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MOLDABILITY OF HIGHLY FILLED POLYMERS

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Injection molding of ceramic and metal powders is relatively new technology applied in automotive, medicine, electronic or military industries. Small and complex-shape parts can be generated with this technology, and material wastage and ecological load are less than in traditional metallurgy.

Feedstocks contain two components: polymer binder and metal or ceramic powder. The main quality factor of the process is the uniform dispersion of a powder within a binder. Since polymer binder is removed after injection molding (prior sintering) a nonuniform powder-binder distribution can cause defects on a final part.

Mixing is the first step to control the powder-binder uniform distribution, where a minimal material segregation and absence of agglomerations as well as voids are desirable. Any weakness occurring during mixing causes problems in the following steps 1,2.

Even if a fairly uniform powder and binder distribution is attained after mixing (as evident from SEM micrograph, Fig. 1) of the sample of the commercially available feedstock prepared by pressing (2 minutes preheating at 200 °C, 3 minutes pressing at 200 °C and 5 minutes cooling), the dispersion of the powder within a polymer binder may dramatically change during high shear processing as injection molding. Thus, moldability of highly filled compounds is the main concern of this paper.

![Fig. 1. SEM of commercially available highly filled (60 vol.%) feedstock](image1)

![Fig. 2. Mold for testing moldability of highly filled polymers](image2)

![Fig. 3. Shear viscosity as function of shear rate for feedstock C, P and E](image3)

Shear rate and corresponding shear stress during injection molding generate local gradients resulting in the nonuniform powder-binder distribution. The critical geometrical elements of a molded part are mostly inner and outer corners, radical thickness changes including gates, weld-lines and thin films or flashes.

Thus, a mold for testing moldability of highly filled polymers was developed at the Polymer Centre, TBU in Zlín (in cooperation with Fraunhofer IFAM, Bremen), which includes the critical geometrical elements mentioned (Fig. 2). The length of the inert walls of the first three elements is 10 mm. Width of the elements wall is gradually decreased from 3 mm to 2.5 mm and 2 mm. Length of the gates between elements is 1 mm with 0.5 mm diameter.

Three commercially available feedstocks (abbreviated C, P and E) were tested; their flow properties are demonstrated in Fig. 3.

Injection molding machine Arburg Allrounder 370S (EUROMAP size 700-100) with a special surface treatment of the screw for highly filled materials was used. Screw diameter was 20 mm with an effective screw length (L/D) of 16.7.

While injection molding of the feedstocks C and P was optimized successfully, the feedstock E, which has demonstrated a high tendency toward the slip during rheological testing, was molded with the following difficulties. The first problem was that the material was entrapped in the feed hopper. After mechanical enhancement, the pellets went through the feed hopper, but stucked just above a screw creating the solid plug and preventing the flow of the rest of the pellets along the screw towards the melting and terminal zones.
After a thorough preheating of the material (50 °C) and setting up rather low speed of a screw (not to exceeding 60 mm s⁻¹) this issue was solved. Plasticity and enhanced adhesion of the feedstock E caused next problem in a sprue bush. Opening of the mold caused a break of the runner system (Fig. 4). A part of the runner system remained in a fixed half of the mold. Removing of this part from the sprue bush was rather complicated. This problem prevented effective injection molding. Thus, various conditions of a molding cycle were tested – nozzle temperature varied from 140 °C to 160 °C, mold temperature from laboratory temperature to 70 °C, injection pressure (900 bar to 2000 bar), holding pressure (900 bar to 1500 bar), injection speed (from 25 mm s⁻¹ to 150 mm s⁻¹). In all cases the problem was observed.

The solution was the reduction of the sprue bush length from the originally 74 mm to 50 mm. It should be noted that after such reduction the nozzle must run inside the mold.

Further, the mold had ejectors located only in the corners of each square element. The molded samples of feedstock E were destroyed by ejectors in B and C square elements. Thus, additional ejectors to B and C square elements were implemented to the mold.

The optimized molding conditions for the particular feedstocks are summarized in Table I.

Nevertheless, all three tested materials exhibit a non-uniform powder distribution after injection molding into a testing mold. The critical changes in powder distribution were detected behind the gates 1, 2 and 3. The segregation of the material components can attain a considerable effect as evident from SEM in Fig. 5, where the completely separated areas (dark areas without a powder) causing warpage of a product structure during sintering can be seen.

The quantification of the powder/binder segregation is provided via combined SEM/EDX analysis followed by an analytical approach developed at present⁴.

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Table I

<table>
<thead>
<tr>
<th>Material</th>
<th>P</th>
<th>C</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1 temperature (°C)</td>
<td>160</td>
<td>160</td>
<td>100</td>
</tr>
<tr>
<td>Zone 2 temperature (°C)</td>
<td>185</td>
<td>170</td>
<td>110</td>
</tr>
<tr>
<td>Zone 3 temperature (°C)</td>
<td>190</td>
<td>180</td>
<td>120</td>
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<tr>
<td>Zone 4 temperature (°C)</td>
<td>195</td>
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<td>130</td>
</tr>
<tr>
<td>Nozzle temperature (°C)</td>
<td>200</td>
<td>200</td>
<td>150</td>
</tr>
<tr>
<td>Mold temperature (°C)</td>
<td>85</td>
<td>85</td>
<td>50</td>
</tr>
<tr>
<td>Injection speed (mm/s)</td>
<td>220</td>
<td>188</td>
<td>150</td>
</tr>
<tr>
<td>Injection pressure (bar)</td>
<td>2000</td>
<td>2000</td>
<td>1000</td>
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<tr>
<td>Injection time (s)</td>
<td>0.19</td>
<td>0.19</td>
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<tr>
<td>Hold pressure (bar)</td>
<td>2100</td>
<td>2100</td>
<td>800</td>
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<tr>
<td>Hold pressure time (s)</td>
<td>4.0</td>
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REFERENCES

THE EFFECT OF ORGANOPHILIC CLAY ON TRIBOLOGICAL PROPERTIES OF GRAPHITE/EPOXY COMPOSITES

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Introduction

Due to remarkable improvement in a wide range of physical and engineering properties polymer nanocomposites are progressively replacing traditional structural materials in the automotive and aerospace industry. Polymer nanocomposite properties are primarily a function of nanofillers particle size, surface properties, distribution in polymer matrix and interactions on filler/matrix interface.

Recently it was found that polymer nanocomposites are also of high importance in applications where low friction of materials is required. Furthermore, a very effective approach how to increase tribological properties of polymers is combination nanofillers with conventional micro sized fillers. Thus, proper selection of nanofillers together with compounding equipment and mixing conditions play a key role in polymer nanocomposite end use properties.

This work highlights the effect of organophilic clay on tribological properties of graphite/epoxy composites. To evaluate the role of compounding parameters on structure and properties composites have been prepared by mixing in high shear (10,000 rpm) as well as standard (500 rpm) mixing equipment.

Materials

As a polymer matrix has been used a resin Bisphenol-A-Epichlorohydrin epoxy resin and a Hardener type Ancamine from Air Products GmbH 3-Aminoethyl-3,5,5-trimethyl-cyclohexylamin (Ancamine 3473), Bisphenol-A diglycidyl ether (BADGE) (Ancarez RZ 4020).

Natural micro crystal structure graphite EPDM 90/91 with the average particle size was 20 µm, product of German company Kropfmühl AG, has been used.

Organophilic clay Nanomer I.30E, modified by 27 \(^\%\) wt. octadecylamine, was obtained from Nanocor Inc. Original Nanomer I.30E particle size 10 µm (Fig. 1) was determined by Laser Particle Sizer (ANALYSETTE 22).

