount of RCC2 in following order: K1127, K1139, and the samples K1148, K1159 and K1147 have the same amount of copolymer.
The growing sequence length of propylene and of ethylene is obvious from Fig. 13 and Fig. 14, where ethylene and propylene distributions are obtained from $^{13}$C NMR data using Markovian statistic. $P(E)_nP$ represents the ethylene sequences length which are not interrupted by propylene unit and $E(P)_nE$ the propylene sequences length not interrupted by ethylene unit. $P(E)_nP$ is depended on RCC2 value, it grows with growing RCC2 value, contrary to $E(P)_nE$, where the trend is descending. The molar fraction decrease of ethylene segment length is the most distinct in the case of the sample K1127 and the most gentle in the case of the sample K1148. The samples are ordered according to the growth of segment length in following succession: K1127, K1159, K1147, K1139 and K1148 and in the case of propylene segment length distribution, the succession, in which the samples are ordered, is inverse (see Fig. 13 and Fig. 14).
Fig. 13: Results of NMR analysis of the original samples – distribution of sequences length of ethylene, which are not interrupted by propylene monomer unit, n describes sequences length of ethylene.

Fig. 14: Results of NMR analysis of the original samples – distribution of sequences length of propylene, which are not interrupted by ethylene monomer unit, n describes sequences length of propylene.
It is obvious, that longer ethylene sequences are present in the sample with growing RCC2 and these sequences are able to crystallize if they contain sequences of the certain length. It is observed using DSC records, where two peaks are visible in the 2\textsuperscript{nd} melting record and in the crystallization (see Fig. 16 and Fig. 17). The smaller peak belongs to crystallizing ethylene segments, whereas the second peak to h-PP. The measurement of original samples was made in the same conditions. The maximum of 2\textsuperscript{nd} melting graph belonging to crystalline propylene segment lies between 160 and 165 °C, the minimum of crystallization graph belonging to propylene segment is at 115 °C.

![DSC - 2\textsuperscript{nd} melting](image)

Fig. 16: Graph of the DSC analysis of original samples expressed as dependence of heat flow changes on the changing temperature during the second melting.
Fig. 17: Graph of the DSC analysis of original samples expressed as dependence of heat flow changes on the changing temperature during the crystallization
**Tab. 2: Results of NMR measurement**

<table>
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<tr>
<th>sample</th>
<th>K1127</th>
<th>K 1159</th>
<th>K 1147</th>
<th>K 1139</th>
<th>K 1148</th>
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<tbody>
<tr>
<td></td>
<td>orig</td>
<td>XI</td>
<td>XS</td>
<td>orig</td>
<td>XI</td>
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<tr>
<td>E (wt%)</td>
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<td>2,0</td>
<td>28,3</td>
<td>13,5</td>
<td>2,9</td>
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<tr>
<td>h-PP(wt%)</td>
<td>71,9</td>
<td>94,0</td>
<td>16,2</td>
<td>69,0</td>
<td>95,9</td>
</tr>
<tr>
<td>h-PE(wt%)</td>
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<tr>
<td>E in EPR (wt%)</td>
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<td>20,8</td>
<td>30,1</td>
<td>36,9</td>
<td>47,1</td>
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**Tab. 3: Results of NMR and FTIR measurement**

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<th>K 1147</th>
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<td>13,5</td>
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</tr>
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<td>RCC2 (wt%)</td>
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<td>—</td>
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<td>RCC2(wt%)</td>
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<td>—</td>
<td>—</td>
<td>32,3</td>
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</table>
### Tab. 4: Chemical composition and internal viscosity values

