A POSSIBILITY OF USING THE FLOTATION PROCESS TO SEPARATE SOLID POLYMERS

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Flotation is a physico-chemical process used traditionally to separate various solid materials, including plastics, basing on a difference in their surface wettability. Unfortunately, the surface of most plastics is hydrophobic which fact makes the selective flotation separation of targeted types of plastics from their mixtures with other types of plastics difficult or even impossible. To render the selectivity of the process itself, the surface of some plastics has to be selectively hydrophilized and so flotationally depressed.

To make the surface of plastics selectively hydrophilic and thus nonfloatable, various methods have been testing such as adsorption of wetting agents1 or a physical treatment2-3 (flame, ozonation, plasma, photocatalytic, etc.). However, a potential of selective chemical treatment by incipient alkanolysis recently emphasized, as exemplified by analyzing the surface hydrophilization of polyethylene terephthalate (PET) submerged with polyvinylchloride (PVC) in NaOH solutions even at ambient temperature and for a very short period of time4.

Indeed, the NaOH-pretreated surface of PET foils was found to become hydrophilic (nonfloatable) to such an extent that the flotation recovery and selectivity of PVC foils, whose surface was left almost untouched (and so entirely floatable), increased appreciably5.

The enhancement of the surface wettability of PET, as measured by contact angle goniometry of water drops, due to the hydrolytic attack is a result of the formation of new hydrophilic groups originating from chain scissions (chemical alteration) as well as of associated dissolution roughening (physical alteration)6.

At the ambient temperature of pretreatment, a descending sigmoidal dependence between the advancing contact angle on the PET surface and the concentration of NaOH solution was observed, being paralleled with the PET/water interfacial tension-vs-concentration dependence. An increase in the temperature of the pretreatment solution up to the temperature of glass transition (~80 °C for PET) further promotes the hydrophilization process and shifts proportionally the latter dependences. The limiting hydrophilicity θa was assessed to occur in 6 % NaOH solution at 60 °C, corresponding to the zero interfacial tension.

The surface roughness and negative charge due to the hydrolytic attack, evaluated by the Atomic Force Microscopy and Streaming Current method, respectively, attain a maximum when pretreated in the NaOH solution whose concentration is exactly the same as that for which the above dependences go through their inflection. This is thought to confirm a general parallelism between the interfacial free energy and the dissolution kinetics.

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CL-21
GENERAL PRINCIPLES OF OPERATION AND CLEANING OF VULCANIZATION MOULDS

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It is a well-known fact, mould fouling occurs during vulcanization, what have negative influence on apperance and dimension stability of moulded parts, and also makes manufacturing costs higher1.

On the basis of conducted analysis hypothesis was accepted, that mould fouling has two stages. In the first stage, insoluble zinc sulphide is formed in the reaction of zinc oxide with sulphur, which makes inorganic deposits on the mould surface. In the second stage, on ZnS crystallites sediment low-
molecular organic ingredients of rubber compound, which carbonize with time\textsuperscript{2,3}. Contamination of vulcanizing mould can be observed as change of colour of its whole surface or deposition of the material in some places of the mould surface\textsuperscript{7}. The speed of mould fouling depends on various factors. Most important of them are: composition of rubber mix, use of anti-adhesive agents, shape and construction of the mould, vulcanization parameters (temperature, pressure) and different reactions between ingredients of rubber compound\textsuperscript{5}.

There are several methods which reduce mould fouling and allow to remove easy an end-product. One can mention among them the use of releasing agents:

- internal – added to a rubber compounds,
- external – modifying the surface of a mould (sacrificial, semi-permanent, permanent). All of them will be shortly described\textsuperscript{6-8}.

Correctly used anti-adhesive agents reduce or even eliminate problem of mould fouling. However, inappropriate selection can generate problems\textsuperscript{9}.

In Branch House of Elastomers & Rubber Technology an investigations over treatment of mould surface by ion bombardment were made\textsuperscript{10}. Due to ion bombardment of metal parts of machines and devices used for compounding, processing or vulcanization of rubber mix, their durability significantly increased. The treatment, preferably of Cr\textsuperscript{+} with energy 20–500 keV in 2.10\textsuperscript{17} cm\textsuperscript{2} i 5.10\textsuperscript{16} cm\textsuperscript{2} dosage carried out under vacuum, makes possible to get rid of the problem arising from adhesion of rubber of its components to metal surface.

Unfortunately, mould fouling occurs sooner or later. Short information about now used methods of cleaning of vulcanization moulds and their efficiency will also be presented\textsuperscript{11-15}.

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CL-22
VISUALIZATION OF THE WEAR TEST OF RUBBER MATERIALS

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Abstract

The article describes the problem of dual shooting and evaluation of high-speed time varying phenomena using high-speed camera systems. It describes necessary steps for the preparation of shooting and how to set up the electronic shutter and also focuses on the processes of calibration and final evaluation of the high-speed phenomena. Dual shooting of high-speed phenomena is very modern while still remaining quite an unexplored field and is at present subject of a research at the Institute of Production Engineering UTB in Zlín. The published processes particularly for the Chip-Chunk test are brand new and at currently being patented in the Czech republic.

Introduction

High-speed camera systems (hereafter referred to as HSC) are well-known not only for the scientific community but also for people from the technical field. Their use has at present been extended from special applications in the military and automobile industry to the common technical practice. The requirements to improve production process, lower costs and increase safety are continuously growing and HSC has a lot to offer in this respect. Using the high recording frequency they enable to examine the given phenomenon, stop the image in a set moment and then examine it as well as detecting the problematic sections.

If we want to do this all, we first need to define the concept “speed, high-speed phenomena”. They are such phenomena for the recording of which it is necessary to use the recording frequency ranging from 100 Hz to 1 000 000 Hz. We also need to specify the type of phenomena. In practice they are periodic, aperiodic and stochastic phenomena, for which it is necessary to determine the time and length of shooting.

Next, we have to consider the type of a HSC. At present there is a number of producers of HSC, which, however, have different configurations. It is also worth noting that the market has recently introduced digital cameras with higher speed of
recording. The recording speeds range up to 100 Hz, which enable to make only very basic evaluations. In the case of professional devices we can distinguish between two basic types: It is a compact type, with a display and most control elements are integrated in the HSC and next, a modular type consisting of a number of modules and peripherals enabling the user to make a recording and evaluation according to the given requirements. The compact systems are more economical, but they are very easy in terms of their operation, setting and evaluation. The modular systems can be adjusted exactly to our requirements with the aid of connectable peripherals and methods of shooting but the setting and evaluation are rather complicated, the price very high.

When shooting with the HSC there are often problems with an insufficient angle of view, which is needed to capture the phenomenon. Common lenses working at angles up to 60° are often not capable to capture the scene shot, on the contrary, the wide-angle lens and special lens, such as Fish Eye, which have the angle of view over 180° can capture the scene but with a subsequent image distortion. Hence, there are two high-speed camera systems used in practice which shoot the parallel phenomena. The two high-speed camera systems are used for parallel shooting of phenomena, which would be difficult or impossible to repeat, with lenses with the angles of view up to 60°.

