



**Sborník příspěvků z konference
s mezinárodní účastí**

Proceedings from the conference

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Konference PLASTKO je nejstarší, mezinárodní, konferencí pořádanou na půdě Univerzity Tomáše Bati ve Zlíně. Je založena na principech spolupráce mezi akademickou i průmyslovou praxí.

Cílem konference je ukázat světu a okolí, že sektor výroby a zpracování plastů není jen zavrženíhodným oborem, jak prezentují mnohá masmédia, ale naopak, že dlouhodobě přispívá k ochraně prostředí, ve kterém žijeme. A samozřejmě také napovědět výrobcům, jakou správnou argumentaci volit při prosazování výrobků na konečných trzích.

Za organizační a vědecký výbor konference Plastko 2022 jsme rádi, že tato konference se těší stálému zájmu firem i akademiků a velmi děkujeme všem návštěvníkům za účast na konferenci.

Organizační výbor konference Plastko 2022

ve Zlíně 21. 9. 2022



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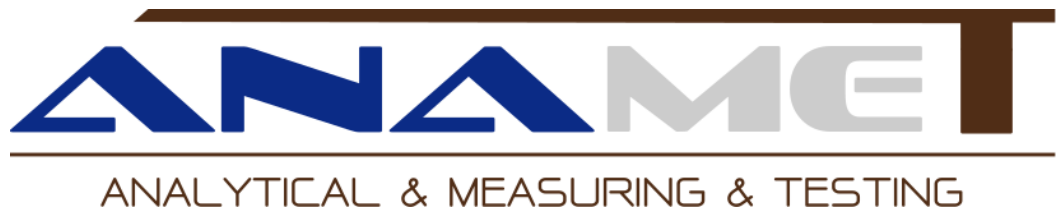
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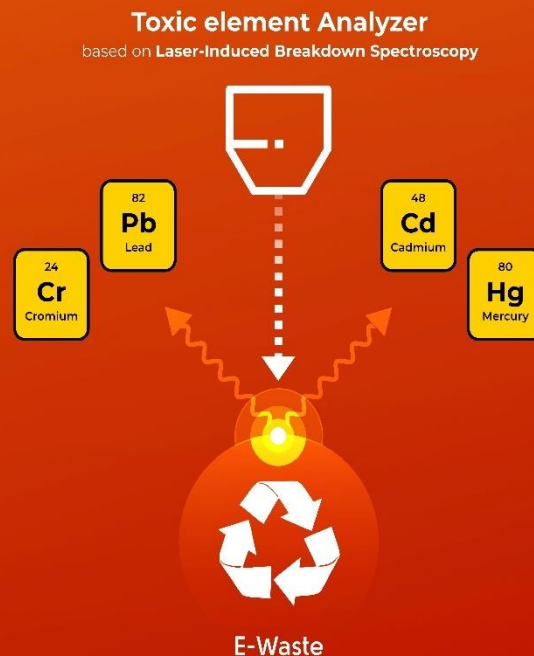
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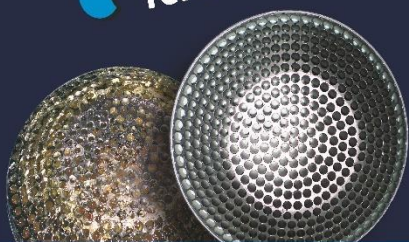
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Přednášky / Lectures

CLUSTERING ACTIVITIES IN EUROPE: THE ROLE OF ECP4

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ABSTRACT

ECP4, The European Composites, Plastics and Polymer Processing Platform is an industry-driven collaboration that unites members from 13 countries amongst the top-level European research institutions, regional plastic clusters, and EU-level industrial organisations of plastics and composites converters.

ECP4 brings innovation partners together to identify opportunities for collaborative Research and Development efforts which yield industrial innovation in the polymer industry.

The key objectives of the platform are:

- To provide networking and collaboration among research institutions and the industry.
- To facilitate the access of the European plastics industry to EU research programs, thus enabling SME's to innovate, gain competitiveness and fulfil sustainable goals.
- To communicate on new technologies and their relevance for the plastics converters and the composites industry.

The presentation gives an overview about the ECP4 organisation, it's activities and an outlook on the most relevant polymer topics expected in the new funding program Horizon Europe.

www.ecp4.eu

CIRCULAR PLASTIC ALLIANCE AND STRATEGIC RESEARCH & INNOVATION AGENDA

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ABSTRACT

The Circular Plastics Alliance (CPA) is an initiative under the European Strategy for Plastics (2018), in particular under Annex III related to voluntary pledges by industry. The European Commission launched the Circular Plastics Alliance in December 2018 to help plastic value chains boost the EU market for recycled plastics to 10 million tonnes by 2025. Between September 2019 and March 2020, the CPA signatories have met in market oriented working groups to identify and confirm the R&D Needs and collectively build the CPA R&D Agenda. The positive outcome is the strong cohesion of R&D needs across the five main CPA value chains or plastics-using sectors, namely: packaging, automotive, construction, agriculture and electronic and electrical equipment (“EEE”). These STRATEGIC R&D NEEDS (common to at least 3 plastics-using sectors) are described in the first section of the document. The market SPECIFIC R&D NEEDS (common to only 1 or 2 plastics-using sectors) are described in the second section of the document.

