8. POLYMERS & POLYMER COMPOSITES

8.1. Lectures

**L01 THE WAY OF STEREOREGULARITY DETERMINATION OF POLYPROPYLENE**

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**Introduction**

Polypropylene (PP) is an important member of the family of the most worldwide produced thermoplastics namely because of its specific properties involving easy processability, low specific gravity and low production cost. One of the key molecular parameters defining physico-chemical properties of PP is the stereoregularity of the polymer chains, i.e. tacticity. It is well known that heterogeneous Ziegler-Natta catalytic systems due to a multiple-site character of active species produce PPs with varying degree of stereoregularity. Since the stereoregularity of polymer chain has an important influence on mechanical properties of PP product, the accurate assessment of PP stereoregularity (isotacticity) is an important task. Stereoregularity can be characterized by isotactic index.

Several methods of PP isotactic index determination differing in principle, complexity of a measurement procedure and an information capability are known from the literature. The most common method used for determination of the isotactic index is an extraction by hydrocarbon solvents (e.g. pentane, hexane, heptane, and octane) at their boiling point. Another method is based on a solubility of the atactic PP in hydrocarbons. Neat PP is divided into fractions (i.e. tacticity). It is well known that heterogeneous Ziegler-Natta catalytic systems due to a multiple-site character of active species produce PPs with varying degree of stereoregularity. Since the stereoregularity of polymer chain has an important influence on mechanical properties of PP product, the accurate assessment of PP stereoregularity (isotacticity) is an important task. Stereoregularity can be characterized by isotactic index.

**Fractionation Methods**

A modified Kumagawa extractor was used for the fractionation according to the ISO 9113:1993 Standard. The extractions were carried out on 5 g of polymer sample in a powder form. The extraction time was 6 h. The soluble fractions were recovered by evaporating the solvent.

The solubility assessment was carried out according to ISO 6427:1982 (E), Annex B Standard. Polymer sample (1.25 g) was completely dissolved during 1 h in o-xylene (125 ml) at its boiling point of 144.4 °C, and in tetralin (125 ml) at 160 °C yielding 1 % wt. solutions. 2 g of PP sample was completely dissolved in decalin (100 ml) at 160 °C during 1 h and 2 % solution was obtained. The solutions were cooled down to 23 °C, and kept at that constant temperature for 18 h. After centrifugation, the insoluble fraction was collected by filtration. The soluble fraction was recovered by evaporating the filtrate. First, fractionations of a standard PP sample were performed by both methods; ten runs were carried out to evaluate the reproducibility of results. The reproducibility of the amount of fractions obtained from original PP using the extraction method was ±0.09 %. The reproducibility of results of ±0.13 % obtained by the solubility method was very good as well.

**Characterization Methods**

13C-NMR spectra were recorded on a 500 MHz Bruker DRX spectrometer operating at 125 MHz. The...
pulse angle was 83 °, pulse interval 20 s, decoupling Waltz 16.

PP melting points were measured with a Perkin-Elmer DSC-7 apparatus. The polymer sample was in the form of thin square-shape films of the weight of about 5 mg. Measurements were carried out using the aluminum pans in the temperature range from 40 °C to 200 °C under N₂ atmosphere (70 ml min⁻¹). The used procedure conditions were as follows: (i) heating from a room temperature to 200 °C at a rate 40 °C min⁻¹, (ii) 10 min isothermal period at 200 °C, (iii) air cooling to 35 °C, and (iv) heating to 200 °C at a rate 10 °C min⁻¹. The second heating data were used for the analysis.

The molecular weight averages (Mₐ, Mₘ, and Mₜ) and the index of polydispersity (Mₘ/Mₐ) of PP and its fractions were determined using a PL-GPC 220 high temperature chromatograph (Polymer Laboratories) equipped with three PL gel 10 μm MIXED-B columns set and two detectors (PL–220DRi and VISCOTEC 220R). Calibration was done with polystyrene standards (Waters and Polymer Laboratories) using 1,2,4-trichlorobenzene solvent (LiChrosolv, Merck) containing 0.025 % Santonox R at a flow rate of 1 cm³ min⁻¹ and 160 °C. The polymer samples were measured as a 0.1 % wt. solution in a mobile phase.

**Results**

**Isotactic Index Determination by Extraction**

Fractions of the representative PP sample H420 obtained by both kinds of separation methods were precisely analyzed using the ¹³C-NMR, DSC, and SEC methods. The insoluble fraction of PP sample consisted of isotactic PP, whereas the soluble one comprised mostly atactic PP. The contents of mmmm pentads present in insoluble fractions were in the range of 93.6–95.5 %, which means that insoluble fraction contains mainly high molecular weight isotactic PP. It was found out that with increasing boiling point of the solvent, the soluble fraction was enriched by low molecular weight isotactic PP, and so-called stereoblocks. An increased content of higher molecular weight atactic PP chains was observed as well.

From the shape of the MWD curve of soluble fractions (see the Fig. 1) it is evident, that pentane and hexane dissolved mainly low molecular weight polymer chains from the original sample. These low molecular weight chains appeared to be short chains of a-PP and short chains of i-PP. Hexane is characterized by slightly higher extraction efficiency in comparison with pentane by 0.4 % wt.

On the other hand, heptane extractable fraction was significantly higher (5.8 % wt.) and contained a much higher portion of high molecular weight chains, mostly of an atactic and stereoblock structure. An asymmetric shape of the distribution curve in the area of the lowest molecular weights is evidently an artefact, caused either by a contamination of the sample during preparation or a measuring error of the SEC method. In the right manner, the distribution curves in the area of the lowest molecular weights for all the three solvents should coalesce.

Then, the fractions of representative sample H420 were characterized by the DSC method; melting points of insoluble fractions and crystallinity of soluble fractions were compared. Calculation of crystallinity α from values of ΔH obtained from the second heating cycle was done according to the equation:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isotactic index [‰]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pentane</td>
</tr>
<tr>
<td>H4b, 17.5.06</td>
<td>99.28</td>
</tr>
<tr>
<td>H449</td>
<td>99.08</td>
</tr>
<tr>
<td>H460</td>
<td>99.15</td>
</tr>
<tr>
<td>H640</td>
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<td>H435</td>
<td>98.63</td>
</tr>
<tr>
<td>H433</td>
<td>99.23</td>
</tr>
<tr>
<td>H526</td>
<td>99.35</td>
</tr>
<tr>
<td>H556</td>
<td>99.17</td>
</tr>
<tr>
<td>H420</td>
<td>98.70</td>
</tr>
</tbody>
</table>

![Fig. 1. Molecular weight distribution of the representative PP sample H420 and of the soluble fractions obtained by extraction with pentane (PS), hexane (HS) and heptane (HS)](image-url)
\[ \alpha = \frac{\Delta H_m}{\Delta H_m^*} \times 100 \]  
(1)

\( \alpha = [\%] \)

\( \Delta H_m \) - melting enthalpy of measured sample

\( \Delta H_m^* \) - melting enthalpy of 100% crystalline polypropylene, \( \Delta H_m^* = 207 \text{ J g}^{-1} \) ref.5.

Fig. 2. shows melting points of insoluble fractions of the representative sample obtained by pentane, hexane and heptane extractions. A decrease of melting points due to increasing boiling point of the solvent is evident. It is probably caused by higher separation efficiency of solvents having higher boiling point. Consequently, a decrease of amount of shorter isotactic PP chains occurred.

From the values showed in the Fig. 3., a dependence of increasing crystallinity on increasing boiling point of the solvent was found out. PP fractions soluble in solvents with higher boiling point contain larger amounts of crystallizable short chains of isotactic PP.

Table III
<table>
<thead>
<tr>
<th>Sample</th>
<th>o-xylene</th>
<th>decalin</th>
<th>tetralin</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3.03</td>
<td>4.07</td>
<td>6.01</td>
</tr>
<tr>
<td>H449</td>
<td>2.43</td>
<td>3.42</td>
<td>4.54</td>
</tr>
<tr>
<td>H460</td>
<td>2.27</td>
<td>3.66</td>
<td>4.58</td>
</tr>
<tr>
<td>H640</td>
<td>2.23</td>
<td>3.10</td>
<td>4.83</td>
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<tr>
<td>H435</td>
<td>2.63</td>
<td>4.37</td>
<td>4.25</td>
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<tr>
<td>H433</td>
<td>2.07</td>
<td>4.06</td>
<td>3.19</td>
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<tr>
<td>H526</td>
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<td>4.67</td>
<td>3.36</td>
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<tr>
<td>H556</td>
<td>3.30</td>
<td>5.01</td>
<td>4.30</td>
</tr>
<tr>
<td>H420</td>
<td>4.18</td>
<td>6.91</td>
<td>7.73</td>
</tr>
</tbody>
</table>

**Determination of Soluble Fractions by Solubility Methods**

PP samples were completely dissolved in three solvents (xylene, decalin, and tetralin) at increased temperature and after cooling at 23 °C, amounts of the fractions, which remained dissolved in solution, were determined. From these values, the contents of fractions, that remained dissolved after cooling the perfect solution of PP down to 23 °C, were calculated. The results are summarized in Table III. For all the PP samples, xylene soluble fraction was the lowest. Generally, it was not possible to specify the difference between the separative efficiency of decalin, and tetralin.

Fig. 4. Comparison of molecular weight distribution of soluble fractions of the sample H420 obtained by solubility methods (XS = xylene soluble, DS = decalin soluble, TS = tetralin soluble)

Characterizations of polymer fractions were carried out for the representative sample H420 by \(^{13}\text{C}\)-NMR, SEC, and DSC methods again. A qualitative composition of soluble fractions determined by \(^{13}\text{C}\)-NMR shows that fractions soluble in decalin and tetralin contain a higher part of longer
atactic chains as well as shorter isotactic chains and stereoblocks in comparison to o-xylene soluble fraction. Insoluble fraction was again marked as isotactic PP.

From the SEC results it is evident, that xylene soluble fraction had the lowest molecular weight part, followed by decalin soluble, whereas the tetralin soluble fraction had the highest content of a high molecular weight portion. The difference consists mainly in the area of higher molecular weights. On the other hand, the decalin soluble fraction contained a much higher portion of high molecular chains of predominantly stereoblock, partially crystalline character. The tetralin soluble fraction was characterized by a similar MWD curve as compared with the xylene soluble fraction, but it contained a portion of much higher molecular weight chains. Average molecular weight $M_w$ of fractions, that remained dissolved, was the lowest for o-xylene, followed by decalin, and tetralin till almost the value of original sample ($M_w = 233,000$ g mol$^{-1}$, $M_w/M_n = 5.3$).

A narrowing of the molecular weight distribution was noted: the xylene soluble fraction had the broad molecular weight distribution ($M_w/M_n = 43.5$), followed by the tetralin soluble one ($M_w/M_n = 34.6$). The decalin soluble fraction had the narrowest molecular weight distribution ($M_w/M_n = 12.2$).

The presence of low molecular chains in the xylene soluble fraction is probably an artefact again.

Fig. 5. shows melting points of insoluble fractions of the representative sample obtained by solubility methods. Melting point values of insoluble fractions increased from decalin, followed by o-xylene to tetralin. It corresponds with the crystallinity values (Fig. 6.), being the highest in the decalin insoluble fraction, followed by the xylene insoluble one, and the tetralin insoluble one. The tetralin insoluble fraction contained probably lower portion of isotactic chains. It follows from the melting point of the tetralin insoluble fraction.

Fig. 6. shows the highest crystallinity in the case of the decalin soluble fraction, followed by the o-xylene soluble one, and the tetralin soluble one. It is probably because of the decalin insoluble fraction contained higher portion of low molecular weight isotactic chains being able to crystallize. It is also confirmed by the results of $^{13}$C-NMR of the representative sample. The tetralin insoluble fraction contained the lowest part of chains able to crystallize.

The highest crystallinity of the decalin soluble fraction can be ascribed to a chemical similarity of decalin, and polypropylene molecules. In both cases, they are aliphatic hydrocarbons with a dominant presence of CH$_2$ and CH groups. Whereas, the molecule of tetralin is half aromatic and the molecule of xylene is fully aromatic.

**Conclusions**

Both kinds of fractionation methods provided very good reproducibility and good fractionation efficiency and can be recommended for determination of the isotactic index of PP.

By the extraction methods, a strong dependence of the isotactic index on the boiling point of the solvent was proved. The highest separative efficiency was found for heptane, which had the highest boiling point of all the solvents used for extractions. With using the high boiling point hydrocarbon (octane), a swelling of polymer sample happened and resulted in impassability of the frit and it was impossible to carry out the extraction. Results of analyses performed on the representative sample showed that increasing the boiling point of the solvent increases the portion of extractable longer atactic chains, shorter chains of i-PP and stereoblocks. Now separative efficiency of pentane, hexane, and heptane by extraction at the same temperature is being examined to prove a dominant influence of increasing temperature of boiling point of solvent on isotactic index.

Results of the solubility methods evaluation showed that the lowest content of the soluble fraction for all the samples under examination was obtained with use of o-xylene. At the same time, this part contained the lowest portion of isotac-
tic PP (measured by the presence of mm triads and mmmm pentads by $^{13}\text{C}$-NMR). Decalin and tetralin showed higher separative efficiency than xylene and also dissolved a higher portion of partially isotactic or stereoblock chains. From the results of analyses, it is evident that in contrast to decalin, which dissolves significantly higher volume of high molecular weight isotactic or stereoblock chains, the efficiency of tetralin and xylene to separate the shorter and also the longer chains is almost the same. It results in a broad molecular weight distribution of soluble fractions.

Upon the performed separations and determination of their structure, the solubility methods using o-xylene, and tetralin at 23 °C can be suggested as the most correct for the determination of the isotactic index. All the other examined methods include an indispensable amount of isotactic or stereoblock chains in separated part of PP.

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REFERENCES
L02 THE CRYSTALLIZATION KINETICS IN SEMICRYSTALLINE NANOCOMPOSITES

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Introduction

Polyolefins represent the most important commodity plastics used in broad range of applications. In majority of cases, their processing is based on the melting step followed by cooling down in various forms and shapes. Properties of semicrystalline polymers are greatly affected by their morphology and, hence, the process of crystallization is of primary importance. High density polyethylene (HDPE) is a semicrystalline polymer with high portion of crystalline phase. The amorphous and crystalline lamellar regions are organized into the spherulites of approximately spherical shape.1,2

Below the melting point, nuclei start to appear in the polymer melt due to the density fluctuations. These local volumes of higher molecular order growth with a rate well described by the Lauritzen – Hoffman surface nucleation theory.3,4 According to the Lauritzen-Hoffman theoretical model, the spherulite growth rate, G, can be expressed for the case of medium undercooling as follows:

\[ G = b_0 (2i\omega)^{1/2} \]  

where \( b_0 \) is the thickness of the crystalline layer added to the surface, \( i \) is the surface nucleation rate and \( g \) is the substrate completion rate. Equation (1) holds for the crystallization regime II in which multiple nucleation that is necessary for a chain segment to be attached to the single substrate takes place.

The expression for the surface nucleation rate, \( i \), has been derived by Hoffman and Miller in the form5:

\[ i = C_0 \left( \frac{kT}{2\omega_0} \right)^{1/2} \frac{h}{4b_0^2 \sigma^2 T_m} \exp \left( -\frac{Q_D}{RT} \right) \exp \left( -\frac{4b_0 \omega_0^2 T_m}{\Delta \Theta} \frac{1}{RT} \right) \]  

(2)

The substrate completion rate, \( g \), involving chain repta-
tion as main diffusion mechanism of chains can be expressed in the form:

\[ g = a_0 \left( \frac{\kappa}{\sigma^2} \right)^{1/2} \frac{kT}{h} \frac{a_0 (\Delta \Theta)}{\sigma T_m} \exp \left( -\frac{Q'_D}{RT} \right) \exp \left( -\frac{Q_D}{RT} \right) \exp \left( -\frac{q}{kT} \right) \]  

(3)

For the case of linear PE, the following parameters were utilized5–6: the activation energy for reptation in the neat matrix \( Q'_D = 24 \, \text{kJ mol}^{-1} \), \( T_m = 418.7 \, \text{K} \), \( \Delta T = 15.8 - 23.8 \, ^\circ\text{C} \) (Regime II), heat of fusion \( \Delta h_p = 2.8108 \, \text{J m}^{-3} \left( 2.8 \times 10^9 \, \text{erg cm}^{-3} \right) \), crystalline surface free energy \( e = 0.093 \, \text{J m}^{-2} \left( 93 \, \text{erg cm}^{-2} \right) \), work of chain folding \( q = 20.48 \, \text{kJ mol}^{-1} \left( 4,900 \, \text{cal mol}^{-1} \right) \), stem dimensions \( a_0 = 4.55 \times 10^{-10} \, \text{m} \) and \( b_0 = 4.15 \times 10^{-10} \, \text{m} \).

Parameter \( \kappa \) used in equation (3) is a result of incorporation of the chain reptation motion into the secondary surface nucleation theory and can be estimated as:

\[ \kappa = h \exp \left( \frac{Q'_D}{RT} \right) \exp \left( -\frac{q}{N_w kT} \right) \left( \frac{z}{g} \right)^2 \]  

(4)

The parameter \( Q'_D \) corresponds to activation energy for reptation motion and the monomer friction coefficient, \( \bar{\eta}_0 \), equals to \( 2.2 \times 10^{-12} \, \text{kg s}^{-1} \). Particular details of the surface nucleation theory can be found elsewhere.3–6

It has been shown by Jancar and Kalfus7, that the chain diffusion can be considerably reduced in nano-filled polymer well above its glass transition temperature. Hence, it is supposed that the presence of weakly interacting silica nanoparticles would be able to increase the activation energy of chain diffusion in the polyethylene melt resulting in the indispensable change of its crystallization kinetics.

Nucleation Activity of Silica Filler in HDPE

To examine the nucleation ability of the silica nano-filer in HDPE, a method suggested by Dobreva et al.8–10 to estimate the nucleation activity of solid substrates in polymer melt was employed. Nucleation activity, \( \Phi \), is a factor by which the work of nucleation decreases with the addition of a solid substrate. Its value is in the range from 0 to 1 from extremely active to inert particles. For homogeneous nucleation in a melt under low undercooling, the cooling rate can be expressed as follows:

\[ \log r = A - \frac{B}{2.3 \Delta T_p^2} \]  

(5)

while for heterogeneous case

\[ \log r = A - \frac{B^*}{2.3 \Delta T_p^2} \]  

(6)

and

\[ \phi = \frac{B^*}{B} \]  

(7)

where \( r \) is the cooling rate, \( A \) is the constant and \( \Delta T_p \) is the undercooling, \( \Delta T_p = T_m - T_c \). \( T_c \) corresponds to the crystallization temperature determined from the DSC curves. Parameter \( B \) can be expressed as:

\[ B = \frac{\omega \sigma^2 V_m^2}{3n k T_m \Delta S_m n} \]  

(8)

where \( \omega \) is the geometrical factor; \( \sigma \) is the specific energy, \( V_m \) is the molar mass volume of crystallizing substance; \( n \) is the Avrami exponent, \( \Delta S_m \) is the entropy of melting and \( k \) is the Boltzman constant.

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Experimental

Fumed silica (Sigma Aldrich, USA) with specific surface area of 390 m² g⁻¹ and mean particle diameter d = 8 nm was used as a nano-filler. High density polyethylene Liten MB 71 (Chemopetrol, CZ) was used as a polymer matrix. Nanocomposite samples were prepared by adding of silica into the polymer solution at 130 °C under ultrasonic filed and intensive mixing. Dried nanocomposite samples were press molded at 170 °C (Fontijne TP400, NL) into the form of 1 mm thick plates. Thin slices cut out from press molded plates were melted between two glass slides at 170 °C. These pressed films of thickness between 5 and 10 μm were used for microscopy observations under polarized light (BX50, Olympus, Japan + hot-stage Linkam LTS 350, UK). Before each measurement of the spherulite radius, the specimen was melted at 170 °C. After 5 min isothermal step, the specimen was cooled below the melting temperature (Tₘ = 147 °C) at a rate of 10 °C min⁻¹. The spherulite growth rate was measured isothermally at temperatures 125 °C, 126 °C, 127 °C and 128 °C, respectively. The nucleation activity of the silica nano-filler in HDPE was estimated according to Dobreva et al. The samples were heated in a differential scanning calorimeter (Pyris 1, Perkin Elmer) up to 170 °C at a rate of heating 10 °C min⁻¹. After 2 min isothermal step at 170 °C, cooling down to the room temperature was carried out at rates of cooling 2, 5, 10, 20 and 40 °C min⁻¹, respectively. Crystalization temperatures were obtained from the peak maxima.

Results

The isothermal crystallization of HDPE was investigated using the polarized light microscopy. Samples with 0–8 % vol of silica nano-filler were analyzed. In Fig. 1., there is shown the early stage of HDPE spherulites growth.

The spherulite radii were analyzed as a function of time. The experimentally obtained data were correlated with the Lauritzen-Hoffmann surface nucleation theory, where the chain diffusion motion via the reptation mechanism was included. The limit value of diffusion motion activation energy was calculated from L-H equation as 24 kJ mol⁻¹ for neat HDPE and with increasing filler volume content considerably higher activation energy of diffusion motion is required (Fig. 2.).

The nucleation activity Φ can be calculated using the equations 6 and 7 as the ratio of slopes of log r versus 1/ΔT_p² for neat HDPE and filled HDPE system. The dependences are shown in Fig. 3. The nucleation factor is unity for all cases within experimental error suggesting that the silica nano-filler does not act as a nucleation agent in HDPE matrix.

Conclusions

Crystallization kinetics of HDPE-silica nanocomposite was shown to be changed significantly by the addition of silica nanoparticles. Based on the correlation between experimental data and the Lauritzen-Hoffman model, the immobi-
lization of HDPE chains in presence of silica of large surface area was identified as the primary mechanism leading to the observed behavior.

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REFERENCES
L03 EFFECT OF HEXAMETHYLDISILOXANE SOLUTION OF ZIRCONIUM PROPOXIDE ON PERMANENCE OF PAPER

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Introduction
Ageing of lignocellulosic carries of information is natural process influenced by different factors. Of the outdoor impacts, relative humidity, oxides of sulphur and nitrogen and others, while of the indoor factors, type of fibres, sizing agent, filling agent, etc. may be introduced1,2,3.

Influence of ageing leads to formation of other compounds, which accelerate degradation of paper, e.g. organic compounds4,5,6.

To stop occurring these processes, conservation techniques, such as deacidification of paper are used7. Efficient deacidification systems have been applied in both polar and nonpolar medium in conservation practice. If this modification system is in the polar medium, it is supposed that diffusion of low molecular compounds to the cell wall, fibrils, microfibrils, elementary fibrils and to the molecular level of other units are to be performed.

Double alkoxides, combination of chemical elements Al-K, Sn-Mg, Zr-Ca are used as a neutralizing agent in suitable solvents, such as alcohols, fluoro-chlorohydrocarbons, hydrocarbons and siloxanes. Disadvantage of the above mentioned alkoxides lies in the formation of visible deposits8,9.

For papermaking industry, water solutions of zirconium compounds are of particular importance, for example adhesions supporting cohesion to the different surface, etc10.

This work was aimed at verifying the effect of hexamethyldisiloxane (HMDo) solution of zirconium propoxide on the permanence of newsprint paper.

Experimental
Raw Materials
Newsprint paper with extract pH 5.5–6.0; grammage \( m_s = 45 \text{ g m}^{-2} \), containing 55 % of mechanical bleached groundwood, 20 % of bleached kraft pulp, 15 % scrap fibres and 10 % clay was used as received.

Modification System
Two different solution of zirconium propoxide (70 % wt. in 1-propanol, Aldrich) in hexamethyldisiloxane (≥ 98 %, Aldrich): 0.02M solution and 0.04M solution were used.

Sheets were modified for 10 minutes at regulat stirring in a laboratory shaker. Subsequently, sheets were dried free in sieves.

Accelerated Ageing
Samples of paper were conditioned for 24 hours at \( T = (23 \pm 1) ^\circ\text{C}, \text{ RH} = (50 \pm 2) \% \) before the accelerated ageing. Subsequently were aged in hermetically sealed bags at 98 ± 2 °C during 0, 1, 2, 3 and 5 days according to standard ASTM D 6819-0211.

Property Measurement
Changes of folding endurance12 (\( \omega \)), breaking length13 (\( \text{lt} \)), Kubelke-Munke intensity of 1,735 \text{ cm}^{-1} peak by FTIR14 (KM intensity), pHextract15 and total color difference16 (\( \Delta \text{E} \)) were studied at modified and aged samples.

Folding endurance was expressed as a coefficient of permanence17, 18 in the time of ageing (t):

\[ S_{\omega,t} = \frac{\omega_{\text{modified,t}}}{\omega_{\text{control,t}}} \]

- if \( S_{\omega,t} > 1 \) – permanence increased
- if \( S_{\omega,t} < 1 \) – permanence decreased
- if \( S_{\omega,t} = 1 \) – is it not change.

Results
The permanence of paper samples modified with HMDO solution of zirconium propoxide was studied. Permanence of paper was evaluated by the change of folding endurance (\( \omega \)), breaking length (\( \text{lt} \)), KM intensity of 1,735 \text{ cm}^{-1} peak (KM intensity), pHextract, and total color difference (\( \Delta \text{E} \)).

![Fig. 1. Dependence of KM intensity peak 1,735 cm^{-1} on the time of accelerated ageing obtained by evaluation of FTIR DRIFT spectra of control (•) and samples modified by 0.02M zirconium propoxide in HMDO (■) and 0.04M zirconium propoxide in HMDO (**)](image-url)
accelerated ageings. Higher concentration of zirconium propoxide in HMDO causes increased formation of carbonyls and carboxyls with unaged control sample immediately after the modification. However during the accelerated ageing a decrease compared with control sample is observed.

Cold extract of pH modified samples are comparable with unmodified sample (pH ≈ 5.5). However pH of sample with lower concentration of zirconium propoxide in HMDO (pH ≈ 4.5) is more mild decreased after 5 days of accelerated ageing in comparison with unmodified control sample (pH ≈ 3.6).

Table I: Breaking length values of samples modified with 0.02M zirconium propoxide in HMDO (0.02M), 0.04M zirconium propoxide in HMDO (0.04M) and unmodified samples (control) during accelerated ageing.