The result of such shooting of one or more phenomena using a set of two camera systems are two films of the same phenomenon, or phenomena from different angles of view according to the position of lenses of the cameras.

The disadvantage is that so far no method has been developed that would combine these separate films, giving a more complex idea about the phenomenon processed. This combination can only be made subjectively in the minds of the viewers watching the films but it is clear that this way of putting images of the two films together may not be precise and sufficiently predictable. So far this process has not been objectivized.

Visualization of the time varying phenomena

This deficiency of the present state of technology can be made up by a method of visualization of the time varying phenomena. The principle of this method is that the images created by shooting a phenomenon with a set of two camera systems (see Fig. 1) are put together at a given time into one dual image according to a characteristic trait of the image, such as a characteristic point, edge or angle.

Practical method of visualization

The example of a practical method of visualization of time varying phenomena is shooting a phenomenon, which takes place during the wear test of rubber materials (referred to as Chip-Chunk test), see Fig. 2 during which a rubber sample of cylindrical shape is penetrated by a pointed tool with defined geometry, see Fig. 3.
Additives with a molecular weight between 900 – 1500 Da have the intention to evaporate partly and pyrolyze slowly. Higher masses (the not volatile ones) degrade according to the pyrolytic fragmentation rules in the furnace. It is expected that there are more than one additive in the extract. Different additives are needed to modify the polymer properties. The additive fraction lower than 900 Da (e.g. Irganox 1050) is expected to slowly degrade and add to the blooming free and the additives are available all over the polymer. Polymeric additives give nearly no emissions, no migration loss and allow higher application temperatures.

The analysis of polymer additives and application of classical gas chromatography is restricted due to low volatility and high molecular weight of some species. Reliable and rapid analytical methods are often needed for the identification of unknown additives, therefore a best available solution need to be developed. For polymeric additives soft ionization methods like fast atom bombardment (FAB)\(^1\) and matrix-assisted laser desorption/ionization (MALDI)\(^2\) are relatively easy and have the ability to analyze high molecular weight compounds, however these methods have limitations. Concerning polymeric additives, soft ionization methods give no clear structural information. The use of a time-of-flight mass spectrometer (TOF-MS) can give a molecular weight distribution of majorities (which means polymer) but under a concentration of 5 % of additives, it is a difficult task to give proper information of the additive, unless extracted\(^3\).

The main focus stays on difficulties concerning volatility, separation and detection, therefore pyrolysis as sample introduction system was evaluated for characterization of some polymeric additives. Pyrolysis as an injection technique coupled to classical gas chromatography with mass detection (PY-GC-MS) makes firstly fragments from the polymeric additive fraction, which are separated by classical gas chromatography and easily detectable by mass spectrometry. This method can be applied if we are interested into the structure of compounds and not primary in the molecular weight.

**Sampling and analysis**

This method is based on separation of the polymeric additives from the polymer matrix by a simple static extraction in toluene. Only a few µl of extract was dried and taken to pyrolysis. The principle of pyrolysis is based on radical reactions induced by heat in an inert atmosphere. These radical reactions continue as radical depolymerization reaction (also called unzipping or back-to-monomer) and might induce a H-transfer between molecules (inter- and intramolecular proton transfer). Pyrolysis fragments are mainly volatiles with molecular weight < 1000 Da and are swept into the analytical column for separation. Mass spectrometry is used for the detection and identification of the fragments.

The ions detected by the mass spectrometer at a certain retention time are very specific for one part of the polymeric additive. The obtained chromatogram (further pyrogram) is often based on a large number of peaks, however, if certain ions are known, the method can be automatized to judge if selected additives are present or not\(^4\).

Additives with a molecular weight between 900 – 1500 Da have the intention to evaporate partly and pyrolyze slowly. Higher masses (the not volatile ones) degrade according to the pyrolytic fragmentation rules in the furnace. It is expected that there are more than one additive in the extract. Different additives are needed to modify the polymer properties. The additive fraction lower than 900 Da (e.g. Irga-
fos 168, Irganox 1076) is also screened by this method. All experiments were carried out with an automated pyrolyzer unit (Frontier Laboratories Ltd. – Kyoto, Japan) coupled to a GC-MS 2010+ (Shimadzu – Kyoto, Japan) with electron impact ionization mode (70eV). The method was optimized, evaluated and proved to be free from memory effects. The optimal pyrolysis temperature was set at 650 °C and the sample extracts were injected by a quick free fall injection of special sample cups. By measurement of sample blanks special attention was taken to assure a clean sample path and avoiding adsorption or condensation of fragments along the sample path.

**Polymeric brominated flame retardants**

Pyrolysis-GC-MS was evaluated for the characterization of polymeric brominated flame retardants (p-BFR). For this the p-BFR needs to be isolated from the polymer matrix. Bromine used as a flame retardant has a long tradition as polymer additive. A recent environmental friendly approach is based on the incorporation of bromine into the polymeric chain (like tetrabromobisphenol A in PC or epoxy resins) or as a polymeric additive (like brominated polystyrene in PET). P-BFRs are mainly used for high-temperature applications like polyesters and polyamides. Flame retardant treated thermoplastics contain generally 5–20 % p-BFR which is for this analytical method an advantage. Most common brominated polystyrenes are produced by the copolymerization of di- and tribromostyrene and are commercially available (Firemaster PBS-64, Sartex HP-7010P). Poly(dibromostyrene), known as PDBS-80, is also commonly used however only for polyester applications

From the legislative point of view, some additive BFRs are restricted to be used. In order to speciate the bromine containing molecule, PY-GC-MS is able to fill this gap in BFR characterization. Here counts the slogan “no data = no market”, sometimes data is missing concerning additive composition

In Fig. 1 is shown a pyrogram of isolated brominated polystyrene from PA6. Main peaks seen in this pyrogram are the isomers from mono-, di-, tri- and tetra-bromostyrene formed after depolymerization. Further a mixture of cyclic side-products from radical recombination can be seen, mainly brominated polycyclic aromates and cyclic hydrocarbons.

The area ratios between the mono-, di-, tri- and tetra-bromostyrene were used to calculate the degree of bromination in this polymeric additive according the equation given in Fig. 2. The measured brominated polystyrene had a calculated number-average bromine degree of 2,7 (2 % RSD, n=3). Technical data from a supplier confirmed that the p-BFR had an average bromination degree of 2,7 (ref.6). Very good match!

$$B_n = \frac{\sum (B_i A_i)}{\sum A_i}$$

**Polymeric hindered amine light stabilizers**

Polymeric steric hindered amine light stabilizers (p-HALS) are improving heat and light stability in thin film polyolefins. The average molecular weight of these p-HALS are ranging from 2000 till 4000 Da. They are added to the polymer in a range of 0,1 till 2 % and appear sometimes mixed with other p-HALS. The importance of detecting p-HALS is mainly based on the need for completing documentation and for quality control/quality assurance purpose.

After extraction and analyzing a LDPE sample containing the commercial p-HALS UVINUL 5050H from BASF (Fig. 3), there were seen 2 regions in the pyrogram (Fig. 4).