VTT PLASTIC VISION AND SOME PRACTICAL EXAMPLES

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ABSTRACT

Plastics are a versatile material for many applications in different fields and a key material in both developed and developing societies. But how can we tackle plastic pollution, greenhouse gas emissions and at the same time preserve the social benefits offered by plastic? A general plastic ban is obviously not a realistic solution. The short answer is through a circular economy of plastics. Plastic recycling offers tools to keep the carbon in the loop and thus reduces the need for fossil raw materials in the plastic value chain.

The main development targets for plastic recycling are increasing the share of recyclable plastic waste, increasing the quality and value of recycled materials, and developing and commercializing industrially implemented recycling processes. Due to lower energy consumption, mechanical recycling is the preferred route to new plastic products, but it often leads to the downgrading of the plastic properties, preventing valuable applications.

Chemical recycling of plastics and advanced waste sorting methods are increasingly being adopted in the industry, providing tools to achieve quantitative and qualitative recycling targets. Today, chemical recycling mainly uses thermal and catalytic pyrolysis techniques to liquefy plastics, with the ultimate goal of producing a feed for steam crackers for light olefin production or directly by depolymerisation to monomers.

The complexity of the plastics value chain with many processes and applications means that there is no one-fits-for-all technology or solution for the circular plastics economy. Here are presented some examples of some technological developments and research topics in plastic recycling.

SOLUTIONS FOR A MORE SILENT WORLD - IMPROVED ACOUSTICS WITH INNOVATIVE POLYMER MATERIALS AND SYSTEMS

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ABSTRACT

Polymer materials are relatively inexpensive, lightweight and easily in 3D shapes formable. Therefore, many articles are made out of polymers today. Among these are various electrical devices, tools and automotive components which housings are made of polymer materials. However due to their low mass density and often relatively low structural damping, polymer materials pose challenges from an acoustic design point of view. Machines, tools or components with polymer housings are often loud.

The Fraunhofer project »PolymerAkustik« – Polymer Acoustics has developed several solutions to reduce sound emissions of devices, tools our household-equipment with housings made of polymers. Tailored polymer materials with improved internal damping and material structures with optimised acoustics offer great potential for noise reduction and sound design. New ventilation slit geometries allow a reduction of tonal components generated for example by the gear or the power electronics without hindering the heat exchange via air flow. For the optimisation the project developed a manageable and efficient vibroacoustic characterisation method. In this paper a summary of the important achievements of the project is given.

REDESIGN WITH REDUCE-REUSE-RECYCLE IN MIND

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ABSTRACT

Plastics have been getting a lot of bad press in recent years. Some of it is totally unjustified. However, all the stakeholders in the plastics industry must address the issues raised in the mass media and try to find technically feasible and economically viable solutions. Plastics pollution must be reduced. Processes and products must be reconfigured. As an example, PET water bottle production and microplastics in bottled water is discussed. It is argued that PP caps should be discontinued, simply because they destroy the excellent quality of HDPE cap post-consumer recycling stream. Microplastics in bottled water have been detected in most brands, in large quantities. Microplastics generation can be traced to injection molding of bottle preforms and caps. Injection mold cavity gate marks, flash and surface porosity are the main sources, due to break off and shedding during subsequent transportation, handling, blow molding of the preforms and during bottling and filling operations. There is no definite information on the impact of microplastics ingestion to human health, but awareness in the general public is increasing and consumers are concerned. There is ongoing research on detection in various laboratories around the world, but hardly any attempts to relate microplastics generation to material properties or processing conditions. To reduce the quantity of microplastics in bottled water, research must be carried out to identify HDPE grades which are less prone to break off and shedding. Production processes and handling of the bottles must be redesigned.

IRGACYCLE ADDITIVATION CONCEPT, AN INDUSTRY FOCUSED CONTRIBUTION TO CIRCULARITY OF PLASTICS

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ABSTRACT

Launched in 2021, BASF IrgaCycle consists of a series of plastic additive formulations, which enable recycled plastics to be reused for the production of high-value plastics in combination with virgin materials. The additive solution addresses specific quality issues associated with recycled resins, such as limited processability, poor long-term thermal stability and insufficient protection from outdoor weathering. Irgacycle concept is also focused on deactivation and compatibilization of various impurities. Compatibilization of various polymer mixtures (PE/PP, PET or PA and PO) is also part of BASF additive solutions. Besides Irgacycle additives, BASF offers also Irgatec CR 76 IC solution for films and fibers recycling, Tinuvin NOR 356 and Irgastab FS products as part of BASF Valeras complex concept for recycling processes and polymers circularity.