<table>
<thead>
<tr>
<th>Days</th>
<th>Control</th>
<th>0.02M</th>
<th>0.04M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3,720 ± 570</td>
<td>3,860 ± 280</td>
<td>3,830 ± 410</td>
</tr>
<tr>
<td>1</td>
<td>3,760 ± 490</td>
<td>3,790 ± 390</td>
<td>4,000 ± 230</td>
</tr>
<tr>
<td>2</td>
<td>3,280 ± 670</td>
<td>3,770 ± 310</td>
<td>3,530 ± 550</td>
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<td>3</td>
<td>3,600 ± 380</td>
<td>3,460 ± 490</td>
<td>3,560 ± 270</td>
</tr>
<tr>
<td>5</td>
<td>2,910 ± 430</td>
<td>3,340 ± 320</td>
<td>3,200 ± 380</td>
</tr>
</tbody>
</table>

Values of breaking length obtained from modified samples were higher than those of unmodified ones. Samples modified with zirconium propoxide in hexamethyldisiloxane show decrease of measured properties in comparison with unmodified control sample. System of modification suppresses the formation of carbonyls and carboxyls. It indicates retardation of ageing process. Effect of modification causes that britliness of paper decreases and that folding endurance rises. Disadvantage of this modification system is low values of pH, which are comparable with unmodified paper. Combination of studied system with compound able to increase pH and thus alkaline reserve (for an instance MgO or other from lines of magnesium or calcium compounds) can help to solve this problem.

Advantage of this modification system is in the presence of polar element, 1-propanol, which is solvent of zirconium propoxide and at the same time, offers the use of non-polar carrier of effective compound. Non-polar solvent causes smooth surface of modified paper without warps and formation of visible deposits on the surface. Polar ingredient compiles presumption of facilitate intersection of effective zirconium compound to the structure of paper.

Lower concentration is more favourable in term of observed properties. This fact is shown on the look of modified paper. At a higher concentration of the effective component, e.g., at 0.04M solution, the total colour difference measured vs. the original unmodified paper is much more expressive (ΔE = 23.6) than that at lower concentration of zirconium compound (ΔE = 17.5).

Conclusions

Solution of zirconium propoxide in HMDO exhibits a positive influence on the permanence of paper, and/or on measured properties. Utilization of studied modification system resulted in smooth surface of modified paper without warps and formation of visible deposits on the surface.
It leads to a decreased formation of carbonyl and carboxyl groups. There was also observed decrease intensity of the peak at 1,735 cm\(^{-1}\) (carbonyl groups) in comparison with control sample measured by FTIR.

It enhances the effect of stability of folding endurance – decreases brittleness of the measured sample in comparison with unmodified one.

Artificial ageing causes decrease of \(I_1\) by about 15% in comparison with the control paper.

A more favourable effect offered solution of zirconium propoxide with lower concentration. Disadvantage of this system is its pH in comparison with pH of unmodified paper.

Combination of studied system with compound able to increase pH and thus alkaline reserve (for an instance MgO or other from lines of magnesium or calcium compounds) can help to solve this problem.

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REFERENCES
**L04 MODIFICATION OF POLYPROPYLENE THROUGH RADICAL GRAFTING IN MELT**

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**Introduction**

Pure polypropylene (PP) is sufficient material for many applications; however utilization of PP in some applications, such as composites, needs improvement of matrix properties for better adhesion, miscibility, dyeability etc. Chemical modification of PP is a way to formation of new material without searching new monomers for polymerization. Industrial and scientific interest gained in recent years grafting of polar monomers onto PP chain\(^1\)\(^-\)\(^5\), most of modification reactions target the change of PP hydrophobia. Reaction of PP with maleic anhydride (MA) is recently the best known modification process\(^6\)\(^-\)\(^7\), which is generally used for improvement of polypropylene adhesion to metals, glass fibres or to other polymers such as nylon or polyethylene terphthalate. Grafting reaction by reactive extrusion can be used for grafting of MA or other polar compounds onto PP chain in a melt state of polymer and in presence of free radical initiator. Possibility of grafting other polar substances, such as other carboxylic derivates, vinyl or acrylic molecules, were studied.\(^8\)\(^-\)\(^11\). Itaconic anhydride (IA), styrene (S) are monomers used for grafting to PP backbone in this work, another monomers such as acrylic acid, methylmethacrylate, vinylacetate etc. can be also tested.

**Experimental**

Two initiators were used for grafting reaction on PP:

- 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane (Luperox 101) for osth styrene and itaconic anhydride monomers
- dicumylperoxide for styrene grafting onto PP backbone.

**Method for PP-g-IA Preparation and Conversion of Itaconic Anhydride Determination**

Experiments of PP-g-IA and preparation were carried out in laboratory mixer Brabender 50 ml at 30 rpm, at temperature 210 °C. Polymer was at first melted about 5 minutes and then was monomer dispergated in polymer for time 1 minute. After that grafting reaction was started by addition of initiator and carried out for time 6 minutes. Unreacted monomer was removed by precipitation amount of 2.5 g sample dissolved in 100 ml of boiled xylene to 700 ml of acetone. Purified PP-g-IA was filtered and washed using 50 ml o acetone and dried in vacuum oven at 40 °C.

Conversion of grafted itaconic anhydride were determined using FT-IR spectroscopy measurement of integral intensity of C=O stretching vibrations at 1,770–1,780 cm\(^{-1}\) and intensity of peak at 1,170 cm\(^{-1}\) belonged to vibration of –CH\(_3\) of PP.

Second method of bounded IA concentration determination was alkalimetric titration. Weight 0.5 g of precipitated PP-g-IA was dissolved in boiling xylene and then titrated using 0.005M KOH and bromthymolic blue as end-point indicator.

**Method for PP-g-S Preparation and Analysis**

Preparation of PP-g-S was carried out the same way as was described in the last section. Styren was poured into mixer using glass pipette.

Analysis was accomplished using FT-IR spectroscopy of PP-g-S. Polymer was at first purified by the precipitation into acetone or ethanole as was described former. FT-IR spectras were taken out using polymeric film. Comparison of integral intensity of peaks of aromatic ring vibration around 700 cm\(^{-1}\) and vibration of –CH\(_3\) at 1,170 cm\(^{-1}\) was used to attached styrene concentration determination.

**Results**

Two molar ratio of initiator to monomer (1:0.6 and 1:0.8) were used in experimental part to comparison efficiency of grating IA and MA. Experimental data of maleic anhydride grafting were get from the same methods as for PP-g-IA. Results of ascertainment monomers conversions are shown in Table I.

**Table I**

<table>
<thead>
<tr>
<th>Monomer</th>
<th>(w_o(\text{monomer})) [% wt.]</th>
<th>(\alpha(1:0.6)) [%]</th>
<th>(\alpha(1:0.8)) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>IA</td>
<td>0.25</td>
<td>23.9</td>
<td>26.7</td>
</tr>
<tr>
<td>IA</td>
<td>0.5</td>
<td>32.4</td>
<td>37.1</td>
</tr>
<tr>
<td>IA</td>
<td>1.0</td>
<td>62.8</td>
<td>55.4</td>
</tr>
<tr>
<td>MA</td>
<td>0.25</td>
<td>47.6</td>
<td>42.4</td>
</tr>
<tr>
<td>MA</td>
<td>0.5</td>
<td>41.9</td>
<td>42.3</td>
</tr>
<tr>
<td>MA</td>
<td>1.0</td>
<td>61.1</td>
<td>64.1</td>
</tr>
</tbody>
</table>

The efficiency of IA grafting in comparison to MA grafting process is apparently less due to probable homopolymerization of IA, which is removed from grafted polymer by purification. Graft length is higher in case of PP-g-IA compare to PP-g-MA and less stability o IA homopolymeric graft less could be the second reason of decreased conversion of IA.

PP-g-PS sample precipitated into ethanol contain both PP-g-PS and PS homopolymer, which could be formed by homopolymerization of styrene. Sample precipitated into acetone contain only PP-g-PS, because PS is in acetone soluble. The grafting efficiency is decreased with increased concentration of initiator. Amount of about 30 to 45 % of bounded styrene was present as a homopolymeric PS, other
Table II
Content of styrene ω(S) in PP-g-PS for concentration 1 % wt. of dicumylperoxide or 2,5-dimethyl–2,5-bis(tert-butylperoxy)hexane for initial concentration of styrene ω₀(S) from 1 to 20 % wt

<table>
<thead>
<tr>
<th>Sample</th>
<th>ω₀(S) [wt%]</th>
<th>ω(S) [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DCP</td>
<td>Luperox 101</td>
</tr>
<tr>
<td>PP-g-PS</td>
<td>1</td>
<td>0.66</td>
</tr>
<tr>
<td>PS + S (non-purified)</td>
<td>5</td>
<td>3.76</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5.28</td>
</tr>
<tr>
<td>PP-g-PS + PS (precipitated into ethanol)</td>
<td>5</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.77</td>
</tr>
<tr>
<td>PP-g-PS (precipitated into acetone)</td>
<td>10</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>6.98</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3.89</td>
</tr>
</tbody>
</table>

as PP-g-PS. Luperox 101 is more efficient initiator for grafting of styrene onto PP.

Conclusions
First part of work was focused to grafting of itaconic anhydride and maleic anhydride onto PP backbone. Comparison of both monomers conversion results shown, that grafting of IA bring about worse conversion due to more complex reaction mechanism and possibility of formation of less stable IA homopolymeric grat.

Second experimental part was concentrated to found better initiator for styrene grafting onto PP. Luperox 101 can be good choice for prepared grafting of mixture IA+S for grafting onto PP backbone. However analysis of amount of homopolymeric PS during radical grafting of styrene onto PP shown that complex mechanism of IA+S mixture grafting could be expected.

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REFERENCES
L05 PROPERTIES OF HOT COMPACTED POLYPROPYLENE PLATES INCLUDING ORIENTED POLYPROPYLENE TAPES

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Introduction

The polypropylene homopolymer (PPH) sheets are used in many common applications. The strength of such material is about 33 MPa, however, the toughness is not very high, especially at low temperatures at which PPH is brittle. The strength can be increased for example by reinforcing PPH with short fibres but the low temperature impact resistance still remains low. The toughness can be improved by incorporating EPR rubber into PPH matrix (impact polypropylene copolymer PPIC), but the strength of such material is substantially lower. Another way of improving both properties is to combine oriented and unoriented PPH and to construct sandwich-like composite plates.

The polypropylene composite plates can be produced by hot pressing several layers of oriented PPH tapes and potentially by adding unoriented PPH thin layers (films). The production conditions must be held in a specific “temperature window” to avoid complete relaxation of the oriented polypropylene chains and to facilitate a lateral welding of PPH.

Some results concerning behaviour of PPH tapes at high temperatures (near to the PPH melting point), lateral welding of tapes or PPH woven fabric and properties of PPH self-reinforced composites are presented in this paper.

Experimental

Material and Samples Preparation

Commercial grade of polypropylene Mosten TB 002 (MFR = 2.73 g 10min⁻¹) was used in this work. A film of 200 or 400 μm thickness (PF) was prepared by chill roll technique. This film was drawn up to ratio 5:1 in the first step, then it was cut into tapes (10 mm width) and those were drawn on a hot plate to the final draw ratio 8:1 in the second step (TB). A part of the tapes was annealed (TB-t) at different temperatures from 120 to 170 °C. Both ends of each annealed tape were fixed to avoid the longitudinal shrinkage of the tape.

To characterise the lateral adhesion a couple of tapes was passed through a tempered channel where a short perpendicularly acting force took place to cause a lateral weld of these tapes. The length of the tempered part of tapes was fixed to avoid the relaxation of tapes.

The composite plates were hot pressed at different temperatures (160 °C to 170 °C) in an open mould. The number of PPH woven fabric layers (WF) was different (four to twelve) and the unoriented PF layers were potentially stuck in between fabric layers to improve the “weld adhesion”.

Measurement

The basic information about the supermolecular structure of PPH tapes was received by recording the fusion curve of a tape using a DSC instrument (TA Instruments Q100) under following conditions: specimen weight about 1.5 mg, heating rate 10°C min⁻¹, initial 50 °C and end temperature 200 °C.

The tensile properties of the tapes were measured at laboratory temperature using an INSTRON 4302 machine. The active length of the specimens were 100 mm, the testing speed was 100 mm min⁻¹ ref.⁵ The tensile properties of pressed plates were measured according to the same method; the strips of 170 mm length and of 15 mm width were cut from the plate.

The lateral weld adhesion of a couple of tapes was characterised by the T-peel test⁶ or the coherence of the composite compact by method for floating roller peel resistance⁷ (INSTRON 4302, 100 mm min⁻¹).

The intensity of the relaxation process in the tape at elevated temperatures was evaluated by a DMA (R.M.I. DX04T) measurement. The constant fluctuating stress \[\sigma_m \pm \sigma_a (\sigma_m = 2, 5, 10, 15, 20 MPa, \sigma_a = 1 MPa), \text{sin oscillations, } 1 \text{ Hz}\] was applied during the temperature scan from 30 °C to 180 °C, 2°C min⁻¹. The initial distance between grips (= gauge distance) was 30 mm and the change of this quantity was recorded during the test. The complex modulus was measured, too.

The ductility of final material was measured by the instrumented puncture test (CEAST 6790/000: inside diameter of clamped support ring = 40 mm, diameter of striker = 10 mm, impact velocity = 3.6 m s⁻¹, T = 23 °C or –20 °C).⁸

Results

DSC Measurements

The information about the changes in supermolecular structure of annealed PPH tapes was evaluated only qualitatively by comparing the shapes of DCS melting records (see Fig. 1.). We interpreted these DSC records based on relaxation of oriented chains and subsequent recrystallization of PPH that took place during annealing of the tape. These processes begin at annealing temperature (approximately at 150 °C). A second melting DSC peak occurs at 155 °C. The recrystallization processes became more intensive at higher annealing temperatures (an example is given for 160 °C); the second melting peak gets larger and it is shifted to higher melting temperature. Process of recrystallization at annealing temperature 170 °C starts to change substantially the crystal lattice character of the tape. The thicker lamellae are built-up (higher \(T_m\)) and the orientation of chains decreases rapidly.

Tensile Tests

The results of tensile tests (tensile strength and elongation at break) are presented in Fig. 2. Tensile strength decreases with annealing temperature in the whole annealing temperature range, because the above mentioned recrystallization process decreases orientation of polymer chains.
Elongation at break increases only up to annealing temperature 160 °C and then it drops. This fact could be also attributed to the polypropylene recrystallization (see above) and subsequent destruction of the tape orientation.

**Adhesion of Tapes**

The strength of lateral weld adhesion of a couple of tapes is depicted in Fig. 3. The adhesion increased with the welding temperature, however, the experimental results exhibited higher scatter. At temperature below 164 °C no measurable adhesion was detected and above 169 °C considerable melting of tapes was observed and this technique of measurement was not applicable.

**Relaxation of Oriented Tapes**

The relaxation of internal stresses was assessed only qualitative till now. The static deformation of a tape specimen with respect to the mean level of a fluctuating stress at constant heating rate were taken as a measure of intensity of the relaxation process at given temperature (see Fig. 4.). It is evident that at low mean stress levels (2, 5, 10 MPa) the shrinkage of the tape is much more intensive than the creep deformation and contrariwise at high stress level (20 MPa). A balance is held for a stress of about 15 MPa.

**Properties of Pressed Composite Plates**

The hot pressed composite plates have a specific structure composed of well distinguishable layers because the pressing requires specific conditions (temperature) for receiving relatively good cohesion and preserving a substantial part of molecular chain orientation in the tapes. An example of a microtomic section is presented in Fig. 5.

**Fig. 4**: Dependence of stationary deformation of the tape under constant fluctuating stress on temperature during the DMA measurements. The mean stress levels are: 2, 5, 10, 15 and 20 MPa and it is remarkable that the strength of the composite is about two times higher than the strength of unoriented PPH. The elongation at break is lower compared with PPH but it is high enough to conclude that the composite materials are not brittle at the laboratory temperature.

The composite samples were further tested by dart drop (Fig. 7). The maximum force (or maximum force at first break) and the puncture energy were recorded. The evalua-
tion was complicated by the fact that the thickness of the composite plates varied from sample to sample and that the simple relation between the value of measured quantity and the thickness of the plate is not known. Therefore the set of unoriented PPH plates (the same type of PPH resin) of different thickness were pressed and the corresponding properties were measured at the same conditions. For evaluation the ratio between the value of composite property and the interpolated value (into the same thickness) of the same property for PPH plate was used. We found that the properties of the composite plates are noticeably better than the properties of PPH unoriented plates in the “pressing window” \(160 \, ^\circ\text{C}/164 \, ^\circ\text{C}\) especially at testing temperature \(-20 \, ^\circ\text{C}\). The common PPH homopolymer is brittle and it splitters during the impact test. To the contrary, the composite plate exhibits no splitter at this temperature (Fig. 9.).

Important factor is the internal cohesion of the composite plates. It was assessed by a modified peeling test. A strip of the surface fabric layer of 15 mm in width was peeled up from the pressed composite plate to evaluate the cohesion of the plate with respect to the different pressing temperatures. The results of measured specific forces are depicted in Fig. 8. It is evident that the welding of oriented tapes starts approximately at 160°C and is significantly better for the material consisting of oriented tapes and unoriented PPH film layers.

Conclusions

It has been demonstrated that a “pressing window” exists for PPH tapes in the temperature range around 164°C where some reasonable adhesion between PPH tapes is formed and the high strength of tapes is kept.

Only a part of the PPH material melted and recrystallized during processing at this temperature.

The complete recrystallization of an oriented tape is connected with the loss of molecular chain orientation and then also with the loss of the tensile strength.
Some distinct layer structure is observed in the composite plates pressed according to described procedure. A shrinkage stress around 15 MPa was found in the PPH tapes at drawing ratio of 8:1 and it has to be compensated during processing.

The decrease of dart drop strength is the main competitive process with respect to the improvement of the homogeneity and the cohesion of the composite plate. This process closes the “processing window” for higher temperatures.

The self reinforced PPH composite plates exhibit very good low temperature toughness comparing to the same grade of polypropylene homopolymer and they do not splitter by the low temperature impact.

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REFERENCES
L06 BIODEGRADATION OF MODIFIED POLYURETHANE FOAMS

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Introduction

Polyurethanes (PUR) are unique family of polymeric materials that is able to pose wide range of properties to suit many requirements. Some of the applications of this versatile polymer include foams, elastomers, paints, fiber, adhesives and sealants.

Biodegradation is natural process of material decomposition which is based on the fact that synthetic polymeric materials could serve as carbon and energy sources for many microorganisms including bacteria, moulds and yeasts. Despite its xenobiotic origin PUR was found to be susceptible to biodegradation by naturally occurring microorganisms.

Biodegradability of material can be influenced by many factors. Very important are structure properties such as molecular orientation, crystallinity, cross-linking and chemical groups presented in the molecular chain. For example, increase of molecular weight or crystallinity usually leads to increasing material durability. Thus, variations in the degradation patterns of different PUR are attributed to many properties of PUR such as topology and chemical composition.

Other important factors which influence process of biodegradation in nature are presence of susceptible microbial population and environmental conditions. PUR biodegradation activity was observed for many microorganisms including bacteria (e.g. Corynebacterium sp., Pseudomonas aureginosa, Comamonas acidovorans, Pseudomonas chlororaphis, Pseudomonas flouscens, Acinetobacter calcoaceticus and Arthrobacter globiformis) and fungi (Culvularia senegalensis, Fusarium solani, Aerobasidium pollulans, Cladosporium sp., Cheatomium globosum and Aspergillus terreus).

In this work, biodegradability of modified PUR foams was tested using single bacterial strain (Arthrobacter globiformis), mixed bacterial culture (Thermophilus sp.) and selected moulds strains (Fusarium solani, Alternaria alternata). In a complex comparative study standard biodegradability tests in laboratory conditions, in model composting conditions and also in different natural environments were used.

Experimental

PUR foams were modified by following biopolymer components: 10 % of acetyl- (AC), hydroxyethyl- (HEC) cellulose, 10; 20; 30 % of carboxymethyl cellulose (CMC), 10% acetylated starch (AS), 10 % glutene (PB). Modifying agents partially replaced polyether polyol. Reference sample without modification agent was tested too.

Flask biodegradation tests were carried out in 50 ml of defined media under permanent shaking (120 rpm). One sample of PUR was represented by 0.25 g of PUR. Growth characteristics and chemical oxygen demand were determined in regular intervals. At the end of cultivation (about 300 hours) PUR mass decreases were measured gravimetrically and PUR surface changes were analysed microscopically. PUR foams were tested in complete medium as well as the only carbon and/or nitrogen source. Single strain Arthrobacter globiformis CCM 193 was cultivated at 25 °C in Nutrient broth NB1 and in Minimal inorganic medium containing glucose as carbon source and (NH4)2SO4 as nitrogen source. Mixed aerobic thermophilic culture Thermophilus sp. was originally obtained from sludge of wastewater treatment in Bystřice pod Hostýnem. Cultivation was carried out at 60 °C on Minimal inorganic medium with minerals and vitamins. The mould strain Fusarium solani F-552 was cultivated on Minimal inorganic medium according A. globiformis. Alternaria alternata was identified during the study with A. globiformis as a common air contaminant. A. alternata was cultivated on Minimal inorganic medium too.

Model composting experiments were carried out under controlled conditions in presence of culture Arthrobacter globiformis. Model experiment under composting conditions was performed according to ref.1. PUR mass changes and surface patterns were analysed at the end of the experiment.

Test of biodegradability in natural condition. PUR foams were exposed to three different natural environment for 50 days. After the end of exposition, mass decreases of foams were analysed and a total bacterial microflora (quantified as colony forming units) in each environment was determined.

Results

All flask biodegradation tests proved that crucial for the course of PUR degradation are type and concentration of modification agent (see Fig. 1. and Fig. 2.).

Generally, PUR mass decreases during flask biodegradation tests were practically identical in presence and/or in

Fig. 1. Mass decreases of PUR samples modified by different agents (flask biodegradation test)
absence of bacterial culture. On the other side, the presence of PUR foam influenced the growth of culture. These two effects could be explained as two-step biodegradation process. First, abiotic destruction of foams occurred, which was followed by the second step – utilization of degradation products by the bacterial culture.

The growth of culture in presence of individual PUR samples was dependent on type of modifying agent. The highest growth of both cultures was observed in PUR modified by CMC.

Experiments with PUR foams used as the only carbon or nitrogen source for thermophilic culture showed that all modified PUR foams could serve as the only nitrogen source. Surprisingly, PUR modified by CMC and AS were better nitrogen sources than inorganic salt. On the other side, only PUR foam modified by AS supported the growth of culture when no other carbon source was present.

In all experiments with fungi, a typical distribution of biomass between PUR surface and medium was observed. *Alternaria alternata* utilized all PUR as the only carbon source. Foams modified by CMC and by AS strongly supported absorption of biomass on PUR surface. Under nitrogen limitation practically the whole biomass was adsorbed on foam surface.

*Fusarium solani* was able to use modified PUR as the only carbon as well as nitrogen source. This strain also strongly preferred growth on surface of PUR foams, mainly under both carbon and nitrogen limitation.

In model composting conditions, the highest loss of biomass was observed in PUR modified by 10% of CMC.

All tested natural environments disposed PUR biodegradation activity. In environments different total bacterial activity was found. Individual environments exhibited also different degree of exposition of foams to natural conditions (weather, water, etc.) which could be considered to be important abiotic factors.

It seems that in early stages of long-term natural degrada-
dation microbial and abiotic factors act simultaneously, but abiotic processes are more efficient. The highest degradability degree was shown repeatedly in PUR modified by CMC and AS.

Conclusions

Tested PUR foams could be biodegraded by microorganisms used in this study. Degree of degradation is strongly dependent on type and concentration of used modifying agents. The highest tendency to biodegradability by most of tested microorganisms was observed in PUR modified by CMC and AS. Mainly in early stages of degradation abiotic and microbial factors act simultaneously. It seems that microorganisms are able to utilize degradation fragments formed during abiotic decomposition.

The effect of mould sorption on PUR surface could be important for biotechnological application. Surface sorption degree depended on type of used modifying agent, mould strain and also on cultivation conditions.

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REFERENCES

REINFORCING MECHANISMS IN LAYERED SILICATE POLYMER NANOCOMPOSITES

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Introduction

In last decade vast literature has been published on polymer nanocomposites reinforced with layered silicate. As it might be thought that the past decade possess a time long enough to fully understand principles of mechanical reinforcement of layered silicate nanocomposites. It is mostly truth in the opposite way. According to the amount of published literature and increasing interest from industrial sphere, we have decided to highlight the reinforcing mechanism in layered silicate nanocomposites. Polymer nanocomposites based on layered silicate were first prepared by Toyota researchers twenty years ago. Compared to the traditional composites, they possess optimal mechanical properties at low filler content, improved barrier properties. Interesting in this material is that a very small amounts of silicate resulted in pronounced improvements of mechanical and barrier properties.

The commonly used layered particles belong to the family of silicates. Among them mmtomorillonite, hectorite and saponite are the commonly used. Their crystal structure consists of layers stacked together. These layers are connected by van der Walls forces and form an interlayer or a gallery. They show two interesting abilities. The first ability is the possibility to disperse into individual layers. And the second is the ability to fine-tune their surface through ion exchange reactions. Layered silicates are mixed with plenty of polymer matrices. Glassy, Semicrystalline, Crystalline, liquid crystal matrices. Glassy, Semicrystalline, Crystalline, liquid crystal matrices were taken into a consideration. The values for polymers were taken into a consideration. The values for amorphous matrices were collected. Amorphous and semicrystalline matrices were taken below their Tg where all the chains are already immobilized the remaining two mechanisms prevails. In semicrystalline polymer between the temperature range Tg and Tm an amorphous phase can contribute to the reinforcement via the chain immobilization. The other remaining mechanisms are active as well. Additionally a neglecting effect must be taken into a consideration like the particle aggregation, low intercalation or exfoliation, voids and bulk non-homogenites. This complicates the modulus predictions based on material parameters and aspect ratio as a function of filler concentration.

In this article we attempt to make an analysis of published data on the elastic modulus of layered silicate nanocomposites for amorphous and semicrystalline polymers. Simple Halpin-Tsai model was used to determine the upper and lower limiting values of the elastic modulus of weakly and strongly interacting systems.

Methodology Used

An experimental data published on clay minerals in polymer matrices were collected. Amorphous and semicrystalline polymers were taken into a consideration. The values for amorphous matrices were taken below Tg and for semicrystalline matrices below Tm. The boundary lines for upper and lower limiting values were calculated using simple Halpin-Tsai model:

\[
\frac{E_C}{E_m} = \frac{1 + \zeta \eta f}{1 - \eta f}
\]  

(1)

where \( E_C \) is the relative modulus, \( E_C \) refers to complex modulus and \( E_m \) is matrix modulus. \( \zeta \) is termed...
as shape parameter and is related to the aspect ratio with equation
\[ \zeta = 2A_R. \]

\[ A_R = \frac{\text{length}}{\text{thickness}} \]

\[ \eta \] is a material parameter related to the elastic modulus of constituents with equation
\[ \eta = \left( \frac{E_f}{E_m} - 1 \right) \left( \frac{E_f}{E_m} + \zeta \right)^{-1} \]

Based on simple micromechanical model represented by Halpin-Tsai model we may consider the aspect ratio equal 1 for no intercalated systems and equal 250 for fully intercalated systems. The values of limiting aspect ratios were roughly estimated from microscopic observations of commercial layered silicate nanocomposites.