Composites preparation

Composites have been prepared in two stages by mixing in low speed and high speed mixing equipments:

- high shear mixer (Ultraturrax 50 E) from IKA
- standard mixer a four paddle-stirrer

Graphite/epoxy and clay/epoxy were prepared by mixing Bisphenol-A-Epichlorohydrin resin and hardener with clay and/or graphite. Hybrid graphite/clay/epoxy composites have been prepared by mixing in two phases:

1. the organophilic clay (Nanomer I30.E) was mixed in the ER (Ancarez RZ 4020) in high shear and/or standard mixer.
2. graphite and the hardening agent was mixed with ER/I30.E composite in a conventional mixer with a four-paddle-stirrer.

Composition of studied composites and corresponding mixing conditions are presented in Table I.

Tribological analyses

The characterization of the frictional and wear behavior was carried out in accordance with the standard test method for ranking resistance of plastics to sliding wear in block-on-ring wear test (cumulative wear method, DIN ISO 7148-2 respective). The tribological properties were determined on a part-test bench (Universalprüfstand Fa. Krauss) as follows:

- abrasive wear (at 1 MPA, 60 °C, 6.6 m s\(^{-1}\))
- static coefficient of friction (at 1 MPA, 60 °C, 6.6 m s\(^{-1}\))
- sliding coefficient of friction (at 1 MPA, 60 °C, 6.6 m s\(^{-1}\))

Results and discussion

In order to eliminate potential mutual effect of the other components (e.g. fibers, lubricants, etc.) and to evaluate solely the effect of clay on tribological performance epoxy/graphite composites, the number of additional components was reduced to epoxy resin, graphite and clay. The clay and graphite content was kept constant on 5 wt.%.

As a polymer matrix has been used epoxy resins due to outstanding tribological and favourable mechanical, thermal, mixing and curing properties. Nanomer I.30E was applied

Table I

<table>
<thead>
<tr>
<th>Composite composition</th>
<th>Epoxy</th>
<th>Epoxy/clay</th>
<th>Epoxy/clay/graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanomer I.30E</td>
<td>0</td>
<td>5 wt %</td>
<td>5 wt %</td>
</tr>
<tr>
<td>Graphite</td>
<td>0</td>
<td>0</td>
<td>5 wt %</td>
</tr>
<tr>
<td>Mixing equipment</td>
<td>Shear mixer 10,000 rpm 30 min</td>
<td>Four paddle stirrer 500 rpm 10 min</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Organophilic clay Nanomer I.30E size distribution
since (as a result of catalytic function of the acidic primary onion ions that facilitate epoxy rings) in this type of organophilic clay the highest level of exfoliation (compared with e.g. Nanomer I.28E, Cloisite C 10, C 15A, C 20A) was achieved.7

To evaluate the effect of compounding on structure and properties composites have been prepared by mixing in high shear (10,000 rpm) as well as standard (500 rpm) mixing equipment.

As it is evident from the Fig. 1, original particle size of Nanomer I.30E was 10 µm. Extensive reduction of transparency of clay/epoxy composites (Fig. 2) indicate, that during both, standard and high speed mixing, the major part of clay particles did not reach nanostructure level. Although the microscopic analyse (resolution microscope 1000×) of clay/epoxy composite structure confirmed significant reduction of clay particle size (up to 0,5 / 1,0 µm), the number of exfoliated particles, if any, was negligible (Fig. 3).

Whilst in both, clay and graphite based epoxy composites by adding of 5 wt.% of single fillers only negligible (16 %) reduction of wear compared to neat epoxy resin was observed, the effect of hybrid clay/graphite fillers was much more significant (Fig. 4). The highest, 48 % wear reduction, was observed in clay/graphite/epoxy composites prepared by standard mixing.

Fig. 2. The effect of clay (I30.E) on transparency of epoxy resin: a) neat epoxy resin, b) clay/epoxy composites prepared by standard mixing, c) clay/epoxy composites prepared by high speed shear mixing

Fig. 3. Structure of epoxy/clay (I30.E) composites prepared by a) standard mixing; b) high speed shear mixing

Fig. 4. Influence of graphite and clay (I30.E) on the wear of epoxy composites prepared by shear mixing

Fig. 5. Influence of graphite and clay (I30.E) on dynamic coefficient of friction of epoxy composites prepared by shear mixing

Fig. 6. Influence of graphite and clay (I30.E) on static coefficient of friction of epoxy composites prepared by standard mixing
Similar, 41% reduction of wear was observed in clay/graphite composites prepared by high shear mixing (Fig. 5). Unlike wear, there was observed negligible only effect of mixing conditions as well as single and also hybrid clay/graphite fillers on the dynamic (Fig. 5) and static coefficient of friction (Fig. 6).

Conclusions

In the paper the effect of organophilic clay Nanomer L30E on tribological performance of graphite/epoxy composites has been studied. It was found that addition of clay lead to comparable wear reduction as in graphite/epoxy composites. However, the most significant improvement of tribological behaviour was observed in hybrid clay/graphite/epoxy composites. In this case important 50% reduction of wear was achieved by addition just 5 wt.% of clay and 5 wt.% of graphite. There was not observed synergistic effect of hybrid fillers on static and dynamic coefficient of friction.

REFERENCES


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POLYMER FLUIDITY INFLUENCED BY THE FILLER

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Abstract

This paper shows the influence of cavity surface roughness and on the flow length of filled polymers by tale into mold cavity. Application of the measurement results may have significant influence on the production of shaping parts of the injection molds especially in changing the so far used processes and substituting them by less costly production processes which might increase the competitiveness of the tool producers and shorten the time between product plan and its implementation.

1. Introduction

Injection molding is one of the most extended polymer processing technologies. It enables the manufacture of final products, which do not require any further operations. The tools used for their production – the injection molds – are very complicated assemblies that are made using several technologies and materials. Working of shaping cavities is the major problem involving not only the cavity of the mold itself, giving the shape and dimensions of the future product, but also the flow pathway (runners) leading the polymer melt to the separate cavities. The runner may be very complex and in most cases takes up to 50% volume of the product itself (cavity). In practice, high quality of runner surface is still very often required. Hence surface polishing for perfect conditions for melt flow is demanded. The stated finishing operations are very time and money consuming leading to high costs of the tool production.

Delivery of polymer melts into the mold cavity is the most important stage of the injection molding process. This paper shows the influence of cavity surface roughness and technological parameters on the flow length of polymer melt into mold cavity. The fluidity of polymers is affected by many parameters (mold design, melt temperature, injection rate and pressures) and by the flow properties of polymers. Results of the experiments carried out with polypropylene contained 5% of graphite proved a minimal influence of surface roughness of the runners on the polymer melt flow. This considers excluding (if the conditions allow it) the very complex and expensive finishing operations from the technological process as the influence of the surface roughness on the flow characteristics does not seem to play as important role as was previously thought.

2. Injection molding

The injection mold for was designed for the easiest possible manipulation both with the mold itself and during injection while changing the testing plates, size of the mold gate etc. The injection mold is inserted into a universal frame (Fig. 2) which was designed for use with many different injection molds that fit the size of the frame. This makes the change of the separate injection molds easier, because the frame remains clamped to the injection molding machine and only the shaping and ejection parts of the molds are changed. Attaching right and left sides of the frame to fixed and moving plates of the injection machine is done using four clamps on each side.

The shaping part of the injection mold is composed of right and left sides, see Fig. 2. The most important parts of the injection mold concerning the measurements are: testing plate, cavity plate and a special sprue puller insert.

The cavity (Fig. 2 – right) of injection mold for is in a shape of a spiral with the length of 2000 mm and dimensions of channel cross-section: 6x1 mm. The cavity is created when the injection mold is closed, i.e. when shaping plate seals the testing plate.

Injection mold can operate with 5 exchangeable testing plates (Fig. 2 – left) with different surface roughness.
The surface of the plates was machined by four different technologies, which are most commonly used to work down the cavities of molds and runners. These technologies are polishing, grinding, milling and electro-spark erosion. The testing plates are used for changing the surface of the mold cavity.