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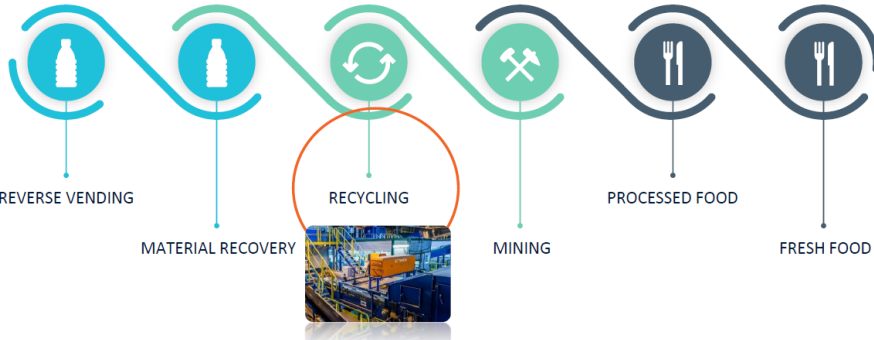
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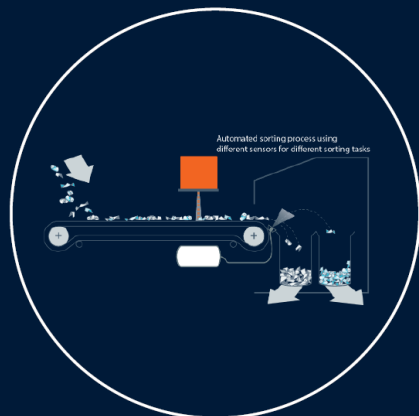
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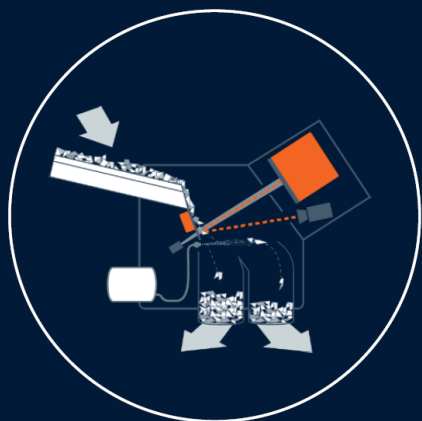
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Správce zálohového systému n.o., Slovensko

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Technologie (1 linka): 2x **Autosort 2800 mm**

Celkový výkon :

Účinnost: > 93% / track

Čistota PET (4-5 různých barev): 93 - 96 % Průchodnost linky: < **4,5 t/h**



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Sortování PE fólie

ATF, Polsko

Linka separovaného odpadu, 24/7, Post consumer PE fólie, 70-80% PE čirá + 20-30% PE barevná

Technologie (1 linka): **Autosort Speedair 2000 mm + Autosort 2000 mm** (čirá fólie) + Kabina (barevná fólie)

Celkový výkon :

Účinnost 1 stroje: 80-85%

Velikost vstupních fólií: 50-300mm

Čistota PE čirá: > 98 %

Průchodnost 1 linky: **2,5 t/h při použití 2000 mm strojů**

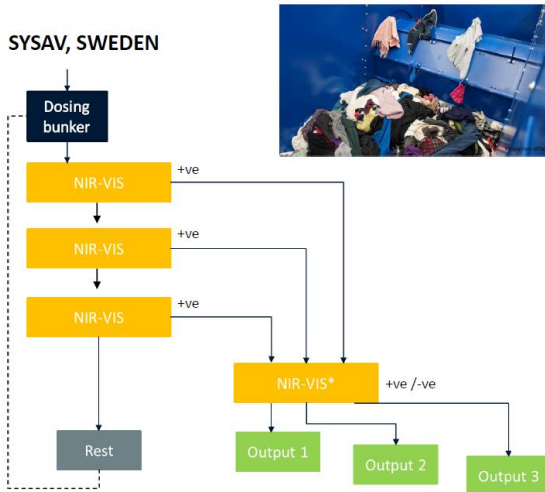


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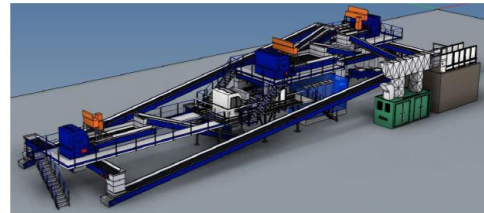
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16

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Sortování PET

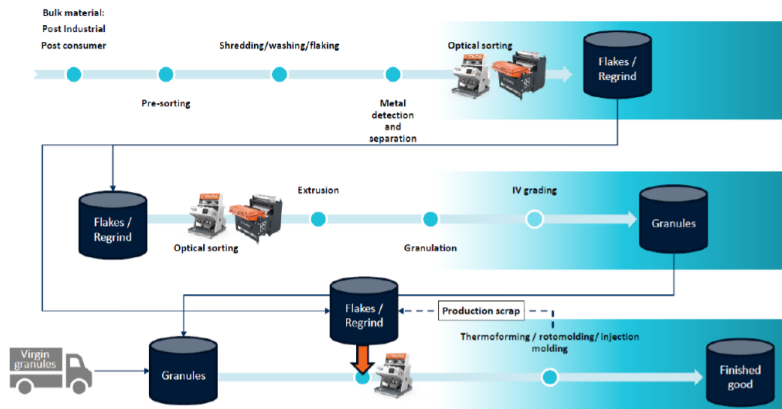
Sortování PO: separace PP/PE

Sortování dle barev

Rozvíjející se trhy: dominantní PET

EU: 50% PET / 50% PO

US: dominantně PO projekty



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CERTIFICATIONS OF RECYCLED CONTENT IN EUROPE

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ABSTRACT

Certifications of recycled content in Europe - Partnerships and tools to achieve the EU objectives

Agenda:

The Circular Plastics Alliance (CPA)

Monitoring Recyclates for Europe (MORE)

PolyCert Europe

The lecture will focus on the existing partnerships and tools that will help Europe to reach the goal of 10 million tons of recycled plastics in new products annually. The lecture will introduce in more details the Circular Plastics Alliance, Monitoring Recyclates for Europe and PolyCert Europe.