**Results and Discussion**

In amorphous polymers below \( T_g \) the chains remain in a frozen state. No low temperature conformations are considered. Hence no further immobilisation can take place while embedded the filler. As a result there are only two reinforcing mechanisms that were left to consider, reinforcement based on elastic modulus and aspect ratio. Experimental data taken from the literature for glassy polymers reinforced mostly with MMT particles completely fell between the boundaries predicted by micromechanical model calculated by equation (1).

In semicrystalline polymers one may take into a consideration an existence of two distinct temperature regions. \( T < T_g < T_m \) for the amorphous phase and \( T_g < T < T_m \). Below the \( T_g \) the reinforcing mechanism is the same as for the amorphous polymers below their \( T_g \). The presence of platelets did not alter the crystalline regions during solidification. On the other hand the semicrystalline polymer in the temperature range \( T_g < T < T_m \) represent more complex behaviour. The amorphous phase above the \( T_g \) shows a nano-scale reinforcement mechanism base on segmental immobilization becomes more important. The overall contribution is proportional to the amount of amorphous portion in semicrystalline polymer able to be immobilized. From H-NMR and Raman spectroscopy measurement only 5–20% of chains is mobile in the case of common polyolefinates at room temperature. It is not surprising that the reinforcement for semicrystalline polymers is not as pronounced as for amorphous polymers. It seems that the main reinforcing mechanism for semicrystalline polymers is the same as for the glassy polymer matrices – stress transfer into a platelet shape filler. This hypothesis is supported by the observation of systems reinforced with fillers with high intercalations like (polyamides) compared with the systems with weakly filler matrix interactions (polyolefinates) at the same filler content.

**Conclusions**

An experimental data published in literature on the relative elastic modulus of amorphous and semicrystalline layered silicate nanocomposites were analyzed using a simple micromechanical model. It was demonstrated that the mechanism of reinforcement for amorphous polymers beneath their \( T_g \) and for semicrystalline polymers beneath their \( T_m \) originates primarily from the substitution of matrix with stiffer filler and from the stress transfer. Most of the published data fell within an upper boundary with aspect ratio 250 and the lower boundary with aspect ration 1. The upper bound has not been achieved because of the low degree of intercalation of platelets, non-homogeneous dispersion and random orientation of the particles. The upper bound is truly related to the idealised dispersion and intercalation.

Authors are very thankful to the Ministry of Education, Sport and Youth for their financial support, grant ID: MSM 0021630501.

**REFERENCES**

**Introduction**

Hornification is one of the main reasons leading to brittleness of fibres on paper recycling\(^1\). Brittleness of recycled fibres is explained by hornification which is measured as a loss of the ability of fibres to retain water. This phenomenon was observed with lignin-cellulose fibres when they were repeatedly wetted and dried.

Hornification is one of the presumed processes occurring also during accelerated ageing of paper. However, the effect of hornification on changes in strength properties of paper has not been expressly proved so far. Hornification manifests itself in lignin-cellulose fibres as their lower ability to retain water and it is determined by WRV.

To determine the degree of hornification and to determine the changes on absorption of water, several methods can be used, for example the method determining the ability to retain water (WRV) or the method determining the point of saturation of fibres (FSP). WRV is calculated as a ratio of the mass of water in saturated fibres dipped into water, with subsequent removal of superfluous amounts of water in a centrifuge to the mass of absolutely dry fibres. The FSP is calculated as the total volume of pores, in other words the total content of water in the pores of the cell wall, and can be determined by free discharge or absorption of nitrogen. If the content of water is lower, WRV decreases linearly with increasing dry matter. This situation shows that hornification can occur when the content of water falls under critical level. If the content does not fall under FSP, hornification shall not occur. Both WRV and FSP fall in value when the fibres get repeatedly wetted, from dry state.

The chemical treatment, that is usually used to prevent hornification, gets effective under the condition that it disrupts the creation of hydrogen bonds between cellulose-cellulose and that it becomes strong enough to inhibit serious changes in the inner structure of the paper.

To prevent the process of hornification one can use chemicals that can cause the fibres to swell. Some studies have shown that alkalic NaOH causes the fibres to swell on the basis of ion-exchange reaction.\(^2\)-\(^6\) The swelling occurs in reaction to osmotic pressure, generated by cations present in the solution (Donnan Effect). The level of swelling increases with the following order of cations: \(\text{Al}^{3+} < \text{H}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Li}^+ < \text{Na}^+\).

The known modification processes that are to protect the lignin-cellulose carriers of information, as for example the Bookkeeper process\(^7\)-\(^\text{11}\) or the Wei T'o Canada\(^9\),\(^\text{12}\), run on the basis of compounds that contain magnesium.

The neutralising agents for the Bookkeeper process are the particles of magnesium oxide (MgO) that are smaller than 1\(\mu\)m and are dispersed in perfluorheptane. Some part of the content of magnesium oxide neutralises the present acids, while the non-regenerated part creates alkalic reserve. The magnesium oxide reacts with the acids and with the moisture in the paper in reactions described in the work\(^\text{13}\).

The deacidification agent of Wei T'o Canada is methoxy-magnesium-methyl-carbonate (MMMK). This alkoxide is soluble in organic solvents. It is an organic-metallic compound, having the formula: \(\text{CH}_3\text{O}–\text{Mg}–\text{O}–\text{CO}–\text{O}–\text{CH}_3\times x\text{CO}_2\), where \(x\) depends on solvents and on temperature\(^\text{14}\).

The MMMK reacts with the moisture of the paper, but most of all with the air humidity, as expressed by the reaction\(^\text{13}\):

\[
\text{H}_2\text{O}–\text{Mg}–\text{O}–\text{CO}–\text{O}–\text{CH}_3 + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{-CH}_3\text{OH} + \text{CO}_2
\]

There occur some other reactions liberating magnesium di-hydroxid Mg(OH)_2, magnesium carbonate MgCO_3 and magnesium oxide MgO, that react with the acids present in paper, thus creating neutral salts. The magnesium compounds, namely, Mg(OH)_2, MgCO_3 and MgO, gradually absorb the moisture and carbon dioxide CO_2 from the air to form basic magnesium carbonate MgO·MgCO_3·Mg(OH)_2, that gets deposited into the fibres of the substrate, thus creating alkalic reserve that is able to protect the paper against acids.

The end-products from the previously mentioned reactions have a deacidification effect on the products of acid hydrolysis in the paper. Simultaneous swelling reactions of the fibres can occur and they lead to increased flexibility and antihornification effect.

This study reports on the effect of some magnesium compounds on improved ability of fibres to retain water in the process of accelerated ageing. The ability to retain water is a measure of hornification that is one of the mechanisms of fibre brittleness.

**Experimental**

**Thermally Accelerated Ageing**

Paper samples held 24 hours in climatic conditions at 23 °C and RH = 50% were put in sacks made of layered polyethylene foils with aluminium layer and hermetically closed. The sacks were conditioned at temperature \(t = 98 ± 2 \, ^\circ\text{C}\), in time periods 0, 1, 2, 3, 5, 10, 15, 20 and 30 days according to standard ASTM D 6819-02 ref.\(^\text{15}\).

**Paper**

The experiment was performed on newspaper produced by Jihočeské papírny Větrní a.s. The newspaper was wood-
based, callendered, nonsized, with basis weight 45 $\text{g m}^{-2}$, containing 55 % bleached ground wood pulp, 20 % white sulphate pulp, 15 % trapped waste fibres, 10 % clay, pH (surface): 4.5–5.0.

Modification Suspensions

In the fight against the ageing processes, the procedures commonly used to modify paper are the processes Bookkeeper and Wei T'o. These processes are based on the concept of binding particles of magnesium compounds onto the paper fibre surface. Used modification suspensions were:

- Suspension of MgO in perfluorheptane (Bookkeeper), Preservation Technologies, L.P. (PTLP), Cranberry Township, PA (USA). The PTLP declares that their dispersion of Bookkeeper contains three basic groups of components
- Methoxy-magnesiummetyl-carbonate in methanol, 2% solution, (MMMK), produced by SNK, Martin.

Measuring of Mechanical Properties

The tensile test to determine breaking length was performed on a universal tensile strength tester INSTRON 1122, Instron Ltd., High Wycombe, Buckinghamshire, England, pursuant to the specification STN ISO 1924–1 (500340): Paper and cardboard. Determination of tensile properties. Changes of folding endurance $W$ were studied on modified and aged samples.

Water Retention Value

The test is carried out by placing a pad of moist fibers in a centrifuge tube that has a fritted glass filter at its base. The centrifuge is accelerated at 900 g to remove water from the outside surfaces and lumens of the fiber (a higher force is used according to some European standards). The remaining water is believed to be associated with submicroscopic pores within the cell wall. The centrifuged fiber pad is weighed, dried at 105 °C, and then reweighed. The WRV equals the ratio of the water mass to the dry mass according to standard ISO 23718:2007.

Results

The previous works report that a modification by Bookkeeper is more or less just a surface modification and a modification of the paper by MMMMK can be considered as running inside the volume because it is present in the whole volume of the paper. A similar difference can be found as to the content of magnesium in the paper on modification.

Fig. 1 shows changes in the WRV parameter of modified papers as related to the period of ageing. The lowest slump of WRV is in connection with the non-modified paper. With the papers modified by compounds of magnesium, the decrease of WRV with time of ageing is less dramatic. The process of modification in surface, that works with a lower content of magnesium than the process of modification in volume, led to an increase of WRV by 17 %, while the modification in volume saw the increase just by 5 %. When one compares the curve of this characteristic and how it develops during ageing, one can see that for the volume modification the trend of WRV to decrease is not significant, the value of WRV decrease is rather stable in the range between 78 % and 72 %. However, in the process of surface modification the WRV value falls from 90 % to 70 %.

When one compares changes of the relative WRV to the changes of WRV for non-aged paper, as dependent on time for given modification processes (Fig. 2.), the trends in decrease for this value are similar. With non-modified paper this relation has a decreasing characteristic, while with modified samples the decreasing trend looks as if it has stopped and is not continuing any more. Out of this relation the best seems to be the modification at which magnesium has been distributed into the whole volume of paper, as the decrease of relative WRV is the slightest. It could be caused by the moisture in the paper itself. Probably, during ageing of the paper, mag-
Fig. 3. Folding endurance as a function of accelerated ageing time period for different modified papers

Fig. 4. Changes in breaking length during accelerated ageing for different modified papers

Fig. 5. Relationship between folding endurance and WRV

Fig. 6. Breaking length as a function of WRV for different modified papers

Magnesium reacted with the moisture present in the paper which caused swelling of the fibres, thus leading to better results of the process of hornification.

Fig. 3. shows the dependence of number of double-folds during accelerated ageing on time. The effect of magnesium compounds on the number of double-folds is clearly positive. Improvements in the number of double-folds can be seen also in non-aged samples, in which case the papers modified in volume or surface prove higher number of double-folds than non-modified paper. The curves reflecting the changes of double-folds are similar for all samples. The greatest decrease can be seen with the non-modified paper. All the samples show the greatest decrease in the number of double-folds in the first ten days of accelerated ageing, later there is a tendency to certain stabilisation of the decrease of the measured quantity. A similar development of relation can be seen for the WRV.

Fig. 4. shows dependences of breaking length on time of accelerated ageing. Even in this relation one can see the positive effect of paper modification via magnesium compounds. Even more, modification in volume increases the breaking length of paper during accelerated ageing. Similarly, paper modification in surface considerably contributes to its breaking length. In the case of non-aged papers, no differences can be seen for the parameter of breaking length.

Fig. 5. documents dependence of the number of double-folds on WRV of papers modified in different way. All the measured dependences reflect the fact that with growing values of WRV the number of double-folds grows as well. For non-modified paper the number of double-folds falls to zero. For modified papers the minimum values are considerably higher and they do not fall to zero.

For non-modified paper, the breaking length depending on WRV changes linearly, but with growing value of WRV the breaking length increases. For paper modified in surface, a similar dependence has been obtained, but with smaller angle of inclination. The paper modified in volume does not show this dependence.
Conclusions
Modification of lignin-cellulose fibres by magnesium compounds leads to their better retention of water. Modification by magnesium compounds inhibits hornification of fibres along the process of ageing. The probable mechanism of the modification is based on reaction of magnesium compounds that are transported into the paper in organic phase by water present in the paper. Magnesium compounds react with residual moisture giving alkalic substances that improve the ability of fibres to retain water. The fibres thus adjusted are more flexible; they undergo only a limited process of hornification and are more stable on bending than non-modified fibres.

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REFERENCES


L09 IMPACT OF PROCESSING ON DEGRADATION OF POLYPROPYLENE IMPACT-COPOLYMER

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Introduction

During processing by extrusion polymers undergo harsh thermo-mechanical exposure, which usually induces chemical reactions leading to the changes in polymer backbone. Conditions in extruder cylinder are very specific as to the access to oxygen, which basically impacts the chemistry of degradation. A certain limited amount of oxygen originally dissolved in polymer matrix is consumed at the initial zone of cylinder. The following path through cylinder is characterized by no oxygen access. Different kinds of reactions thus take place during extrusion.

In the case of polypropylene homopolymer (PPH), the traces of oxygen are consumed by the reactions with R’ radicals, originating from the thermo-mechanical cleavage of C–C and C–H bonds. These reactions give rise to the formation of oxygen containing intermediates such as RO’ and ROO’ radicals, the cleavage of which leads to the decrease in molecular weight. These reactions, however, are of limited extent just because of the limited amount of oxygen entering the reaction. When oxygen is consumed, the thermomechanical cleavage of C–C backbone plays the dominating role. This mechanism is typical for the processing in an extruder. Carbon centered R’ radicals formed in this way are not able to propagate in the absence of oxygen and in the case of polypropylene they terminate by disproportionation giving rise to CH3 = C(CH3)- end groups. Due to the methyl substitution, the end double bond cannot add R’ radicals. Thus in the case of PP no crosslinking occurs and processing degradation leads exclusively to the decrease in molecular weight, reflected by the increasing melt-flow rate.

PP homopolymer degradation mechanism has been well described in literature. On the other hand degradation of PP impact-copolymer is much less documented. PP impact-copolymer is typical with the heterogeneous structure, consisting of PP homopolymer, ethylene-propylene rubber and a relatively small portion of PE homopolymer phases. The degradation processes induced here by extrusion are thus more complicated and influenced by the presence of ethylene units, the quantity and distribution of which substantially influences the overall behaviour of the material. The target of this work is to elucidate phenomena taking place in PP impact-copolymer during extrusion.

Experimental

Materials

Polypropylene, a medium-impact copolymer of Innoven technology (gas-phase process) – (i) non-stabilized fluff (total ethylene content 6.4 % wt.) and (ii) commercial grade (total ethylene content 5.4 % wt.) both of melt-flow index (MFI) 6 dg min\(^{-1}\). (230 \(^\circ\)C 2.16 kg\(^{-1}\)) were used for the experiments. Polypropylene homopolymer of the same technology, commercial grade of MFI 6 dg/min. (230 \(^\circ\)C 2.16 kg\(^{-1}\)) was used as a reference. Both commercial grades were pelletized and stabilized with the same stabilizer system.

Methods and Measurement

Processing stability was carried out on a Brabender single-screw extruder 19 mm, l/d=30, at 260 \(^\circ\)C 100 rpm; Melt-flow index (MFI) was measured at 230 \(^\circ\)C, 2.16 kg (ISO EN 1133).

Yellowness index (YI) – according to ASTM D 1925 (DataColor SF650) measured on pellets

GPC analysis – carried out at PL-GPC 220 with detectors PL–220DRI and VISKOTEK model 220R, 3 × column PL gel 10 µm MIXED-B, 300 × 7.5 mm, mobile phase TCB, flux 1.0 ml min\(^{-1}\).

Mechanical properties were measured on Instron 4466 and Zwick 5102; specimens injection moulded at 200–230 \(^\circ\)C were used.

Solvents successive extractions were carried out using a Soxhlet extractor. Extractions varied from 12 to 20 hours; 5 g of polymer were extracted, solvent volume was 800 ml.

Results

Processing of Commercial Grades

Processing stability

A commercial PP impact-copolymer (ICPP) and its homopolymer reference (PPH) were subjected to multiple extrusion on a laboratory Brabender extruder at 260 \(^\circ\)C. Because both the starting materials were received in the form of pellets, the pelletization step at the producer’s facility at 240 \(^\circ\)C was denoted as zero extrusion, while the other ones carried out on a Brabender at 260 \(^\circ\)C were numbered 1\(^{st}\) to 5\(^{th}\) extrusion. After selected extrusions, material properties were determined (Tables I and II).

In spite of the different chemical compositions of both of the polymers, processing characteristics induced by multiple extrusion were found very similar. The presence

<table>
<thead>
<tr>
<th>Table I</th>
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<tr>
<td>--------------------------------</td>
</tr>
<tr>
<td>0. extrusion</td>
</tr>
<tr>
<td>1(^{st}) extrusion</td>
</tr>
<tr>
<td>3(^{rd}) extrusion</td>
</tr>
<tr>
<td>5(^{th}) extrusion</td>
</tr>
</tbody>
</table>
of ethylene units in ICPP did not exhibit any special impact on melt behaviour, so that as to the melt rheology, one could conclude that both the materials behaved similarly. Higher levels of colour development in ICPP may be accounted for to the phenol conversion, favoured by a higher level of oxygen dissolved in its amorphous phase. The presence of oxygen and phenol consumption are also likely responsible for faster OIT drop in ICPP. Regardless to their absolute values, OIT changes also indicate that the stabilizer system is faster consumed in ICPP.

More intensive changes in ICPP macromolecules are indicated by GPC data. It shows that average number molecular weight Mn drops due to multiple extrusion by 21 % rel. in ICPP and only about 8 % rel. in PPH (Tables III and IV).

Table III
Molecular weight distribution of ICPP after multiple extrusion at 260 °C

<table>
<thead>
<tr>
<th>PP-impact copolymer</th>
<th>(M_n) (\times 10^3)</th>
<th>(M_w) (\times 10^3)</th>
<th>(M_z) (\times 10^3)</th>
<th>(M_w/M_n)</th>
<th>Intrinsic viscosity [mlg(^{-1}) (GPC)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0. extrusion</td>
<td>62</td>
<td>342</td>
<td>1,059</td>
<td>5.6</td>
<td>166.6</td>
</tr>
<tr>
<td>1st extrusion</td>
<td>49</td>
<td>262</td>
<td>708</td>
<td>5.4</td>
<td>135.6</td>
</tr>
</tbody>
</table>

Table IV
Molecular weight distribution of PPH after multiple extrusion at 260 °C

<table>
<thead>
<tr>
<th>PP-impact copolymer</th>
<th>(M_n) (\times 10^3)</th>
<th>(M_w) (\times 10^3)</th>
<th>(M_z) (\times 10^3)</th>
<th>(M_w/M_n)</th>
<th>Intrinsic viscosity [mlg(^{-1}) (GPC)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0. extrusion</td>
<td>51</td>
<td>314</td>
<td>986</td>
<td>6.2</td>
<td>158.4</td>
</tr>
<tr>
<td>1st extrusion</td>
<td>47</td>
<td>260</td>
<td>705</td>
<td>5.6</td>
<td>138.3</td>
</tr>
</tbody>
</table>

**Mechanical properties**

The changes in mechanical properties, as a consequence of processing, were monitored. It was found that in spite of relatively strong thermo-mechanical impact of multiple extrusion at 260 °C, tensile and flexural properties did not change substantially. Attained values, such as shown in Tables V and VI, more or less lie within the range of experimental error in the cases of both polymers.

Table V
Mechanical properties of ICPP after 0. and 5th extrusions at 260 °C

<table>
<thead>
<tr>
<th></th>
<th>0. extrusion</th>
<th>5th extrusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress at yield</td>
<td>29.9 ± 0.1</td>
<td>29.2 ± 0.1</td>
</tr>
<tr>
<td>Elongation at yield [%]</td>
<td>3.8 ± 0.1</td>
<td>3.9 ± 0.1</td>
</tr>
<tr>
<td>Elongation at break [%]</td>
<td>67.3 ± 23</td>
<td>56.3 ± 18</td>
</tr>
<tr>
<td>Flexural modulus [MPa]</td>
<td>1,671 ± 15</td>
<td>1,647 ± 19</td>
</tr>
<tr>
<td>Impact strength Charpy +23 °C [kJ m(^{-2})]</td>
<td>8.6 ± 0.3</td>
<td>7.0 ± 0.3</td>
</tr>
</tbody>
</table>

Table VI
Mechanical properties of PPH after 0. and 5th extrusions at 260 °C

<table>
<thead>
<tr>
<th></th>
<th>0. extrusion</th>
<th>5th extrusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress at yield</td>
<td>33.9 ± 0.4</td>
<td>34.2 ± 0.2</td>
</tr>
<tr>
<td>Elongation at yield [%]</td>
<td>7.5 ± 0.1</td>
<td>7.5 ± 0.1</td>
</tr>
<tr>
<td>Elongation at break [%]</td>
<td>101–&gt;335</td>
<td>101–&gt;335</td>
</tr>
<tr>
<td>Flexural modulus [MPa]</td>
<td>1,597 ± 24</td>
<td>1,566 ± 30</td>
</tr>
<tr>
<td>Impact strength Charpy +23 °C [kJ m(^{-2})]</td>
<td>3.6 ± 0.1</td>
<td>2.6 ± 0.3</td>
</tr>
</tbody>
</table>
However, the presence of rubbery (EPR) domains in ICPP causes that crack propagation rate is still fairly moderated and the loss of some portion of tie molecules is thus compensated. Then the relative drop in Charpy +23 °C values is rather moderate in ICPP.

Despite certain degradation changes, such as partial crosslinking, may also take place in EPR phase, their role as energy dissipaters is still not lost\(^8\). Hence, coming out of the above results it can be confirmed that as to mechanical properties, the negative consequences of processing degradation are less pronounced in ICPP than in PPH.

**Processing of Non-Stabilized ICPP**

In the previous part, commercial ICPP and its PPH reference were investigated. Both were stabilized. Since the stabilizer system moderates degradation and diminishes its consequences, another measurements were carried out with a non-additivated ICPP fluff. With respect to the absence of stabilization only three processing extrusions were adopted. Samples after 0. and 3\(^\text{rd}\) extrusion were tested.

Degradation of non-stabilized ICPP was found very intensive even after three extrusions at 260 °C, strong increase in melt-flow index was observed. The samples after 0. and 3\(^\text{rd}\) extrusion were subjected to successive extraction by organic solvents in order to separate individual polymer fractions and determine changes in their quantities as a consequence of processing.

As solvents, non-polar hydrocarbons with increasing boiling temperatures – n-hexane, n-heptane and n-octane were used according to scheme in Fig. 4. Polymers were dissolved in boiling solvent and precipitated from the solution at room temperature. Each solvent extracted different fraction of polymer. In this way, four fractions – hexane solubles (HEX-sol), heptane solubles (HEP-sol), octane solubles (OCT-sol) and octane insolubles (OCT-ins) were attained. Their composition, previously determined by NMR, FTIR and DSC techniques\(^9,10\) is shown in Table IX.

<table>
<thead>
<tr>
<th>Table VII</th>
<th>Melt-properties of non-stabilized ICPP after multiple extrusion at 260 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICPP fluff</td>
<td>MFI [dg min(^{-1})]</td>
</tr>
<tr>
<td>0. extrusion</td>
<td>6.0</td>
</tr>
<tr>
<td>1(^\text{st}) extrusion</td>
<td>20.1</td>
</tr>
<tr>
<td>3(^\text{rd}) extrusion</td>
<td>42.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table VIII</th>
<th>Molecular weight distribution of non-stabilized ICPP fluff after triple extrusion at 260 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP- impact copolymer</td>
<td>(M_n) [(\times 10^3)]</td>
</tr>
<tr>
<td>0. extrusion</td>
<td>46</td>
</tr>
<tr>
<td>3(^\text{rd}) extrusion</td>
<td>30</td>
</tr>
</tbody>
</table>

**Fig. 2.** Molecular weight distribution of PPH after multiple extrusion at 260 °C, (full line = 0.extrusion; shredded line = 5\(^\text{th}\) extrusion)

**Fig. 3.** Molecular weight distribution of non-stabilized ICPP fluff after triple extrusion (full line = 0. extrusion; shredded line = 5\(^\text{th}\) extrusion)

**Fig. 4.** Scheme of successive extractions of a non-stabilized ICPP

Considering the effect of processing on quantities of individual fractions it was found that hexane and heptane solubles mostly vary only within an experimental error and their quantities do not exhibit any impact processing.

Biggest changes due to processing took place in both octane fractions. Drop in octane insolubles indicates that the longest isotactic homopolymeric chains were reduced.
in molecular weight. Increase in octane solubles portion on the other hand provides information on the degree of solubility of the scission products. No increase in heptane solubles then confirms, that the scission products are only highly crystalline PP homopolymeric chains.

The solvent successive extraction thus provided evidence that in ICPP the biggest extent of degradation changes induced by processing took place in a PP homopolymeric phase.

### Conclusions

The above processing experiments have revealed, that despite higher extent of backbone scission taking place in ICPP, in terms of melt viscosity both polymers behaved in a similar way. It can be concluded that both ICPP and PPH, tested under the same processing conditions and using the same stabilizer systems, exhibit the same processing stabilities.

In the solid state some differences were observed. While the tensile and flexural characteristics were not affected by processing at all, impact properties dropped down and indicated certain changes in polymer morphology. Although the biggest portion of degradation changes took place in the homopolymeric phases of both polymers, the presence of rubbery domains diminished their effect in ICPP. Due to the ability of moderating the crack propagation rate, EPR phase compensated the loss of some tie molecules and partly retained the impact resistance. Then it is evident that multiple extrusion caused relatively less harm in ICPP also in its solid state.

The results obtained in this work, together with the data of our previous experiments, step by step reveal the mechanism of ICPP processing degradation and allow us to learn where and in what extent degradation takes place.

The authors thank Jaroslav Kučera for mechanical tests and Radek Matuška for GPC measurements. Financial support from the Czech Grant Agency under project 104/07/1638 is greatly appreciated.