The first region exist mainly of linear (saturated and unsaturated) hydrocarbons (C\textsubscript{9}–C\textsubscript{24}) with some higher peaks from 2,2,6,6-tetramethylpiperid-4-yl derivates after unzipping of the monoamid side of this monomer (shown with an asterisk). In the second region are nicely seen the distribution of the monomer in its whole. The appearance of the monomer is in analytical pyrolysis no surprise as depolymerization is one of the main processes.

Mass spectrometry is playing a major role for the interpretation of the results. As shown in Fig. 5, by using a selective scan for ion 57 M/z, all hydrocarbon fractions can been taken out and the theoretical C\textsubscript{17}–C\textsubscript{21} distribution is appearing more in detail. The maximum of the hydrocarbon distribution is approximately at C\textsubscript{19}, which is also given in the technical data.

A scan of ions with masses in the monomer range (M/z 500–700) shows nicely the distribution of the monomer (Fig. 6).

\[\text{Fig. 2. Equation used for calculation of number-average bromination degree in brominated polystyrene (B}_n\text{). Where: B}_i\text{ means number of bromine atoms (here used e.i. 1, 2, 3 and 4) } \sum (\text{peak area}) \text{ means certain amount of brominated styrene monomer containing the same amount of bromine atoms i}\]

\[\text{Fig. 3. UVINUL 5050 (BASF)\textsuperscript{9}}\]
Polymeric hindered amine light stabilizers in a mixture

The depolymerization mechanism of p-HALS is a practical mechanism for identification by monomer composition. The condensed types of p-HALS like the poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidine-ethanol–alt-1,4-butanedioic acid, further called light stabilizer 622 (Fig. 7) will difficult decompose to monomers.

Due to advantages related to mass spectrometry, these fragments can be fully identified and selected as typical fragmentations for a certain polymeric additive. By use of a spectral database containing reference additives made in-house, mixtures of additives can be detected according to their retention time and mass spectra. Complex mixtures like commercial TINUvin 783, which is a synergistic mixture of light stabilizer 944 and light stabilizer 622 can be identified using reference pyrograms from both compounds.

For light stabilizer 944 there can be taken one major characteristic peak which is the monomer peak at retention time 24.9 minutes (Fig. 9) with a typical fragmentation ion at...
460 M/z. The light stabilizer 944 is also presented in Tinuvin 783 as shown in Fig. 10, but here are already single ions selected for light stabilizer 944 and light stabilizer 622. Some information is lost but the main conclusion stays, the target analytes are detected and the “noise” from all other fragmentations are reduced.

**Conclusion**

PY-GC-MS seems to be a useful tool for polymeric additive characterization. Each polymeric additive has its own decomposition mechanism with possibility to get very specific information about the structure. A comparison with reference standards is recommended as well as automatisation of data processing by measuring selected ions.

The extraction procedure seems to give a satisfying sensitivity and suppresses the background sufficiently to make proper conclusions.

The main drawback of PY-GC-MS is that there is no molecular mass detectable; it is up to the customer to decide what is more important, structural information or an average mol weight distribution of used additives.

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**CL-24**

REINFORCEMENT OF RECYCLED BUMPER MATERIAL WITH WOOD FIBERS: STRUCTURE DEFORMATION MECHANISMS, PROPERTIES

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Recently the production and application of thermoplastics reinforced with forest-derived fibers increased considerably. The application of wood fibers in polymer composites has several advantages: the fibers are obtained from natural resources, they are available in various forms in large quantities, they are light, cheap, and can be added to commodity matrices in considerable amounts. As plastics contribute to the amount of solid waste in increasing volumes, waste utilization has become an attractive alternative to disposal. Today the main application of recycled car bumpers is the production of new bumpers, but the reinforcement of this material with wood fibers could open up new possibilities for the automotive industry and be a solution for an environmentally friendly, high quality and cheap material. Since such a composite consists of at least four components, its structure can be quite complicated. The elastomer added for impact modification and the reinforcement can be distributed in the matrix separately from each other, but the elastomer may also encapsulate the filler. The properties of the resulting composite depend very much on the extent of encapsulation. Stiffness was shown to depend mainly on embedding, while impact resistance was influenced also by other factors¹. The extent of encapsulation depends on the relative magnitude of adhesion and shear forces acting during homogenization and processing². Since interactions are relatively weak, while the particle size of the reinforcement is quite large, mostly separate distribution of the components is expected in PP/elastomer/wood composites. Structure can be and often must be controlled by the addition of functionalized components, like MAPP or MAEPM. However, changing composition and structure modifies the mechanism of deformation, the extent of reinforcement and final properties. In this study composites modeling wood reinforced bumper material as well as actual recycled bumper regrind/wood composites were prepared and studied in detail. Filler content was varied in a wide range. Structure and interfacial adhesion was modified with the use of different functionalized polymers. Mechanical characteristics were studied on injection molded parts by tensile testing and by the measurement of impact resistance. The structure of the composites was analyzed by SEM and model calculations. Deformation mechanism was studied with the help of acoustic emission and volume strain measurements. A wide variety of deformation mechanisms and behaviors were found as composition, interactions and structure changed.

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**CL-25**

EU TIRE LEGISLATION - HOW SSBR HELPS TO MEET THE CHALLENGE

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The Kyoto Protocol as the first globally agreed contract on reducing greenhouse gas emissions requires industrialized
nations to reduce their CO₂ emissions significantly already in near future. In general, Transportation is contributing about 26 % of the overall anthropogenic CO₂ emissions in the EU (Michelin Fact book 2008) and 18 % can be directly correlated to road transport. Thus, tire rolling resistance reflects 4 % of the overall emissions and is a significant contributor to fulfilling the global requirements.

The improvement of the CO₂ balance in Transportation was clearly correlated to tire design and put forward to the tire industry by several legislators worldwide. Tire manufacturers in the European Union are facing challenging target limits required by legislation taking effect as of 2012. The European Regulation (EC) No 443/2009 from 2009 is setting emission performance standards for new passenger cars as part of the Community’s integrated approach to reduce CO₂ emissions from light-duty vehicles. Additionally as of 2012 all tires marketed in the European Union will be rated concerning type-approval requirements based on Regulation (EC) No 661/2009 and labelled regarding Regulation No 1222/2009 (Fig. 1) with respect to fuel efficiency, wet grip and external noise.

As of 2012 the label will increase the level of consumer information on tires regarding wet grip and environmental aspects and increase market transparency. As 2014 tires not meeting the requirements will not be allowed to be sold in the EU. This trend is not limited to Europe. Several countries as Japan, Korea, Canada or US have already or are planning to implement similar schemes.

Major performance targets of tire treads as rolling resistance, wet grip and wear are inversely correlated to each other. The reduction of fuel consumption must be achieved at the expense of neither safety (wet grip) nor wear (Abrasion resistance).