KLÍČOVÉ ASPEKTY K DOSAŽENÍ RECYKLAČNÍCH CÍLŮ

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ABSTRAKT

Evropská legislativa oběhového hospodářství definovala jasné strategické nastavení ve vztahu k nakládání s odpady na dalších minimálně 15 let. Strategie byla stvrzena konkrétními cíli pro recyklaci komunálních odpadů a také cíli pro vybrané obalové materiály a jejich recyklaci. Nezbytnou podmínkou k možnému dosažení vysokých recyklačních cílů je efektivní třídění, používání spektra dobře recyklovatelných materiálů, ale také ekonomická smysluplnost recyklace jako takové. Ekonomická smysluplnost souvisí s velikostí trhu druhotných surovin a s velikostí poptávky po produktech recyklace. ČAOH, jakožto svaz sdružující největší kapacity recyklačních technologií v České republice aktivně hledá cesty k řešení jmenovaných aspektů, tedy k podpoře recyklace. V prezentaci se dozvíte vhodné efektivní formy třídění, dozvíte se podrobnosti o roli primárního a sekundárního třídění, řekneme si jaká množství odpadů budou muset procházet třídícími procesy, aby bylo možné splnit závazné legislativní cíle. Sdělíme si vhodné aktivity, na které by se měli zaměřit výrobci obalů a uvedeme si informace k tomu, jakou může mít v budoucnu roli chemická recyklace odpadů. Krátce bude komentována i aktuální krize na trhu energií a její dopady na systémy sběru a recyklace.

COMPARISON OF MECHANICAL PROPERTIES OF SENTRYGLAS IONOPLAST AND STANDARD PVB INTERLAYER

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ABSTRACT

Laminated safety glass (LSG) is commonly used for a wide variety of building projects. Additional benefits such as post-glass breakage, structural safety, security from natural and man-made threats, acoustic and energy performance have led to the expanded use of LSG.

A typical laminated glass construction consists of two or more glass panes bonded together by an interlayer such as Standard PVB (polyvinylbutyral), Ionoplast Inter layer (SentryGlas®), Stiff PVB or EVA (Ethylene-vinyl acetate) [1] Laminated glass has become a major interest in structural applications after the adoption of “Effective Thickness Method” by ASTM E 1300 in 2009. In recent years, more structural engineers are becoming aware of the viscoelastic behavior of the interlayers [1,2-4] SentryGlas® Ionoplast Inter layer, from Kuraray (originally invented by DuPont), was developed with the aim of achieving higher stiffness, temperature resistance, and resistance to tearing applications, briefly superior post breakage strength. The glass fragments adhere to the interlayers so that a certain remaining structural capacity is obtained as the glass fragments arch or lock in place and it depends on the fragmentation of the glass. Stiff PVB process is similar to standard PVB while standard ionoplast interlayers require some special processing [2] But recent improvements in ionoplast interlayer technology enable ionoplast to be laminated more similar to PVB [2] To evaluate the impact resistance we have used mainly ball-drop tests but also pendulum impact tests according to EN 12600 & ANSI can be conducted on laminated safety glass in order to measure the effects of dynamic loads and to analyze the post-breakage performance. Stiff PVB and Ionoplast behave differently at higher temperatures, which can affect the post breakage strength of the laminate. The post-glass breakage behavior of laminated glass is defined as the state when one or more glass sheets are cracked and the broken pieces of glass remain bonded to the interlayer.

The aim of tests in Kuraray was to evaluate the post breakage behaviour when the load was up to 400 Kg, with weight increments of 100 Kg, with a 15 minute time interval between each load

increment [3] Laminates with SentryGlas® Ionoplast and Stiff PVB inter layers sustained this load of 400 Kg without collapse at -20°C and + 21°C temperatures, while Standard PVB laminate could not sustain the 100 Kg imposed load at +21°C as it collapsed in few seconds [3,4] At room temperature, PVB is soft with an elongation at break of more than 250 per cent. For higher temperatures and durations, the shear transfer is strongly affected. Low stiffness of the PVB interlayer results in blanket effect as soon as the glass breaks even for vertical applications because of the self-weight of the panel, especially with large panel sizes and minimal supports [4] The laminate construction made with 0.89 mm SentryGlas® Ionoplast inter layer sustained a weight of 100 Kg for more than 30 minutes and collapsed when load was ramped up to 200 Kg. Similarly, 1.52 mm Ionomer laminate could sustain a load of 200 Kg for more than 30 minutes after breakage and collapsed when load was ramped up to 300 Kg.

As a conclusion, we can say, that Ionoplast should be used in cases of higher temperature and longer load durations. While Stiff PVB are perfectly suitable when lower design temperatures are specified [4,5] In general, the experiments demonstrate that the post-breakage performance of laminates with SentryGlas® ionoplast interlayer are superior to those with PVB.

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ARPRO, EXPANDOVANÝ POLYPROPYLEN S RECYKLOVANÝM OBSAHEM

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ABSTRAKT

Společnost JSP, výrobce materiálu ARPRO, je světovou jedničkou na trhu expandovaného polypropylénu (EPP). ARPRO je pěna s jedinečnou kombinací vlastností – výborně absorbuje energii v kombinaci s vysokou strukturální pevností, má velmi nízkou hmotnost, vysokou chemickou odolnost a mimořádné tepelně a zvukově izolační vlastnosti. Tento materiál je využíván především v automobilovém průmyslu a oboru HVAC, je vhodný také pro různá použití ve stavebnictví, strojírenství a obalovém průmyslu.

ARPRO je 100% recyklovatelný. Na podporu oběhového hospodářství vyvinula společnost JSP materiál s 25% obsahem recyklovaného EPP z dílů na konci životního cyklu. Tyto díly jsou mechanicky recyklovány podle přísných požadavků na kvalitu, díky kterým jsme pak schopni vyrábět ARPRO RE se stejnými vlastnostmi jako ARPRO z primárních surovin. ARPRO RE je tedy materiálem vhodným pro výrobu bezpečnostně kritických a funkčních dílů v automobilovém průmyslu.