### REFERENCES


### Table IX

Overview of fractions available by successive solvents extractions from ICPP matrix\(^9,10\)

<table>
<thead>
<tr>
<th>Fraction</th>
<th>PE-homo</th>
<th>PE-homo</th>
<th>PP-atactic</th>
<th>PP-isotactic</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEX-sol</td>
<td>•</td>
<td>XX</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>HEP-sol</td>
<td>x</td>
<td>x</td>
<td>XX</td>
<td></td>
</tr>
<tr>
<td>OCT-sol</td>
<td>•</td>
<td></td>
<td>XX</td>
<td></td>
</tr>
<tr>
<td>OCT-ins</td>
<td></td>
<td></td>
<td>XX</td>
<td></td>
</tr>
</tbody>
</table>

XX – prevailing, X – much, x – little, • – nearly nothing


L10 POLYMER SEMICONDUCTORS FOR FUTURE MOLECULAR ELECTRONIC DEVICES

MARTIN WEITER and MARTIN VALA
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Introduction

Polymer semiconductors are poised as never before to transform the world of circuit and display technology. After more than 20 years of academic and industrial research worldwide the conjugated polymers has reached a very high level of outstanding material properties that are particularly attractive for the electronic industry. There are many potential applications including light-emitting devices, photovoltaic solar cells, plastic field-effect transistors, non-linear optical devices. Major electronics firms such as Sony, Philips, Samsung, Siemens and Pioneer are now developing the low cost and sometimes surprisingly high performance organic electronic and optoelectronic devices. Large-scale multicolor displays together with flexible active matrix of organic thin film transistors (OTFT) are now commercially available. Functional polymers are applied even in the logical circuits, which give rise to a new branch – “Plastic Logic”.

For this to become a reality, an intensive research has to be done. The first highly conducting organic polymer, chemically doped polyacetylene, was reported in 1977. Although initially these doped conducting polymers were unstable in air, brittle, and difficult to process, new generations of these materials are stable and easily processable from a wide variety of solvents. The electrical conductivities now range from those typical for insulators (<10^-10 S cm^-1), to those typical of semiconductors such as silicon (~10^-5 S cm^-1), to those greater than 10^4 S cm^-1 (nearly that of copper, 5×10^4 S cm^-1). At the end of the 1980s poly(phenylenevinylene) (PPV) has been one of the most studied polymers. This intense research led to the discovery of the polymer-based light emitting diode (LED) in 1990 by the Cambridge group in England. At the same period the high-performance electroluminescent devices made of multilayer of vacuum-sublimed dye films at Eastman Kodak, field-effect transistors made from polythiophene and from small conjugated oligomers were demonstrated. This was a breakthrough improvement since it made it possible to combine the good mechanical and processing properties of polymers with semiconducting behavior (providing processibility under well established techniques, such as spin or dip coating). From that time, wide range of semiconducting polymers is now commercially available from different suppliers, for different quantities and qualities.

In spite of great progress that has been made, there is still much to be understood about the underlying science that controls the properties of the organic electronic devices. Organic materials have often proved to be unstable and when exposed to air, water, or ultraviolet light, their electronic properties can degrade rapidly. Making reliable electrical contacts to organic thin films is difficult and the metal-polymer interface is a matter of intensive study. The low carrier mobilities characteristic of organic materials obviates their use in high-frequency (greater than 10 MHz) applications. These shortcomings are compounded by the difficulty of both purifying and doping the materials. Finally, in many types of organic semiconductors, the processes connected with the photogeneration and transport of charge carriers under the influence to electric field are still not well understood and are open to conjecture. The better understanding of these basic phenomena can enhance speed and efficiency of organic electronic devices, which is the fundamental motivation of our work.

Organic photovoltaics currently lag behind the inorganic one because of low solar energy conversion efficiency about 1–6%. It is well known that photodissociation can be highly efficient in two component donor-acceptor systems, as evidenced by the photovoltaic response of several systems. To improve the efficiency, the combination of photoconducting polymer substrates and quest materials such as fullerenes were employed, nevertheless the experimental results published by different authors are diverse. In order to enter an electrode the photogenerated charges have to move over the bulk of the solar cell and overcome the potential barrier in electrode region. On molecular level the charge transport can be affected by introducing the guest molecules, whose energy levels are in general different from the energy levels of the host. The transport of charges is affected by recombination during the journey to the electrodes – particularly if the same material serves as transport medium for both electron and holes. Also, interaction with atoms or other charges may slow down the travel speed and thereby limit the current. It is often observed that the distribution in the length of the conjugated segments caused by kinks or chemical defects increases disorder in conjugated polymers as compared to their oligomeric counterparts or other small molecules. Thus, in organic photovoltaic devices based on the combination of additives and polymer substrates the interaction between the moving charges and the additives seems to be a crucial process affecting the efficiency of photovoltaic conversion. Therefore, the aim of our study was to describe the influence of charge traps induced by additives on the efficiency of charge carrier transport.

Experimental

Polymer devices were manufactured as a sandwich cell with a dielectric multilayer. Samples consisted of transparent indium tin oxide (ITO) electrode on a glass substrate on to which the 15 nm thin layer of poly(2,3-dihydrothieno-1,4-dioxin) (PEDOT) was spin cast from water solution to decrease the injection barrier for holes. Then, the active polymer layer, typically 150 nm thick, was spin coated from chloroform solutions of MDMO-PPV (Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] ) with 0/30 % wt. of spiropyran 6-nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] (SP). To decrease the contact injection
barrier for electrons a thin 10 nm layer of Alq3 (8-hydroxyquinoline, aluminium salt) was vacuum evaporated and the structure was completed by evaporating of aluminium top electrode 100 nm thick. Average device area was 3 mm².

The photochromic reaction of SP was activated using a Xenon lamp with band filter (360 ± 20) nm. In our previous work it has been shown that after photochromic conversion the charge traps are created in the vicinity of a polymer chain and charge carrier mobility decreases which lead to to the current decrease. The electric response of the samples on the spiropyran photoswitching was studied by measuring the current-voltage (I-V) characteristics of the samples by Keithley 6517A electrometer.

Results

The photoswitching of polymer conductivity and photoconductivity was studied by standard current-voltage j(V) measurement. The results for typical devices are shown as log-log plot in Fig. 1. The variation of the dark current before and after photochromic conversion is depicted by dark symbols, whereas the variation of the photocurrent during irradiation of the sample with halogen lamp with cut off UV filter (< 420 nm) is shown by white symbols. In organic thin film devices the current is typically contact limited in low field region, whereas at higher field region space-charge or charge-trap limited conductivity are commonly accepted. The results show this behavior. At low forward-bias voltages below 10 V the increase of j with V is relatively small, whereas in the higher field region the slope of the dependence is more pronounced, which is in accordance with Space-charge limited current (SCLC) theory. This theory proposes that the space charge which limits conduction is stored in the traps. In the case of energetically discrete trapping level, the SCL current can be expressed as

\[
j_{SCL} = \frac{9}{8} \varepsilon \varepsilon_0 \mu \theta \frac{V^2}{L^3},
\]

where \( \varepsilon \) and \( \varepsilon_0 \) is the relative permittivity and permittivity of vacuum, \( \mu \) is the charge carrier mobility, \( V \) is the applied voltage, \( L \) is the electrode distance and \( \theta \) is the ratio of free to total charge carriers.

However, in cases of practical interest traps are usually distributed in energy. In that case traps will be filled from the bottom to the top of the distribution as applied electric field increases. This is equivalent to an upward-shift in the quasi-Fermi level with electric field. As a consequence, \( \theta \) increases with electric field and the j(V) characteristics becomes steeper. In terms of present work, the distribution of charge traps describes those induced by spiropyran to merocyanine photochromic conversion. The presence of distribution of traps opens additional pathways to the relaxation of charge carriers towards steeper states. A zero order analytic description of the effect can be based on the Hoesterey and Letson formalism. The latter is premised on the argument that the carrier mobility in a system with relative trap concentration \( c \) is the product of the mobility in the trap-free system \( \mu_0 \) multiplied by trapping factor:

\[
\mu(c) = \mu_0 \left[ 1 + c \exp \left( \frac{E_t}{kT} \right) \right]^{-1},
\]

where \( E_t \) is the energy of trapping level, \( k \) is the Boltzmann constant and \( T \) is the temperature. Consequently, the current flowing in a sample with enhanced number of trap states will be less than in sample without traps.

The surprisingly large increase of the photocurrent after the photochromic conversion can be explained by the charge transfer mechanism and by the presence of polar merocyanine molecules. This phenomenon indicates that there is a high tendency for charge separation as well as good ability to retain charges once induced by electric field. However the elucidated the detailed mechanism of the photogeneration, a detailed studies of exciton generation, charge separation and following transport should be done.

Conclusions

The utilization of organic semiconductors in electronic and optical devices was described. The new molecular device based on photoswitching of polymer conductivity and photoconductivity was demonstrated. The experimental behavior of the system explored by means of SCLC method showed
a change of the density of states in the bandgap of the polymer. Reversible creation of new trapping level during the photochromic conversion was observed. According to the trap controlled hopping model for the description of charge transport, the presence of new trapping level results in the decrease of the charge carrier mobility as predicted by the theoretical calculations.

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REFERENCES


L11 MOLECULAR MODELING OF MATERIALS WITH NETWORK STRUCTURE

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Introduction
Numerous different polymeric materials are from structural point of view macromolecular networks. Network-like polymers can have various forms, such as gels, rubbers and glasses. Their properties depend on microscopic properties such as crosslink density, chemical composition. Variability of behaviors is caused by different theoretical principles influencing their properties. Deformation properties can be as a consequence either of intermolecular interactions or of the change of combinational entropy.

Macromolecular networks are known for a long time. First theories were proposed by Flory, Kuhn and Grun1, and James and Guth2. In the 70s as a consequence of the single chain elasticity model proposed by Treloar3

\[ \sigma = \frac{1}{3} E \sqrt{N} L^{-1} \left( \frac{\lambda}{\sqrt{N}} \right), \]  

(1)

where E was Young modulus; N – number of segments of the chain; \( \lambda \) – draw ratio (elongation) of the chain and \( L^{-1} \) was the inverse Langevin function.

Since the development of this theory, have been many refinements and extensions, such as the model of 8 chains cell proposed by Arruda and Boyce4 which approaches to the real behavior of rubbery networks. The main results about rubbery networks were summarized on a large review work by Puso5. In the first work of Termonia6, was the single chain elasticity theory was successfully applied to the prediction of spider silk elasticity. However, the simple network is not realistic. Therefore the models should reflect real structure of the networks.

Second principle of polymer loading is acting of intermolecular interactions7. The interactions can be either bonding or nonbonding. During the deformation, the bonds and the nonbonding pairs are shifted from their equilibrium positions. The exact molecular theories were introduced by Lennard Jones potential. This is a model of potential where the atoms approaching each to other are subjected to strong repulsive interaction whereas in the long distance are not interacting. The distance of such potential is a function of interatomic distance:

\[ U = 4\varepsilon \left( \frac{r_{12}^0}{r_{12}} \right)^6 + \left( \frac{r_{12}^0}{r_{12}} \right)^{12}, \]  

(2)

where \( \varepsilon \) is energy of nonbonding interaction and \( r_{12}^0 \) is distance where the energy is zero.

Intermolecular interaction is mostly used in the Molecular Dynamics and Molecular Mechanics. These two techniques are used to investigation of molecular theories. The molecular mechanics is to find the optimum atomic positions in the molecule. Molecular dynamics is based on solution of Newton equations. It enables to describe effects hanging together with molecular motion such as effect of temperature and pressure. Task of molecular dynamics simulation can be defined in the box with periodic boundary conditions.

Position restraints are the functions that can fix the nod at one certain position.

Experimental
The simulation consisted of three phases: (i) system building, (ii) simulations, and (iii) calculation of material properties.

Building of Rigid Networks
The material was considered a network composed of macromolecular chain. The chains were composed of atoms and atomic groups. The atomic groups were coupled together according to their connectivity. Building of network was made by in-house builder. Input properties of the builders were crosslink density and the density of material. The results of the builder were coordinates of atoms and topology of groups. The material is represented by representative sample volume (RSV). The RSV was a cubic box.

Deformation of Network
The cubic box was deformed and the position restraints were set to the model. The position restraints were introduced to topology and applied to boundary atoms. Two types of deformation were applied. Tensile deformation was applied to one boundary in perpendicular direction to plane of box side. The shape in other axes was compressed. The second was shear deformation applied to the boundary atoms. It was applied in parallel direction to the boundary plane of cubic box.

Optimization of structure and calculation of potential energy was applied by GROMACS software. Input properties were coordinates of atomic groups and topologies of atoms. The result was a potential energy calculated for each deformed state. The potential energy density was considered a function of deformation tensor.

\[ u = f(\varepsilon) \]

(3)

Calculation of Material Properties
Important material properties are Young Modulus and Poisson ratio. The tensile curve was calculated as a gradient of equation (1).

\[ \sigma(\varepsilon) = \text{grad}(u) = \left( \frac{\partial u}{\partial \varepsilon_{xx}}, \frac{\partial u}{\partial \varepsilon_{yy}}, \frac{\partial u}{\partial \varepsilon_{zz}}, \frac{\partial u}{\partial \varepsilon_{xy}}, \frac{\partial u}{\partial \varepsilon_{yz}}, \frac{\partial u}{\partial \varepsilon_{zx}} \right) \]

(4)
Material described here was isotropic; therefore, the deformation was performed only in one axis. The Young modulus was considered a derivative of the tensile curve.

\[ E = \left( \frac{d\sigma}{d\varepsilon} \right)_{\lim \varepsilon \to 0} \]  \hspace{1cm} (5)

Poisson ratio was calculated from shear modulus (\(\mu\)) and tensile modulus.

\[ \nu = \frac{E}{2\mu} - 1 \]  \hspace{1cm} (6)

Rubbery Networks

The polymer material was considered affine rubbery network. It was composed by tetra-functional affine nods and freely joined chains with both fixed ends. The deformation of single chain was calculated from Treloar equation.

The input properties of the model were crosslink density and number of segments between two nods. The network was built and deformed. The result of the software was a tensile curve. Young modulus of rubbery network was calculated from tensile curve. Poisson ratio for rubbery network is from theory 0.5 as the networks are incompressible.

Results

Three types of macromolecular network of crosslink density were built. All the networks were composed of carbon or hydrocarbon groups and they differed in crosslink density. The set of materials was composed of one example of sparse network (vulcanized rubber), one example of dense network (ebonite) and one example of the crystalline structure (diamond).

First was a rubbery network where the distances between crosslinks were too long. There was presumed rubbery behavior of network. Example of predictive power can be shown on example of vulcanized natural rubber. Network model was applied to the measured data from literature. The recipe of natural rubber contained 1.96 % sulfur. Theoretical crosslink density considering only the disulfide bridges was 337 mol m\(^{-3}\). Tensile curve is shown in Fig. 1. The modulus was higher than measured modulus. The measured experimentally crosslink density was 91 mol m\(^{-3}\). It can be caused by two reasons. First, not all the sulfur will participate on reaction. The disulfide bridge is only a model crosslink. In reality, the crosslinks are poly-sulfide bridges.

In the ebonite, crosslink density was calculated from composition. The average fraction of sulfur in ebonite is 30 weight percent. Considering that two atoms of sulfur form a tetrafuctional nods are connected by connected 6 freely joined segments. Taking density 1.3 g cm\(^{-3}\) we get 0.006 crosslinks cm\(^{-3}\). That means 0.012 elastically active chains. The volume of nods was negligible. The chain with 6 segments cannot be considered a statistical chain. Therefore the rubber elasticity of such network was not calculated. The potential as a function of deformation is shown in Fig. 2.

The tensile curve was calculated from the potential energy density of ebonite network. The stress strain characteristics was calculated as a gradient of function of energy density. Function of stress on relative elongation is shown in Fig. 3.

All the stress-strain functions were applied to calculation of material properties. As the method was not sensitive to shear deformation, the poisson ratio could not be calculated. The Young modulus was calculated and compared to experimental data in Table I.

The vulcanized rubber properties are driven by entropic interaction whereas the ebonite and diamond were influenced by intermolecular interactions.

In the rubbery material, the modulus calculated from theoretical crosslink density is higher than experimental modulus. The modulus calculated from experimental crosslink density is lower than the experimental modulus. The model network even with experimental crosslink density is not yet realistic description of structure. It was negligible the volume
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Fig. 3. Stress-strain function of model material ebonite calculated from intermolecular interaction

of crosslinks, that will act as increase of Young modulus. Moreover, the model and material showed different elongation at break. It shows that there could be some unstable crosslinks such as two macromolecular chains coupled with weak interaction. These nods can disappear and re-appear during the tabnsile test.

The calculated modulus of ebonite and diamond was lower than experimental. It can be caused by not exact structure of both models and non exact force fields. The ebonite had model density 0.5 g mol\(^{-1}\) whereas the real density was 1.4 g mol\(^{-1}\). Also the diamond had density 11 g mol\(^{-1}\) whereas experimental density of diamond was 3.45 g mol\(^{-1}\).

Conclusions

Macromolecular networks show different deformation behavior even if they have composition. It is caused by different principles of their deformation. Loading of materials can be caused by rubber elasticity or by intermolecular interactions.

The vulcanized rubber, ebonite and diamond are material based on carbon structures. The vulcanized rubber is a sparse network, ebonite is a dense network and diamond is a regular lattice. Their deformation properties were calculated: vulcanized rubber from rubber elasticity theory, ebonite and diamond by molecular mechanics. The calculated values were lower than the experimental data. The densities were different form experimental densities of material. It is necessary to approach the structural properties to real structure of materials.

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REFERENCES
8.2. Posters

P01 PHYSICO-CHEMICAL PROPERTIES OF FUNCTIONALIZED TEMPERATURE-SENSITIVE BIOMATERN JANIČÁŘ, MUDRÁKOVÁ, JANČÁŘ, AND MARTIN CHYTLIK, MILOS VÁVROVÁ, and JAN ČEPÍK

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Introduction

Copolymers of poly(lactic acid), poly(glycolic acid) and poly(ethylene glycol) (PLGA-PEG) are presenting interesting features, such as biodegradability, no toxicity and thermal induced sol-gel transition, for their potential use in tissue engineering and controlled drug delivery. The aqueous solution of the copolymer is free flowing sol at room temperature and becomes a non flowing gel at body temperature.

Various architectures of PLGA copolymers with PEG were studied in the past few years and they have been also modified with different kinds of crosslinkers. The goal of this work is to discover the possibilities of synthesis of PLGA-PEG copolymer and its modification with itaconic anhydride (ITA) in order to prepare crosslinkable macromonomer for the use in tissue engineering and bone repair. ITA is obtainable from natural resources and was recently used for functionalization of poly(ε-caprolactone).

Experimental

Raw Materials

Poly(ethylene glycol), (PEG, M<sub>n</sub> = 1,500, Aldrich, Germany), D,L-lactide and glycolide (DLLA, GA, 99.9%, Polysciences, U.S.A.), stannous 2-ethylhexanoate, (95%, Aldrich, Germany), itaconic anhydride (ITA, 97%, Aldrich, Germany). All chemicals were used as received.

Synthesis

The PLGA-PEG triblock copolymer (see Fig. 1.) was prepared via ring opening cationic polymerization of DLLA and GA in a bulk using the PEG as initiator and stannous 2-ethylhexanoate as catalyst under inert atmosphere. PLGA-PEG product was modified by ITA in the bulk under inert atmosphere.

Characterization

The molecular weight and the molecular weight distribution (PDI) was determined by gel permeation chromatography (GPC) using Agilent technologies 1100 Series GPC with RI detector at the temperature of 30 °C in tetrahydrofurane mobile phase.

The product structure was studied by means of Fourier transformed infra-red spectroscopy on Nicolet Impact 400D FTIR spectrometer using KBr pellets. Proton nuclear magnetic resonance spectra (1H NMR) analysis was performed on the Bruker 500 MHz nmR spectrometer, when 20 mg of copolymer sample were dissolved in 1 ml of CDCl3.

Thermal analyses (TA) of copolymer sample were made using TA Instruments TGA Q500 machine for thermogravimetric analysis (TGA), temp. ramp of 10 °C min<sup>−1</sup> from 40 °C to 600 °C under 25 ml min<sup>−1</sup> nitrogen purge and also by means of TA Instruments DSC Q200 machine for differential scanning calorimetry (DSC), temp. ramp of 3 °C min<sup>−1</sup> from −90 °C to 200 °C under 50 ml min<sup>−1</sup> nitrogen purge.

Sol-Gel Transition Assessment

The sol-gel transition was determined by the test tube inverting method (TTIM) in the temp. ramp from 24 °C to 50 °C by the 1 °C 10 min<sup>−1</sup> rate in a water bath. Samples of copolymers were dissolved in the vials in the concentration step of 2% wt. from 2% wt. to 24% wt. The transition temperatures were determined according to a flow (sol)/no flow (gel) criterion.

Moreover, rheology was used for the sol-gel transition determination. Samples of copolymers were dissolved in the vials at the concentrations of 15, 20 and 25% wt. and measured by the TA Instruments AR-G2 rheometer equipped with plate-plate geometry using 25 mm standard steel parallel plate and 1,000 μm gap. Measurements were proceeded at the temp. ramp step tests of 0.5 °C min<sup>−1</sup> rate from 15 to 60 °C under oscillation stress of 0.40 Pa and angular frequency of 1 rad s<sup>−1</sup>.

Results

Polymer Characterization

The GPC analyses of PLGA-PEG (M<sub>n</sub> = 4 861; M<sub>w</sub> = 6 392; PDI = 1.32) and PLGA-PEG/ITA (M<sub>n</sub> = 4 989; M<sub>w</sub> = 6 663; PDI = 1.34) showed very similar values of molecular weight and molecular weight distribution (PDI) before and after the functionalization by ITA indicating no side reactions within functionalization process. The 1H nmr spectroscopy proved the incorporation of itaconic acid to the end of polymer through the characteristic peaks of lactic acid (O−(CH<sub>2</sub>CHO) protons (δ = 1.5–1.75 ppm) and (O−(CH<sub>2</sub>CHO) protons (δ = 5.1–5.35 ppm), glycolic acid (OCH<sub>2</sub>O) protons (δ = 4.6–4.95 ppm), backbone PEG (OCH<sub>2</sub>CH<sub>2</sub>O) protons (δ = 3.55–3.8 ppm) and itaconic acid double bond (OC(CH)<sub>2</sub>CCH<sub>2</sub>COOH) protons (δ = 5.7–5.8 ppm and δ = 6.35–6.5 ppm).

Fig. 1. PLGA-PEG-PLGA/ITA macromonomer structure
Ftir spectroscopy analysis showed characteristic ester, \( \text{C=O} \), acidic and alkyl bands. The spectra are presented on Fig. 2.

### Thermal Analysis

Thermal degradation of copolymers proceeds in two steps, the first is ascribed to PLGa blocks, the second to PEG chain, as it is described in the literature. Indistinctive degradation step around 110 °C by the PLGA-PEG/ITA copolymer can be assigned to the ITA groups. ITA itself tends to degrade from 90–110 °C which has a conclusion for further modification conditions. The thermograms are shown in Fig. 3.

DSC analysis showed a broad glass transition peak in temperatures from −65 °C to 0 °C with inflexes at −14.9 °C and −23.9 °C for PLGA-PEG and PLGA-PEG/ITA copolymers, respectively.

### Sol-Gel Transition

Rheology showed two storage modulus (\( G' \)) peaks and tan δ valleys for PLGA-PEG copolymer sol, which are assigned to amber and white gel respectively, but one \( G' \) peak and tan δ valley for PLGA-PEG/ITA copolymer. Both TTIM and rheological analysis proved the uprise of amber gel state of both the copolymer sols in concentrations higher than 15 % wt. and temperatures from 35 °C to 45 °C. In higher temperatures, the gels turn white and then separate to suspension. The TTIM phase diagram and rheology charts are shown on Fig. 4 and Fig. 5.

### Conclusions

PLGA-PEG copolymer and PLGA-PEG/ITA macromonomer were synthesized successfully and characterized via FTIR, GPC and \(^1\)HNMRR. The molecular weight of both products is similar. The presence of ITA in the polymer chain caused decrease in temperature stability, glass transition temperature and critical gel temperature. Storage moduli of gels increase with concentration. TTIM results correspond with those obtained by rheology. Both gels exhibit suitable mechanical properties at the concentrations of 15 % wt. and higher for biomedical applications (bone adhesives).

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**Fig. 2.** FTIR spectra of copolymers

**Fig. 3.** TGA curves of copolymers, PEG and ITA

**Fig. 4.** Sol-gel phase diagram obtained by TTIM

**Fig. 5.** Rheology analysis of 20 % wt. copolymer sols
REFERENCES
**P02 PROPERTIES OF RECYCLED CARBON FIBERS**

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**Introduction**

Fibers in high performance composite materials are very expensive. For this reason it is suitable to interesting about recycling waste products from fabrication of composites and composite parts after its lifetime. We made some experiments to obtain reinforcing carbon fibers from waste products and we evaluated properties of this recycled fibers. These fibers can be suitable for next exploitation. In contribution we demonstrate products of recycling and its properties. In Aeronautical Research and Test Institute, Prague are developed experimental test system for fibrous thermosetting composite breakdown. This system was designed and realized during 2006 in cooperation with the company Elektrické pece Svoboda, Světice near of Říčany. The base of the system consists of a thermal reactor, where under conditions of high temperatures and normal or inert atmosphere, decomposition of composite takes place. The results of process are remaining fibrous or other reinforcement and gasified components of matrix, which are conducted into cooling and filtration parts. These parts enable to obtain additional components from material breakdown, depending on the type of material and processing technology. The whole system is fully programmable and variably adjustable as to temperature or inert media flow. Several restrictors, suck-in valves and flaps can also control the movement of gaseous products. The system also allows for monitoring of many parameters of the process, in particular the temperature inside of furnace inside of charge, temperature at cooler and filter unit outlets. Furthermore the mass decrement of the material processed and, gaseous products of breakdown are monitored, especially \( \text{O}_2, \text{CO}, \text{CO}_2, \text{H}_2, \text{NO}, \text{NO}_2, \text{SO}_2 \) or \( \text{C}_x\text{H}_y \) contents. Of course, it is possible to transmit measured values to PC for further analyses.

**Experimental**

On the Department of Textile materials, Faculty of textile engineering and Department of chemistry, Faculty of education, Technical university of Liberec are develop testing methods for evaluating of recycled high performance fibers. We made analysis by the optical, gravimetric and SEM method; we realized tests of strength and wetting characteristics of these fibers.