3. Results

Natural polypropylene and polypropylene with different amount of filler – talc (10 %, 20 %, 30 %, 40 % of talc) has been used for the experiment.

The aim of the measurements was to find out the influence of separate parameters, especially the quality of the injection mold cavity surface and filler amount, on the flow length. The main results are given on the Fig. 3–6.

### Table I

<table>
<thead>
<tr>
<th>Surfaces of testing plates</th>
<th>Flow length [mm]</th>
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<tr>
<td>Polished plate</td>
<td>212</td>
</tr>
<tr>
<td>Ground plate</td>
<td>210</td>
</tr>
<tr>
<td>Electro – spark machined</td>
<td>208</td>
</tr>
<tr>
<td>plate (fine design)</td>
<td>206</td>
</tr>
<tr>
<td>Milled plate</td>
<td>204</td>
</tr>
<tr>
<td>Electro – spark machined</td>
<td>202</td>
</tr>
<tr>
<td>plate (rough design)</td>
<td>200</td>
</tr>
</tbody>
</table>

Fig. 1. **Assembly of injection mold;** 1 – frame, 2 – injection mold, 3 – ejection system

Fig. 2. **Cavity plates** (left – testing plate, right – shaping plate)

Table I

<table>
<thead>
<tr>
<th>Polished plate</th>
<th>Ground plate</th>
<th>Electro – spark machined plate (fine design)</th>
<th>Milled plate</th>
<th>Electro – spark machined plate (rough design)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_a$ [µm]</td>
<td>$R_z$ [µm]</td>
<td>$R_a$ [µm]</td>
<td>$R_z$ [µm]</td>
<td>$R_a$ [µm]</td>
</tr>
<tr>
<td>0.102</td>
<td>0.172</td>
<td>4.055</td>
<td>4.499</td>
<td>9.566</td>
</tr>
</tbody>
</table>

Fig. 3. **Dependence of the flow length on surface quality (0 % talc)**

Fig. 4. **Dependence of the flow length on surface quality (20 % talc)**

Fig. 5. **Dependence of the flow length on surface quality (40 % talc)**
4. Conclusion

This research looked into the influence of technological parameters on filling of the injection mold cavity and the flow length respectively. The differences in flow lengths at the testing cavity plates with different surface roughness were very small, rather higher in case of rougher surfaces. But there is demonstrable difference of worse flow properties on each testing plate with increasing percentage of filler (talc). The measurement shows that surface roughness of the injection mold cavity or runners have no substantial influence on the length of flow. This can be directly put into practice. It also suggests that final working and machining (e.g. grinding and polishing) of some parts of the mold, especially the flowing pathways, are not necessary.

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REFERENCES


Abstract

The understanding of dynamic behavior as well as fracture behavior of rubber-like materials is of great practical importance for the prediction of rubber-like product’s life time. The aim of this work is concentrated (i) to the description of mechanisms leading to rubber failure with respect to real loading conditions of the products and (ii) to a proposal resp. discussion of future trends in practical rubber characterization. We firstly demonstrate a relationship between Fatigue Crack Growth (FCG) behaviors under different loading conditions. Concluding we introduce a closed characterization method of dynamic rubber behavior with respect to tyre tread wear including the specific role of the FCG behavior of the rubber materials.

Introduction

The most important high dynamically loaded technique rubber parts are especially tyres, which are very important parts for the life-safety in the daily usage. The mechanical behaviour of tyre can be observed from two different views, because of the anatomy and functionality of tyre. The design of tyre consists from the in- and outside parts, which are exposing different conditions as loading, ozone concentration, temperature etc. The most affected part in tyre is the tread, because of the contact with the roughness of the road, high dynamic loading conditions, variation of fatigue dynamic and quasi-static loading, impact, influence of high temperature fluctuation, ozone concentration, solar radiation, influence of fluid medium etc. The composition of the compound has a highly important influence on the mechanical behavior of the tread. The standard used rubber types by compounding of tread are also depend on anatomy of tyre and consist of SBR (styrene-butadiene rubber), NR (natural rubber) and/or BR (Polybutadiene rubber). Whereas the other important technical rubber products are mostly based on EPDM (ethylene propylene diene monomer)

It is well known that the extreme requirements for the high dynamic loading conditions, composition of tyre compound as well as the design of tyre tread have an effect on the fatigue and failure of tyres. These processes lead to the
The dissipated energy increase in the smallest asperity surface. The real dynamic loading condition is defined due to loading and detail of the contact between tyre tread and road visualization of real dynamic loading, denoted as pulse area is just a few per cent of the nominal footprint contact the tyre tread relaxes until the next contact (revolution of tyre) milliseconds, after that the contact is enable and the zone in loading conditions. Most efforts in this field are based on the investigating of fracture mechanics of tyre tread under the real main important subjects of scientific research for FCG velocity and FCG orientation? These are the local and propagation and what are the influences of the initiation time, the contact regions causes, that the tyre rubber–road contact over the whole footprint area (s. Scheme 1). The asperity of proceeds. A tyre does not make perfect contact with the road degradation of the mechanical behaviour of rubber matrix. The initiation of local instability in tyre tread due to failure is particularly caused by micro-crack initiation. Its propagation could have fatal consequences because of the resulting global tyre’s instability and thus danger caused due to car’s accident. The understanding of the relationship between the crack initiations caused by impact, fatigue or combination of both and its propagation is a subject of high scientific interest, therefore its description will improve the safety, a higher durability and life service of the tyre as well. The tests and determination of tyre failure are time and money consuming and thus the effective testing method in laboratory condition is highly appreciated.

The exact description of the real dynamic behaviour and failure of tyre tread in the laboratory depends on many conditions, which are listed in the previous paragraphs and therefore the realisation of the analysis is very complicated. The main important question from the tyre producers is: “Which methods could lead to the exact prediction and quantitative characterization of tyre tread behaviours while the tyre development process?”. According to the character of cyclic loading of tyre (s. Scheme 1) only dynamical loading test conditions can lead to a proper description of mechanical behavior and investigation of tyre failure. Thus the efficient approach for the exact characterization of tyre tread behaviour is defined as follows: “The development of new methods or utilization of the systems and equipment for physical material testing of polymeric materials has to be performed under the application of real loading conditions”.

What are the reasons for the crack initiation, its propagation and what are the influences of the initiation time, FCG velocity and FCG orientation? These are the local and main important subjects of scientific research for investigating of fracture mechanics of tyre tread under the real loading conditions. Most efforts in this field are based on the fundamental work of Rivlin and Thomas. The Scheme 1 represents the tyre rolling with the visualization of real dynamic loading, denoted as pulse loading and detail of the contact between tyre tread and road surface. The real dynamic loading condition is defined due to proceeding of loading at the orange denoted region (correspond to the tyre footprint) in the timing range of milliseconds, after that the contact is enable and the zone in the tyre tread relaxes until the next contact (revolution of tyre) proceeds. A tyre does not make perfect contact with the road over the whole footprint area (s. Scheme 1). The asperity of the contact regions causes, that the tyre rubber–road contact area is just a few per cent of the nominal footprint contact area. The dissipate energy increase in the smallest asperity contact regions and the material forces as crack driving forces are applied. Thus the fracture processes with the micro-crack initiation of the tyre tread have been started!