Na základě studie LCA jsme vyhodnotili environmentální dopady výroby ARPRO RE s obsahem 25 % recyklovaného obsahu a porovnali je s ARPRO vyrobeným z primárních zdrojů. Výsledkem je 12% snížení uhlíkové stopy u recyklovaných typů ARPRO. Do studie nejsou započítány žádné environmentální kredity, jak požaduje automobilový průmysl.

Letos jsme uvedli na trh ARPRO REvolution s téměř 100% recyklovaným obsahem. Tento materiál je určen pro netechnické aplikace, jako jsou obaly, výrobky pro volný čas, nábytek apod. Je to expandovaný polypropylén s nejnižší uhlíkovou stopou na současném trhu, emise CO₂ má o 43% nižší než ARPRO vyrobené z primárních zdrojů.

Mechanická recyklace je stále neekonomičtější a neekologičtější metoda pro řešení odpadu z EPP. Díky obsahu přísad zajišťujícím tepelnou stabilitu a dobře kontrolovanému recyklačnímu cyklu jsme schopni zabránit degradaci materiálu. Otestovali jsme tři po sobě jdoucí recyklační cykly a výsledky ukazují, že konečné mechanické vlastnosti recyklovaného ARPRO jsou stejné jako ARPRO vyrobené z panenských surovin.

Současné lineární hospodaření s plasty je už dále neudržitelné. ARPRO Recycled reaguje na současnou poptávku po oběhovém hospodářství. Nabízíme řešení, jak zachovat přírodní zdroje a zmírnit klimatické změny. Je čas jednat - průmysl musí změnit svoji předpojatost spojenou s používáním recyklátů.

FOOD PACKAGING TRENDS: INNOVATION, SUSTAINABILITY AND SAFETY

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ABSTRACT

The packaging sector, including flexible films and rigid containers, represents the largest single market for plastic consumption. In Europe, about 62 million tons of plastic are produced each year. Of these, 23 million tons are used to produce packaging (92 million tons expected in 2050), representing more than 40% of the total weight of all plastic inserted in the market and more than 60% of the fraction of post-consumer plastics, with a significant environmental impact [1-3]. In order to stop the environmental pollution caused by this sector all over the world, the value chain of plastic packaging needs a deep transformation in the perspective of sustainability and the Circular Economy principles.

The main challenges in developing sustainable food packaging involve the realization of effective systems, with satisfactory functional properties, easy-to-produce by conventional technologies and, last but not least, that are safe and suitable for food contact.

In this context, scientific and industrial research is focused on the development of innovative solutions in terms of materials and processes, with a multidisciplinary approach where technological innovation, sustainability, and food safety become an inseparable threesome. On one hand, the realization of new eco-sustainable packaging promotes the use of raw materials from renewable and/or recycled sources, the reduction of thickness and weights, the development of 100% monomaterial packaging, and the transition from plastic packaging to mostly paper/plastic packaging. On the other, it also makes use of innovative technologies, such as nanotechnologies, active packaging, coatings, the optimisation of orientation techniques, which are capable to give the packaging all the functional properties it needs. At the same time, the respect of food suitability implies the use of FDA and EFSA-approved materials and the verification of compliance with the requirements of the European regulation [4].

These considerations constituted the starting point for three case studies carried out by the Polymer Science and Technology group at the University of Salerno.

The first one involved the realization of PLA-based 3-layer nanocomposite films, having different positions and relative thicknesses of the layers, through a blown film coextrusion plant. The nanocomposite PLA layer was inserted between two pure PLA layers for safe food contact; the structures, 100% biodegradable and/or recyclable, showed a marked improvement in processability, mechanical performance and barrier properties, allowing to extend the shelf life of packaged products. The nanocomposite films were also easily sealable and did not show significant alterations in transparency, color and overall migration compared to the pure PLA matrix [5].

The second case study concerned the functionalization of PBAT/PLA-based films by spreading (PVOH)/(PLA+Wax) double coating layers, to produce high performance biodegradable films. The careful design of the films allowed to combine the ductility of the substrate with the excellent barrier properties of PVOH and with the sealability and hydrophobicity provided by the PLA layer with natural wax. The strategy employed also demonstrated to be promising for the use of the films for the packaging of sensitive foods with high gas barrier requirements and extended shelf life [6].

The last case study involved the realization of monomaterial active films based on PET and a food-approved oxygen scavenger, with prolonged effectiveness over time. Three-layer structures were realized by cast co-extrusion, inserting the active layer, at an optimized concentration (10% w/w) of the scavenger, between two PET inert barrier layers. Four different configurations were designed, and the scavenging properties were extensively investigated; the films demonstrated their effectiveness in extending the durability of the oxygen scavenger over the time, avoiding its premature exhaustion. Finally, the possibility of modulating the films' layout allowed to adapt and optimize the scavenging performance according to the specific preservation requirements of the food to be packaged [7, 8].

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CHEMCYCLING AND BIOMASS BALANCE

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ABSTRAKT

Udržitelnost je neoddělitelnou součástí DNA společnosti BASF. Už více než 150 let přispíváme k tomu, aby se svět stal lepším místem pro život. Proto je i nadále jedním z klíčových témat, které formuje a spoluutváří nejen současné postoje firmy, ale zásadně ovlivňuje její směřování do budoucna.