**Results**

Fibers at standard temperature of recycling are much damaged. The standard temperature is temperature optimized for perfect decomposition of epoxy resin in composite. Ends of fibers are etched after oxidative treatment of air oxygen. In probe are much released microfibrils. Damaging after treatment on temperature below 50 °C on air is also obvious. Some ends of fibers appear as hollow fibers. On the surface are etch pits and released microfibrils. Surface of fibers after recycling at standard temperature minus 100 °C in nitrogen is smooth without remarkable contents.

Table I

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<th>Environ</th>
<th>Diameter [μm]</th>
<th>Yield [%]</th>
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<td>36</td>
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<tr>
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Table II

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Table III

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<td>102</td>
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<tr>
<td>st. –100 °C – ( \text{N}_2 )</td>
<td>2.04</td>
<td>1,731</td>
<td>105</td>
</tr>
<tr>
<td>virgin</td>
<td>1.53</td>
<td>990</td>
<td>91</td>
</tr>
</tbody>
</table>

Fig. 1. **SEM image of the most damaged fiber end**
damaging. On the surface of virgin fibers are fine striation advanced with structure of polyacrylonitrile precursor.

Conclusions

In this time we are trying to another way of recycling of carbon composites. We study surface properties of recycled fibers and hazard factors of carbon fiber dust. We searching possibilities of utilization of recycled carbon fibers no only for termoplastioc composites, but also for special purpose for example electric conductive paper and so on. We assume that recycling of composites will be in next time very significant.2–6

This work has been supported by Aerospace Research Center 1M0501 and Textile Research Center 1M0553 of Czech Ministry of Education.

REFERENCES
**HALOSILYL-SUBSTITUTED CYCLOPENTADIENYL TITANIUM COMPLEXES AS CATALYSTS FOR STYRENE SYNDIOSPECIFIC POLYMERISATION**

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**Introduction**

Syndiotactic polystyrene (s-PS) is an interesting material with a high melting point of 275 °C and a fast crystallization rate as compared with isotactic polymer. Its interesting properties which are similar to those of some more expensive engineering plastics are the reason for further scientific interest. In our previous work we reported the catalytic behaviour of novel half-sandwich titanium complexes in syndiotactic styrene polymerisation (see in Fig. 1). The variation of halosilyl substituent on cyclopentadienyl ligand affected both the catalytic activity and the properties of s-PS.

In this contribution a series of polymerisation runs was carried out in a time scale of 20–120 min in order to compare the activity dependence of examined complexes on reaction time and thus to better evaluate their polymerisation behaviour.

**Experimental**

All manipulations of air- and moisture-sensitive materials were carried out under nitrogen atmosphere, using either a dual vacuum/nitrogen line and standard Schlenk techniques or a high vacuum line. Methylaluminoxane (MAO) was purchased from Crompton GmbH (10 % wt. in toluene). Toluene (Lachema) was freshly distilled from sodium benzophenone ketyl prior to use. Styrene (Aldrich) was dried over calcium hydride and freshly distilled under vacuum prior to use. Investigated complexes and reference compounds CpTiCl3, Cp*TiCl3, [Si(CH3)2F2Cp]TiCl3 (F1), [Si(CH3)2F2Cp]TiCl3 (F2), [Si(CH3)2C1Cp]TiCl3 (C1), [Si(CH3)2C1Cp]TiCl3 (C2) were prepared according to the known procedure.

**Polymerisation and Polymer Characterisation**

Styrene polymerisations were carried out in a magnetically stirred (600 rpm min⁻¹) glass double-jacket reactor (100 ml) under nitrogen atmosphere. The reactor was successively charged by toluene (30 ml), styrene (0.0156 mol, 1.8 ml) and MAO. The MAO/Ti ratio of 800 was used for all polymerisation runs. Afterwards the reactor was thermostated at 50 °C and titanium complex in toluene (9 × 10⁻⁶ mol) was injected to initiate the polymerisation. After selected period of time (20–120 min) the reaction was quenched by adding 10 ml of sec-butyl alcohol. The resulting mixture was poured into acidic methanol (500 ml). The polymer was collected by filtration and dried under vacuo to constant weight. The reproducibility of obtained polymer yields was estimated to be ±10 %. Representative PS samples were extracted with boiling methyl ethyl ketone for 6 h to remove any atactic material. The syndiotactic polymer was determined as the amount of material insoluble in methyl ethyl ketone. 

¹³C nmr spectra were recorded on a 500 MHz Bruker Avance spectrometer operating at 125 MHz. The pulse angle was 83 °, pulse interval 20 s, decoupling Waltz 16. Melting points were measured with a Perkin-Elmer DSC–7.

**Results**

The catalytic behaviour of four titanium complexes with varying halosilyl substituent on Cp ligand and MAO for syndiospecific styrene polymerisation was investigated. Polymerisations were performed in toluene at 50 °C in the range of polymerisation time of 20–120 min.

The catalytic efficiency of complexes was evaluated according to the polymerisation activity, which is defined as a yield of PS per mol of titanium and per 1 h of polymerisation (see in Fig. 2). The activity of all studied complexes was dependent on the polymerisation time. A maximum activity was reached after a short induction period of about 20 min whereafter the activity decreased. The decrease could be attributed to the deactivation of the active species or to the occlusion of part of the catalyst in the precipitating polystyrene.

The average catalytic activity decreased in the order F1 > F2 > C1 > C2. Such decrease of activities may result from an increase of steric bulk of halosilyl substituent hindering the monomer coordination to active species. The highest activity was 207 kgPS mol⁻¹Ti⁻¹ h⁻¹ using [Si(CH3)2F2Cp]TiCl3 (F1)/MAO catalytic system.

Further the polymerisations catalyzed by well known complexes CpTiCl3 and Cp*TiCl3 (Cp* = C5Me5) and MAO were carried out under identical experimental conditions. Complex CpTiCl3 in combination with MAO reached maximum polymerisation activity of 91 kgPS mol⁻¹Ti⁻¹ h⁻¹. However, the complex with Cp ligand, which is a stronger electron
donor and exerts a greater sterical hindrance, possessed a slightly lower maximum activity of 86 kgPS mol\(^{-1}\) h\(^{-1}\) at the same polymerisation conditions. In all cases halosilyl-substituted titanium complexes were more active than the reference CpTiCl\(_3\) and Cp\(^*\)TiCl\(_3\) compounds.

Polystyrenes prepared by examined substituted half-sandwich titanium complexes and MAO exhibited melting points in the range of 264–266 °C. Melting point of PS obtained by CpTiCl\(_3\)/MAO system was lower approximately by 10 °C. The percentages of fractions insoluble in boiling methyl ethyl ketone were in the range of 92–99.9 %. The syndiotacticy of PSs was not possible to be evaluated by means of \(^{13}\)C nmr namely because of the insolubility of highly syndiotactic fractions obtained after extraction procedure.

Conclusions

The introduction of halosilyl substituent onto Cp ligand of half-sandwich titanium complex affected both the catalytic activity and syndiotacticity of product. The catalytic acitivity on average decreased in the order F1 > F2 > C1 > C2.

This work has been supported by Project MSM0021630501.

REFERENCES

**P04 SYNTHESIS OF MODIFIED CUCURBIT[n]URILS**

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**Introduction**

Cucurbit[n]urils (cB[n], n = 5–10), a remarkably robust macrocyclic host molecule, have gained much attention in the new millennium for their exceptional molecular recognition ability. The pumpkin-shaped molecule has a hydrophobic cavity and two identical carbonyl-laced portals. While the hydrophobic interior provides a potential inclusion site for nonpolar molecules, the polar ureido carbonyl groups at the portals allow cB[6] to bind ions and molecules through charge-dipole and hydrogen bonding interactions. The unique structure and recognition properties make cB[n] attractive not only as a synthetic receptor but also as a building block for the construction of supramolecular architectures. Compared to the chemistry of cyclodextrins and calixarenes, however, that of cB[n] has developed slowly until recently, which may be attributed mainly to their poor solubility in common solvents and inability to functionalize these molecules. Our research is aimed to the synthesis, characterization, purification and separation of new functionalized cB[n].

**Experimental**

Generally modified cB[n] was synthesized from an acid-catalyzed condensation reaction of glycoluril or substituted glycoluril and formaldehyde (paraformaldehyde) or mixture of aldehydes.

The indirect method of functionalization of cB[n] involves acid-catalyzed self-assembly of an equimolar mixture of unsubstituted glycoluril (A) with two different aldehydes (B and C), the results of which would give cB[n] functionalized at the methylene bridges of cB[n] (Scheme 1).

![Scheme 1](image)

**Purification**

Isolation of mono-functionalized cB[6] from the crude mixture was a very tedious and time consuming job which took most of our research time. The primary purification was based on the preferential solubility or stepwise precipitation of variously substituted and unsubstituted cB[n] as well as other glycoluril oligomers. Water, methanol, acetone and 2-propanol were used to precipitate solids from the crude mixture. MALDI-TOF MS was used to determine molecular weight distributions of all collected fractions and the results were compared to select the most relatively pure fraction for further purification treatment. It was found that for some specifically substituted CB[n] 0.1M NaOH can selectively extract monosubstituted and unsubstituted CB[6] from di- and tri-substituted CB[6] and other minor components. Dilute aqueous HCl (for example 7% or 21%) solution was also used in the combination with the basic medium. Component enriched with the monosubstituted CB[6], was subjected further purification on the strong acid cation exchange resin. As a solvent system mixture of HCl and HCOOH was used and numerous fractions were collected and analyzed by 1H-NMR. Please note that in no case completely pure monosubstituted CB[6] was obtained although MALDI spectrum in some case showed a single molecular ion peak for the corresponding component. This might be rationalized due to lack of optimization of chromatographic conditions such appropriate composition of mobile phase and right length of stationary bed. As stationary phase, we used DowEX50WX8(mesh no. 100–200) in one case and DowEX50WX2(mesh no 200–400, p.a) in other case.

**Characterization**

The purified sample was analyzed by 1H and 13C-NMR spectra using Bruker AVANCE 300 MHz and 75 MHz spectrometer respectively and molecular weight distribution was obtained on a MALDI-TOF mass spectrometer Reflex IV, Bruker Daltonics.

![Fig. 1. 1H nMR spectrum (300 MHz, D2O)](image)
C calendar mmr spectrum shows two C = O peaks at δ 156.66, and 157.49 ppm, one of which nicely indicates the formation of a second type of CB[6], that is, monomethylated CB[6]. The peak at δ 53.60 ppm indicates -CH3 substitution at the methylene bridge position.

MALDI-TOF MS spectrum shows that the purified sample contains mixture of monosubstituted CB[6] (m/z 1,127.5 as complexed with hexamethylenediamine (HMDA) as well as unsubstituted CB[6] (m/z 1,113.5 as complexed with HMDA) as major product. HMDA was used to improve the sample solubility.

Conclusion and Perspectives

Though the parent molecule CB[6] is a century old, the chemistry of the CB family seems beginning to blossom. The recent developments, including the synthesis of CB homologues and derivatives, have brought dynamism to CB chemistry, as witnessed from the increasing interest in various interdisciplinary application fields such as artificial ion channels, vesicles, stationary phases in chromatography, ISEs, polymers, nanomaterials, and many others for the last several years. In this poster we have demonstrated a new one pot synthetic method for the preparation of new functionalized CB[n] derivatives. As the yield and purity of compound is not yet satisfactory more time is still required to optimize the purification method.

The authors are grateful to the Grant Agency of the Czech Republic for providing financial support (grant 203/07/P382) for this research work.

REFERENCES

Determination of Color Transition Temperature for Processing of Thermochromic Polymeric Materials

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Introduction

Thermochromic behaviour means a reversible colour change with temperature change and it has been observed for a variety of compounds with temperature variation. A more precise definition has been given by Day: “Thermochromism is defined operationally as an easily noticeable reversible colour change in the temperature range limited by the boiling point of each liquid, the boiling point of the solvent in the case of solution or the melting point for solids.” While Day’s definition is applicable for majority of inorganic and organic substances, we can use the term thermochromic also in important technical fields, which demands another external impulse together with temperature of the observed colour change (e.g. thermochromic pigments).

Thermochromic dispersions are manufactured for use in aqueous ink and coating systems, but can be applied in dried encapsulated form also into polymeric materials such as polyolefines. As the temperature rises, they change from coloured form to colourless one. They get back their coloured state when the temperature is decreased again. Colour change induced by thermochromism occurs when certain temperature of thermochromic transition is reached. This transition temperature varies for different thermochromic compounds. Colour change is usually slow process; hence it can appear to occur in some temperature range. There can be observed a kind of thermal hysteresis, which means that the temperature needed to regain its former colour is significantly less than the temperature needed to obtain required colour change.

There are two components in thermochromic dispersion systems: a solvent and a colorant. If the temperature is below the melting point of the solvent, these two parts stick together and the system is coloured because of the electron interaction. But if we increase the temperature of the system and this temperature reaches the melting point of the solvent, these two parts separate resulting in decolorization of the system (see Fig. 1.).

Fig. 1. Principle of colour change in thermochromic dispersions

Experimental

Experimental part is based on the usage of the thermochromic granules of ThermChrom BG, VB, OY containing about 20% of thermochromic compound in polypropylene matrix. Temperatures used in the polymer processing could be relatively high (from 200 to 260 °C) so it was essential to find out how the thermochromic compounds respond to exposure to temperatures.

Determination of Thermochromic Transition Temperature

Determination of thermochromic transition temperature (TTT) needed to be stated for further processing with the thermochromic compounds. Sample of thermochromic material was fixed to the tip of the thermocouple. Thermocouple with the granule of pigment was placed into the beaker with distilled water. Magnetic stirrer was set to warm up distilled water to 37 °C. Colour of the thermochromic granule was observed using Gretag Macbeth SpectroScan. Process was repeated five times for each type of thermochromic pigment and average TTT value was calculated.

Determination of the Thermal Color Stability of Thermochromic Compound

First tests of thermal stability of color transition were done in drying oven Venticell, BMT, a.s. (200 °C, 230 °C and 260 °C) as Method 1. Tests served as preliminary ones because the ovens did not have the exact control of temperature. Deviation was ± 10 °C. One pellet of each sample of thermochromic material was heated at appropriate temperature for 5 minutes and pellet was left in the opened and turned-off drying oven to cool down slowly to the room temperature. There was a necessity of tempering the oven before placing samples in it, the tempering period was 20 minutes.

Other tests (by Method 2) were done using hot-air pistol Steinel HL2305LCD and a thermocouple for determination of the exact temperature of test. Hot-air pistol was placed on a stand by holders and under the pistol there was a basin made of tinfoil. Hot-air pistol was turned on and the temperature nearby tinfoil basin was measured by thermocouple. When the temperature reached desired value (either 260 °C, 280 °C), a granule of thermochromic material was placed into the basin. Pellets were placed into the basin separately (unlike heating in an oven) and were heated for 5 minutes.

Results

Determination of Thermochromic Transition Temperature

Samples were heated to pre-set temperature (37 °C) and they were observed during the whole process of heating. Tem-
perature was written down when the colour of the samples began to change. The colours of the samples returned to the initial ones after cooling samples down to room temperature. We can state that the thermochromic transition is reversible for these types of thermochromic compounds after testing at given temperatures.

Table I. shows the temperatures of thermochromic transition of samples used. The lowest TTT was measured for the sample VB and it was 29.6 °C, almost the same TTT was measured for sample GB –29.8 °C. The highest measured TTT was 30.6 °C of the sample OY.

Table I
Temperatures of thermochromic transition of thermochromic compounds

<table>
<thead>
<tr>
<th>ThermChrom Measurement number</th>
<th>BG</th>
<th>VB</th>
<th>OY</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>29.5</td>
<td>29.6</td>
<td>30.4</td>
</tr>
<tr>
<td>2</td>
<td>29.8</td>
<td>29.7</td>
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</tr>
<tr>
<td>5</td>
<td>29.9</td>
<td>29.6</td>
<td>30.7</td>
</tr>
<tr>
<td>Average TTT</td>
<td>29.8</td>
<td>29.6</td>
<td>30.6</td>
</tr>
</tbody>
</table>

Determination of the Thermal Color Stability of Thermochromic Compound

Samples were heated to 37 °C and sample colour was observed during the whole process of heating. Temperature was noted when the colour of the thermochromic material changed.

Table II shows the measured temperatures of thermochromic transitions for all three samples tested after the thermal conditioning. There is only slight difference between those temperatures for each sample at given temperature. For example TTT of sample BG varies only by 0.3 °C and this difference can be caused by measurement deviation. Generally were TTTS slowly decreased after melting of samples. After materials cooling down they all got into their beginning colours. Thermochromism was not lost by exposing thermochromic granules to the temperatures up to 260 °C.

Temperature of thermochromic transition has decreased by approximately 1.5 °C for the sample BG and 2 °C for the sample OY when heating up. The changes in TTT were almost the same no matter if we heated it to 200, 230, 260 or 280 °C.

Measured temperature of thermochromic transition for VB has not almost changed. The difference between all done measurements is 0.8 °C which can be neglected having in mind that the observation was only visual and on that account subjective. The fault of the measuring TTT of VB is also because the change in colour from violet to blue was not as obvious as when measurements were done with BG and OY.

Table II
Temperatures of thermochromic transition of thermochromic compounds after the test of thermal stability at 200 °C, 230 °C and 260 °C (by Method 1) and 260 °C, 280 °C (by Method 2)

<table>
<thead>
<tr>
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<th></th>
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</thead>
<tbody>
<tr>
<td>BG</td>
<td>1</td>
<td>28.3</td>
<td>28.5</td>
<td>28.5</td>
<td>28.4</td>
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</tr>
<tr>
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<td>28.6</td>
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<td>28.6</td>
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<td>Ø</td>
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<td>28.6</td>
<td>28.6</td>
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<tr>
<td>VB</td>
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<td>29.9</td>
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<td>29.4</td>
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</tr>
<tr>
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<td>Ø</td>
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<td>29.2</td>
<td>30.0</td>
<td>29.7</td>
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</tr>
<tr>
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<td>28.3</td>
<td>28.5</td>
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<td>28.5</td>
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</tbody>
</table>

Fig. 2. Comparison of TTT before and after the thermochromatic material tests of thermal stability
Conclusions
Preliminary tests were done with samples to see how they behave at increased temperature. All of them exhibited thermochromic colour transition at approximately 30 °C. Another set of tests was done to find out the ceiling temperature they can be exposed to. These tests of thermal stability were important because thermochromic compounds were intended to manufacture by processes where temperatures reach 260 °C. It was found out that ThermChrom BG and OY stand the temperatures up to 280 °C whereas ThermChrom VB is suitable for using at 260 °C at most. Tests of thermal stability proved the thermochromic compounds are suitable for processing without substantial TTT change by all common technology for plastics materials.

This work has been supported by grant Czech Ministry of Education MSM 0021630501.

REFERENCES
P06 POLYMER PHOTOELECTRONIC DEVICES
BASED ON INTERACTION BETWEEN 
\(\pi\)-CONJUGATED POLYMER MATRICES 
AND PHOTOCHROMIC MOLECULES

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Introduction

Nowadays, after more than 15 years of academic and industrial research worldwide, the class of organic materials, conjugated polymers has reached a very high level of outstanding material properties and the potential for different industrial applications is now emerging. Various polymers are used in organic light-emitting diodes (OLED) and flat organic displays equipped with organic field-effect transistors, some other expect applications including optical sensors are very close to industrial applications. Printing technology is currently enabling the production of these high-efficiency organic devices. Given the need for very low-cost circuits for everything from smart cards carrying personal information, to building entry cards, to inventory control, it is reasonable to assume that within 10 years, the square footage of organic circuitry might exceed that of silicon electronics, though one expects that silicon transistors would still vastly outnumber and outperform those fabricated from organic materials\(^1\).

Experimental

Polymer devices were manufactured as a sandwich cell with a dielectric layer of MDMO-PPV (Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]) containing 0–30 % wt. of admixed spiropyran (6-nitro-1',3',3',-trimethylspiro[2H-1-benzopyran-2,2'-indoline]). The device and material structure is depicted in Fig. 1. The active polymer layer was spin coated from chloroform solutions on transparent indium tin oxide (ITO) electrode covering part of the glass substrate. The thickness of the active layer was about 150 nm. The structure was completed by evaporation of aluminium top electrode. Average electrode area that delimitate the active area of the device was 3 mm\(^2\). The same solutions of active materials were spin cast on quartz substrates for optical measurements. The photochromic reaction of spiropyran was activated using a Xenon lamp with blue filter transmitting UV light 340 nm. Optical switching was studied using standard absorption and photoluminescence spectroscopy (PL) with excitation at 450 nm. The electric response was studied by measuring the current-voltage \(j(V)\) characteristics of the samples in the dark with Keithley 6517A electrometer. The measurements were performed in vacuum cryostat at room temperature.

Results

Optical Switching

Under irradiation of an appropriate light energy, the spiropyran exhibits photochromism as shown in Fig. 2 and Fig.3. The photochromic reaction is accompanied by a charge redistribution resulting in a significant increase of the dipole moment of the molecule. The studied spiropyrany (SP) is stable in its colourless closed ring isomeric form, while UV irradiation produces a metastable open ring isomer merocyanine (MC) absorbing at 550–600 nm. The maximum of absorption band of MDMO-PPV is situated at 450 nm, the addition of SP increases the absorption of the sample in the UV region as shown in Fig.3. After irradiation with UV light the spectra exhibit a significant absorption band at 590 nm caused by the colored merocyanine form. Annealing in dark or irradiation with a red light gradually restores the original spectrum, the change is fully reversible.

A strong photoluminescence (PL) quenching after the photochromic conversion caused by radiative energy transfer was observed as figured in Fig. 4. The stable form of spiropyran does not show any luminescence contrary to its MC form. MDMO-PPV show their own luminescence and creation of MC form via the photochromic reaction therefore could result in the photoluminescence bands decrease of the MDMO-PPV. However, MC possesses a high dipole moment which generally causes a quenching of luminescence. The quenching was found to be strong even in the case when the SP \(\rightarrow\) MC conversion was very weak, even not observable in absorption spectra. Furthermore the PL of MC could be triggered through the polymer excitation. This means that the energy absorbed by polymer (donor) is transferred to MC molecules (acceptor). According to the Forster-Dexter theory the dipole-dipole energy transfer probability is, among other, related to the overlap of donor emission and acceptor absorption. After the reverse (MC \(\rightarrow\) SP) reaction was com-

Fig. 1. Schematic structure the devices used for characterization

Fig. 2. Photochromic reaction of the spiropyran (SP) into (photo)merocyanine (MC) manifests itself as color change of the system
pleted, the polymer PL was recovered, the reversibility of the process was, however, influenced by photodegradation of the polymer matrix.

**Current-voltage Measurements**

The photoswitching of charge carrier mobility was studied by standard current-voltage $j(V)$ measurement. The results for typical devices are shown as log-log plot in Fig. 5. The current-voltage characteristics show a typical decrease of the current after the excitation of photochromic spiroparane. These prove that the presence of created polar MC molecules in the vicinity of a polymer chain modifies the distribution of on chain site energies. Thus the distribution of hopping transport states is broadened and charge carrier mobility decreases which lead to a decrease. These findings are in good agreement with our previous theoretical studies by means of quantum-chemistry calculations.

**Conclusions**

The experimental behaviour of the system explored by means of current-voltage characterization showed a significant decrease of the current thorough the sample after irradiation.

**REFERENCES**

P07 ANALYSIS OF THE WOOD SURFACE TREATED BY DIFUSE COPLANAR SURFACE BARRIER DISCHARGE TYPE ATMOSPHERIC PLASMA

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Introduction
DCSBD plasma sources proved their potential for surface treatment of wide spectrum of polymer materials\(^1\). The treatment of wood with atmospheric-pressure plasma offers at least three advantages: expensive vacuum equipment is not required, continuous in-line processing can be realised and processing times are short\(^3\).

Surface treatment of wooden materials by atmospheric coplanar barrier plasma discharge can improve homogeneity of wood surface, which has mostly unequal structure. Unequality comes from the fact, that wood surface contains spots with different affinity to water (hydrophobicity and hydrophilicity).

Changes of wood surface pH and composition of water extract influence the adhesion of urea-formaldehyde resins\(^4\). Therefore the study of plasma treatment effect for surface pH can contribute to the improvement of coating technology.

Experimental
Wood surface was treated by atmospheric plasma generated by diffuse coplanar surface barrier discharge (DCSBD) in air atmosphere. The plasma exposure time of wood surface was 5 s.

pH Measurement
Determination of surface pH of three wood species was performed according to standards (STN ISO 50 0374 and Tappi T 529 om-88). Measurement was carried out with electrode with flat head Sentek P17/BNC conected with Jenway 3510 pH-meter. Clean (dustless) wooden surface was air-conditioned for 24 hours at 23.5 °C and at 48.65 % of humidity prior the measurement. Wooden surface was during experimental can contribute to the improvement of coating technology.

Results
Table I
Surface pH of three wood species before and after the plasma treatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH value before plasma treatment</th>
<th>pH value after plasma treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce</td>
<td>6.23 ± 0.03</td>
<td>4.18 ± 0.03</td>
</tr>
<tr>
<td>Beech</td>
<td>5.77 ± 0.02</td>
<td>3.72 ± 0.03</td>
</tr>
<tr>
<td>Oak</td>
<td>4.74 ± 0.02</td>
<td>3.68 ± 0.03</td>
</tr>
</tbody>
</table>

Cold water extract was titrated with 0.01M solution of sodium hydroxide on phenolphthalein indicator. Amount of acid components was determined from sample surface treated in distance 0 mm, 0.39 mm, 0.65 mm up to 1.04 mm from plasma electrode.

Isotachophoretic Determination
Extraction time of cold water extract was 60 minutes. Wooden surface was in direct contact on plasma electrode surface (0 mm).

Electrophoretic analyser type EA 100 (Villa, SK) was applied for electrophoretic determination of carboxylic acids, which is given for capillary isotachophoresis (ITP). Standards of formic acid, acetic acid, propionic acid and butyric acid were used for determination.

Composition of electrolytes: 5 mol m\(^{-3}\) MES (Morpholineethanesulphonate) + HIS (Histidine buffer), 10 mol m\(^{-3}\) HISCl (Histidine chloride buffer) + 10 mol m\(^{-3}\) HIS + 0.1% MHEC (Methylhydroxyethylcellulose), pH = 6.

Total change of acid components concentration was determined by the acid-base titration. In this case was also measured dependence of concentration of acid content on distance between wood surface and surface of plasma electrode. The highest concentration of acid content was observed when surface of wood was in direct contact with plasma electrode. By increasing the distance between surface plasma electrode and surface of wood, concentration of acid content was falling down gradually (Table II).