The micro-crack initiation proceeding during frictional sliding of a hard blade abrader on the rolling rubber surface is termed a stick-slip motion. This fracture process is caused due more different mechanisms regarding to the real rolling of tyre. Generally the process could start with the dynamic impact of the strange object (profile of the road surface asperity), which has a considerable higher E-modulus in comparison with the impacted tyre tread. The impactor stresses the tread in the direction of loading and currently influences the stress at the contact zone with the frictionally sliding. After the proceeding of loading in the timing range of milliseconds the contact is enable and the zone in the tire tread relaxes. This mechanism repeats in the frequency of rolling and depends on road surface, because of its fractal 3D structure. The micro-crack can be initiated and proceeds in the phase of the impact or the initiation can start in the phase of sliding, whereas the both processes are characterized due to unreproducible high dynamics change of stress and energy dissipation in the material between relaxed and stressed conditions. The first measurements of rubber abrasion at steady state started Liang et al.8 and the method demonstrating the Chip & Cut effect introduced Mañas et al.7.

As tyre undergoes millions of fatigue cycles, these initiated micro-cracks propagate continuously and lead to catastrophic failure. The observation of rubber resistance against the FCG is necessary to characterize. The tearing energy criterion is commonly used for the fatigue dynamic fracture analysis. There is only one commonly used test equipment for the quantitatively description of dynamic crack propagation working under the real loading conditions. This is the Tear Analyzer made by Co. Coesfeld GmbH & Co. KG.

Materials and experimental details

Three different rubber compounds firstly based on 50/50 SBR/NR (denoted: S-NR-N) and secondarily on 50/50 SBR/EPDM (denoted: S-E-N) blends were filled with 60 phr of normal carbon black N234. The third compound, also based on 50/50 SBR/EPDM (denoted: S-E-M), was filled with carbon black N234 in the masterbatch form. The additional typical curatives corresponding to the composition of the real tyre compound were added. The rubber compounds were prepared using a laboratory internal mixture. The test specimens were cured in a compression mould according to
the determined rheometric properties.

The experimental analysis were performed according to the real rolling condition of tyre 215/70 R16 at a speed of 8 Kmph corresponding to the pulse loading frequency 1 Hz whereas the loaded tyre footprint consists of 35° segment of the whole tyre. Thus the pulse width was determined on 100 ms.

FCG measurements were carried out using Tear Analyzer under pulse as well as sinusoidal loading conditions for the comparison of the real and unrealistic simulation of tyre rolling. The frequency for the pulse loading was set on 1 Hz, while the sinusoidal loading was carried out at frequency 10 Hz, to measure under the identical impact duration while 100 ms. The strain was varied between 5 % and 25 %. The analysis was performed at room temperature. In this study, two double notched and one not-notched pure shear test specimens were simultaneously analysed, whereas the un-notched test specimen was used for determination of tearing energy. The standard pure shear test specimen with the geometry ratio \( L_0/(\text{length})/Q/(\text{width}) = 1.8 \) was used. Each of the pure shear test specimen was notched with notch length \( a_0 = 21 \text{ mm} \) in the both side of test specimen calculated from the definition of minimal notch length \( a_{\text{min}} \) in dependence on geometry ratio \( L_0/\text{Q} \).

The analysis of the frictional sliding of a hard blade abrader on the rolling rubber test specimen has been performed using the test equipment developed by Maňas et al. The standard cylindrical test specimens with the diameter of 55 mm were used and the testing conditions were set according to the above denoted tyre rolling. The energy \( E = 2.77 \text{ J} \) impacted the revolving test specimen in frequency 1 Hz.

**Results and discussion**

In Scheme 2, the influence of the real (pulse) and unrealistic (sinusoidal) loading conditions simulation of impact to the rolling tyre as well as the different types of compounds on FCG rate becomes apparent. It was found that the FCG rate at a given tearing energy as well as the FCG trend increase significantly under the pulse in comparison to the sinusoidal loading conditions independent on type of analysed compound. Therefore, the real pulse loading represents a more critical condition for the fracture behaviour of tyre! The reason for this behaviour is the effect of stress relaxation in the test specimen occurred in the un-loaded phase of tyre rolling. When the deformation forces are removed, the rubber network adopts a state, that is different from the initial state and the rubber relaxes. The again dynamically applied stress, after the relaxation, the fracture and recombination of crosslinks take place. The comparison of pulse and sinusoidal loading conditions also shows different trends in the FCG resistances. The FCG resistance for the compounds analysed under sinusoidal loading conditions were determined in the following order: S-E-N < S-E-M < S-NR-N, whereas under pulse loading the different trend is shown: S-E-M < S-E-N < S-NR-N. As expected, the blend based on SBR/NR shows the highest FCG resistance due to the strain induced crystallinity in NR.

The relationship between the FCG rate and tearing energy is compared to the independently measured rate of wear. In the Scheme 3 the wear resistance of the compounds were determined in the following order: S-E-M < S-E-N < S-NR-N, whereas the compound based on SBR/NR shows the highest wear resistance. A significantly decrease in the wear resistance measured in the remaining compounds is caused due to EPDM basis. The trend of wear resistance diverges with the FCG resistance determined under sinusoidal loading, while the trend corresponds with the FCG resistance of the compound analysed under the pulse loading. The simulation of near to similar testing conditions between the FCG rate and Chip & Cut measurement provides the identical trends of mechanical behaviours.

The future trends for the characterization of the relationship between the structure of rubber matrix and fracture mechanical behaviours are conditioned with the development of new measuring system for simulation of frictional sliding of a hard blade abrader on rubber test specimen corresponding to the real loading of a rolling tyre. The measuring method and equipment based on real pulse simulation in dependence of tyre dimension is objective of the common research of Co. PRL Polymer Research Lab. The future measuring system takes in to account the on-line

![Scheme 2. Influence of sinusoidal and pulse loading conditions on FCG](image1)

![Scheme 3. Comparison of the mass loss respectively wear rate](image2)
controlling of the time and depth as well as the impact frequency of abrader sliding on the rubber test specimen during the complete analysis. The process of analysis is electronically controlled with force respectively energy of sliding or with defined depth of sliding abrader in test specimen. Thus the real testing condition of rolled tyre can be simulated and the energy dissipation during the sliding of hard abrader can be firstly exact determined.

**Conclusion**

The work deals with description of influence of the real (pulse) and unrealistic (sinusoidal) loading conditions corresponding to the rolling tyre on FCG rate. It was demonstrated, that the real pulse loading represents a more critical condition for the fracture behaviour of tyre. This fact together with the diverse relationship between the evaluated wear and determined FCG resistance under sinusoidal loading pointed out the relevance of the analysis under the real loading conditions. As future trends for the exact characterization of the relationship between the structure of rubber matrix and fracture mechanical behaviors caused due to the frictional sliding of a hard blade abrader on rubber according to the tyre rolling conditions a new measuring method and system has been introduced.

This contribution was written with support of Operational Program Education for Competitiveness co-funded by the European Social Fund (ESF) and national budget of Czech Republic, within the framework of project Advanced Theoretical and Experimental Studies of Polymer Systems (reg. number: CZ.1.07/2.3.00/20.0104).

**REFERENCES**


**CL-26 COMPOSITION OF TIRE PYROLYSIS PRODUCTS**

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1. Introduction

This contribution deals with pyrolysis of waste tires and the influence of various process parameters on product distribution and composition. Waste tires are composed of more than 100 substances, the main of them being: rubber (50 wt.%), fillers like carbon or silica gel (25 wt.%), steel cords (10 wt.%), sulphur (1 wt.%), zinc oxide (1 wt.%), and many other additional substances such as processing oil, plasticizer, anti-degradants and vulcanization accelerators. Due to their high heating value, carbon and volatile matter content, waste tires are a valuable material for energy recovery.

Pyrolysis experiments were carried out in a laboratory screw type reactor, under different conditions, by varying temperature and residence time. The effect of above mentioned parameters was investigated with regard to composition of process gas and mass yields. Liquid and solid products were analysed by elemental analysis and gas compositions were determined by gas chromatography.

It was found that the liquid fraction decrease with higher temperature and increase with longer residence time. The gas fraction consisted mainly of hydrogen, methane and light hydrocarbons. The formation of hydrogen and methane was preferred at higher temperature and shorten residence time, opposite to the light hydrocarbons formation.