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<thead>
<tr>
<th>sample</th>
<th>XS (wt%)</th>
<th>E/P copolymer calculated from polymerization ratio (% wt.)</th>
<th>MFI 21 N (g/10min)</th>
<th>fraction</th>
<th>(^{13}\text{C}-\text{NMR analysis} )</th>
<th>FTIR analysis</th>
<th>IV (mg/ml)</th>
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<td></td>
<td></td>
<td></td>
<td>(^{12}\text{C}-\text{NMR} )</td>
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The second melting of DSC measurement shows growing peak belonging to crystalline ethylene with the maximum 116 – 120 °C with growing RCC2. It is possible to observe the display of crystalline ethylene sequences in the crystallization record of the samples K1148 and K1147 in a form of a small minimum in temperature between 105 and 110 °C. Not only the height of the peak, but its maximum moves to higher temperatures. Very interesting information has been obtained by SSA analysis, where information about crystallizing segment length of ethylene in E/P copolymer is given. The SSA method proceeds from the supposition, that lamella thickness is given by ethylene segment length, which is not interrupted by an abnormality, in this case by propylene unit. The graphic dependence of the quantity segment in mol/g unit on the segment length in nm expresses the distribution of crystalline structure in E/P copolymer. It was used the calculation according to ethylene, because in the case of using the calculation according to propylene, what is possible too, the obtained results would not be relevant due to the excess of propylene in the analysed samples. Samples K1139 and K1148 are similar concerning the segment length distribution, the difference is in their quantity. K1148 contains the most of crystallizing copolymer. The other samples are ordered with descending amount of copolymer segments: K1147, K1159 and K1127 (see Fig. 18). The segment length and the content of these segments visibly grow with growing RCC2 value. RCC2(E) value, which represents the amount of ethylene in impact copolymer, grows with growing RCC2 value. (see Fig. 15)

![SSA-E/P region - (E)](image)

Fig. 18: SSA analysis of E/P region expressed as crystalline segment length distribution. The calculation of segment length and quantity of segment was made according to ethylene. Analysis of the original samples.

### 4.2 Fractions

Original samples were fractionated using o-xylene extraction into two fractions, the results of the o-xylene extraction are in Tab. 5 as XS value. XS and XI fractions were obtained using the o-xylene extraction. XS fraction would contain E/P copolymer, primarily in the form of EPR, and amorphous or low-molecular h-PP. XI fraction would contain high-crystalline structure, primarily h-PP and crystalline E/P copolymer.
Extracted amount of XS fraction does not correspond to the content of E/P copolymer in the case of all samples, which was calculated from weight polymerization ratio (see Tab. 4). The reason is imperfection of the o-xylene extraction in the comparison with some other methods of fractionation, consisting in that a part of high-crystalline E/P copolymer could stay in XI fraction. The most distinct is this fact in the case of samples K 1127, whose RCC2 value is the lowest, and K1148, whose RCC2 value is the highest. It results in the fact, that these two samples have the lowest XS value (see Tab. 5).

IV value of each original sample and its fractions was determined. Great differences are visible in IV values of XS fractions, whereas IV values of XI fractions change only little (see Tab.5).

Tab. 5: Viscosity measurement results

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<td>K 1148</td>
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<td>182,31</td>
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If only h-PP, forming homopolymer matrix, stayed in XI fraction after the fractionation, the IV values would be equals because all samples contain the same homopolymer matrix. But IV values of XI fractions grow, what is caused by the fact that a part of E/P copolymer with higher IV value stays in XI fraction. Because of the rising IV value of E/P copolymer, the IV value of XI fraction grows. Moreover, it is possible to see great differences in parallel measurements of IV, which can be caused by the fact, that the samples are inhomogeneous. The rising molecular weight, which influences the IV value, is evident in the decrease of melt flow index (see Tab. 4).

ATREF was used for certification if XI fractions did not contain amorphous EPR (Fig. 19). This presence of EPR would show as a signal at the temperature between 10 and 30 °C. No signal of amorphous polymer, which occurs in the form of a peak, is observable in this temperature interval. It is possible to deduce, that preparative fractionation, o-xylene extraction, was effective.
Fig. 19: Results obtained from ATREF analysis in the graphic form as normalized IR response to crystallization of fractions at certain temperature. This analysis was made on XI fractions.

The great peak with maximum at 115 °C is observable in ATREF record of XI fractions. This peak belongs to isotactic h-PP, moreover, it is possible to find signal belonging to polymer, which crystallizes at lower temperatures and whose amount increases with increasing value of RCC2. The elution temperature of this polymer lies between 40 and 100 °C. E/P copolymer, which contains ethylene or propylene sequences, will probably present in XI fractions in a form of semi-crystalline structure. This presence of E/P copolymer caused differences in parallel measurement of IV and is expressed in $^{13}$C NMR analysis as EPR (see Tab. 2).