Přinášet na trh řešení, která jenž přispívají ke snížení uhlíkové stopy, představují úsporu ve využívání fosilních zdrojů nebo umožňují recyklování použitých výrobků po skončení jejich životnosti, je důležité nejenom pro nás, ale i pro naše zákazníky napříč všemi průmyslovými odvětvími.

Máme nejenom vizi, ale i konkrétní projekty směřující ke snižování uhlíkové stopy v rámci našich výrobních procesů. Zefektivňujeme naši výrobu a spotřebu energie, investujeme do obnovitelných zdrojů a urychlujeme vývoj, abychom mohli splnit námi stanovený cíl uhlíkové neutrality do roku 2050.

Ku příkladu, náš projekt ChemCycling, který je založený na chemické recyklaci, otevírá možnosti transformace směsného plastového odpadu nebo použitých pneumatik na surovinu nahrazující klasické fosilní zdroje. Dalším příkladem je metoda Mass Balance, která umožňuje výrobu technických plastů s obsahem recyklované složky v primární kvalitě. Stejná metoda se využívá i při použití surovin z obnovitelných zdrojů. V BASF tvoříme svět chemie pro udržitelnou budoucnost.

STRUCTURAL SUPPORT FOR R&D PROJECTS
TECHNOLOGY AGENCY OF THE CZECH REPUBLIC

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ABSTRACT

The Technology Agency of the Czech Republic is an organizational unit of the state that was founded in 2009 by Act No. 130/2002 Coll. on the support of research, experimental development, and innovation. The creation of TA CR is one of the cornerstones of the fundamental reforms in research and development (R&D) in the Czech Republic. The key feature of the reform is the redistribution of financial support from the national budget. The Technology Agency of the Czech Republic simplifies the state support of applied research and experimental development. TA CR prepares and manages state funding programs whose purpose is to stimulate the interconnection of organizations working on applied research with innovative activities in business and the state administration. TA CR develops new tools to support closer collaboration between research organizations, the business sector, and the state administration. TA CR's objective is to offer our support in research, development, and innovation to as many partners as possible so that they can help us change the world for the better. TA CR supports international cooperation in the area of applied research, development and innovation and collaboration with similar agencies abroad. TA CR is interested in cooperation with agencies and institutions developing international collaboration around the world to connect, identify mutual priorities, exchange know-how, and support joint applied research projects to ensure the development of innovation and competitiveness of partners. TA CR also establishes cooperation with embassies of foreign countries in the Czech Republic in collaboration with the Ministry of Foreign Affairs, with Czech embassies abroad, and with other ministries and organizations to increase the awareness of TA CR activities and programmes, and of the situation in applied research, development and innovation in the Czech Republic. TA CR is a member of the TAFTIE European network of innovation agencies, which allows us to share experience and information with partner organizations that also support research, development, and innovation in various parts of the world.

VČASNÉ A SPOLEHLIVÉ ODHALENÍ VAD VE VÝROBNÍM PROCESU

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ABSTRAKT

Zvýšení efektivity výroby, snížení zmetkovitosti a odhalení vad co nejdříve ve výrobním procesu. To jsou hlavní body, které dnes musí řešit každý výrobce. Ponořte se s námi do tajů strojového vidění, které toto vše umí zajistit. Těžištěm našich řešení jsou systémy založené na vizuální inspekci a strojovém vidění s využitím průmyslových kamer světových výrobců. Výroba a recyklace plastů jde ruku v ruce a je nutné obě oblasti co nejvíce automatizovat, abyste dosáhli snížení nákladu a vysoké rentability.

Kamerové technologie, které je vhodné pro tyto účely použít, umí pracovat nejen ve viditelném spektru. Některé vady či materiály je totiž výhodnější kontrolovat např. v infračervených vlnových délkách. Samozřejmostí je kontrola rozměrů a celistvosti výrobku. Výhody kamerového systému jsou především nepřetržitý provoz 24/7, objektivní zhodnocení problému a možnost jej umístit i do stísněných prostor, a tím odhalit případný problém již v zárodku a ne až při výstupní kontrole. Díky tomu lze velmi výrazně snížit náklady na výrobu a případnou recyklaci již hotového výrobku k opětovnému využití materiálu.

Dnešní nejmodernější kamerové technologie umožňují dokonce rozlišit i druh materiálu, např. jako vstupní suroviny, a vytřídit tak kontaminanty ještě dříve, než začne proces výroby. Díky tomu je konečný výrobek homogennější a méně náchylný na vady, které se mohou projevit v průběhu času.

Možností, jak automatizovat výrobu, je celá řada. Proto jednotlivá řešení, která nabízíme, jsou vždy šitá na míru zákazníkovi podle jeho potřeb a technických možností.

POLYLACTIC ACID COMPOSITES WITH VEGETABLE FIBERS FOR APPLICATIONS IN PACKAGING INDUSTRY

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ABSTRACT

The companies SYNPO, akciová společnost, and SPA 2000 s.r.o. in cooperation with scientists from the University of the Azores, Portugal, and from the Nanomaterials and Nanotechnology Research Center (CINN CSIC), Spain, are involved in the development of a new type of biodegradable polymer composite usable as a packaging material, especially in the food industry. This composite consists of a biodegradable polymer based on polylactic acid reinforced with plant fibers with the addition of antibacterial glass. The plant fibers used, provided by the University of the Azores, were obtained from a *Hedychium gardnerarium* plant. This highly invasive plant represents a significant problem for the environment of the Azores and must therefore be eradicated. The commercial use of the fibers from this plant would thus reduce the financial cost of this eradication. The development of new packaging material will make it possible to replace packaging materials produced from petroleum derivatives and to use waste material from the disposal of invasive plants and antibacterial glass from recycled materials. The developed material is compostable, and thus represents a lower burden on the environment than packaging materials used so far. During the solution of the project, the process of incorporating plant fibers into the polymer matrix was successfully mastered. Packaging materials of a new type, aimed at their use in the food industry, were prepared from the thus obtained composite. In cooperation with Tomáš Baťa University in Zlín, a procedure for composting of these packaging materials was also developed. The research was carried out

within the European project M-Era.Net "Vegetal fibers-reinforced PLA antimicrobial composites for packaging applications" with the financial support of the Technology Agency of the Czech Republic (project no. TH06020002).