2. Experimental

Shredded steel-less tire sample was used for the experiments. In order to quantify the amount of volatile and non-volatile components thermogravimetric and elemental analysis of raw sample was performed. The volatile fraction was determined to be 63.5 mass% and the non-volatile one was 36.5 mass%. Elemental composition of tire sample is shown in Table I.

The pyrolysis experiments were carried out in a laboratory pyrolysis reaction unit in a nitrogen atmosphere. The pyrolysis unit consisted of a continual screw type reactor, a cooling system and a gas analyser. The flow reactor was working under isothermal conditions and the residence time of the solid particles was controlled by a frequency circle of rotating metal screw. The pyrolysis experiments were performed over the range of temperatures of 600–750 °C and at residence times R1 (135.4 s), R2 (99.4 s) and R3 (75.5 s). A detailed description of the apparatus is provided in ref. 1.

Solid and liquid fractions were analysed using an elemental analyser Vario Macro Cube (Elementar Analysensysteme, Hanau, Germany). The analysis of gaseous phase was done on a Micro Box III (SLS MICRO TECHNOLOGY, Hamburg, Germany).
3. Results and discussion

Solid and liquid pyrolysis yields were determined in each experiment by weighing the obtained amount and calculating the corresponding percentage. The gas yields were determined by difference and, therefore, include all the experimental errors and inaccuracies. Product yields of solid, gaseous and liquid (tar) fraction at various temperatures and residence times are shown in Fig. 1. An increase in the amount of gases and a consequent decrease in the amount of liquids can be seen. This decline in the liquid fraction and increase in the gaseous yields was also observed by other authors and can be explained by the stronger thermal cracking processes taking place at higher temperatures. Concerning residence time, there was a slight increase in liquid yields with temperature as a result of shorter time for decomposition to take place.

Tire pyrolysis gases were mainly composed of light hydrocarbons (ethane, ethene etc.), hydrogen and methane together with some CO, CO₂ and H₂S. The results for the composition of the gases are shown in Fig. 2, where it is to be observed that the higher the pyrolysis temperature is, the more methane and hydrogen is present in the gas, while the remaining hydrocarbons decrease. This drop in the light hydrocarbon chains and the rise in the methane and hydrogen with temperature is due to the mechanism of the pyrolysis process itself. As temperature rises, the heavier hydrocarbons are cracked, giving rise to lighter ones, methane and hydrogen. Consequently, the gas samples become enriched with the lighter hydrocarbons as the temperature increases. Furthermore, the higher the final temperature of pyrolysis is, the less CO₂ is produced, while CO increases, probably because of the secondary reactions taking place during the pyrolysis process. In this last step CO is formed from reactions in the gas phase between CO₂ and hydrocarbons or from other cracking reactions.

Pyrolysis liquid is a very complex mixture of organic compounds of 5–20 carbons and with a great proportion of aromatics and aliphatic. The elemental analysis results are shown in Table II. There can be seen a decrease in carbon fraction at higher temperature, possibly due an increase of aliphatic, nitrogenated and benzothiazol compounds. It may be concluded that in the low temperature pyrolysis, there are more free aliphatic compounds, while in the higher-temperature liquid, many of such aliphatic are linked to aromatic structures. Similar results concerning the increase of aromatics with temperature have been observed at other residence times.

The increase in oxygen could be caused due to the production of oxygenated compounds at higher temperatures.

Table I
Elemental composition of raw tire sample

<table>
<thead>
<tr>
<th>Component</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>Oa</th>
<th>Residueb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content/? mass %</td>
<td>0.4</td>
<td>80.4</td>
<td>7.4</td>
<td>1.6</td>
<td>2.7</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Note: a Calculated from the difference to 100 %, b residue: non-combustible matter

Table II
Elemental composition of liquid at Rt1

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>O+othersa</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>1,24</td>
<td>89,91</td>
<td>7,53</td>
<td>1,15</td>
<td>0,17</td>
</tr>
<tr>
<td>650</td>
<td>2,03</td>
<td>85,91</td>
<td>7,67</td>
<td>1,17</td>
<td>3,22</td>
</tr>
<tr>
<td>700</td>
<td>2,13</td>
<td>85,31</td>
<td>7,64</td>
<td>1,15</td>
<td>3,77</td>
</tr>
<tr>
<td>750</td>
<td>1,14</td>
<td>83,12</td>
<td>7,71</td>
<td>1,14</td>
<td>6,89</td>
</tr>
<tr>
<td>800</td>
<td>1,21</td>
<td>82,56</td>
<td>7,37</td>
<td>1,12</td>
<td>7,74</td>
</tr>
</tbody>
</table>

Note: a Calculated from the difference to 100 %

FIG. 1. Product yields as a function of temperature and residence time

FIG. 2. Composition of key gas components
These compounds have been identified by several authors. The presence of these compounds can be explained as a result of the thermal degradation of oxygenated compounds of tires, such as stearic acid, extender oils, etc.

Pyrolysis char is composed mainly of carbon black and ash. The elemental composition of the solid obtained at every temperature and residence time is presented in Table III. The ash contained in the pyrolytic residues come from the inorganic fillers of the original tire. It can be seen that there is almost no effect of pyrolysis temperature on the elemental composition of the chars. This is logical since the main polymeric component of automotive tires is styrene–butadiene rubber and temperature above 600 °C is sufficient for release of all volatiles. Similar results have been observed at other residence times Rt2 and Rt3.

4. Conclusions

Yields of solid, liquid, and gas obtained from isothermal pyrolysis of waste tire have been calculated. The studied parameters were: temperature and residence time. Increasing the temperature resulted in an increase of gas fraction and a decrease of liquid and solid fraction. The influences of residence time on the product distribution is negligible compared to the influence of temperature.

The gas fraction was a mixture of hydrocarbons of low molecular weight (ethane, ethene) methane and hydrogen. The composition of this gas fraction depends on the final temperature of pyrolysis. High temperatures favour the presence of hydrogen and methane, while low ones mean a higher proportion of light hydrocarbons.

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CL-27
INFLUENCE OF PA6 GF25 REGRINDS CONTENTS ON THE MECHANICAL PROPERTIES OF THE OIL FILTER CORE

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marek.szostak@put.poznan.pl

Filters for internal combustion engine vehicles appeared shortly after the construction of the first vehicles of this type of drive. Currently, each vehicle equipped with elements for removing impurities from the oil, fuel, air supplied to the engine and the passenger compartment. The continuous development of engine components increases the demands on the filter, the more strained and finely crafted units must be better protected from pollution. In addition to the technical requirements of the growing ecological requirements. The objective is to design the filter to minimize the negative impact on the environment. At the same time consumers demand the best performance at the lowest price. For several years popularity of EKO filter, in which plastic parts replace metal details is growing. This solution lowers the cost of production and facilitates the recycling of used filters. Manufacture of large quantities of plastic parts leads to the formation of waste products that must be exploited. Transformation of plastics by injection makes it possible to re-use material by grinding and recycling in injection molding technology. Reprocessing materials may change its properties, which in some, especially high loaded elements disqualifies its use.

The aim of this study was to determine the maximum content of PA6 GF25 regrind in the oil filter core C-2073 by examining the influence of regrind on the mechanical properties of that part.

EKO-type oil filters are mounted in demountable enclosures, which are an integral part of the engine. His filter cartridge consists of filter paper fused in upper and lower bottom. The oil supplied from the oil pan through the oil pump is purified by flow through the filter medium in the direction of the filter interior. OE673 oil filter is one of the most popular filter installed in many modern cars such as: Citroen C2, C3, C4, Ford Focus, Kuga, Peugeot 207, 308, 407, both gasoline and diesel engines.