A major contribution to decreasing rolling resistance and optimizing heat built up of tire tread comes from limiting hysteric energy loss and improving filler distribution. A major part of passenger car tread compound is SSBR. The next generation of functionalized SSBR enhances the interaction of polymer chain ends with fillers as silica or carbon black. As shown in Fig. 3 the new functionalization technology leads to an overall expansion of the magic triangle without loosing performance in any of the three categories. Beside DIN abrasion, tan δ 0 °C is reflecting wet grip performance and the rolling resistance is indicated by tan δ 60 °C. As an example the new generation of chain end modified SSBR grades, e.g. Sprintan® SLR 4602-Schkopau, enable in a silica compound (80 phr) a significant improvement of 28 % in tan δ 60 °C, enhanced DIN abrasion and heat build up, while maintaining wet grip characteristics.

In general, improving polymer-filler interaction is leading to increased compound viscosity levels, which could impose limitations regarding compounding or output characteristics depending on mixing and extrusion equipment. However, diverse processing aids could be applied to reduce compound viscosity and assist filler distribution, but these changes may affect compound performance as well as add undesired raw material cost.

In a comparable silica formulation the newest generation of functionalization technology developed by Styron Synthetic Rubber results in enhanced processing index and additional performance regarding rolling resistance and wet grip.
CL-26
STUDY OF THERMOELASTIC PROPERTIES OF ACRYLATE COMPOSITES IN AUTOMOTIVE INDUSTRY – PART I

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Abstract

The wide spectrum of composite materials application in automotive, aerospace and military industry, heterogeneous and their large scale utilization requires necessary demanding accurate knowledge of material parameters those materials.

The thermal expansion behaviour and elastic properties of acrylate resin MODAR reinforced by glass fibre are studied. MODAR – Modified Acrylic Resins offers a series of unique thermoset polymers used in many markets such as automotive, mass transit, railways, building, rods for optical cable, structural parts and profiles and optical fire retardant/low smoke / low toxicity composite parts. MODAR resins offers: low viscosity, rapid cure, fast cycle times, superior physical properties, and resistance to cracking, long shelf-life and stability (valuable for hot climate countries).

Introduction

Properly designed composite materials can produce thermal expansion coefficients lying well outside the range shown by homogeneous materials both in a single direction and in a plane. Much lower negative values may be produced compared with single materials as well as larger positive values. Such extreme values may be coupled with a choice of other mechanical properties, e.g., Young’s modulus or breaking strength or toughness. In this paper we demonstrate influence of two kind of reinforcement to linear coefficient of expansion and elastic properties, too. The investigated sample contains different kind of reinforcement, UNIFILIO and ROVICORE. ROVICORE consists of a non-woven core sandwiched between Chopped Strand Mat (CSM.) This fabric is ideal for Closed Mould production, for example RTM (Resin Transfer Moulding.) Each square metre x 1mm thickness will absorb approx. 600g of resin. UNIFILIO is an E-glass continuous strand mat of random orientation in multiple layers and held together by a binder. Dilatometry is a method by which the thermal expansion of a material may be measured. There are many types of dilatometers. Dilatometers may use a pushrod, capacitor, or optical system to sense expansion and

Study of thermoelastic properties

may be configured in horizontal, vertical, or in-between configurations. Materials expand because an increase in temperature leads to greater thermal vibration of the atoms in a material, and hence to an increase in the average separation distance of adjacent atoms. Thermal expansion of investigated composite materials was measured on the Dilatometer DIL 402 PC, Scheme 1, which is a universal applicable instrument for routine investigations of ceramic, glass, and metal samples, this dilatometer meets all normal requisites regarding resolution, calibratability, precision and sample atmosphere. This is an easy-to-operate, entry-level instrument for materials characterization for in-plant quality control.

Dilatometers utilize a Linear Differential Variable Transformer (LVDT) to convert a pushrod displacement to a voltage. This voltage is recorded and converted to a recordable displacement signal by software. By carefully controlling and recording, via thermocouple, the temperature of a sample at the free end of the pushrod, the thermal elongation characteristics of a sample may be determined. When changes in length are driven by changes in temperature, it must be recognized that dilatometer components can also be affected. For that reason, two test runs are required for each experimental sample. The first run is performed using a material with known thermal expansion characteristics. This first “correction” run allows determination of changes in length of the dilatometer components (sample holder and pushrod) by subtracting changes of the known material from the total. The second run is performed with the experimental sample. Changes in length of the experimental sample can be determined by subtracting changes in length of the system components from the total changes in length. Horizontal and vertical dilatometers each have advantages and disadvantages due to orientation. Horizontal dilatometers minimize thermal expansion of components because convection effects are minimized, whereas component expansion in vertical dilatometers may be much greater as heat is carried by convection along the length of the sample holder and pushrod. A disadvantage of horizontal dilatometers is friction. Typically, the sample is placed in contact with the sample holder, and it must expand

Scheme 1. Schematic of dilatometer in horizontal configuration
along the surface. This is not a problem with vertical dilatometers\footnote{Využitie statických metód a kmitov v diagnostike materiálov: Diagnostické metody v materiálovým inžinierstve. UKC ZSVTS, 2009.}. The sample is set on a fixed plate, and the pushrod is lowered to contact the sample. On the investigated samples are impose requirements on permanent specific length, eventually only little exchanging, so push rod was perpendicular on base (cross-sectional area). The measurement can be doing only to critical temperature – gas evolution, burning, diffusion and so on\footnote{Daw J. E., Rempe J. L., Knudson D. L., Condie K. G., Crepeau J. C.: Viability of Pushrod Dilatometry Techniques for High Temperature In-Pile Measurements.}. The software allowed calculates two kinds of thermal expansion coefficient. The first is technical coefficient of thermal expansion, which is calculated by using equation (1), during exactly required value of reference temperature $T_0$ standartly indicated $T_0 = 20\, ^\circ C$. The second is physical coefficient of thermal expansion. For both cases is coefficient linear expansion constant or practically constant. The coefficient linear expansion is determined like average value on this interval, more detailed is referred in \footnote{Viability of Pushrod Dilatometry Techniques for High Temperature In-Pile Measurements.}.

$$\alpha = \frac{1}{L_o} \frac{L - L_o}{T - T_o} = \frac{\varepsilon}{T - T_o}$$

(1)

Results and discussion - part A

The diagrams of work for the sample A are described on the schemes 2, 3, 4, 5.

Sample A: measurement 1,
Mode of heating, $T = 50\, ^\circ C$, $\alpha_f = 23,070.10^{-6}\, K^{-1}$,
Mode of cooling $T = 52,6\, ^\circ C$, $\alpha_f = 73,725.10^{-6}\, K^{-1}$.

Sample A: measurement 2,
Mode of heating, $T = 50,1\, ^\circ C$, $\alpha_f = 61,573.10^{-6}\, K^{-1}$
Mode of cooling $T = 52,6\, ^\circ C$, $\alpha_f = 64,347.10^{-6}\, K^{-1}$.

Scheme 4. Behaviour dependency $\varepsilon$ to $T$, sample A, measurement 2

The diagrams of work for the sample B are described on the schemes 6, 7, 8, 9.