Total acidity in comparison to untreated sample demonstrated the least increase (43 %) of acid components after the plasma treatment at spruce sample. The highest increase of acid components up to 95 % was achieved at oak wood, which surface was in direct contact with plasma electrode.
Value of increase of acid components in beech sample was similar to oak sample (94%). Value of acid components in the distance of 1.04 mm from surface of electrode was near to value of untreated sample (Table II, III).

Table II
Acid components concentration (c) of three wood species in air atmosphere in different distances of wood surface from surface of electrode (d)

<table>
<thead>
<tr>
<th>d [mm]</th>
<th>c Spruce [10⁴ mol dm⁻³]</th>
<th>c Beech [10⁴ mol dm⁻³]</th>
<th>c Oak [10⁴ mol dm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.3972</td>
<td>4.9259</td>
<td>6.9643</td>
</tr>
<tr>
<td>0.39</td>
<td>2.8876</td>
<td>3.7369</td>
<td>5.2657</td>
</tr>
<tr>
<td>0.65</td>
<td>2.5479</td>
<td>3.0575</td>
<td>4.5862</td>
</tr>
<tr>
<td>1.04</td>
<td>2.3780</td>
<td>2.7178</td>
<td>3.7369</td>
</tr>
</tbody>
</table>

Table III
Acid components concentration at wood samples before the plasma treatment (c)

<table>
<thead>
<tr>
<th>Sample</th>
<th>c [10⁴ mol dm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce</td>
<td>2.3780</td>
</tr>
<tr>
<td>Beech</td>
<td>2.5479</td>
</tr>
<tr>
<td>Oak</td>
<td>3.5671</td>
</tr>
</tbody>
</table>

By means of carboxylic acids standards (formic acid, acetic acid, propionic acid, butyric acid) we confirmed presence of these carboxylic acids in the samples of spruce, beech and oak. We found that plasma treatment caused increase of formic acid content. It was located at all measured wood samples against to untreated samples. The highest increase of formic acid concentration up to 56.2 % was achieved at oak sample (Table VI). Otherwise the least increase of this acid was measured at spruce sample where percentage of increase moved at level 11 % against to untreated sample (Table IV). Concentration of formic acid increased up to 39.2 % in the beech sample (Table V). On the other hand, concentration of acetic acid decreased after the plasma treatment at all wood species. The highest decrease was observed at spruce sample up to 49.7 % and the least decrease was measured at oak sample where concentration dropped to level 6.4 %. Concentration at oak sample dropped to 11.2 %.

The highest concentration among investigated acids had propionic acid but change of concentration influenced by the plasma treatment was in this case the least. It is only one acid which demonstrated both increase and decrease in dependence of wood species. Propionic acid concentration decreased by plasma treatment against to untreated sample (3.3 % and 7.2 %) at the spruce and oak sample. Concentration of propionic acid increased at oak sample up to 7.8 % against to untreated sample.

After the plasma treatment, decrease of concentration in case of butyric acid in all wood species as in case of acetic acid occurred. Concentration decreased up to 15.2 % at spruce sample, 23.8 % at beech sample and 27.2 % at oak sample.

Conclusions
Formic, acetic, propionic and butyric acid were in water extract before and after plasma treatment, but their concentration differed. As formic acid is out of the all above mentioned acids strongest one and it can be stated, that this acid contributes to the total acidity of wooden surface the most. The highest increase of formic acid concentration was found at oak wood (56 %). The lowest fall of concentration was found at propionic acid, which dropped down just about 3 % after the plasma treatment in comparison to untreated sample.

Extraction method allows semiquantitative determination of acids and relative comparison of plasma treated and plasma untreated samples. Therefore the data of acids concentrations relate only to the volume of water extract and to area of exposed surface of sample.

This work was financially supported by the Slovak Research and Development Agency, Project No. APVT–20-033004 “Study of atmospheric plasma surface treatment of solid wood materials”
REFERENCES
P08 STRATEGIES FOR ENHANCING POLY(3-HYDROXYBUTYRATE) PRODUCTION IN SELECTED BACTERIAL STRAINS

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Introduction
Polyhydroxyalkanoates (PHAs) are a group of hydroxyacid polyesters that are produced and accumulated in the form of intracellular granules by a wide variety of bacterial strains. These strains use PHA as carbon, energy and reducing power storage material. Of the big family of PHAs, a homopolymer of 3-hydroxybutyrate, poly(3-hydroxybutyrate) (PHB), is the most widespread in nature and the best characterised. PHB aroused much interest in industry and research thanks its biocompatible, biodegradable, thermoplastic and piezoelectric properties. PHB appears to find many potentional applications in medical, industrial and agricultural fields.

Generally, the main problem of PHB is high cost in comparison with traditional plastics from petrochemical routes. That is why strategies for enhancing PHB production are developed. Typical strategy, which is widely used for enhancing PHB production, is limitation with nitrogen, phosphorus or another element when excess amount of carbon source is present.

Among the factors restricting the economy of PHB production very important is the cost of carbon source. In PHB production, about 40% of the total cost is for raw materials. Cheap waste substrates, for instance cheese whey or waste potato starch, are very attractive from this point of view. Effective utilization of waste substrates should lead to reduction of PHB cost.

The positive influence of stress factors (such a peroxide stress, osmotic stress, ethanol stress or heavy metal stress) on accumulation of different secondary metabolites were reported. However, to this time only little is known about accumulation of PHA under exogenous stress condition.

The aim of this work was to compare different strategies that could enhance PHB production and reduce costs of PHB. Limitations with nitrogen and/or phosphorus source were tested. The influence of several exogenous stresses on PHB production was compared. Finally, production of PHB was studied in synthetic and organic medium as well as using cheese whey as a cheap waste substrate.

Experimental
Bacterial Strain
Cultivations were performed with culture Bacillus megaterium CCM 2037.

Cultivation Condition
Cultivations were carried out at 30°C under permanent shaking (150 rpm) in 100 ml of media. Several media were tested, as the first synthetic medium (SM) containing glucose as the only carbon source, KH₂PO₄ and Na₂HPO₄ (1:1) as the phosphorus source and (NH₄)₂SO₄ as the nitrogen source was used. SM was used for limitation experiments. Culture was transferred (centrifugation 20 min., 6,000 rpm) into limited medium (medium without nitrogen or/and phosphorus source) after 20 hours of growth on complete medium. After following 15 hours, biomass and PHB concentration were determined. SM was also used for stress experiments. The second tested medium was Bacillus medium (BM) containing peptone and beef extract. The last medium was cheese whey obtained from cheese manufactury Pribina Příbraslav. Thermal denaturation and sulphuric acid were used for precipitation and removing of whey proteins before cultivation. Whey was tested with and/or without addition of salts according to SM.

Analytical methods
Biomass concentration was analyzed spectrophotometrically at 630 nm after suitable dilution with distilled water. Relationship between absorbance A 630 nm and dry cell mass was evaluated. Before PHB determination biomass was lyophilized. Dryied cell material was hydrolyzed and derivatized in a mixture of 0.8 ml acidified methanol (15% v/v H₂SO₄) and 1 ml chlorofrom at 100°C for 140 min. Resulting methyl esters of 3-hydroxybutyric acids were determined using gas chromatography with MS or FID detection. Commercial PHB (Fluka) was used as the external standard.

Results
First, the effect of nitrogen and/or phosphorus source limitation was tested. All tested limitations led to enhancing PHB content in bacterial cell biomass in comparison with cultivation without limitation. However, it seems that for Bacillus megaterium limitation with nitrogen source is probably the best stimulating factor for PHB production (see Table I).

Table I
PHB production under limitation (35 hours)

<table>
<thead>
<tr>
<th>Limitation</th>
<th>PHB content [% dry weight]</th>
<th>PHB yield [g dm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without limitation</td>
<td>14.164 ± 1.248</td>
<td>0.234 ± 0.025</td>
</tr>
<tr>
<td>N limitation</td>
<td>24.035 ± 1.406</td>
<td>0.360 ± 0.029</td>
</tr>
<tr>
<td>P limitation</td>
<td>14.857 ± 0.826</td>
<td>0.177 ± 0.009</td>
</tr>
<tr>
<td>N + P limitation</td>
<td>17.648 ± 0.691</td>
<td>0.237 ± 0.018</td>
</tr>
</tbody>
</table>

Also some other tested exogenous stress factors influenced positively the productivity of culture in comparison with control. Ethanolic stress as well as Na₂SO₄ supported PHB accumulation.

Mainly ethanolic stress resulted in improving PHB production. This effect could be caused by the fact, that ethanol...
is metabolised via acetyl-coenzyme A, which is starting metabolite for PHB production. It is not clear if enhanced PHB production was caused by ethanolic stress or by utilization of ethanol alone. Both factors could be involved. The culture could utilize ethanol with the aim to remove toxic substance from medium. Increase of acetyl-coenzyme A concentration led then to enhanced PHB accumulation.

**Table II**

<table>
<thead>
<tr>
<th>Stress Factor</th>
<th>Biomass [g dm⁻³]</th>
<th>PHB content [%]</th>
<th>PHB yield [g dm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂</td>
<td>0.047 ± 0.001</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.134 ± 0.039</td>
<td>6.864 ± 0.082</td>
<td>0.016 ± 0.001</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.812 ± 0.029</td>
<td>20.793 ± 0.358</td>
<td>0.377 ± 0.007</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>0.053 ± 0.000</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Citrate</td>
<td>1.739 ± 0.025</td>
<td>14.620 ± 0.054</td>
<td>0.254 ± 0.001</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>1.744 ± 0.050</td>
<td>19.881 ± 0.612</td>
<td>0.345 ± 0.011</td>
</tr>
<tr>
<td>Control</td>
<td>1.762 ± 0.009</td>
<td>17.030 ± 0.179</td>
<td>0.300 ± 0.003</td>
</tr>
</tbody>
</table>

* no PHB production was observed

**Table III**

<table>
<thead>
<tr>
<th>Media</th>
<th>Biomass [g dm⁻³]</th>
<th>PHB content [%]</th>
<th>PHB yield [g dm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>1.288 ± 0.015</td>
<td>0.050 ± 0.011</td>
<td>0.001 ± 0.000</td>
</tr>
<tr>
<td>BM + glucose</td>
<td>2.602 ± 0.050</td>
<td>44.720 ± 3.290</td>
<td>1.164 ± 0.086</td>
</tr>
<tr>
<td>BM + starch</td>
<td>2.150 ± 0.110</td>
<td>21.054 ± 0.711</td>
<td>0.453 ± 0.012</td>
</tr>
<tr>
<td>Whey</td>
<td>0.389 ± 0.033</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Whey + salts</td>
<td>1.612 ± 0.033</td>
<td>15.464 ± 0.181</td>
<td>0.249 ± 0.003</td>
</tr>
</tbody>
</table>

* no PHB production was observed

Addition of Na₂SO₄ led to higher PHB production too. This effect could be caused by reducing properties of Na₂SO₄, but the effect on PHB production was relatively low.

Other stress factors inhibited the growth of culture and/or PHB accumulation. Because of relationship between stress factor concentration and its biological effect further experiments will be needed. Detailed analysis of concentration effects was not included into this pilot study.

Because of relatively low PHB amount (14–20 % of total biomass) other media then SM were tested. Culture growing on BM medium itself did not contain almost any PHB after 45 hours of growth. However, when glucose was added, production of relatively high PHB amount was observed. This is probably caused by the fact, that culture depleted nitrogen and phosphorus sources of BM medium, but carbon source (sugar) was still present. Culture was able to utilize sugar for the growth as well as for PHB accumulation.

Finally, cheese whey was tested as a component of medium for PHB production. Low growth and no PHB production were observed when cultivations were performed on whey itself. Addition of salts (according to SM) led to the strong increase of growth and production properties of culture.

**Conclusions**

All strategies tested in this work could be used for enhancing PHB production in Bacillus megaterium CCM 2037. Limitation with nitrogen seems to be a strong stimulating factor for PHB production.

Positive effect of two exogenous stress factors on PHB production was observed. Ethanolic stress and Na₂SO₄ enhanced PHB production. However, the mechanism and optimal concentration of stress factors have to be clarified.

Culture was able to utilize organic substrates (BM, cheese whey) and product high amount of PHB. The highest yield of PHB (1.16 g dm⁻³) was obtained during growth in BM medium with glucose. Bacillus megaterium is also able to use cheap cheese whey or starch as a carbon source. That should lead to reducing of PHB cost. However, further optimization studies are needed.

This work has been supported by project MSM 0021630501 of Czech Ministry of Education.

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Comparison of Biodegradability of Modified Polyurethane Foams and Polyurethane Elastomeric Films

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Introduction
Polyurethanes (PUR) are a widespread group of polymeric materials involved in many aspects of modern life. They are widely used in medical, automotive or industrial fields. PUR are very variable group of materials because they could be prepared in many forms ranging from flexible or rigid foams, solid elastomers, coating, adhesives and sealants. Polymeric materials could serve as carbon (but also nitrogen and other atoms) and energy source for heterotrophic microorganisms including bacteria, moulds and yeasts. This natural process of material decomposition is called biodegradation.

After the years of PUR production manufactures found PUR susceptible to biodegradation. Microbial degradation of PUR as well as other polymeric materials is dependent on many properties of the polymer such as molecular orientation, crystallinity, cross-linking and chemical groups present in the molecular chain. Very small variations in the chemical structure may result in large differences in the term of biodegradability.

This work was focused on the comparison of biodegradability of two different forms of the same PUR material - modified PUR foams and modified PUR elastomeric films. Several types of biopolymers were used as modifying agents that should enhance biodegradability of both PUR forms. For laboratory biodegradation tests mixed thermophilic culture Thermophilus sp. was used.

Experimental
PUR foams and elastomeric films were modified by 10% of acetyl-cellulose (CA), 10% carboxymethyl cel- lulose (CMC) and 10% acetylated starch (AS). Modifying agents partially replaced polyether polyol. Both PUR foams and PUR elastomeric films were prepared from the identical raw materials. The only difference was that in film preparation blowing agent (water) was not used.

Biodegradation Tests
Biodegradation tests were performed with mixed thermophilic culture Thermophilus sp. Cultivations were carried out at 60 °C under permanent shaking in 100 ml of defined media. One sample of PUR was represented by 0.25 g of PUR. Growth characteristics, chemical oxygen demand and glucose concentration were determined in regular intervals. At the end of cultivation (about 100 hours) PUR mass decreases were measured gravimetrically and PUR surface changes were analysed microscopically.

Results
The presence of PUR material influenced growth of bacterial culture in comparison with culture without PUR. Generally, PUR foams supported the growth of bacterial culture, on the contrary PUR elastomeric films weakly inhibited biomass production. The inhibition effect was exhibited mainly during early stages of growth when long lasting lag-phase was observed. This effect was probably caused by formation and/or release of some toxic component(s) which inhibited the start of the growth. Because toxic effect was not observed in PUR foams, it is possible that toxic component(s) was by some way removed during the foaming process.

Modifying agent type was other important factor which influenced the growth of culture. From this point of view, CMC seems to be the best modifying agent because it strongly supported the growth of culture grown both in presence of PUR foams as well as PUR films.

Mass decreases of foams and films were very similar, however, in some experiments higher degradation degree was observed in PUR films. It is surprising because PUR films are expected to be more rigid than PUR foams.

It seems that modification agent type is probably more important factor than the form of PUR material. The highest losses of material were observed in PUR foams and films modified by CMC (see Fig. 1.). High mass decreases of CMC PUR materials could be partially caused by water solubility of carboxymethyl cellulose itself.

Conclusions
In conclusion, modified PUR foams as well as elastomeric films could be degraded by thermophilic bacteria. Differences between foams and films are surprisingly small. It seems that for biodegradation degree more important factor is the modification agent type than PUR material form. Carboxymethyl cellulose appears to be the best modifying agent.
from biodegradation point of view. In relatively short-time lasting tests (about 100 hour) PUR materials modified by carboxymethyl cellulose exhibited almost 7 % of weight loss. CMC PUR materials also strongly supported the growth of bacterial culture.

This work has been supported by project MSM 0021630501 of Czech Ministry of Education.

REFERENCES
SYNTHESIS OF SUBSTITUTED POLYSILYLENES USED AS SEMICONDUCTIVE POLYMERS

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Introduction

Polysilylenes are of considerable research interest because of their electronic, photoelectrical and nonlinear optical properties.

Polysilylenes are most often obtained by Wurtz reductive coupling of organosilanes with sodium metal in refluxing toluene (Scheme 1). Therefore the metal is easily distributed throughout the solution. Unfortunately, the yields of polymers and the reproducibility of the reaction are usually quite poor. Up to now there is no satisfactory mechanistic theory to determine the best procedure, and the reaction conditions must be optimized for each polymerization. Reaction conditions close to optimum could be achieved by evaluating the trends. This contribution reports on the methods and procedure based on new operatory conditions that allowed us to gain in yield and quality of product obtained.

Experimental

General Synthesis (Procedure A) of Poly[methyl(phenyl)silylene] PMPSi

The polymers were prepared by the Wurtz synthesis from dichloro(methyl)phenylsilane with sodium dispersion in refluxing toluene under inert and dark atmosphere during the whole process. To a three-necked Schlenk flask equipped with stirring bar, condenser and dropping funnel was added freshly cut sodium (7.5 g, 0.33 mol). Dry toluene (100 ml) was transferred with a canula to the reaction flask and heated to reflux. The solution of freshly distilled dichloro(methyl)phenylsilane (25 ml, 0.13 mol) in 25 ml of toluene was added dropwise into the dispersion until the color of the reaction mixture changed to blue, indicating the start of the reaction. The rest of the monomer solution was then dropped in the course of 1 h. After 1 h 30 min under reflux, the reaction was quenched at room temperature by addition of 1 ml of BuLi solution. The residual sodium was reacted, under ice bath cooling with 25 ml of ethanol and then with 25 ml of water. The organic layer was separated and taken directly to centrifuge. Cross-linked and insoluble portions were separated by centrifugation at 12,000 rpm for 15 min. Desired polymer fraction was recovered by precipitation of the toluene solution into methanol. For purification, it was reprecipitated from THF solution with methanol. The white solid was collected by filtration, washed with methanol and dried in a vacuum oven.

Modified Procedure (B) for the synthesis of Poly[methyl(phenyl)silylene] PMPSi

The solution of freshly distilled dichloro(methyl)phenylsilane (25 ml, 0.13 mol) in 25 ml of toluene was added rapidly (5 min) into the dispersion. Extreme care had to be exercised due to great rate of polymerization. After that the reaction mixture was stirred under mild reflux for 1 h. The mixture was then allowed to cool to room temperature for quenching with 1 ml of distilled water. While cooling in an ice bath water (2 × 25 ml) was added carefully to neutralize the excess of sodium.

Polymer Characterization

1H, 13C NMR spectra were recorded with a Bruker Avance 300 Varian apparatus at a working frequency of 300 MHz for 1H and 75 MHz for 13C in CDCl3 using TMS as the internal standard. Chemical shifts are given in ppm. The molecular weight and the molecular weight distribution of the polymers were determined by GPC method using Agilent Technologies 1100 Series instrument equipped with a refractive index detector and UV detector, two PLgel Mixed C columns of 300 × 7.5 mm with particle size of 5 mm, degasser, pump and auto sampler. Tetrahydrofuran was used as the mobile phase at a flow rate equal to 1 ml min−1. The average molecular weight was calculated using a series of polystyrene standards (Mw = 316,500–162).

Fig. 1. Molecular weight distribution of polymer products obtained by route A, Mw = 6.2 kg mol−1, Mw/Mn(PD) = 2, Mw = 47 kg mol−1, Mw/Mn(PD) = 14
Results

The present study is focused on properties of polymers obtained using proposed experimental conditions.

The data collected on NMR indicates the presence and purity of the product obtained: The peaks of methyl group resonating around 1.2 ppm and the aromatic protons of the phenyl group resonating around 7 ppm. Peaks are slightly shifted due to the silicon bonding compared to the Carbone one.

Typical analytical data after precipitation: $^1$H NMR (CDCl$_3$): $\delta$/ppm = –1.0–1.3 (br, m, 3H, CH$_3$), 6.0–8.4 (br, m, 5H, aromatic H). $^{13}$C NMR (CDCl$_3$): $\delta$/ppm = –6.3 (br), 127.1 (br), 129.1 (br), 133.3 (br), 134.8 (br), 136.2 (br).

GPC analyses (Fig. 1.) confirmed that the new procedure (Fig. 2.) allowed us to access to new longer chain polymers with higher polydispersity(PD). The yields of such kind of synthesis varies from 40–60 % and is well described in literature.

The Wurtz coupling reaction was conducted in low quantities and many times extracted so that we could obtain more or less pure long chain polymers separated from oligomers. Some low yields obtained are due to a lower scale reaction and drastic separation methods. Better yields can be obtained working on higher scale and determining better single chain molecular weight as we observed total conversion of starting products.

Conclusions

Methods used for the synthesis of PMPSi are well known in chemical industries and are usually drastic and therefore expensive and polluting. The way we explored allowed us to access higher yield polymers of very reasonable cost. The biggest advantage of it is that it uses also less hazardous products or polluting solvent. We could get through this new fashion synthesis high value polymers at lower cost and using only water and ethanol for reaction’s ending and extraction which makes it part of the “green chemistry” or at least towards it.

The other aim of our work would be to synthesize new model of polysilylenes attached directly to functional chromophores throughout a Suzuki coupling and investigate their electrical and optical properties. The proposed structure should be capable of light driven switching between high conductive and low conductive regime, and therefore to be used as current switch or actuator.

REFERENCES

PI1 AUTOMATION OF PE-CVD PROCESS FOR PREPARING OF NANOSTRUCTURED FILMS

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Introduction
Plasma Enhanced Chemical Vapor Deposition (PE-CVD) is a powerful tool for designing of nanostructured films. The PE-CVD technology is relatively complicated and condition-intensive in terms of resulting material’s reproducibility. The deposition system has many input parameters have to be set or continuously regulated. A controlling of the process parameters using an automation technique can increase a reproducibility of experiments. The automated measured data recording enables additional check of deposition process. The aim of presented work is a design and development of programmable automation system for deposition process with a view of parameters controlling.

Plasma polymerization is a powerful tool for a deposition of thin films whose physicochemical properties can be controlled in wide ranges and thus the technology enables adjusting of the material properties with respect to an application. Recently the interest in nanolayers and nanostructures preparation increases. Preparation of the layers and/or complicated structures offers controlling of many process parameters in real time. A success of the coating technique depends on a suitable technological system, as the vacuum quality and film reproducibility are the crucial parameters. With respect to the necessary accuracy of synchronization of all controlling component during the plasma processes the high level of deposition process automation is requisite.

The Developed System
We have developed a capacitive coupling system for creative design and application of complex film systems in smart materials. The internal setup of our deposition chamber using plan-parallel electrodes was derived from a typical capacitive coupling system, but our apparatus was equipped with many non-standard components described in other papers. The electronic components of the deposition system were choosing according to the possibility of remote controlling in terms of needed deposition system automation during the system designing. The wiring of the components, its communication ports or bus channels and/or analog channels was realized.

The system for PE-CVD process controlling used for a research in the lab conditions is complicated in terms of a needed great versatility of the system, its peripherals, and
a variability of deposition process conditions. The setup of the technological system to an exactly defined state requires a data reading from many sensors and offers controlling of many components of the system. The needed parameters of the deposition process are a function of time in the case of a multilayer or a gradient structures preparation. In fact the process is synchronized controlling and/or tracing regulation of process parameters defined in the real time. The full controlling of the system is realized using three computers - control units:

- The first of them controls spectroscopic in situ ellipsometer Yobin – Ivon. The communication is realized by TCP/IP protocol via commercially used software.
- The second control unit communicates with mass spectrometer Hiden and oscilloscope Hameg using serial channel RS – 232 via commercially made software.
- The third of control units supplies a pressure measuring, a process gases flow, a temperature measurement and a regulation, a vacuum valves position controlling, a communication with rf plasma generator and so on.

A block scheme in the Fig. 1. describes the realized solution of communication between the third control unit and the connected peripheries. The system was designed according to a possibility of basic operation of the deposition process independently of the control units operation in case of their failure. Therefore all sensors and actuators are connected via their autonomic primary control units equipped basic user interface which enables to obtain the needed values and/or elementary control the sensor/actuator function. The interfaces are relatively complicated and not user friendly, therefore they are not usable for common work of operator. The primary control units are connected via RS-232 serial channel to a multi-serial interface installed in the main control unit. The system of vacuum control is realized using digital input/output interface of the multi-channel measuring card Advantech. The digital signal is adjusted by system of electronic switches controlling electro pneumatic actuators of the vacuum valves.

The plasma polymerization technology often uses a pulsed mode of the plasma discharge. The plasma generator Cesar 1310 (Advanced Energy company) is equipped with an internal timer for the pulse mode. The change of pulse mode parameters is belated by a time needed for a communication between the control unit and the generator. Therefore the solution is not suitable for stepless control of the pulse mode parameters. For the reason the main control unit is equipped with a multi-channel timer/counter module Advantech working in the pulse width modulation (PWM) regime. The signal controls the pulse mode parameters during complicated high-speed process operations.

The developing of control software for the main control unit was necessary as well. The elemental control units are not distributed with suitable communication software mostly. Therefore the software components for the communication between the elemental control units and the main control unit were developed using Borland Delphi tool. The components were implemented to a developed main software user interface named as A3-Controller. The software enables to an operator comfortably and easily to control all peripheries mentioned in the block scheme in Fig. 1. as well as to obtain and record the process values. In addition the main software was equipped with a timing functions, an automated control of a pumping speed, and a module fore a vacuum tightness checking etc. The three main control units are connected via Ethernet to the Internet network therefore the PE – CVD system is controllable from any PC connected to Internet.

REFERENCES
P12 CRYSTAL STRUCTURE OF A LANTHANIDE SANDWICH COMPLEX (C₅Me₅)₂NdCl₂Li(OEt)₂

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Introduction

The potential of lanthanide sandwich complexes of general formula (C₅Me₅)₂LnCl₂Li(OEt)₂ (where Ln = Nd, Sm) in polymerisation catalysis is nowadays well established. In situ alkylation of the dichloro lanthanideocene precursor by dialkylmagnesium results in a production of efficient active species for ethylene oligomerisation. The propagation takes place via a controlled ethylene growth chain transfer reactions between active centres and dialkylmagnesium yielding tailor-made oligomers possessing narrow molecular weight distributions. These transfer reactions are reversible, very effective even at higher temperature and could thus be considered as living.