Possible presence of crystallizing components in XS fractions was investigated using DSC (see Fig. 21 and Fig. 22). Some peaks have been found in the record of 2$^{nd}$ melting and more in the record of crystallization, but their intensity shows, that only minimal amount of crystalline phase is present in XS fraction.
DSC - 2nd melting

**Fig. 20:** Graph of the DSC analysis of XS fractions expressed as dependence of heat flow changes on the changing temperature during the second melting.

DSC - crystallization

**Fig. 21:** Graph of the DSC analysis of XS fractions expressed as dependence of heat flow changes on the changing temperature during the crystallization.

DSC and ATREF results show, that all amorphous material was extracted to XS fraction with only minimal amount of the crystalline or semi-crystalline phase.
4.2.1 XS fractions

The composition of XS fraction was determined from $^{13}$C NMR analysis (see Fig. 24). The content of ethylene, expressed as E in the figure, increases with growing RCC2 value. The majority of h-PP in impact copolymer sample is crystalline, so its content is very small in XS fraction. Atactic or low-molecular PP is soluble in xylene, so atactic or low-molecular PP is present in XS fraction. But the found content of h-PP is not equal in all XS fractions, it gradually decreases in the line of the analysed samples.

![NMR XS](image)

**Fig. 24:** Results of NMR analysis of XS fractions separated from the original samples – amount of components forming the analysed samples

It is possible to suppose, that if the h-PP matrix is equal in all samples, the ratio of atactic and low-molecular h-PP would be equal too, then showed trend would be similar to the trend of original samples. But due to the statistical model influence, a part of E/P copolymer, whose propylene sequences are longer, is considered as h-PP. It leads to the increasing trend of h-PP content in $^{13}$C NMR analysis results in the line of the analysed samples. On the other hand, h-PE content is only lightly increasing.

But this value of the sample K1148 is abnormally low, which is caused probably by sample inhomogeneity or it can be caused by measurement error.

The calculated content of h-PP decreases, because E/P copolymer with longer propylene sequences is added if RCC2 value is low. This E/P copolymer is missing and is not considered by the statistical model as E/P copolymer, what is the reason why E/P copolymer grows. h-PE does not change distinctly, because E/P copolymer containing longer ethylene sequences is not extracted into XS fraction.

The ethylene amount grows with growing RCC2 value and contrary, the amount of propylene descends (see Fig. 24). Ethylene sequence length is maximally 11 length units, only the sample K1148 is an exception because this sample contains a high amount of ethylene in E/P copolymer (see Fig. 22)

SSA analysis was not made because XS fractions contained amorphous material and cannot be tested using SSA-DSC.
Fig. 22: Results of NMR analysis of XS fractions separated from the original samples – distribution of sequences length of ethylene, which are not interrupted by propylene monomer unit, n describes sequences length of ethylene.

Fig. 23: Results of NMR analysis of XS fractions separated from the original samples – distribution of sequences length of propylene, which are not interrupted by ethylene monomer unit, n describes sequences length of propylene.
4.2.2 XI fractions

The fractions contain mostly high isotactic h-PP, what is visible in DSC graphs (see Fig. 25 and Fig. 26). The maximum at 165 – 166 °C belongs to h-PP in the case of all measured samples. Samples K1148 and K1139 have another maximum at 115 °C, this maximum belongs to crystalline PE.

Fig. 25: Graph of the DSC analysis of XI fractions expressed as dependence of heat flow changes on the changing temperature during the second melting

Fig. 26: Graph of the DSC analysis of XI fractions expressed as dependence of heat flow changes on the changing temperature during the crystallization

The DSC measurement of crystallization showed the presence of crystalline PP, whose crystallization temperature is 115 °C. It exist an analogy between XI fractions and their
original samples, the maximum occurs at the same temperature, but the maximum is higher in XI fractions than in original samples, because XI fractions contain higher amount of crystalline structures than original samples and melting enthalpy and crystallization enthalpy are higher in XI fractions than in original samples (see Tab. 6).

In the case of XI fractions of samples with high RCC2 value, E/P copolymer with long crystallizing ethylene sequences present in E/P copolymer is not fractionated using o-xylene extraction and stays in XI fraction (see Fig. 29). It is caused by high crystallinity of these sequences.