The material used for the oil filter bottoms is polyamide 6 with talc, which as filter lowers the cost and makes it easier to fusion barrier filter into the bottom. Cores are produced from polyamide 6 reinforced with glass fiber, which improves its mechanical properties. The core in EKO type oil filter prevents the paper collapse into the filter, in some of the solutions have also some other functions. The OE673 oil filter core has a cross (Fig. 1), whose task is to close the oil drain into the oil pan. At the time of the filter changing after unscrewing the housing nut, the trigger is opened and the oil can flow from the filter housing. In the case of the cross cracks in the core, the oil from filter housing drains into the sump, which caused the reducing the pressure in the oil system. The loss of oil pressure in the lubrication system may result in damage to the engine; therefore, it is very important
to provide adequate mechanical properties of the core.

Core C-2073 is produced from polyamide 6 with 25 % glass fibers (Tarnamid T-27 GF25) on the injection molding machine MARS 1600 from HAITIAN Company. The parameters of the injection molding process are as follows:
melt temperature 260–280 °C, mold temperature 65 °C, drying temperature 110 °C, injection pressure 65 MPa, injection speed 40–65 mm s⁻¹, holding pressure 40 MPa, holding time 2 s, cooling time 8 s.

To carry out the test, samples containing regrind from 0 to 50 % weight contents were prepared. In addition, the cores made from 100 % regrind have been prepared too. The regrind has been obtained from production wastes by grinding them in the mill. The regrind has two times bigger size (around 5 mm) to compare with original polyamide 6 granulates (grains about 2.5 mm). From each samples with different regrind content, 20 cores has been obtained by injection molding from which 6 was selected for further study. Selected cores were measured before conducting the tests. The results of dimension measurement are presented in Table I and II. The cores strength tests has been preceded on the Zwick testing machine and consisted of pushing the special rod into the core cross. An attempt was to simulate the operation of the core in the filter housing. In order to check the strength of the internal core cross, the axial load was applied (Fig. 2 and 3). The results of mechanical tests are shown in Table I.

The minimum reference force is 650 N which has been determined on the basis of strength tests of the OE filter cores, which are regarded as a model. Differences in the strength results can be partly due to the lack of perfect eccentricity during conducting the tests. As shown in Table II, the increase of the regrind contents does not change the force required to destroy the sample. Therefore, the use of regrind not adversely affects the mechanical properties of the C-2073 core.

As it is seen from the Tables II and III, with increasing of regrind content in the input material, the core diameter decreases gradually, obtaining a dimension smaller of

<table>
<thead>
<tr>
<th>Test no.</th>
<th>0%</th>
<th>10%</th>
<th>20%</th>
<th>25%</th>
<th>40%</th>
<th>50%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>783</td>
<td>741</td>
<td>728</td>
<td>769</td>
<td>772</td>
<td>714</td>
<td>726</td>
</tr>
<tr>
<td>2.</td>
<td>787</td>
<td>759</td>
<td>720</td>
<td>747</td>
<td>767</td>
<td>729</td>
<td>757</td>
</tr>
<tr>
<td>3.</td>
<td>719</td>
<td>763</td>
<td>776</td>
<td>737</td>
<td>751</td>
<td>782</td>
<td>758</td>
</tr>
<tr>
<td>4.</td>
<td>781</td>
<td>718</td>
<td>781</td>
<td>732</td>
<td>742</td>
<td>779</td>
<td>775</td>
</tr>
<tr>
<td>5.</td>
<td>766</td>
<td>775</td>
<td>762</td>
<td>782</td>
<td>738</td>
<td>753</td>
<td>765</td>
</tr>
<tr>
<td>6.</td>
<td>719</td>
<td>782</td>
<td>771</td>
<td>741</td>
<td>759</td>
<td>774</td>
<td>752</td>
</tr>
<tr>
<td>Average</td>
<td>759</td>
<td>756</td>
<td>756</td>
<td>751</td>
<td>754</td>
<td>755</td>
<td>756</td>
</tr>
</tbody>
</table>

Table II
Results of core diameter [mm] measurements in dependence on the regrind content. Nominal diameter 29 (+/-0.2)mm

<table>
<thead>
<tr>
<th>Test no.</th>
<th>0%</th>
<th>10%</th>
<th>20%</th>
<th>25%</th>
<th>40%</th>
<th>50%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>29,11</td>
<td>29,05</td>
<td>29,09</td>
<td>29,07</td>
<td>29,02</td>
<td>28,98</td>
<td>28,94</td>
</tr>
<tr>
<td>2.</td>
<td>29,15</td>
<td>29,04</td>
<td>29,12</td>
<td>29,06</td>
<td>29,04</td>
<td>28,97</td>
<td>28,90</td>
</tr>
<tr>
<td>3.</td>
<td>29,12</td>
<td>29,03</td>
<td>29,13</td>
<td>29,06</td>
<td>29,01</td>
<td>28,98</td>
<td>28,93</td>
</tr>
<tr>
<td>4.</td>
<td>29,09</td>
<td>29,05</td>
<td>29,11</td>
<td>29,05</td>
<td>29,01</td>
<td>28,99</td>
<td>28,94</td>
</tr>
<tr>
<td>5.</td>
<td>29,11</td>
<td>29,04</td>
<td>29,09</td>
<td>29,06</td>
<td>29,02</td>
<td>28,96</td>
<td>28,95</td>
</tr>
<tr>
<td>6.</td>
<td>29,08</td>
<td>29,05</td>
<td>29,06</td>
<td>29,07</td>
<td>29,03</td>
<td>28,95</td>
<td>28,92</td>
</tr>
<tr>
<td>Average</td>
<td>29,11</td>
<td>29,04</td>
<td>29,10</td>
<td>29,06</td>
<td>29,02</td>
<td>28,97</td>
<td>28,93</td>
</tr>
</tbody>
</table>
The location of the injection point (Fig. 4) causes the problem of an accurate determination of the various types of contractions in different areas of the analyzed part. We suppose that grinding in the sieve mill can cause a degradation of polymer, which may have a direct effect on the processing shrinkage. Longitudinal shrinkage, most noticeable to the core height, seems to be smaller. That dimension for core obtained from 100% regrind material achieved the upper tolerance limit – 64.30 mm. For the outer core diameter, it is very difficult to determine clearly which type of shrinkage predominated and what their size is. The nominal outer core diameter is 29.00 +/- 0.2 mm and with increasing the regrind content it decreases but remain within the established tolerances.

- The research has shown that adding the polyamide regrind does not affect the mechanical properties of the oil filter core C-2073.
- Dimension analysis of the molded part has shown that the optimal content of the PA6 regrind material is 25%, due to assurance of the tolerance field for the molded C-2073 core.
- It is possible to use the regrind from production PA6 wastes for manufacturing the new elements with good mechanical properties and suitable dimensional tolerance.

REFERENCES


Fig. 4. The injection point on the C-2073 core

0.19 mm. In that same time the height of the core is increasing of 0.15 mm.

Key words: recycled plastic, ant flooding, Watergates

This contribution describes developments in the area of plastic recycling aimed at the reuse of waste materials for the manufacture of a useful product. Throughout development of the concept “modular flood barrier structure”, the recovery of plastic materials was assessed, primarily, plastic waste from automobiles and industry. For the modular design of the structure a utility model was prepared. In terms of the type and composition of source material, polypropylene (PP) and polyethylene (PE) were the materials chosen. When designing the geometry and constructing the barrier, the first stage was to design the structure based on the shape of unified blocks made from PP and PE. These unified blocks were designed in Slovakia at Chemosvit Environchem, a.s. but are also available internationally. In cooperation with Chemosvit, the focus was to produce blocks made from recycled materials and their subsequent application for beneficial use. The present need for flood protection inspired its production from these recycled materials. The suitable shape and strength characteristics of the plastic blocks provided sufficient grounds for the development of the flood barrier. In the first phase, different structural shapes were assessed in terms of their stability to determine their suitability for the given application. The results of these efforts were the initial design of the whole structure and its parts. Following this, the structure was revised and a prototype was constructed. The structure underwent numerous optimization processes including finite element analysis (FEA) and internal/external stability analysis. Production documentation, prototypes, and field tests were also performed. Currently, changes to the design are being performed in order to prepare it for mass production.