BIOREAGENT FOR CHEMICAL RECYCLING OF PLASTICS FROM END-OF-LIFE VEHICLES

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ABSTRACT

In this contribution, polyurethane (PU) and polycarbonate (PC) scraps from end-of-life vehicles are chemical recycled by means of a renewable bio-reagent. The bio-reagent, synthesized from a waste fraction of vegetable oils, is able to convert the PU and PC scrap into liquid recycled polyols. The prepared recycled polyols can be reused for fabrication of low-density rigid PU foams designed as thermal insulation panels. It was found that up to 50 wt % of the virgin petrochemical polyol can be replaced by the recycled polyols without any negative effect on the foaming process. The prepared PU foams exhibit the apparent density around $40 \text{ kg}\cdot\text{m}^{-3}$, the homogeneous cellular structure with a high content of closed cells (>91 vol %), the beneficially low value of lambda coefficient ($\sim 23 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and water absorption (~ 0.35 vol %) compared to the reference PU foam without recycled polyol. Surprisingly, the highest content of recycled polyol derived from PC scrap causes the exceptionally high compressive strength (>350 kPa in parallel to foam rise direction) of the produced PU foams, due to the unique polyol structure combining rigid aromatic segments with flexible oil glyceride units. All the prepared PUR foams were thermally stable up to 220 °C.

OPERAČNÍ PROGRAM ŽIVOTNÍ PROSTŘEDÍ 2021 - 2027
PODPORA PŘECHODU NA OBĚHOVÉ HOSPODÁŘSTVÍ
ÚČINNĚ VYUŽÍVAJÍCÍ ZDROJE – PLÁNOVANÁ OPATŘENÍ

Jaromír Manhart

Státní fond životního prostředí České republiky, Odbor odpadového hospodářství
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Cílem **Operačního programu Životní prostředí 2021–2027 (OPŽP)** je ochrana a zajištění kvalitního prostředí pro život obyvatel, přechod k oběhovému hospodářství a podpora efektivního využívání zdrojů, omezení negativních dopadů lidské činnosti na životní prostředí a klima, zmírňování dopadů změny klimatu a příspěvek k řešení problémů životního prostředí a klimatu na evropské a globální úrovni.

V rámci specifického cíle **1.5 Podpora přechodu na oběhové hospodářství účinně využívající zdroje** budou podporována zejména **opatření** vedoucí k přechodu na principy oběhového hospodářství a zlepšení uplatňování hierarchie nakládání s odpady, a to prostřednictvím investic zejména do prevence vzniku, znovuvyužití a recyklace odpadu.

V oblasti **prevence vzniku odpadů** budou podporovány zejména:

- kompostéry pro předcházení vzniku komunálních odpadů,
- RE-USE centra pro opětovné použití výrobků včetně aktivit pro opravy a prodloužení životnosti výrobků, podpora prevence vzniku odpadu,
- budování infrastruktury potravinových bank,
- podpora prevence vzniku odpadů z jednorázového nádobí nebo jednorázových obalů.

V oblasti **sběru, zpracování a využití odpadů** bude podporována zejména:

- výstavba a modernizace sběrných dvorů, doplnění a zefektivnění systému odděleného sběru/svozu zejména **komunálních odpadů**, včetně podpory door-to-door systémů a zavádění systémů PAYT ("Pay-as-You-Throw"),

- podpora třídících a dotřídňovacích systémů, včetně úpravy, pro separaci odpadů kategorie ostatní,
- budování zařízení pro úpravu a zpracování **čistírenských odpadních kalů** z čistíren odpadních vod, včetně úpravy vyčištěných odpadních vod pro jejich opětovné využívání
- výstavba a modernizace zařízení pro **materiálové a jiné využití odpadů**, včetně **bioplynových stanic** pro zpracování odpadů,
- budování a modernizace zařízení pro chemickou recyklaci odpadů,
- budování a modernizace zařízení pro sběr a nakládání s **nebezpečnými odpady**.

Očekávaným příspěvkem uvedených opatření ke specifickému cíli je z hlediska dalšího směřování odpadového hospodářství naplňování strategických cílů **Plánu odpadového hospodářství České republiky**, a to:

- 1) předcházet vzniku odpadů a snižovat měrnou produkci odpadů,
- 2) minimalizovat nepříznivé účinky vzniku odpadů a nakládání s nimi na lidské zdraví a životní prostředí,
- 3) zajistit udržitelný rozvoj společnosti a přiblížení se k evropské „recyklační společnosti“, a
- 4) maximálně využívat odpady jako náhradu primárních zdrojů a přechod na oběhové hospodářství.