Sample B: measurement 1,
Mode of heating, $T = 48,9\, ^\circ C$, $\alpha_f = 39,289.10^{-6}\, K^{-1}$,
Mode of cooling $T = 52,6\, ^\circ C$, $\alpha_f = 39,342.10^{-6}\, K^{-1}$.

Scheme 5. Behaviour dependency $T$ to $\alpha$, sample A, measurement 2

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CL-27
DEFECT ANALYSIS FOR AUTOMOTIVE INDUSTRY – FROM THE ANALYTICAL POINT OF VIEW

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Introduction

Already ancient Romans knew that “making haste slowly” was not just an aphorism, but a reflection based on experience. Defects always will appear, as they are part of daily life. Nowadays many defects in automotive industry are raising-up caused by higher production speeds, shorter leading times, changing of suppliers or simply human abstraction.

However, sometimes a product looks good during storage but in real use discolors, shows mechanical defects like cracking, blooming or has adhesive problems. It is impossible to keep everything for 100 % under control, therefore production lines count always with a few % of defect end products. If the number of defects are significantly increasing, there is need to investigate the problem. Defects can have a wide range of causes/consequences and should be used as data for continuous quality improvement.

Economical and technical aspects

Defect analysis acts in many cases not to find the “bad guys and good galls”, but mainly to clarify unexpected inversions which are leading to new approaches and mainly prevention. Analytical chemistry can support the automotive industry to characterize defects if results are properly interpreted. Working out cases scientifically needs afterwards a technical correction by the producer. After characterization a certain defect, conclusions are important for further prevention.

Defect analysis need to be considered as a feedback mechanism to improve the quality and productivity with overall prevention of historically determined mistakes. This prevention can save manufacturers lots of money.

Strategy: comparison and elimination

According to the location and shape of the defect spectral, microscopic or separation techniques can be applied. According to the desired uncertainty of measurement, the best available technology should be chosen.

Basically a defect is best detectable if there is a possible comparison with a reference sample (or more samples). Many methods used in the scientific community are based on this principle. By elimination of possibilities, a solution can be found for further prevention.

Non-destructive first! - spectral methods

The use of spectral analytical tools is preferred in order to know in which direction the analyst should speciate. Common spectral tools like fourier transformed infrared spectrometry (FTIR) and X-ray fluorescence spectrometry (XRF) can be equipped with a microscope, (e.g. scanning electron microscope coupled to energy-dispersive X-ray spectroscopy / SEM-EDX). From these visualizations lots of basic information can be achieved. Mainly defects like small impurities, spots, adhesive problems and surface defects can be easily characterized. Spectral methods are non-destructive and very quick.

One case of a defect appearing on the surface of a multi-layer car profile made from EPDM. On the surface were seen...
''dots''. In Fig. 1 is seen by SEM that a ''dot'' is located between 2 polymer layers. After gold sputtering for SEM-EDX measurement there was detected that the material is foreign and contains typical elements from talc \((H_2Mg_3(SiO_3)_4)\), which the other parts did not have. This was once more confirmed by measurement on FTIR by microscope (Fig. 3). The polymer in the ''dots'' is foreign due to the fact that it contains talc and the other test parts (from the layers) not. All results were obtained by comparison the defect test point with reference test points.

Both spectral methods come to the same conclusion. In many cases these spectral analysis can direct the analyst in the direction of organic defects or inorganic defects.

**Separation sciences**

To identify a small amount of macromolecules as impurities, pyrolysis-GC-MS can be applied. The power of pyrolysis is that it requires a small amount of sample (0.5 mg) and is able to fully characterize pyrolysis fragments by classical gas chromatography/mass spectrometry (GC-MS). In Fig. 4 is seen a picture of white fibers coming out of a cover intended to use for car interior. After isolating them, extracting and applying a pyrolysis analysis on this part, this foreign material was identified to be a copolymer PC/ABS.

For characterization of fogging, thermal desorption (TD) coupled with GC-MS is the best available technique. It is possible to simulate on a test part the whole temperature range over a longer time and identify the emissions produced. Fig. 6 shows a fogging comparison test of 2 car sealants. One sealant (lower chromatogram, Fig. 6) give no emissions while the other/defect one (upper chromatogram, Fig. 6) shows a Gaussian distribution of polydimethylsiloxanes. Such a comparison is commonly done for screening of additives, searching for batch-to-batch differences and looking for foreign reaction products.

Non-adhesive behavior of materials can have a broad range of causes, however, if there is a possibility for comparison with previous batches it makes sense to compare. In the following case a defect with adhesive properties of leather on a steering wheel was solved by thermal desorption. Low molecular weight analytes were expected, therefore thermal desorption GC-MS was applied. The absence of 2 commonly used amine catalysts in the PU-glue at the defect test point prove the bad-adhesive properties on the defect test point (Fig. 7).
Elements, lower detection limits please!

Element analysis for automotive industry is in evolution toward trace levels. Therefore special analytical tools like inductively coupled plasma spectrometry (ICP) is getting more and more important for defect analysis. Differences between batches for an element like sulfur might be critical fur rubber mixtures.

The use of inorganic additives, fillers, inorganic acid scavengers can be characterized on its element composition. Differences in homogeneity of hydrotalcites used as an acid scavenger in PP pellets can give already huge effects of yellowing, if a phenolic stabilizer is mixed. Therefore the ratio Mg/Al should be screened on raw materials.

Conclusion

New trends in modern analytical chemistry are focussed on many fields in the scientific world. However for automotive industry with common analytical instrumentation and experienced people, defect analysis can support the QA and QC for many automotive applications. As defect analysis is a part of its prevention itself and process optimization, it might not be ignored as defect analysis can save the producer lots of money.
At the same time, the designer is expected to design the gate in such a way so that it fulfills its function. It is one of the reasons why it is necessary to study the influence of gates on the injected product. More profound knowledge of this problem can help designers of injection molds to make the right decision.

Experimental conditions

Parts with ejecting mechanism to fit the universal frame of the injection mould were designed for the experiments. The cavity of the mold was of square board shape with the dimensions (100 × 100 × 3) mm. The design of the runner system enabled to fill the cavity by different ways – by different types of gates.

Gates were divided into three groups (A, B and C) according to the way of filling the mold cavity. Out of these groups representative gates were selected in respect of their practical application. In total four gates were selected:

- A1 – film gate on the side of the board;
- A3 – fan gate on the side of the board;
- B1 – fan gate in the corner of the gate;
- C1 – cone gate in the centre of the board.

Square boards from the selected gates were manufactured on the injection molding machine ARBURG Allrounder 420 C. Test samples were cut out of the boards to be used for mechanical tests. The test samples were prepared in two directions:

- In the direction of the melting from the gate – L direction (longitudinal).
- Transversally to the direction of the melt from the gate – T direction (transversal).

The following mechanical tests were carried out on the test samples:

- Tensile test – performed on a universal testing machine ZWICK 1456 according to ČSN EN ISO 527-1 and ČSN EU ISO 527-2. To increase the precision of measurement an extensometer was used during testing.
- Bend test – performed on a universal testing machine ZWICK 1456 according to ČSN EN ISO 178.
- Impact test – performed on the hammer CEAST Resil Impactor Junior according to ČSN EN ISO 179.
- Hardness test – carried out on the hardness testing machine AFFRI using the method of Shore D according to ČSN EN ISO 868.