Development

The Slovak university of technology in Bratislava is currently involved in the project “research of progressive technologies for the recovery of waste from scrap automobiles” in harmony with the priorities of the Slovak
ministry of environment (SME). The principal coordinator of
the project is the faculty of mechanical engineering, and the
project is financed by the recycling fund in Slovakia. SME
has stated in a press release that: “foremost, the effective
protection against flooding, and the reduction of
environmental burdens in sensitive and national park zones
remain a priority”. Ing. Peter Žiga, PhD., press release
minister of Environment SR, (SME, 1.7.2012 and HN,
28.2.2013).”

The primary objective of the project is to increase the
effectiveness and sustainability of developing ecological
security in the collection and processing of scrap automobiles
and solving problems in their recycling. To meet the goals of
the project, specific objectives were set, whose integrated
results satisfy the main goal. The specific goals of the project
can be divided into four parts:

1) Prediction, determining optimal technologies, methods
and logistics in processing automobiles.

2) Proposal of optimal structure and function from research
centers in collaboration with the automotive industry in
the Slovak republic and processors of scrap vehicles.

3) Specification in the areas of research and development of
new technologies and specific machine nodes on the
basis of waste and secondary materials.

4) Research of new products which increase the recovery of
recycled materials and ensure its demand in the synergy
of waste processes.

The key requirement of the project results are that the
results of the research were not tied to one processor but
rather to be implemented in all processors of scrap vehicles in
the SR under the auspices of the Slovak automotive industry.
In terms of the current state of scrap vehicle processing, three
consecutive and chronological stages with two main branches
(analytic and scientific research) are proposed. In order to
ensure the highest quality of the results, individual parts of the
project are solved in cooperation with qualified external
organizations with unique or otherwise appropriate
specializations.

The first stage of the project was performed from May
2011 to June 2012.

The major challenges that emerged from the analysis are
“Research of technology for the effective processing of car
car bodies” and “research of technologies for the recycling of
difficult to recover waste, proposal of new products which
increase the usage of recovered materials” – and applying this
to successfully develop a needed product “flood barriers”.

Modular structure of mobile flood barrier
concept manufactured from recycled plastic

Integrating the outputs of cooperating groups, the
investigators began to explore possibilities in applying plastic
waste from scraped vehicles as recycled material in the
production of new products. Many types of flood barriers
exist internationally. During the implementation of the
project’s first phase (May 2011 to June 2012) problems in
mobile flood barrier concepts were explored. The structure,
shape, material and operation of a wide range of flood barrier
products were analyzed with the intention of identifying
strong and weak points of each individual design and applying
the knowledge obtained in the research of a new
concept. This new concept was based on the integration of
existing systems, using their benefits to design a new flood
barrier. The basic requirements for the new barrier were that it
would be: produced from recycled materials, self-anchoring
but not permanently anchored to the ground, could be used on
firm and soft ground, allow for convex and concave
configurations, can copy rough terrain, can be easily deployed
and removed, and can adjust the barriers height. The
investigators filed a utility model application no. SK 5847
Y12 entitled “Modular flood barrier structure”. This utility
model serves as a basis for more detailed solution of flood
barriers. The proposed design structure theoretically allows,
from one system, to create two similar configurations and
arrangements from the modular flood barrier structure.

The first modular flood barrier structure has a vertical
wall constructed of braced, L-shaped structures seen in Fig. 1.
The water enters the barrier from the inside and the braces are
loaded in tension. The stability of the barrier (in terms of
shifting and tipping) is guaranteed by the force action of
hydrostatic pressure in the vertical direction.

The second modular structure consists of an angled and
horizontal part (Fig. 2). In this design, the water acts on the
barrier from the outside were the connecting braces are loaded
in compression. The hydrostatic pressure of the water on the
sloped surface ensures adequate anchorage to prevent its
movement.

If the barriers are installed on firm ground, then a rubber
seal is placed below the horizontal parts of both water
barriers. In the case that the barriers are located on uneven or
soft ground, then anchoring pikes are used on the horizontal

Fig. 1 Flood barrier with vertical wall, 1-base, 2-vertical wall, 4-
brace

Fig. 2 Flood barrier with sloping wall
parts. Connecting the vertical parts is done by using attachment bars. To obtain greater stability, the vertical parts are mounted to each other in a pattern (long to short to long etc...) and are connected with bars. The structure, to a certain extent, allows for a curved barrier. For a convex shape (Fig. 3a) the horizontal parts are not necessary to connect. For concave shape (Fig. 3b) it is only necessary to connect every other horizontal part. The modular structure of the flood barrier also allows for deployment over uneven terrain (Fig. 3c). In this configuration, the horizontal bars are not necessary.

The most practical realization indicated a sloped configuration. The main reason for this was the undesirable effect of submerged functional parts in the L configuration. The sloped barrier consists of a system of horizontal parts and sloped parts. The angle of the sloped part is adjustable by the length of the braces and the position of their attachment point. The modular structure allows for the change in length of the sloped parts. The technical advantages of the modular structure are evident in the effects induced externally.

Calculation of the barriers under static loading was performed through two independent methods. The results from the faculty of mechanical engineering STU (SjF STU, Table I) in Bratislava and the results from external experts at the faculty of civil engineering at STU (SvF STU, Table I) in Bratislava where compared for different angles of the barrier under given loading conditions (Table I).

An important part of the development process was the constant assessment of the structure by experts in the area of FEA and statics (Fig. 4). The initial, relatively simple, simulation indicated that the system can become unstable and therefore it was necessary to perform a more complex analysis of the assembly which included all important interactions so that the simulated state best represented real conditions.

In the next phase, the construction was optimized, mainly with respect to satisfy the manufacturing processes for the test model. A parametric simulation model was constructed with variable geometry in order to obtain the most suitable shape of the structure. The simulation consists of the load $F_1=17720$ N, pressure acting on the walls at a water level of 1.6 m, water pressure on the flap $p=0.016$ MPa, and the assumption of terrain between the base and the surface $f=0.55$. All of which resulted in the stress spectrum and deformation of a system which best represents the real conditions, states, and reactions in important nodes of the device (Fig. 5).

### Table I

Forces acting on the wall segment with a width of 1.12m at different angles and water depths

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<td>-</td>
<td>5,783</td>
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</table>

Fig. 3. Modular flood barrier structure

Fig. 4. MKP analysis of a system of blocks, Von Mises stress assessment [MPa]
Ambition and direction of further research

In terms of the optimization of the structure, the investigators will focus on factors affecting the mass production of the flood barrier and its effectiveness, Fig. 6. Another goal is to determine a simpler construction for less demanding operational conditions, Fig. 7. The optimal manner for production seems to be injection. However, to this point, there have not yet been any producers capable or willing to realize such a process. Despite this, the proposed design has been considered very successful so far.

This contribution was made by realization of the project Development of progressive technology of compacting biomass and manufacture of prototypes and highly-productive tools (ITMS code of the project: 26240220017), based on the support of operational system of program Study and development financed from European fond of regional improvement.