The reaction mechanism of ethylene oligomerisation was published few years ago but there was no reliable proof of the structure of (C₅Me₅)₂LnCl₂Li(OEt)₂ even though its synthesis was described already in 1981 by Tiley et al. and well grown blue crystals of this compound could be easily isolated. The structure of (C₅Me₅)₂LnCl₂Li(OEt)₂ was first proposed based on the similarity with the spectral data of compounds (C₅Me₅)₂LnCl₂Li(OEt)₂ (Ln = Ce, Sm) whose structures were known as well as for some other lanthanide sandwich complexes (Pr, Nd, Gd, Dy, Yb and Lu) with different organic donors (e.g. THF or TMEDA) and various substituents on the cyclopentadienyl rings.

Although many structures of lanthanidenocenes with the general formula Cp₂LnCl₂MD₂ (Cp = cyclopentadiene or its derivative, Ln = lanthanide, M = alkali metal, D = organic donor) are known, others have been reported to have a quite unconventional structures and/or coordinations numbers. Therefore we have focused on the determination of the crystal structure of the title species (i) to confirm or negate the structure predicted in already published studies; (ii) to get the missing experimental data for quantum mechanical study of this compound.

Experimental

The density data were collected on a KUMA KM-4 CCD kappa-axis diffractometer using a graphite monochromatized Mo-Kα radiation (λ = 0.71069 Å).

Results

The selected compound (C₅Me₅)₂LnCl₂Li(OEt)₂ was prepared according to the known procedure. Blue crystals were obtained from the reaction mixture and after various kinds of recrystallization in diethylether suitable crystals for X-ray analysis were obtained. The data collection details are tabulated in Table I and selected bond lengths and angles are reported in Table II.

Conclusions

The title compound crystallizes in the tetragonal space group P 4₃,m with one quarter of a molecule in the asymmetric unit and it is isomorphous with the cerium analogue. The molecule is localized on the mm symmetry site, which together with a heavy disorder of all organic residues made the structure determination rather difficult. However, it was possible to obtain data of satisfactory quality and finally confirm the molecular structure of this species (see in Fig. 1.).

Table I

<table>
<thead>
<tr>
<th>Crystal data and structure refinement for (C₅Me₅)₂NdCl₂Li(OEt)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
</tr>
<tr>
<td>formula weight</td>
</tr>
<tr>
<td>crystal system</td>
</tr>
<tr>
<td>space group</td>
</tr>
<tr>
<td>temp [K]</td>
</tr>
<tr>
<td>λ [Å]</td>
</tr>
<tr>
<td>a = b [Å]</td>
</tr>
<tr>
<td>c [Å]</td>
</tr>
<tr>
<td>V, [Å³]</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>ρ calcld. [g cm⁻³]</td>
</tr>
<tr>
<td>μ [mm⁻¹]</td>
</tr>
<tr>
<td>F(000)</td>
</tr>
<tr>
<td>crystal size [mm³]</td>
</tr>
<tr>
<td>θ range for data collection, deg</td>
</tr>
<tr>
<td>no. of reflns collected</td>
</tr>
<tr>
<td>no. of indep. reflns (Rint)</td>
</tr>
<tr>
<td>no. of data/restraints/parameters</td>
</tr>
<tr>
<td>GoF on F²</td>
</tr>
<tr>
<td>wR²</td>
</tr>
<tr>
<td>R₁</td>
</tr>
<tr>
<td>R₁, wR²</td>
</tr>
<tr>
<td>abs. struct. par.</td>
</tr>
<tr>
<td>largest diff. peak / hole [e Å⁻³]</td>
</tr>
</tbody>
</table>

Table II

<table>
<thead>
<tr>
<th>Bond lengths [Å] and angles [°] for (C₅Me₅)₂NdCl₂Li(OEt)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonds and angles</td>
</tr>
<tr>
<td>Cl(1)–Li(1)</td>
</tr>
<tr>
<td>Li(1)–O(1)</td>
</tr>
<tr>
<td>Nd(1)–Cl(1)</td>
</tr>
<tr>
<td>Li(1)–Cl(1)–Nd(1)</td>
</tr>
<tr>
<td>O(1)–Li(1)–O(1A)</td>
</tr>
<tr>
<td>Cl(1)–Li(1)–Cl(1A)</td>
</tr>
<tr>
<td>Cl(1)–Nd(1)–Cl(1A)</td>
</tr>
</tbody>
</table>
Acknowledgement is given to Project MSM0021630501 for financial support of this work.

REFERENCES

Fig. 1. Crystal structure of (C₅Me₅)₂NdCl₂Li(OEt₂). All hydrogen atoms as well as second positions of the disordered moieties have been omitted for clarity.
### P13 COMUTING EFFECTIVE PROPERTIES OF COMPOSITES VIA FEM SIMULATIONS

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**Introduction**  
Composite materials take more and more important role in modern material science. It is influenced by several reasons, however mainly for their good mechanical properties and very cheap preparation. For estimation of properties of such materials were introduced many models with different assumptions and with different quality of approximation. The method which was used by us was mathematical homogenization method which follows from asymptotical properties of differential equations describing given physical phenomenon – linear elasticity in our case, however method can be used for wider spectrum of equations. The input of this method is representative volume element (RVE) – unitary cube (denoted by \( Y \)) which represents whole material. It has to be determined theoretically or from experimental results. The space conformation of phases can be arbitrarily complex also we can compute with more than only two phases (matrix, reinforcements). We supposed spherical shape of reinforcements, the inclusions are uniformly distributed in matrix and have random diameters. For generating such conformation was used discrete version of random sequential algorithm (RSA). All computings were done in Matlab 7.1 and in Comsol Multiphysics 3.2.

Aromatic thermotropic liquid crystalline polymer (TLP) dispersed in polypropylene (PP) could serve as high modulus and high strength deformable inclusions. Modeling of relation between its morphology and mechanical behavior is useful way in development of new materials with tailored properties. It can eliminate certain polymer structures prior to the costly process of its preparation, processing and testing.

### Experimental

**Hard Sphere Problem, RSA Algorithm**  
Problem of placing spheres in unit cube is in literature referred as hard sphere problem – we have to randomly place \( n \) spheres with radius \( r_i \) to which corresponds volume \( V_i \) in such way that following holds:

(i) \[ \sum_{i=1}^{n} V_i = \varphi, \ 0 \leq \varphi < \]

(ii) the spheres do not intersect each other

(iii) the spheres are uniformly distributed in space

(iv) the space is composed from periodical copy of this unit cube so it has to be periodic wrt. spheres

For creating of such structure were designed several algorithms, we introduce two of them:

- **Algorithm 1.** we randomly generate new position of sphere and then we test if it satisfies conditions (ii) and (iii), if it does then we save this position and generate position for next sphere, if it doesn’t we generate again new position and do test, we repeat this procedure until we place all spheres, this algorithm is denoted as random sequential algorithm (RSA)

  - **Algorithm 2.** we begin with all spheres placed in some lattice (often it is FCC lattice) and then we randomly move each sphere so that condition (ii) holds, after enough movements the condition (iii) is also satisfied.

#### Table I

Illustration of quality of an approximation of disc with different fineness of space division

<table>
<thead>
<tr>
<th># of units per radius</th>
<th>( S_{disc}/S_{orig} )</th>
<th># of units per radius</th>
<th>( S_{disc}/S_{orig} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.9099</td>
<td>50</td>
<td>1.0590</td>
</tr>
<tr>
<td>2</td>
<td>1.8209</td>
<td>75</td>
<td>1.0395</td>
</tr>
<tr>
<td>5</td>
<td>1.4565</td>
<td>100</td>
<td>1.0298</td>
</tr>
<tr>
<td>10</td>
<td>1.2796</td>
<td>200</td>
<td>1.0149</td>
</tr>
<tr>
<td>20</td>
<td>1.1450</td>
<td>300</td>
<td>1.0099</td>
</tr>
<tr>
<td>30</td>
<td>1.0986</td>
<td>400</td>
<td>1.0075</td>
</tr>
<tr>
<td>40</td>
<td>1.0737</td>
<td>500</td>
<td>1.0059</td>
</tr>
</tbody>
</table>

On the other hand disadvantage of algorithm 1 is possible infinite time or sometimes impossibility to successfully finish algorithm. This disadvantage was partially removed by our improvement of this algorithm. The space was divided to small cubes (discretization), which then form unity in discrete space the approximation of sphere in this space is shown on Fig. 1., Table I gives us information about quality of such
approximation). Possibility of placing the center of the next sphere to some cube was indicated by 1 and negative of this by 0. By this algorithm we can also trace the decreasing amount of free space available for place center and from this value we can estimate how much effort we need in algorithm 1, this is shown on Fig. 2. One of generated structures used for computing is shown on Fig. 3.

Mathematical Homogenization Method

Mathematical theory of homogenization was developed in early 60s of 20th century by many mathematicians. We used results of this theory for system of elliptic PDE’s (linear elasticity equation)\(^1\) to computing mechanical properties of composites. Formulas for tensor describing material characteristics of resulting composite material are (we are using Einstein summation convention, \(A\) is tensor of original material, \(A^0\) is tensor of homogenized material)

\[
A_{ijkl}^0 = \frac{1}{V} \int_Y A_{ijkl} \chi_{ijkl} \, dx,
\]

(1)

where \(\chi_{ijkl}\) are solutions of following problems

\[
\frac{\partial}{\partial x_i} \left( A_{jlm} \frac{\partial \chi_{ijkl}}{\partial x_l} \right) = -\frac{\partial A_{ijkl}}{\partial x_j} \quad \text{in} \ Y, \ i = 1, ..., n,
\]

\(\chi_{ijkl} \quad Y \text{– periodic}
\]

\[
\int_Y \chi_{ijkl} \, dx = 0
\]

and

\[
e_{ijkl}(\chi) = \frac{\partial}{\partial x_i} \chi_{ijkl} + \frac{\partial}{\partial x_j} \chi_{ijkl}
\]

is linearized strain tensor.

Results

Computed results compared with experimental ones (PP matrix reinforced with TLCP, where portion of TLCP goes from 0 % to 40 %) are shown on Fig. 4. We can conclude that for small amounts of TLCP prediction is quite good and our curve fits well to experimental data, for bigger amounts of TLCP this doesn’t hold, this can be influenced by the fact that particles of TLCP can interact between them or by the fact that our sphere model is inadequate to reality.

Conclusions

Discrete version of RSA seems to be good way how to analyze evolution of algorithm. It shows us that possibility of place another sphere goes rapidly down. So ordinaly RSA can be insufficiently slow or it won’t lead to solution at all.

Prediction possibilities of homogenization algorithm are sufficiently good, for better description of behaviour is needed to know much precisely microstructure of composite material.

REFERENCES

P14 EFFECT OF THERMAL HISTORY ON STRUCTURE-PROPERTY RELATIONSHIP IN ORIENTED POLYPROPYLENE FILMS AND TAPES

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Introduction
The orientation is technological process for foils, tapes and fibrils preparation. Oriented monofilaments have better mechanical properties (e.g. tensile strength, modulus, resistance to cyclic deformation) than unoriented.

Annealing of an oriented sample causes relaxation, polymeric chains integrate into the existing lamellae and the lamellae thicknesses increase. An increase of crystallographic symmetry, decrease of orientation of crystalline phase, disorientation of amorphous phase and a decrease of some mechanical properties is caused by annealing.

Experimental
Material and Samples Preparation
Commercial grade of polypropylene Mosten TB 002 was used in this work (MFR = 2.73 10 min⁻¹). This material was extruded and film of 400 µm thickness was prepared by chill roll technique. Primary film was drawn up to ratio 5:1 in the first step, then the film was cut to tapes (10 mm) and those were drawn on the hot plate to the final draw ratio 8:1 in the second step.

A part of tapes TB(4)-8/10 were continual annealed in the next step. This lable of tapes means: TB is polypropylene Mosten TB 002, (4) is thickness of primary foil (400 µm), 8 is drawn ration and 10 is cutting width of tape before drawing (10 mm). Testpieces passed throught tempered channel; both ends of samples were fixed to minimize shrinkage and annealed at 150, 160 and 170 °C.

Unannealed and annealed testpieces were tested. Strength and elongation at break (tensile properties), degree of crystallinity and structure characteristics (DSC) and chain orientation (RTG) were measured.

DSC, Tensile Tests and RTG
A circle specimens of 1 to 4 mg of weight were cut from the tapes. Each specimen was put into the aluminum pan and heated up in apparatus TA Instruments Q100. The test conditions were: heating rate of 10 °C min⁻¹, inert nitrogen atmosphere, the test was started at 50 °C and stopped at 200 °C. The endotherm peaks were recorded out and the fusion enthalpy, maximal temperature and the half-width of the peak were evaluated.

The tensile properties of unannealed and annealed polypropylene tapes were tested using INSTRON 4302. Tensile tests were performed at laboratory temperature and at test speed of 100 mm min⁻¹. The cylindrical iron clamps of the axises distance (100 mm) were used. The maximal tensile strength and elongation at break were recorded.

The RTG measurements were done in a laboratory of UTB FT Zlín using diffractometer HZG-6 in transition and reflection modes. The tapes were measured longitudinal and transversely to the draw direction.

Results
DSC
The melting curves of polypropylene tapes are shown in Fig. 1, the main characteristics are given in Table I. The first curve represents melting of unannealed oriented material TB(4)-8/10 - 23 °C and the others with changed shape represent melting of annealed tapes.

We interpreted change of shape in this way. Structure has changed during recrystallization. The part of the oriented chains relaxed and a lamellar structure was created. The beginning of the process is represented by the curve of TB(4)-8/10-150 °C.

Annealing at 160 °C. The peak is higher and is shifted to higher temperature. Lamellae of regular structure increased in the thicknesses.

Process of recrystallization at annealing temperature 170 °C starts to change substantially the crystallite character in the tape. The thicker lamellae are built-up (higher Tm) and the orientation of chains becomes to decrease (see RTG).

Fig. 1. Heat fluxes of PP tapes – TB(4)–8/10. Test were done with heating rate of 10 °C min⁻¹. Materials were without ageing (23 °C ×-) and aged at 150 °C (×), 160 °C (○) and 170°C (++)

Table I
DSC characteristics of PP tapes

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔHm [J g⁻¹]</th>
<th>Half-width [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB(4)-8/10-23 °C</td>
<td>114.7</td>
<td>10.80</td>
</tr>
<tr>
<td>TB(4)-8/10-150 °C</td>
<td>118.5</td>
<td>10.1</td>
</tr>
<tr>
<td>TB(4)-8/10-160 °C</td>
<td>119.9</td>
<td>6.83</td>
</tr>
<tr>
<td>TB(4)-8/10-170 °C</td>
<td>116.4</td>
<td>4.42</td>
</tr>
</tbody>
</table>

Tensile Test
The results of tensile tests are presented in Table II (tensile strength and elongation at break). Tensile strength...
decreases with annealing temperature in the whole annealing temperature range, because the above mentioned recrystallization decreases orientation of polymer chains.

Elongation at break increases only up to annealing temperature 160 °C and then it drops. This fact could be attributed to polypropylene recrystallization process (see above) and subsequently destruction of the tape orientation.

Table II
Results of tensile tests

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength [MPa]</th>
<th>Elongation at break [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB(4)-8/10-23 °C</td>
<td>513 ± 20</td>
<td>41 ± 3</td>
</tr>
<tr>
<td>TB(4)-8/10-150 °C</td>
<td>419 ± 40</td>
<td>96 ± 14</td>
</tr>
<tr>
<td>TB(4)-8/10-160 °C</td>
<td>328 ± 16</td>
<td>158 ± 8</td>
</tr>
<tr>
<td>TB(4)-8/10-170 °C</td>
<td>201 ± 14</td>
<td>97 ± 7</td>
</tr>
</tbody>
</table>

R T G

Fig. 2. WAXS patterns measured longitudinally to draw direction (tapes TB(4)-8/10, unannealed (23 °C -☐-) and annealed at temperatures (150 °C -×-, 160 °C -○-, 170 °C -+-))

The maximums of diffraction intensity are located at the same 2Θ angles for tape annealing temperatures 23 °C, 150 °C and 160 °C (Fig. 2.). TB(4)-8/10-170 °C sample has those maxima shifted to higher angles. The intensities of peaks are changed in accordance with annealing temperature, because the number of crystallites in the drawing direction has decreased.

Measured intensities in transversal direction are very low, i.e. the tapes have practically no reflection planes perpendicular to the draw direction. Material TB(4)-8/10-170 °C has some few crystallites in the transversal direction. Probably, some of crystallites were created during recrystallization in this direction.

Conclusions

Results of DSC, tensile tests and RTG are presented in this paper.

DSC results show that annealing of PP tapes increase dimensions of crystals and above 170 °C a complete recrystallization started.

The tensile strength decreases in the whole range of the annealing temperature. Deformation increases up to 160 °C, then it decreases. This phenomenon should be interpreted by above mentioned recrystallization processes.

The crystallite orientation decreases in the drawing direction with increasing annealing temperature. The samples have no or very low amount of crystallites orientated in transversely direction, because of absence of WAXS peaks.

We thank the Board of Industry and Trade for financial support, grant: 1H-PK/39

REFERENCES

P15 BIORESORABLE COLLAGEN-HYALURONIC ACID SCAFFOLDS CROSS-LINKED USING A WATER-SOLUBLE CARBODIIMIDE

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Introduction
Porous collagen scaffold matrices containing hyaluronic acid (HA) are promising materials for tissue regeneration. Collagen, a well-known material has been widely used in medical applications. It is extensively used for wide-area parenchyma bleeding and for laparoscopic procedures as a haemostatic agent. HA is important component of extracellular matrix, having high water retention capacity. HA is involved in cell migration and cell differentiation which support wound healing process. By combination of collagen and HA, the material with haemostatic and healing properties can be created.

In this study, collagen was blended with hyaluronic acid and cross-linked by carbodiimide at different period of time in order to evaluate the swelling and degradation properties used for certain biological applications.

Experimental
Bovine collagen type I (VUP a. s., CZ) and hyaluronic acid (CPN spol. s.r.o., CZ, Mn = 150 kDa) were used. Cross-linking solution mixture of 25 mmol.l⁻¹ of N-(3-dimethylamino-propyl)-N'-ethylcarbodiimide hydrochloride (EDC, Sigma Aldrich, D) and 12.5 mmol.l⁻¹ of N-hydroxysuccinimide (NHS, Sigma Aldrich, D) in 98 % of ethanol was prepared.

Sample Preparation
Collagen and hyaluronic acid were mixed in two different ways. The Coll-HA-1 matrix was made by combination of freeze drying and air drying method while the Coll-HA-2 one was only freeze dried which is commonly used method.

Prepared matrices were subsequently cross-linked using EDC/NHS system for three periods of time: 0.25, 1 and 2 h.

Characterization
The morphology of a surface structure and cut profiles of collagen-HA matrices was compared using scanning electron microscopy (SEM).

For water uptake determination each scaffold was cut up and weighted. The pieces were consequently immersed to physiological solution (PS) and in 1 hour the pieces were removed and re-weighted. The water content was calculated according to formula (1), where \( w_s \) is weight of swollen scaffold and \( w_d \) is weight of the dry scaffold.

\[
\text{Water uptake} = \left(\frac{w_s - w_d}{w_d}\right) \times 100
\]

The hydrolytic degradation of collagen-HA samples was studied in PS at 37 °C which simulated human body fluids. The degradation resistances were measured within a period of 30 days and determined using gravimetric method.

The bioinduction differences were evaluated just between matrices of pure collagen and collagen includes hyaluronic acid. The samples were tested at the laboratory of cells regeneration and plasticity (Liběchov, Czech Republic). The collagen scaffolds were colonized with mesenchymal cells and cultivated for 10 days in order to monitor both the stability in the cells solution and cells activity.

Results
SEM images of collagen-HA surfaces at Fig. 1.a and Fig. 1.b demonstrate differences between scaffold structures. Samples of Coll-HA-1 embodies smooth surface in comparison with porous surface of Coll-HA-2. Cut profiles scan (Fig. 1.c and Fig. 1.d) show that Coll-HA-1 is porous only in the middle part but the smooth just on the surface. The Coll-HA-2 shows porous structure in all volume.

The fastest hydrolytic degradation (of about 1 hour) yield the non cross-linked Coll-HA-2 porous sample while the other non cross-linked Coll-HA-1 sample exhibit higher stability by degrading up to 90 % in physiological solution at 37 °C within 30 days. The degradation stability of all samples increased markedly after the cross-linking by EDC/NHS, however, the different cross-linking period of time did not shown considerable dependences. Based on the results, the samples truckled to the degradation between 20–30 % (Coll-HA-1) or 30–40 % and (Coll-HA-2) in 30 days as can be seen in Fig. 2 and Fig. 3 respectively.

Fig. 1. Scanning electron images of collagen-hyaluronic scaffolds a) Coll-HA-1 surface, b) Coll-HA-2 surface, c) Coll-HA-1 cut profile, d) Coll-HA-2 cut profile
Moreover, different water uptake behavior of collagen-Ha matrices were observed. As presupposed, more stable Coll-Ha-1 samples absorbed smaller amount of water in comparison with Coll-Ha-2 samples. The time of cross-linking did not have considerable influence on the water uptake behavior as shows Fig. 4.

Compared with pure collagen the collagen-Ha scaffolds indicated higher shape resistant and better density of cultivated mesenchymal cells after 10 days of cultivation.

Conclusions

Collagen and hyaluronic acid are poorly miscible when the amount of hyaluronic acid increases. Two different samples of collagen-HA were prepared (Coll-HA-1 and Coll-HA-2), cross-linked by EDC/NHS system and analyzed.

Scanning electron images showed differences in porosity of both samples. The Coll-HA-1 sample was porous just in the middle part between two smooth surface layers which probably protect the material against external effects resulting to slowest degradation rate and lower uptake in comparison with fully porous Coll-HA-2 sample. While non cross-linked Coll-HA-1 sample degraded at 90 % after 30 days, the non cross-linked Coll-HA-2 sample fully disintegrate in one hour. The cross-linking of both samples stabilized the matrices against the hydrolytic degradation. In 30 days the cross-linked Coll-HA-1 sample degraded to 30 % compared to 40 % of Coll-HA-2. As for water uptake behavior, the Coll-HA-2 sample absorbed 90 % wt. of water in one hour in contrast to 60 % wt. of Coll-HA-1 samples where the bilayer decreases the water absorption. However, the cross-linking time did not have considerable influence in both swelling and degradation behaviors.

It is assumed that after the formation of collagen-hyaluronic acid mixture, carboxyl groups of hyaluronic acid react promptly with amino groups of collagen. This result in small amount of free amino groups applicable to cross-linking thereupon the time, needed for the sufficient cross-linking degree, is surprisingly short – 15 minutes.

The collagen-HA matrices showed better bioinduction effect in both shape resistance and cells density in comparison with pure unmodified collagen samples.

The results showed that collagen-HA materials prepared in various ways exhibited different properties useful for wide range of applications. Particularly, Coll-HA-1 might be used as material needed higher stability, whilst Coll-HA-2 is suitable for systems required higher absorption ability.

Financial support of this research under the NPV II project 2B06130 and project MS 0021630501 from the Ministry of Education, Youth and Sports of the Czech Republic is greatly appreciated.

REFERENCES

**P17 SPIN PROBE DYNAMICS IN RELATION TO FREE VOLUME AND RELAXATION DYNAMICS OF POLY(ISOBUTYLENE)**

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**Introduction**

The local structure and dynamics of glass-forming systems can be studied by means of reporter stable free radicals, the so-called spin probes.1–4 The ESR spectra reflect rotational mobility of paramagnetic molecules which is closely related to both internal and external factors. We attempt to understand the rotational dynamics of the spin probes which is dependent on the microstructure of a matrix and its static and dynamic fluctuations as well as the spin probe parameters, i.e. the size (volume, mass) and shape as a function of temperature.

The physical microstructure of disordered former can be characterized using the free volume concept5–6. In the past, this idea was utilized to interpret spin probe dynamics by formulating the various versions of free volume models of spin probe rotation in polymers.7–9 Recent progress in positron annihilation lifetime spectroscopy (PALS)10,11 allowed to relate the directly measurable free volume to individual matrix dynamics12 as well as to the spin probe mobility13,14. Recent PALS and ESR studies on a series of polymers revealed the connection between crossover of regimes for the small spin probe TEMPO at characteristic ESR temperature $T_{50G}$15 and the appearance of a certain mean free volume hole which confirmed the independence of the chemical structure of matrices13,14. For further clarification of the role of free volume in spin probe mobility are needed more detailed free volume PALS data.

Investigations of glass-formers within ESR vs. PALS analysis supported the idea that primary α-process in the matrix plays the role in mobility of larger spin probes4,16 and that the secondary processes are important for the smaller ones16. We present cross analyses of the spin probe dynamics results in the context of the microstructure and microdynamic data of pure matrix from PALS and BDS studies.

**Experimental**

Poly(isobutylene) $-[\text{CH}_2-\text{C(\text{CH}_3)}_2]_n$ from a recent PALS study18 was used. Molecular weight $M_n = 1.3 \times 10^6$ g mol⁻¹ and glass transition temperature from differential scanning calorimetry (DSC) $T_{g_{\text{DSC}}} = 207 \pm 1$ K. The spin probes 2,2,6,6-tetramethyl-1-piperidinyloxyl, known as TEMPO, 4-Maleinimido-2,2,6,6-tetramethyl-1-piperidinyloxyl (MI-TEMPO) from Aldrich Chemical Comp., Inc and 1,5-dioxa-3,3-bis(brommethyl)-8,8,10,10-tetramethyl-9-azaspiro [5,5] undecaneoxy (Br-TEMPO) were used. They were introduced into the polymer matrix by diffusion from the vapour phase at a temperature near their corresponding melting points. The structure and basic molecular parameters of spin probes are presented in Fig. 1 obtained by means of the simulation software Cerius², Accelrys Inc.

**Results**

The ESR signal of all the three nitroxyl radical change from a broad triplet at lower temperatures to a narrow triplet in a higher temperature region, which corresponds to a slow rotational regime with a high spectral parameter of the $2A^{zz} \sim 68$ G changing to a rapid rotational regime with lower values of $2A^{zz} \sim 35$ G. Fig. 2. shows the spectral parameter of mobility, $2A^{zz}$, and the correlation time, $\tau_c$, being determined by the standard formulae.