![Fig. 29: Results of NMR analysis of XI fractions separated from the original samples – distribution of sequences length of ethylene, which are not interrupted by propylene monomer unit, n describes sequences length of ethylene – amount of components forming the analysed samples](image)

The $^{13}$C NMR results shows following: The ethylene content in XI fractions grows but it is lower than in original samples because a part of it was extracted to XS fraction in a form of EPR. In the XI fraction, there are, according to statistical model, h-PE and E/P copolymer with either high or low RCC2 value according to 21 – 92 wt%. XI fractions of samples K1127 and K1159 have quite low RCC2 value, respectively 21 and 47 wt%, but RCC2 values of other samples are high. The h-PP content is very high in all samples, what is caused by h-PP, present in XI fraction after the o-xylene extraction. Only atactic and low-molecular h-PP was extracted into XS fraction.

It is visible, that E/P copolymer is not perfectly separated from h-PP using o-xylene extraction, so this E/P copolymer stays in XI fraction and another E/P copolymer was analysed as h-PE. If h-PE was not found using $^{13}$C NMR in the case of some samples, it can be caused either by the inhomogenenity of the sample or by measurement error. This is the case of XI fractions of samples K1147 and K1148 (see Fig. 29).

Graphs, where sequences length distributions are represented show, that XI fraction of the samples K1127 and K1159 contains quite short ethylene sequences, maximal length is 11 units. But the other XI fractions are completely different, where $^{13}$C NMR analysis
determined long sequences, in the case of K1148 even 61 length units. In the case of propylene segments, the situation is exactly opposite. E/P copolymer present in XI fraction contains long propylene sequences in the case of samples K1159 and K1127 (see Fig. 27 and Fig. 28).

Fig. 27: Results of NMR analysis of XI fractions separated from the original samples – distribution of sequences length of ethylene, which are not interrupted by propylene monomer unit, n describes sequences length of ethylene.

Fig. 28: Results of NMR analysis of XI fractions separated from the original samples – distribution of sequences length of ethylene, which are not interrupted by propylene monomer unit, n describes sequences length of ethylene – distribution of sequences length
of propylene, which are not interrupted by ethylene monomer unit, n describes sequences length of propylene

It is possible to find a connection between RCC2 values and SSA results. If RCC2 value is low, the XI fraction contains copolymer with short ethylene sequences which are not able to crystallize and are not analyzed by SSA as crystalline material. Short ethylene sequences are able to form, if the amount of ethylene in E/P copolymer is low as in the case of samples K1127 and K1159 (see Fig. 30).

![SSA-E/P region - (E)](image)

**Fig. 30:** SSA analysis of E/P region expressed as crystalline segment length distribution. The calculation of segment length and quantity of segment was made according to ethylene. Analysis of the XI fractions.

The greatest amount of crystaline E/P copolymer is present in the case of samples K1148 XI, with the highest RCC2 value. The other samples are ordered with descending amount of ethylene sequences: K1147, K1139, K1159 and K1127 (see Tab. 4).
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5 CONCLUSION

Detailed structural analysis of five different impact copolymer samples was realised on the original samples and on their fractions. These fractions were obtained using o-xylene extraction into in o-xylene soluble and in o-xylene insoluble fraction. The aim of fractionation was to analyse in detail composition of EPR present in XS fraction and crystalline polymer present in XI fraction. O-xylene extraction was used because it is not so time exacting.

The analysed samples are distinctly different in some mechanical properties, primarily in low-temperature Charpy impact strength. The samples contain the equal homopolymer PP matrix and the equal content of E/P copolymer but the composition of E/P copolymer is different from sample to sample, which is the consequence of different polymerization conditions.

Different structural-analytical methods such as $^{13}$C NMR, FTIR, DSC, SSA and TREF were verified and tested as suitable for structural analysis of impact copolymer samples. The calculation using statistical model in $^{13}$C NMR analysis was verified if it is suitable for calculation of main components content from measured $^{13}$C NMR spectra in the case of impact copolymer analysis. It showed that this model considers long ethylene sequences as h-PE such as long propylene sequences are considered as h-PP. But it is possible to say, that this statistical model gives important information about composition of the analysed sample.

ATREF method was used to verify the o-xylene extraction effectiveness and to determine that in XI fraction remains not only h-PP from homopolymer matrix but crystallizing E/P copolymer too.