REFERENCES


CL-29
BIODEGRADABLE POLYMER BLENDS FROM RENEWABLE RESOURCES

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Abstract

In this work, attention was focused on study of polylactic acid (PLA) and thermoplastic starch (TPS) blends modified with modifier M. In these blends, the content of each component was gradually changing and influence of modifier on mechanical properties was studied.
**Introduction**

Biodegradable polymeric packaging materials, especially polymers from renewable resources, represent a new generation of packaging materials. Their main advantage is a fact, that their whole life cycle is oriented to protecting environment and human healthy. But these polymers have some disadvantages like sensibility on water and air moisture, they have worse thermal stability, worse some mechanical and barrier properties. The solution of these problems lays in finding appropriate modification techniques, either by adjusting the processing conditions, a suitable composition of polymer blend, or combination of both.

Polylactic acid (PLA) is semi-crystalline, linear, thermoplastic polyester with good processability, biocompatibility and biodegradability as well. PLA is the front runner in the emerging bioplastics market. PLA can be produced by condensation polymerization directly from its basic building block lactic acid or by conversion of lactide— the cyclic dimer of lactic acid—to PLA via ring-opening polymerization. PLA exists in two enantiomeric forms – L-lactic acid and D-lactic acid. It has similar mechanical properties like polystyrene (PS), with elastic modulus of 3000-4000 MPa, tensile strength of 50–70 MPa, glass transition temperature of about 60–70 °C and elongation at break of 2–10 %. It is a versatile polymer, with high transparency, high molecular weight, good processability and water solubility resistance. Its usage is oriented in packaging, biomedicine, electronics, automobile and other consumer applications like blown bottles, extruded cast and oriented films, and melt-spun fibers for nonwovens, textiles and carpets.

Starch is a renewable and widely available raw material, being the end product of photosynthesis. It is the storage polysaccharide of cereals, legumes and tubers. Starch is composed of a mixture of two substances, an essentially linear polysaccharide-amylose and a highly branched polysaccharide-amylopectin. The size, shape, and morphology of the starch granules are characteristic of the particular botanical source. The glass transition temperature of the dry starch is in the range of 240–250 °C (ref.). Native starch is a nonplasticized material because of the intra- and intermolecular hydrogen bonds between hydroxyl groups of starch molecules. In order to process thermoplastic starch, it is necessary to disrupt its crystalline structure. The physical properties of the thermoplastic starch (TPS) are greatly influenced by the amount of plasticizer present. Mostly, polyols are usually used as plasticizers, of which glycerol in combination with water is the major one. Main application areas of TPS or starch based materials include foams for the loose-fill foam market, films for agriculture, shopping bags and mouldable products like pots, cutlery or fast food packaging.

**Experimental**

**Materials**

- Polylactic acid – PLA 4042D from NatureWorks, LLC, USA
- Starch – Meritena 100 from Amylum Slovakia, SR
- Glycerol – GL from H.C.I. Slovakia, SR as starch plasticizer
- Water – as auxiliary starch plasticizer
- Modifier M as blend modifier

**TPS preparation**

Thermoplastic starch (TPS) was prepared directly in process of PLA/TPS blending by means of twin-screw extruder using glycerol and water as starch plasticizers.

**PLA/TPS blends preparation**

PLA/TPS blends were prepared using twin-screw extruder at thermal profile 140 – 150 – 160 – 160 – 160 – 160 – 160 – 160°C. Extruded material was chilled with air on the belt loop and granulated into small pellets.

**PLA/TPS films preparation**

Granulated material was used to PLA/TPS films preparation on single-screw extruder at thermal profile 160 – 165 – 170 – 180 °C, where flat die and chill-roll technology were used.

**Measurement of mechanical properties of prepared blends**

Yield strength (σy), tensile strength at break (σb) and the elongation at break (εb) were done according to ISO 527 standard using Zwick machine at cross-head speed 1 mm/min in the deformation range of 0–3 % and after this value of elongation the speed increased up to 50 mm min–1. These properties were determined based on recorded tensile curves.

**Results and discussion**

At first, an influence of modifier M on mechanical and rheological properties was studied. Modifier content in PLA/TPS blends varied from 0 to 1 %wt., and content of TPS, PLA, GL and water was constant. Figures 1–2 show dependencies of chosen properties: tensile strength at yield and elongation at break on modifier content in PLA/TPS blends.
Fig. 2. Dependence of elongation at break on modifier M content in PLA/TPS blends.

Fig. 3. Dependence of tensile strength at yield on starch content in PLA/TPS blends prepared with and without modifier M.

Fig. 4. Dependence of elongation at break on starch content in PLA/TPS blends prepared with and without modifier M.

Blends.

Fig. 1 shows that tensile strength at yield ($\sigma_y$) has its maximum at modifier content of 0.2 %wt. Above this concentration, tensile strength at yield was decreased. Modifier M has positive influence on elongation at break of prepared blends. A small addition of modifier (0.1 %wt.) caused an increase of $\epsilon_b$ from 0 % to 250 %. Prepared blends have value of elongation at break above 200 % up to modifier content of 0.4 %wt. Above this concentration of modifier, elongation at break was decreased to almost zero value.

On the next figure, there is a dependency of chosen mechanical property of prepared biodegradable blends PLA/TPS on starch content. Content of GL and water was constant, it was varied the content of starch in blends, from 40 %wt. up to 70 %wt. It was studied an influence of starch content on properties of PLA/TPS blends prepared with and without modifier M at its one concentration.

Tensile strength at yield (Fig. 3) of studied blends PLA/TPS was decreased with increasing content of starch. Blends prepared without modifier M have 2 times lower values of studied property than those prepared with modifier M.

Blends prepared without modifier M have almost zero value of elongation at break (Fig. 4). But blends with modifier have value of this property from 150 up to 300 %, maximum was reached at starch content of 50 %wt.

Besides changing modifier and starch content in PLA/TPS blends, content of GL and water was gradually varied as well. After research of basic properties of modified PLA/TPS blends, Design of experiment (DoE) method was used and

Fig. 5. Tensile strength at yield of optimized modified PLA/TPS blends with various composition.

Fig. 6. Elongation at break of optimized modified PLA/TPS blends with various composition.
after evaluating of DoE, optimization of blend composition followed. Blends were optimized according to 3 criteria: A, B, C. Fig. 5 and 6 show results of measurement of chosen mechanical properties.

Obtained results presented on Fig. 5 shows, that values of tensile strength at yield of optimized modified blends are higher than values of $\sigma_y$ of standard polyolefins like LDPE, HDPE or PP. In the case of elongation at break (Fig. 6) of optimized blends PLA/TPS, it can be concluded that all 3 optimized blends have similar or higher $\varepsilon_b$ than LDPE, its value is approximately 300 %.

Conclusion

Based on reached results it can be concluded that it is possible to set up composition of modified PLA/TPS blends with required properties which are comparable with properties of polyolefins usually used in packaging applications. Present material has high potential for its practical usage.

REFERENCES


CL-30
RECYCLING OF USED TIRES AND REUSE OF RUBBER GRANULATE

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There are several methods of material recovery of used tires like: mechanical recovery, pyrolysis recovery, cryogenic recovery or ozone recovery. The most popular method in the world is mechanical recovery which is also used in our company.

Mechanical recovery

The actual process of recovery could be described in a simple form as a continuous multi-stage mechanical crushing of tires into rubber granules of the desired fractions, during the process the metal and textile components of the tire are separated. Last machinery in line is Aspirator. Aspirator sorts the resulting rubber granulate (0–4 mm) into required fractions (for example: 0,0–0,5 mm / 0,5–1,0 mm / 1,0–3,0 mm).

Reuse of rubber granulate

The main final product material of material recycling is rubber granulate, which is used in many areas. For example: filling for artificial turf (grass surfaces), safe children playground surfaces, rubber tiles for animal housing, replacement of concrete and ceramic tiles, noise protection walls and barriers, rubber plates to absorb underground vibrations, rubber side-way panels for the rails, sorbents, modified asphalt, rubber mixtures (compounds) that are used in the rubber industry. The waste is then converted into a finished product, thereby closing the recycling circle.