Polymer material used for the experiments was Polyamid 66 produced by company BASF.

![Injected board – types of gates](image)

Results and discussion

Tensile test proved the influence of the filler and its orientation. The orientation of fibres is what makes the gate different. In the case of A1 film gate, in which fibres have the greatest possibility of orientation and the gate enables the best balanced application of holding pressure, the influence of the filler on the product properties in the L direction of the flow and T direction of the flow were most visible. In the case of other types of gates this influences is not so apparent and depends on the shape and location of the gate.

The values of tensile modulus obtained from the samples taken in the direction of the flow (L direction) and transversally to the direction of the flow (T direction) were different as expected. The interesting fact was that in the case of 15 % filling and 50 % filling, the values in the T direction were higher than in the L direction. The greatest difference between the L direction of the flow and T flow was shown by 30 % filling. At the same time it was shown that in the case of this filling the type of the gate used made no difference, because the values measured are almost identical in both directions regardless of the type of the gate.

The bend test in many respects confirmed the tendencies found by the tensile test. Also, lower values of flexural modulus of elasticity compared with the tensile test were confirmed. The values were about 10 % to 20 % lower in the L direction than in the tension and in the T direction the values were 30 % to 40 % lower. By comparing the results obtained for all the gates and materials it was found that the values of individual fillings in the T direction do not show any significant difference and therefore the type of gate does not make any difference. However, in the case of filled materials, in the L direction A1 gate is considerably dominant compared to A3 and B1 gates, which show significantly lower values in this direction. It does not apply to 35 % filing which
shows minimal differences in both directions.

In the case of unfilled material the type of the gate showed a great influence during the impact test. A1 film gate showed only minor difference when comparing the values in the L and T directions, only about 6 %, but the difference was quite significant for A3 and B1 gates with approx. 25 %.

In the impact resilience there was an interesting development in the values measured. While at other measurements it is common that the value measured rises in parallel with the increasing amount of filling, there was at first a considerable drop and then a gradual growth to the original value. The reason is the glass fibres. The unfilled material showed its resilience as expected and it was necessary to apply higher energy to fracture the test sample. However, only 15 % of glass was sufficient to decrease the energy needed by as much as 65 %. With the growing content of the filler, material strength was gradually increasing and the values measured slowly approached those of the basic material. The values were, however, leveled at 35 % filling.

The polymer filled with 15 % and 35 % of glass fibres showed the greatest stability of the values measured regardless of the type of the gate used. The difference between the gates was more significant in the other filled materials.

Measurement of the hardness showed the expected fact that the higher the content of the filling, the greater the hardness of the material. The tests further showed that when using A1, A3 and B1 gates the values of hardness are very similar for all materials. C1 gate showed the lowest hardness for all materials, but it is lower by 4 % compared to the other gates, which can in general be considered negligible.

Conclusion

The presented results showed interesting correlations between the type of the gate and the selected material. In general the most suitable material appears to be polymer with the filling of 30 % or 35 % of glass fibers. The reason is the greatest stability of values measured for all types of gates. At present it would not be right to make recommendations for designers, because more tests and experiments are in progress.

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REFERENCES


CL-29

HOW THE FILLER INFLUENCE THE FLUIDITY OF POLYMER

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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 40 % 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 different amount of filler 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 mov-
ing 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 side. 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: 6 \times 1 \text{ 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 (Table I). The testing plates are used for changing the surface of the mold cavity.

### 3. Results

Natural polypropylene and polypropylene with different amount of filler – glass fibers (10 %, 20 %, 30 %, 40 % of GF) 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 following pictures.

#### Table I

<table>
<thead>
<tr>
<th>Surfaces of testing plates</th>
<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>$R_a$ [\mu m] $R_a$ [mm]</td>
<td>$R_a$ [mm]</td>
<td>$R_a$ [mm]</td>
<td>$R_a$ [mm]</td>
<td>$R_a$ [mm]</td>
<td>$R_a$ [mm]</td>
</tr>
<tr>
<td>0,102</td>
<td>0,172</td>
<td>4,055</td>
<td>4,499</td>
<td>9,566</td>
<td></td>
</tr>
</tbody>
</table>

### Fig. 3. Dependence of the flow length on surface quality (0 % GF)

### Fig. 4. Dependence of the flow length on surface quality (20 % GF)
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 the there is demonstrable difference of worse flow properties on each testing plate with increasing percentage of filler (GF – glass fibers). 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.

This article is financially supported by the Czech Ministry of Education, Youth and Sports in the R&D projects under the titles ‘Modelling and Control of Processing Procedures of Natural and Synthetic Polymers’, No. MSM 7088352102 and ‘CEBIA Tech’, No. CZ.1.05/2.1.00/03.0089.

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fications. This procedure uses aqueous \(^{10-12}\) and organic \(^{13-16}\) methods. Non-aqueous methods are mostly based on thermal decomposition of organic iron precursors in the presence of a surfactant. The resulting magnetite nanoparticles can be stabilized in water or organic solvents depending on the reaction method.

In this work a simple and direct method for the preparation of magnetite nanoparticles with diameters ranging from 5 to 30 nm is presented.

The synthesized magnetite particles are functionalized with different silanes in ethanol and dispersed in silicon rubber. The physical properties of anisotropic composites are presented.

**Eperimental**

**Synthesis of magnetite nanoparticles**

Magnetite particles were prepared by coprecipitation, adding 5 mol l\(^{-1}\) NaOH solution at 30 °C into the mixed solutions of 0.25 mol l\(^{-1}\) FeCl\(_2\)*4 H\(_2\)O and 0.5 mol l\(^{-1}\) FeCl\(_3\) (molar ratio 1:2) until the pH reached 11. The slurry was magnetically separated and washed three times with demineralized water until the pH became neutral. The solid was dried at 5 mbar and room temperature\(^{1,2,17}\).

**Functionalization of magnetite nanoparticles**

The dry magnetite nanoparticle powder was dispersed in ethanol (96 %) in an ultrasonic bath for one hour. 100 wt.% of silane was added to this dispersion, stirring rapidly. After 20 h the reaction was quenched with water, washed three times with demineralized water and dried at 5 mbar at room temperature\(^{17}\).

In this work two silanes were used for functionalization: tetraethyl silicate (TEOS) and triethoxyoctylsilane (Si\(_{208}\)).

**Magnetite nanoparticles in silicon**

Different amounts of dry, functionalized magnetite nanoparticle powder were dispersed in a two-component silicon in an ultrasonic bath for 30 minutes. The composite was cured at 30 °C for 24 h with and without a magnetic field in a 2 mm Teflon-mould.

**Results and discussion**

The synthesized magnetite nanoparticles are identified by XRD. The XRD-pattern (Fig. 1) shows the typical structure for magnetite\(^{6}\) with broad peaks showing the nanoparticularty of the powder. The room temperature Mössbauer spectrum of the magnetite sample is typical for nanocrystalline magnetite particles with a diameter about 10 nm (ref.\(^{18}\)).