The aim of DSC analysis was to measure $2^{nd}$ melting and crystallization and to assign peaks, which belong to high crystalline h-PP and to crystallizing ethylene segments. Moreover, DSC analysis of XS fractions was used to confirm the effectiveness of the fractionation.

The unique SSA technique was used to study the microstructure of the analysed samples from the point of view of lamellas formation of crystalline structures.

After the comparison with $^{13}$C NMR results, it was deduced, that the content of the crystalline ethylene segment and thickness of the lamella belonging to crystallizing E/P copolymer rise with rising ethylene content in E/P copolymer. Ethylene sequence length increases with increasing ethylene content in E/P copolymer.

If this knowledge about E/P copolymer structure is compared with measured physical properties, especially with low-temperature Charpy impact strength and with FM, it is possible to suppose, that optimal ratio of ethylene and propylene in E/P copolymer lies in quite large area around 1:1. Charpy impact strength shows some extremes, whereas measured FM shows constant growth. FM increases with growing RCC2 value and with IV, with the concentration of ethylene units and with the concentration of homopolymer PE. FM is determined by homopolymer matrix in the sample. It influences flexibility of the material which the sample is composed of.

In the case of extreme ratios of both monomers such as in the case of the sample K 1127, where RCC2 value is equal to 28 wt%, and K 1148 with RCC2 value equal to 70 wt %, there is a distinct decrease of impact strength.

It is caused by formation of long propylene sequences in the case of low RCC2 value and E/P copolymer probably starts to be well compatible with h-PP matrix and it is possible to consider, that certain dissolution of EPR domains will take place in homopolymer matrix. After this dissolution, the EPR domains cannot have their toughening function and impact strength decreases.
The second extreme case leading to the impact strength decrease occurs, if ethylene amount is so high, that long ethylene segments can be formed and can crystallize. Therefore, the content of amorphous E/P copolymer decreases and/or the quality of amorphous EPR changes so substantially, that toughening function of amorphous E/P copolymer decreases.

It would be suitable to continue with further studies of impact copolymer samples to explain more detailed mechanisms leading to properties deterioration. For this purpose, it would be suitable to study impact copolymer morphology but this was not possible due to demands and extent of the experiments used in this work. It can be supposed, that proposed hypotheses could be verified using microscopic analysis of rubber particle size distribution in the analysed samples.

It is necessary to note, that different molecular weight of the rubber, which was determined using IV measurements, could influence properties of the analysed samples, too. It would be interesting to find it out but study of E/P copolymer MW influence on impact copolymer properties is out of possibilities of this bachelor thesis.
6 REFERENCES


7 List of Abbreviations

acc. according
ATREF analytical temperature rising elution fractionation
CaSt calcium stearate
C2 content of ethylene in whole sample
$^{13}$C NMR nuclear magnetic resonance using nucleus $^{13}$C
DSC differential scanning calorimetry
E ethylene
EN European norm
E(P)$_n$E propylene sequence length isolated by ethylene monomer unit
E/P copo copolymer polyethylene-polypropylene
EPR ethylene-propylene rubber
FM flexural modulus
FTIR Fourier transform infrared spectroscopy
H enthalpy
$^1$H NMR nuclear magnetic resonance using $^1$H nucleus
h-PE polyethylene homopolymer
h-PP polypropylene homopolymer
ID internal diameter
IR infrared spectroscopy
ISO International Standard Organisation norm
IV intrinsic viscosity
MFI melting flow index
MW molecular weight
n sequence length
NaBz sodium benzoate
orig original sample
P propylene
PE polyethylene
P(E)$_n$P ethylene sequence length isolated by propylene monomer unit
PP polypropylene
Q heat flow
RC content of E/P copolymer in impact copolymer
RCC2 ethylene content in E/P copolymer
RCC2(E) ethylene content in E/P copolymer and in h-PE
SS stainless steel
SSA successive self-nucleation annealing
T$_c$ crystallization temperature
T$_m$ melting temperature
TREF temperature rising elution fractionation
XI xylene insoluble fraction
XS xylene soluble fraction

Units
°C degrees Celsius
$\text{cm}^{-1}$ centimetres power -1
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<td>gram</td>
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<td>Hz</td>
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