**Fig. 1. Structure, molar mass in g mol⁻¹, and van der Waals volumes in Å³ of a series of spin probes used**

<table>
<thead>
<tr>
<th>Spin Probe</th>
<th>Molar Mass (g mol⁻¹)</th>
<th>Van der Waals Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMPO</td>
<td>156.1</td>
<td>50G</td>
</tr>
<tr>
<td>MI-TEMPO</td>
<td>251.1</td>
<td>265–s1311 (2008)</td>
</tr>
<tr>
<td>Br-TEMPO</td>
<td>412.0</td>
<td>230.6</td>
</tr>
</tbody>
</table>

ESR investigations were performed on the X-band Brucker-ER 200 SRL with a Brucker BVT100 temperature variation controller unit. The ESR spectra were registered over a wide temperature range from 100 K up to 400 K. The ESR spectra were analyzed via two parameters of the rotational dynamics. The spectral parameter of mobility, $2A^{zz}$, and the correlation time, $\tau_c$, being determined by the standard formulae. 

For the quasi-spherical spin probe TEMPO $T_{50G} = 263$ K. In addition, crossovers in the $2A^{zz}$-$T$ plot within the slow and rapid regimes define the two characteristic ESR temperatures at $T_{2A^{zz}} = 205$ K or $T_{2A^{zz}} = 347$ K, respectively. On the other hand, the temperature dependences of the spectral parameter $2A^{zz}$ for the two larger non-spherical spin probes MI-TEMPO and Br-TEMPO, which differ in their volume by a factor of 1.35 and in their masses by a factor of 1.64, are rather similar with the corresponding $T_{50G}$ values of 330 K or 333 K, respectively.
estimated by using the standard formulae\textsuperscript{1,2,16}. In the case of a slow motional regime, the Goldman – Bruno – Polnaczek – Freed equation (1) has been applied:
\begin{equation}
\tau_c = a[1-S(T)]^b \tag{1}
\end{equation}
where, $S(T) = A_{XX}(T)/A_{ZZ}(T_{ref})$ and represents the extrema line separation $2A_{ZZ}$ of the triplet spectra at temperature $T$ and some reference value of $2A_{ZZ}$, usually at $T_{ref} = 77$ K. The a and b coefficients depend on the motional model of spin probe reorientation used. In the case of organic matrices/ small spin probe systems such as our PiB/temPo pair, the jump diffusion mechanism was found to be hold, for which $a = 2.55 \times 10^{-9}$ s and $b = -0.615$ (ref.\textsuperscript{1,2,16}). In the rapid rotation regime the Freed – Fraenkel equation (2) was used:
\begin{equation}
\tau_c(T) = A\Delta H_{11}[1/L_{11} - 1]^{1/2} \tag{2}
\end{equation}
where $A = 6.7 \times 10^{-10}$ s, $\Delta H_{11}$ = the line width of the low-field line of the triplet spectrum and $L_{11}$, $L_{12}$ are the intensities of the lines of the low- and high-field component of the triplet spectrum. The results are displayed in the Arrhenius representation in Fig. 3. Four regions of different motional regime having the Arrhenius character:
\begin{equation}
\tau_c = \tau_e \exp[E_e/RT] \tag{3}
\end{equation}
where, $\tau_e$ is pre-exponent and $E_e$ is activation energy, can be distinguished. Intersection points of the linear regimes define the characteristic ESR temperatures $T_{XX}^{\tau_1} = 208$ K, and $T_{XX}^{\tau_2} = 320$ K. The first two bend effects in Fig. 3. are consistent with the characteristic ESR temperatures $T_{XX}^{\tau_1}$, $T_{90G}$ from Fig. 2. Dynamic change between the rapid sub-regimes at $T_{XX}^{\tau_2}$ is approximately consistent with $T_{XX}^{\tau_1}$ vs. T plot.

The observed reorientation behaviour of a series of spin probes can be related to the o-Ps annihilation and free volume information from PALS\textsuperscript{18}, as well as to the relevant literary dynamic results from broadband dielectric spectroscopy (BDS)\textsuperscript{19} and nuclear magnetic resonance (NMR)\textsuperscript{20}.

**PALS Data in Relation to ESR Findings**

The PALS technique provides a unique information about the free volume microstructure of a matter\textsuperscript{10,11}. This method is based on the annihilation behaviour of microscopic ortho-positronium probe (o-Ps) which is very sensitive indicator of local regions of low electron density, the so-called free volume. According to quantum-mechanical model\textsuperscript{21–23}, the o-Ps lifetime, $\tau_3$, is a measure of the radius, $R_h$, of a spherical free volume hole by equation (4):
\begin{equation}
\tau_3 = \tau_3(0)\{1-R_h/(R_h + \Delta R) + (1/2\pi)\sin[2\pi R_h/(R_h + \Delta R)]\}^{-1} \tag{4}
\end{equation}
where $\tau_{3(0)}$ is the statistically averaged para-Ps and ortho-Ps lifetime (0.5 ns) and $\Delta R = 1.66$ Å is the thickness of electron layer around the hole whose value is determined by fitting the observed lifetimes in molecular crystals and zeolites of known vacancy or cages sizes.\textsuperscript{21–23} The corresponding mean hole volume is simply $V_h = (4/3)\pi R_h^3$. In reality, however, the shape of free volume holes is not strictly spherical, so that equation (4) is used as the equivalent sphere radius or volume. In addition, free volume holes in condensed media, generally, have no uniform size, so that the free volume size distribution function is relevant\textsuperscript{22}. If a one-to-one correspondence between the o-Ps lifetime and the free volume hole radius is assumed to be valid, the o-Ps lifetime distribution can be transformed into the free volume hole radius distribution, $f(R_h)$:
Intersection points define two characteristic PALS temperatures $T_g^{PALS}$ and $T_{b1}$. Similarly, four different regions in the $\sigma_g^3$-$T$ plot can be distinguished. The first two characteristic PALS temperatures $T_g^{PALS}$ and $T_{b1}$ agree with the previous ones, while the third one lying at $T_{c5} = 320$ K has not direct analogy in the o-Ps lifetime.

By comparing ESR and PALS responses, following coincidences were found. The bend effect within the slow rotational regime of TEMPO at $T_g^{34}$ = 205 K (Fig. 2.) lies in the vicinity of the glass transition. Further, a crossover between slow and rapid regimes at $T_{50G}$ = 262 K is in an approximate coincidence with $T_{b1}$ = 270 K in $\tau_1$, $\sigma_g$ vs. $T$ plot. The acceleration of TEMPO in a rapid rotational regime at $T_g^{2}$ = 320 K is comparable to the plateau at $T_{b2}^{a}$ from Fig. 4. Moreover, a crossover of MI-TEMPO and Br-TEMPO at $T_{50G}$ = 330 or 333 K in Fig. 2. lies slightly above $T_{b2}^{a}$.

All these phenomenological coincidences suggest the common origin in the underlying processes. This aspect will be discussed later by considering the dynamic data of PIB.

Geometrical aspect consists in a direct comparison of the spin probe sizes $V_p^{W}$ with free volume hole sizes as well as free volume hole distributions as obtained from analysis of PALS spectra by using the LT 9.0 programme. Fig. 5. shows the mean hole volume, $<V_h^{\infty}>$, and the mean hole volume dispersion, $\sigma_h$, as a function of temperatures in relation to $V_p^{W}$ (Fig. 2.) lies in the vicinity of the glass transition. Further, a crossover between slow and rapid regimes at $T_{50G}$ = 262 K is in an approximate coincidence with $T_{b1}$ = 270 K in $\tau_1$, $\sigma_g$ vs. $T$ plot. The acceleration of TEMPO in a rapid rotational regime at $T_g^{2}$ = 320 K is comparable to the plateau at $T_{b2}^{a}$ from Fig. 4. Moreover, a crossover of MI-TEMPO and Br-TEMPO at $T_{50G}$ = 330 or 333 K in Fig. 2. lies slightly above $T_{b2}^{a}$.

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All these phenomenological coincidences suggest the common origin in the underlying processes. This aspect will be discussed later by considering the dynamic data of PIB.
On increase the temperature, \( g_n(V_h) \) approaches the vdW volume of TEMPO and at \( T_{50G} \), it crosses the high-value tail of the corresponding distribution. Similar finding is valid for the MI-TEMPO and Br-TEMPO probes at \( T_{50G} \approx 330 \, K \). However, the same values of \( T_{50G} \) suggest that the presence of local free volume is a necessary condition, but not a sufficient condition for a crossover phenomenon. Finally, at higher temperatures, the bend effect in the rapid regime of the TEMPO at \( T_{50G} = 343 \, K \) in Fig. 2, is related to the maximum of \( g_n(V_h) \), when is the maximal probability of the occurrence of free volume holes being almost equal to the vdW volume of the TEMPO probe. This is fully consistent with Fig. 5.

**PALS and ESR Data vs. Dynamics Relationships**

This section discusses the ESR crossover phenomena in relation to internal dynamics of PIB. Fig. 7 displays the relaxation map for the all relaxation processes in PIB as obtained from BDS and NMR studies\(^{19,20}\). Amorphous PIB exhibits a slow primary \( \alpha \) process and two secondary \( \beta \) – and \( \delta \) – processes. In this plot, the o-Ps lifetimes at the characteristic ESR temperatures \( T_{50G} \) are compared with the mean characteristic times of the secondary relaxation processes. In the case of the smallest probe TEMPO, the \( \alpha \) – process at \( T_{50G} = 270 \, K \) and not too distant from the \( T_{50G} = 263 \, K \). On the other hand, the \( \alpha \) – process lifetime \( \tau_2(T_{50G}) \) for larger spin probes \( \delta \) – process at around 282 K. The longer arrow marks the o-Ps lifetime \( \tau_3(T_{50G}) \) for larger spin probes which crosses the extrapolated \( \beta \)– process at 322 K.

**Conclusions**

In summary, from the mutual cross-comparisons of three responses it follows that the changes in the spin probe TEMPO dynamics are closely related to the fluctuation of the local free volume due to secondary \( \delta \)– process. On the other hand, the local dynamics of the \( \beta \)– process is responsible for the occurrence of plateau at \( T_{b2} \) as well as for the ESR crossovers at \( T_{50G} \) for the larger spin probesMI-TEMPO and BR-TEMPO in PIB.

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**REFERENCES**

TOUGHNESS VERSUS STRENGTH AND STIFFNESS OF POLYPROPYLENE FILLED WITH SUBMICRON \( \text{CaCO}_3 \) PARTICLES

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Introduction
Polypropylene (PP) as one of the most important commodity polymer is widely used in technical applications. The advantage of this material is good processability, relatively high mechanical properties, great recyclability and low cost. However, due to its impact resistance especially, the usefulness of PP as an engineering thermoplastic is still limited. The challenge of improving the impact toughness of this semi-crystalline polymer continues to receive considerable interest in recent years. It is well known that the addition of the mineral fillers to PP can profoundly change the mechanical properties of a polymer system. The properties themselves (size, shape, material properties, surface treatment) and distribution of this particles can have a significant effect on the global behavior of the composites. Generally, the addition of rigid particles to a polymer matrix will have an embrittling effect on the composite. A new concept is the usage of filler particles as toughening agent. The general idea is to mimic the rubber toughening mechanism using rigid filler particles. The rigid particles must debond and create free volume in the blend on a sub-micron size level. This is much like the cavitation mechanism in rubber toughened systems. The micro-mechanistic model for this toughening effect is consisting of three stages (stress concentration, debonding and shear yielding).

In this paper, the toughening of polypropylene with calcium carbonate particles on submicron size level is studied. First, the influence of matrix molecular weight and the nucleation agent on the toughening behavior was evaluated. Following results of this experiment were preparing optimized polymeric matrix. The next step was compounding of a composites system from optimized matrix and submicron size \( \text{CaCO}_3 \) particles. The influence of the size and mass content of the particles on the mechanical properties of composites were investigated. Particularly, the stiffness, strength and toughness were chosen as relevant parameters. The stiffness and strength were estimate by the means of tensile test while for toughness the J-R curve procedure was utilized. The results were correlated with microscopic observation. Further we were interested on deformation behavior of the composite system.

Experimental
The isotactic polypropylene (iPP) matrix with MFR 37 g 10min\(^{-1}\) (230 °C, 2.16 kg) and molecular weight \( M_w = 194,000 \) was prepared. Further, this iPP matrix was modified by beta nucleation agent NJ Star NU-100 from Rika International (GB).

As filler we used to commercial available \( \text{CaCO}_3 \) particles from Solvay production concretely SOCAL 312 with these parameters: Average diameter \( d_{50} = 0.07 \mu m \) and specific surface (BET) 19 m\(^2\)g\(^{-1}\), that was with surface treatment already from production. The composite was prepared with two weight percents of filler (5 % wt., 10 % wt.), see (Table I).

<table>
<thead>
<tr>
<th>Types of prepared composites</th>
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<tbody>
<tr>
<td>Sign as</td>
</tr>
<tr>
<td>N5</td>
</tr>
<tr>
<td>N10</td>
</tr>
<tr>
<td>B5</td>
</tr>
<tr>
<td>B10</td>
</tr>
</tbody>
</table>

Compounding of the materials was done using APV 25 twin screw extruder. After compounding, the blends were injection moulded into “dog-bones” using Battenfeld 750 CD injection moulding machine in accordance with ČSN EN ISO 527-1.

Tensile Test
The tensile tests were carried out on the testing machine ZWICK Z020 in accordance with ČSN EN ISO 527-1. The deformation rate was 10 mm min\(^{-1}\) and the temperature of measurement was 23 °C. The following values were estimated: Tensile Modulus (E), Tensile Stress at Yield (\( \sigma_y \)), and Tensile Strain at Yield (\( \varepsilon_y \)). Extensometer with accuracy class 0.5 was used to measure the strain during the tensile test.

The tensile test results (Figs. 1., 2.) exhibit lower tensile modulus and slightly lower yield strength with the increasing of fillers content. This trend was shown distinctive in the case of composite with beta nucleated matrix.

Comparing of tensile plots (Fig. 3.) and energy to break Wb (Fig. 4.) from these composite materials interpret the
Composite materials with beta nucleated PP matrix exhibit higher elongation to break and higher energy to break. This enhancement grown to double in composite with 5 % wt. (material B5).

Resistance curve tests were made by multiple specimen technique in accordance with ASTM 6068-96 on the testing machine ZWICK Z1120 (deformation rate was 10 mm min⁻¹, support distance 40 mm).

The fracture toughness of composites with native PP matrix and beta nucleated PP matrix were determined in terms of the J-R curves. As the fracture characteristics the J integral value at crack extension of 0.05 mm (Δa = 0.05 mm) was chosen (J₀.₀₅).

The results of fracture tests are summed up in (Fig. 5.) and (Fig. 6.), respectively. Particularly, J-R curves of individual composite systems are given in (Fig. 5.) and the J₀.₀₅ values for native or beta nucleated PP matrix with 5 % wt. and 10 % wt. composite systems are shown in (Fig. 6.).

As shown in Fig. 6. the composite material with beta nucleated PP matrix and 10% wt. content of CaCO₃ particles (material B10) exhibit decrease trend of J₀.₀₅ characteristic. This effect means possible lower crack resistance of mentioned system. Generally, the crack resistance of all this systems is considerably higher in comparison with PP matrix materials without CaCO₃ fillers.

The structure of composite materials was evaluated by optical microscopy in polarized light on microscope Zetopan-Pol. It was preparing by the method of ultrathin cuts (5 µm) on Mikrotron Leica. Ultrathin cuts were extracted from the middle part of injected molded specimens perpendicularly to this direction (Fig. 7.).
We can see markedly difference between composites with native PP matrix and beta nucleated PP matrix. The native matrix composites shows spherulite structure with small size of spherulites. In the case of beta nucleated PP matrix composites is any spherulite structure visible. Further it was the crystallization process examined under temperature 135 °C. The addition of CaCO₃ particles affect this behavior and reduce the crystallization time from 1 hour to 10 min. The filler particles increase number of crystallization centers and accelerate the crystallization process. In the case of beta nucleated matrix is mentioned effect involved by higher ability of this nucleation agent.

Morphology of PP specimens was study by scanning electron microscopy (SEM).

These samples were prepared from part of composite material specimens after tensile test in axial direction. Separating of samples was in liquid nitrogen and than they was evaporate coated. The fracture areas were observed in 5,000 × total magnification (Fig. 8.). Not least we evaluated distribution of CaCO₃ filler particles.

The characteristic morphology changes of samples in a study are shown in (Fig. 8.). The particles are dispersed reasonably well, although there are only small agglomerates visible. On both pictures we can see formation of tree stage micro-deformation mechanism. This result is in good agreement with literature³,⁴.

Conclusions

The mechanical properties and morphologies of PP composites filled with CaCO₃ particles are in good accordance with literature. It was clear that type of PP matrix had key effect on composite properties and behavior. The addition of fillers particles lead to increase stiffness and crack initiation resistance and improve too the deformation behavior especially in the case of beta nucleated PP matrix. Further the filler particles increase number of crystallization centers and accelerate the crystallization process. It was confirmed forming of 3-stage deformation mechanism in investigated systems.

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REFERENCES

**Introduction**

Polyurethanes (PUs) are widely commercially produced material because of possibility to obtain various properties by changing raw materials resulting in flexible or rigid foams, solid elastomers, coatings, adhesives and sealants. PUs are usually produced by the polyaddition reaction of a polyfunctional isocyanate with polyol or other reactants containing two or more groups reactive with isocyanates. Nowadays, with increasing PUs consumption, the chemistry of preparation is focused on the possibilities of recycling and/or degradation of the plastic materials in order to avoid environmental pollution by non-degradable polymer waste dump. The elimination of expenses connected with recycling of these materials becomes a vital target of all producers. One of the ways how to reduce the price along with increasing the degradability of these materials is addition of cheap biodegradable filler to the structure of PURs, which can partly or fully substituted one of the raw material, mostly polyol. Several research works using bio-polyols containing more than one hydroxyl group (–OH) in the main chain suitable for coupling reaction has been carried out.

In this paper, new elastomeric PUs with specific mechanical as well as biological properties were prepared by one-shot process. Commercial non-degradable polyether polyol derived from petrochemical feed stocks was partly substituted by the bio-polyols based on cellulose or starch derivatives. Prepared samples were tested for mechanical properties by tensile measurements. Moreover, the biodegradability was evaluated by thermophilic bacteria.

**Experimental**

Briefly, water-free tolylene diisocyanate (TDI), water-free polyether polyol (PEP), tin catalysts and degassed biopolyol (cellulose or starch derivatives) were mixed together in one-shot process, stirred under the vacuum and poured into the 1 mm thick metal frame placed between two polypropylene sheets. The reacting mixture was left to cure for 2 days at laboratory temperature. Cellulose or starch derivatives with different degree of substitution (DS) of –OH groups like acetylated starch (DS = 0.1), acetylcellulose (DS = 2.4), 2-hydroxyethylcellulose (DS = 0.6) and carboxymethylcellulose sodium salt (DS = 0.7), AS, AC, CMC, HEC, respectively, were used for substitution of common PEP in amount from 1 to 10 % wt.

**Biodegradation Evaluation**

Based on the SEM pictures (Fig. 1.) of PU specimens it is evident that all added fillers were not dissolved in polyol and prepared samples have character of composite materials. Fig. 1.a shows one big particle of CMC (approx. 250 μm) with bad adhesion to the PU matrix. The surface of HEC particles looks flat with several sharp borders showing little bit better adhesion to the matrix than CMC (Fig. 1.b). On the other hand, some molecules from the bio-filler surface could be dissolved in the polyether polyol and thus integrated to the polymer structure. This probably happened in the case of AC and AS bio-polyol because their surface is smooth and particles are fully incorporated in PU matrix (Fig. 1.c and d). The AC particles are strongly porous and their adhesion to the matrix is very good. There is no evident separation between the AC and PU surface. However, specimens filled by AS shows excellent adhesion to the PU matrix which either stays on the surface of particles or the particle breaks apart with the matrix during the breaking of the specimen.

All mentioned SEM pictures show evident influence on both size and chemical composition of filled bio-polyols on the modified PUR morphology. The best adhesions show both AC and AS even if their particle sizes and shapes are...
different. However, the morphology does not say anything about the mechanical properties of resulted polymer composite materials, which have to be evaluated by tensile measurement.

**Tensile Characteristics**

Based on the stress-strain curves all prepared specimens behaved like tough materials without yield point. The reaching the elasticity limit was followed up by a long extension ended with the break. Better elongation at break then reference PU sample embodied only specimens having 1 and 5 % wt. of CMC and all PU elastomers filled with hyperbranched AS polysaccharide. Fig. 2. shows that the addition of the bio-filler increased the Young’s modulus in all cases except the specimens filled with 1 % wt. of HEC, AC and AS, which should not be taken into deep account due to the relatively high standard deviation of \( \varepsilon_B \).

Based on the results it is evident that there are two groups of fillers which influence the properties of final material. CMC, HEC and AC forms the first group of the linear cellulose molecules incorporated in PU matrix. 1 % wt. of these bio-polymers in PU matrix increase the tensile strain at break \( \varepsilon_B [\%] \) of prepared specimen and in the case of 1 % wt. of CMC also tensile stress at break \( \sigma_B [\text{MPa}] \). \( \sigma_B \) of 1 % wt. of HEC and AC is lower than \( \sigma_B \) of REF. All cellulose based derivatives filled specimens with content of 5 % wt. of fillers in polyol part have increased \( \sigma_B \) but only in case of 5 % wt. of CMC increased also \( \varepsilon_B \). In case of substitution of 10 % wt. of polyol by CMC, HEC or AC have all specimens slightly increased \( \sigma_B \) but decreased \( \varepsilon_B \), whereupon, it is possible to say that only addition of 5 and 10 % wt. of CMC can improve the mechanical properties of PU matrix, which corresponded with stress-strain curves, even if SEM microscopy had not proved good adhesion of CMC to PU matrix. The CMC particles are probably very tough composed of long agglomerated fiber, which might improve the elongation during the mechanical straining. On the other side, porous particles of AS showing good adhesion resulting in increase the Young’s modulus but also reduce the elongation at break.

The second group include the specimens made of polyol partly substituted by AS which consists of branched amylpectin and linear amylose whose -OH groups of their polymer chains are partly substituted by acetate group – \( \text{C(O)CH}_3 \) with degree of substitution \( DS = 0.1 \). Addition of 1 % wt. of AS has increased \( \varepsilon_B \) and its values of \( \sigma_B \) are very close to REF sample whereas addition of 5 and 10 % wt. have both values higher resulting in improved mechanical properties of above mentioned samples in comparison with reference PU elastomer also proved by SEM pictures. Starch particles are probably more flexible then cellulose ones implicating the increase in elongation at break.

**Biodegradation**

The growth of thermophilic bacteria in the presence of control and modified PU elastomeric films is illustrated in Fig. 3. It is evident that PU films weakly inhibited the initial growth of thermophilic bacteria in the presence of control and modified PU elastomeric films is illustrated in Fig. 3.
growth phase of bacterial culture where the lag-phase is dependent on the type of modification agent.

**Conclusions**

Proposed work proved that synthesis of the new cost-effective biodegradable PU elastomers can improve mechanical properties of commercially available polyurethane materials. Applied methods showed that prepared samples have character of particle reinforced composite materials.

In a pilot study, biodegradation of modified polyurethane elastomers by mixed culture of thermophillic bacteria exhibited unusual growth characteristics strongly dependent on the type of biopolymer filler.

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P20 MODELS OF ORGANIZED SUPERMOLECULAR STRUCTURES: APPLICATION TO COLLAGEN FIBRILS AND DENDRIMERS

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Introduction

Contribution describes simulation of selected supermolecular structures: dendrimers and collagen fibril. Research was focused to relation between its supermolecular structure and macroscopic physical properties derived from the structure.

Dendrimers are synthetic macromolecules with regular and highly branched architecture. They are synthesized with series of controlled reactions, where each step (generation) results in an exponential increase in the number of monomers. Structure of such materials has also impact on their applications such as catalysis or biomedical applications.

They are interesting from viewpoint of theoretical research because they have simply defined supermolecular structure. It enables building a model of such structures with high fidelity. Second, they have no more structural levels between supermolecular and macroscopic structure. This enables instant validation of modeling results with measured properties. Mainly the dendrimer solutions are described in literature. Therefore, modeling of its solvation can be useful.

Collagen is fibrous protein that is found in connective tissue – bone, tendons, and skin. This function requires special properties. The crucial property is high elasticity. The tendons are deformed and relaxed many times during life. Dissipation of a lot of energy could lead to its damage. Moreover, the plastic deformation would lead to permanent deformation of tendons. Neither dissipation of energy nor the permanent deformation is observed in nature.

One of collagen components is composed from complex helical structure. Three factors were taken into account: triple helical supermolecular structure, presence of strong intermolecular interaction, and the layout side chains outside the triple helical structure. Model can be helpful in analysis of factors. Unlike real experiment, in the model one factor can be switched off and isolated effect other factors can be analyzed separately.

Experimental

Building of supermolecular structures as well as deformation and salvation of supermolecular structures were performed by in house software.

Molecular simulations and visualization were realized by general public license software GROMACS and Argus-Lab.

Building Structure of Dendrimer and its Solvation

Input properties of dendrimers are shown in Fig. 1. The result of the model is a molecule. The molecules were built either in vacuum or in water.

Building structure and Deformation of Collagen Fibrils

Parameters of collagen triple helix are shown in Fig. 2. Builder outputs are analogous to previous chapter.

The structure was optimalized by energy minimalization method. A deformation was applied to the collagen fibril by position restraints.

Results

Solvation of Dendrimers

Dendrimer of CH₂ group was build of 1st, 2nd and 5th generation. The structures were optimized in vacuum. Introduction of solvent led to steep increase of potential energy. 3.7 x 10⁶ kJ mol⁻¹.

However, the increase of energy may be caused by repulsive intermolecular energy. Two atoms were in close vicinity. The interactions must be analyzed and dendrimer builder with higher fidelity should be programmed.
Deformation of Collagen Fibrils

First, structure of collagen without hydrogen bonds was built. Structure was optimized. The combination of triple helix and weak London interactions were sufficient to conserve main helices; however, they were not sufficient to conserve secondary helix. In this structure, increase of energy during deformation was lower than statistical deviation of energy in undeformed state. Thus, the deformation was not calculated.

In case of structure with hydrogen bonds, increase of energy was significant. Deformation was performed until the elongation limit 0.0035 nm. The resulting force is shown in Fig. 3.

Until elongation 0.001 nm no force was registered. Then, the interaction increased. The atoms were probably slightly out of equilibrium in the first phase of simulation.

Conclusions

Properties of selected supermolecular structures: dendrimers and collagen fibrils were investigated. They were calculated by molecular mechanics method. First process was salvation of dendrimer by water. Energy of molecular box increased significantly during solvation. It is not in correlation with real solution. The factor responsible for increase of energy should be analyzed. Deformation of collagen model molecule corresponded to real behavior of collagen fibrils.

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