The size of the magnetite particles is measured by TEM and DLS.

The TEM images show a average particle diameter of 17.9 nm. Fig. 3 shows a TEM image and the histogram of the particle size. The unfunctionalized particles have a tendency to agglomerate which is confirmed by DLS results. Here the unfunctionalized particles have a solvodynamic average diameter in ethanol of 1.66 μm, the particles which are functionalized with TEOS have a average diameter of 51 nm and the particles which are functionalized with acrylsilane have a average diameter of 35 nm. This tendency shows the deagglomeration of functionalized particles and indicates a monolayer of acrylsilane on the magnetite particle surface instead of a multilayer of TEOS.

The SQUID-measurements (Fig. 2) show a high saturation magnetization and no hysteresis at room temperature this indicates superparamagnetic properties in the material.

The effect of functionalization of the magnetite particles is investigated by TGA and FT-IR. The TGA of the particles functionalized with Si\(_{208}\) indicate a 4 mass% coverage with organic material, this equates to 5 mass% of silane. The FT-IR spectrum of the functionalized particles shows typical aliphatic bands.

The transition temperature of Fe\(_3\)O\(_4\) (magnetite) into Fe\(_2\)O\(_3\) is also given by TGA at 168 °C. After functionalization with TEOS the transition temperature rises to 188 °C. This fact indicates a good coating of the surface and a protection of the surface atoms against oxidation by the functionalization.
Magnetite-polymer composites

The magnetite-silicon composites show a switching effect to higher stiffness in presence of an magnetic field as a function of field strength. This property can be used to build actuators and sensors based on elastomers.

Physical properties

During incorporation and curing the magnetic particles can be oriented within the polymer matrix. The orientation is establishing a memory effect in as much as physical properties changes significantly when the composite is deformed in absence or on presence of an external magnetic dynamically field.

Summary and outlook

The combination of magnetic nanomaterials with polymeric matrix materials opens new ways to synthesize different composite materials with adjustable characteristics. These materials can be used for example as new sensors, actuators or in biotechnologies.

The main problem, a good dispersion of the nanoparticles in the polymeric matrix, was solved by functionalization with silanes, which have organic groups that are similar to those used in this work.

A better control of the particle size and particle dispersion will be part of the next steps of this work.

The authors want to thank Prof. V. Šepelák (University of Braunschweig) for the Mössbauer measurements, Dr. Ch. Menneking (Laser Zentrum Hannover e.V.) for the DLS measurements and the BMBF for financial support of this work.

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CL-31
RECYCLING OF PP/EPDM/TALC CAR BUMPERS

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In the work the comparison of mechanical properties of recyclates from Volkswagen car bumpers obtained after the grinding and regranulates from the same wastes but produced in the extrusion process on the twin screws extruder (type ZAMAK, L/D = 40) has been presented. The original bumpers has been produced from the PP blends with 20 % EPDM and 10 % of talc. The example of passenger car bumper is presented on the Fig. 1.

Materials and technology used in car industry were always connected with technical knowledge in the time of its production. First cars were based on wood and steel. In 1930 same elements has been produced from polymeric materials. In 1955 the average car have 5 kg of parts made from plastics. Between the years 1960–1970 the contents of plastics part in
the cars increase from 11 kg to 45 kg, but still it were mostly rather the decoration part than constructional one. In next years together with development of polymer processing technologies the car parts produced from plastics became the real construction elements and now we can find about 145 kg of plastics parts in every produced passenger car (it is around 12–15 % of car weight). The amount of plastics used in production of average passenger car is shown on the Fig. 2.

One of the most common application of polymer materials in the car are bumpers. They are produced mostly from modified PP material. The front bumpers are made from PP+EPDM polymer blends (to have more elastic properties) and the rear bumpers are made from PP+EPDM blends modified by some amount of talc (to decrease a cost of production).

The wastes from such a bumpers have been put on the recycling test. The PP/EPDM/Talc recyclates obtained during the grinding process have been compared with PP/EPDM/talc regranulates obtained during extrusion and regranulation process made on the twin screw extrusion line. The static tensile test and dynamic mechanical thermal analysis (DMTA) have been done for both materials. The measurements of melt flow index (MFI) of the PP blends recyclates and regranulates has been made too.

The research results of rheological (MFI) and mechanical properties (max. tensile strength – $\delta_{\text{max}}$, elongation at break – $\varepsilon$, Young Modulus – E) are presented in table I while the results of DMTA tests are shown on Fig. 3,4 and in Table II.

The results of the measurements have been presented on the line diagrams (Fig. 3 and 4) of $E'$ and $\tan \delta$ dependence in a function of temperature. The full line designation the results for 1 Hz frequency testing while the broken line the results for 10 Hz. On the diagrams the $T_g$ temperatures for the components of the blends have been shown. For the sample obtained from PP recyclate the $T_g$ temperature for EPDM component was determined as $-42.5$ °C for 10Hz frequency and $-46.3$ °C for 1Hz frequency testing. The $T_g$ temperature for PP in the same sample was found as $+5.1$ °C for 10Hz and $+1.4$ °C for 1 Hz frequency. For the sample obtained from PP regranulate the $T_g$ temperature for EPDM was measured as $-42.7$ °C for 10Hz and $-46.8$ °C for 1Hz frequency testing, while the $T_g$ temperature for PP was: $+3.4$ °C for 10Hz and $+0.8$ °C for 1 Hz frequency testing.

![Fig. 1. The example of passengers car bumper](image1)

![Fig. 2. The amount of plastics used in production of average passenger car](image2)

![Table I: Results of mechanical and rheological properties tests](table1)

<table>
<thead>
<tr>
<th>Type of polymer</th>
<th>Stress at peak [MPa]</th>
<th>Strain at break [%]</th>
<th>Young Modulus [MPa]</th>
<th>MFI [g/10min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP blend Recyclate</td>
<td>17,5</td>
<td>167</td>
<td>932</td>
<td>35,5</td>
</tr>
<tr>
<td>PP blend regranulate</td>
<td>16,3</td>
<td>168</td>
<td>802</td>
<td>27,5</td>
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</tbody>
</table>

![Fig. 3. DMTA study of $E'$ and $\tan \delta$ in dependence of temperature for PP+EPDM+talc recyclate. Full line: $f = 10$ Hz, broken line = 1 Hz](image3)

![Fig. 4. DMTA study of $E'$ and $\tan \delta$ in dependence of temperature for PP+EPDM+talc regranulate. Full line: $f = 10$ Hz, broken line = 1 Hz](image4)
The results of the measurements have shown that both materials have good mechanical properties (tensile strength 16–18 MPa, Young Modules 800–930 MPa and elongation above 160%), good procesability – MFI above 27 g/10 min (recyclate – 35 g/10 min, regranulate – 27 g/10 min) and good thermal behaviour (glass transition temperature 1,4–5,1 °C for PP recyclates and 0,8–3,4 °C for PA regranulates) what is very important for the materials used in the production of car bumpers.

On the basis of the research results it was fund that the differences in samples properties produced from recyclates and regranulates of PP/EPDM/talc blends are very small. The differences in mechanical and rheological properties are negligible only the glass transition temperature for PP regranulates (after the thermal treatment in extrusion and regranulation process) has shown a small shift into the more negative value. Such a results allowed to conclude that regranulation of tested PP/EPDM/talc blends in the recycling process is useless. Due to the lower price of reprocessing of PP/EPDM/talc wastes from car bumpers, for the production purposes, using only the grinding process is more effective than extrusion and regranulation processes of such a wastes and that’s why the cheaper material – recyclates, should be selected for further recycling technologies.

The influence of plasticizers on thermoplastic processing, rheological and thermal properties of CA necessary for foam sheet extrusion were investigated by rotational and capillary rheometer, rheotens test, melt flow rate (MFR) and differential scanning calorimetry (DSC).

Introduction

Today, oil-based polystyrene (PS) is a standard material for producing thermo-formable extruded foam sheets using physical blowing agents (PBA). PS is a non-biodegradable polymer based on non-renewable resources. Cellulose acetate (CA), as a cellulose ester, is a biodegradable polymer based on renewable resources and therefore particularly suitable for producing sustainable foams and thermoformed trays.

CA exhibits mechanical properties as well as heat distortion resistance comparable to or better than those of PS. Thus, CA is a good candidate to replace PS. Generally, CA has to be modified for thermoplastic processing. The most common way is external or physical plasticization with suitable plasticizers like phthalates.

For effective foam sheet extrusion using PBAs, CA has to fulfill specific rheological and thermal properties. In particular a specific melt viscosity, melt elongation and melt strength is required for sufficient nucleation, cell growth and cell stabilisation to prevent cell collapse. To adjust these requirements, suitable eco-friendly non-toxic plasticizers like citrates can be used.

Experimental

Cellulose acetate was supplied as white powder with a degree of substitution (DS) of about 2,4 and a solubility parameter δ between 22 to 25 MPa^{1/2} [4,5]. Different types of...
plasticizer in different concentrations (15, 20, 25 wt%) were used (table I).

An internal mixer (Plasti-Corder® Lab-Station, Brabender) with a chamber volume of approx. 370 cm³ and a kneader temperature of 180 °C was used for compounding. The plasticizer and the CA powder were premixed and then fed into the chamber. After feeding had been completed, mass temperature and torque were measured as a function of mixing time. To minimize the thermo-mechanical induced degradation of CA, the mixing time was fixed at 3–4 min.

The glass transition temperature \( T_g \) was investigated from the second heating cycle of DSC measurements with 10 K min\(^{-1} \) heating and cooling rate under \( N_2 \) atmosphere. The MFR was measured at 230 °C with 5 kg. Melt viscosity was measured with rotational rheometer (cone-plate modus) and capillary viscosimeter (str and die 30/1). Melt strength was investigated with rheotens test. The temperature of the extruder was set from 210 to 220 °C with a throughput of 0,5 kg h\(^{-1} \) and a strand die of 30/2.

### Results and discussion

For thermoplastic processing of CA, the addition of an appropriate compatible plasticizer is necessary. With increasing plasticizer content, maximum torque as well as mass temperature decreased considerably (scheme 2). Thus, thermo-mechanical stress decreased, degradation of CA can be minimized and thermoplastic processing at lower temperatures is possible.

The plasticizer efficiency was studied by measuring the glass transition of CA. The data were extrapolated using the Fox-Flory-Equation. With increasing plasticizer content, the \( T_g \) decreased significantly (scheme 3). Therefore, melting and thermoplastic behaviour of CA can be improved. The decrease in \( T_g \) is a function of plasticizer type and its compatibility as well as mutual behaviour with CA. The use of the Hansen solubility parameter is one option to predict plasticizer miscibility with a polymer\(^6\). For good solubility, it is generally accepted that \( \Delta \delta = (\delta_{\text{poly}} - \delta_{\text{plast}}) \leq 3 \). However, this is almost a rough estimation as the solubility depends also on functional groups in the molecules and the diffusion behaviour of the plasticizer into the polymer\(^6\).

The rheological properties are very important for effective nucleation, cell growth and foam stabilisation to prevent cell collapse. Therefore melt viscosity, MFR and melt strength were investigated. The melt viscosity decreased considerably in the low shear region due to lower polymer content and more plasticizer-plasticizer as well as plasticizer-polymer interaction leading to higher free volume in the compound\(^6\). At high shear rates, the concentration influence diminished due to shear thinning.

As mentioned above, the compatibility between plasticizer and CA has a tremendous influence on the flow behaviour of the polymer (scheme 5).

Generally, the more compatible the plasticizer is with CA, the better the interaction and mutual behaviour. The plasticizer efficiency was studied by measuring the glass transition of selected plasticized CA as a function of plasticizer type and content (n DSC-data / – Fox-Flory).

### Table I

<table>
<thead>
<tr>
<th>Plasticizer</th>
<th>Synonym</th>
<th>( M_w ) [g/mol]</th>
<th>( \delta ) [MPa(^{1/2} )]</th>
<th>( \text{bp} ) [°C]</th>
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<tbody>
<tr>
<td>Acetate-1</td>
<td>CA-A-1</td>
<td>176,17</td>
<td>23,4</td>
<td>259</td>
</tr>
<tr>
<td>Acetate-2</td>
<td>CA-A-2</td>
<td>218,21</td>
<td>21,8</td>
<td>260</td>
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<td>Benzoate</td>
<td>CA-B</td>
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<td>CA-C</td>
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<td>20,9</td>
<td>294</td>
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<td>Phosphate</td>
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<td>326,00</td>
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</table>

### Scheme 2.

Kneader graphs of CA-P as a function of plasticizer content

### Scheme 3.

Glass transition of selected plasticized CA as a function of plasticizer type and content (n DSC-data / – Fox-Flory)
ticizer disturbs the structure of loose attachments between polymer chains because of shielding effects and thereby, the intermolecular forces between polymer chains weaken and segmental motion increases. As a result, the free volume increases and improves flow behaviour of CA. The clear increase in MFR with increasing plasticizer content confirms the observed melt viscosity results (Table II).

Melt strength is a key characteristic for stable cell growth. If the melt strength and viscosity is too high, insufficient cell growth occurs due to fast hardening of the melt. If the melt strength is too low, cell collapse (rupture) can occur due to strong biaxial stretching at the growing cell surface. Therefore melt strength was measured with rheotens test. The melt elongation of CA increases significantly with an increase in plasticizer content (scheme 6). The draw resonance (curve oscillation) is diminished compared to lower plasticizer content. Thus, indicating an improvement in melt flowability and melt elasticity with an increase in plasticizer content.

Conclusions

Thermoplastic processing behaviour, rheological and thermal properties of externally plasticized CA were investi-

Table II

<table>
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<tr>
<th>Compound</th>
<th>15 wt.%</th>
<th>20 wt.%</th>
<th>25 wt.%</th>
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<td>22,8</td>
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<tr>
<td>CA-C</td>
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<td>CA-P</td>
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REFERENCES


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