Cílem je dosáhnout intenzivního přechodu **odpadového hospodářství** na principy **oběhového hospodářství** tak, aby byla splněna nově stanovená pravidla pro nakládání s odpady – závazné cíle pro recyklaci komunálních odpadů, závazné cíle pro omezení skládkování odpadů, nové povinnosti pro třídění komunálních odpadů, závazné cíle pro recyklaci obalových odpadů, závazné cíle v oblasti třídění jednorázových plastových výrobků vyplývající z evropské legislativy, a byla dodržována **evropská hierarchie nakládání s odpady**.

Vybrané podmínky podpory:

- projekt plně respektuje hierarchii nakládání s odpady,
- projekt musí být v souladu se závaznou částí Plánu odpadového hospodářství České republiky i krajských plánů,
- u projektů materiálového využití odpadů musí být využito minimálně 50 % odpadů vstupujících do zařízení,

- nebudou podporována zařízení spadající do systému obchodování s emisními povolenkami (EU ETS), zařízení vedoucí ke zvyšování množství zbytkových odpadů a zařízení na energetické využití smíšeného komunálního odpadu (ZEVO),
- u projektů na mechanicko-biologické úpravy odpadů bude podpora poskytována v závislosti na poměru vytríděného odpadu.

Tab. Předběžný odhad alokace finančních prostředků ve specifickém cíli 1.5 (2022, srpen)

SC 1.5 Podpora přechodu na oběhové hospodářství	Celkem cca. 6,51 mld. Kč
Kompostéry pro předcházení vzniku komunálních odpadů	580 mil. Kč
RE-USE centra pro opětovné použití výrobků	290 mil. Kč
Infrastruktura potravinových bank	189 mil. Kč
Prevence vzniku odpadů z jednorázového nádobí nebo obalů	392 mil. Kč
Sběrné dvory a systémy odděleného sběru a svozu odpadů	1,45 mld. Kč
Třídící a dotřídňovací linky	452 mil. Kč
Úprava a zpracování kalů z ČOV	632 mil. Kč
Zařízení pro materiálové využití odpadů	903 mil. Kč
Zařízení pro energetické využití odpadů včetně BPS	1,08 mld. Kč
Zařízení pro chemickou recyklaci odpadů	226 mil. Kč
Zařízení pro sběr a nakládání s nebezpečnými odpady	316 mil. Kč

Zdroj: SFŽP, 2022, září <https://opzp.cz/dokumenty/>; <https://opzp.cz/nabidka-dotaci/>; <https://opzp.cz/>

Hlavními cílovými skupinami jsou:

- obce jako původci komunálního odpadu, přičemž se může jednat o samotné obce, jejich svazky nebo obchodní korporace vlastněné veřejnými subjekty;
- subjekty podnikající v oblasti nakládání s odpady nebo nakládání s potravinami bez ohledu na jejich právní formu;
- subjekty podnikající v oblasti výroby a průmyslu bez ohledu na právní formu.

V rámci specifického cíle nejsou podporovány žádné aktivity přímo cílící na zajištění rovnosti, inkluze a nediskriminace. Nastavení podmínek podpory i proces výběru projektů bude nicméně respektovat obecné principy včetně rovnosti mužů a žen tak, aby poskytovanou podporou nedocházelo k vytváření nerovného a diskriminačního prostředí.

ZKUŠENOSTI SE ZPRACOVÁNÍM PLASTOVÝCH ODPADŮ NA VŠTE

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ABSTRAKT

Příspěvek pojednává o dosavadních zkušenostech se zpracováním plastových odpadů (a souvisejícím výzkumu v oboru environmentálních technologií) na VŠTE. Je poukázáno na technické obtíže spojené se zpracováním netříděného plastového odpadu. V příspěvku je zmíněna zejména (1) výroba tvarovek z netříděného plastového odpadu; (2) rafinace procesní kapaliny z pyrolýzy plastů; (3) využití pevného pyrolyzního rezidua jako náhrady cementu; (4) rafinace polyuretanu, či (5) zkušenosti s biologicky rozložitelnými plasty. Jsou diskutovány aspekty pyrolýzy a plazmového zplyňování. Je deklarována ochota vstoupit do společných vědecko-výzkumných projektů.

EKO MATERIÁLY – SUROVINY A DOSTUPNOST

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ABSTRAKT

Eco polymerní materiály – nazývám tak souhrnně materiály s určitým pozitivním přínosem pro ekologii.

Spadají sem klasické recykláty polymerů i nově zavedené primární (Virgin) polymery vyrobené bez ropného základu.

Eco polymerní materiály se na evropském trhu pohybují dlouho, např. PBAT (polybutylene adipate terephthalate) již od roku 1998.

Snahy o opakované používání plastových materiálů jsou viditelné asi posledních 10 let.

Zhruba 5 let běží silná kampaň na podporu ekologizace plastových výrobků.

První polymerem, recyklovaným ve větším měřítku byl PET – dáno masou jeho použití a dobře dostupným, organizovaným a relativně čistým zpětným sběrem obalů.

Recyklační firmy pracovaly na velmi podobném technologickém postupu: díky kontaktům na, pokud možno, stálý zdroj odpadu (= suroviny) byly schopny nastavit třídění, čištění a další úpravu materiálu tak, že na konci byl dobře použitelný materiál. Kolem roku 2010 již byly k dispozici velmi sofistikované “black boxy“, které na základě většinou fyzikálních vlastností byly schopny roztřídit a zpracovat směs polymerního odpadu. Stále však mějme na paměti, že materiál vstupující do procesu byl již poměrně dobře vytříděn!

Logicky největší podíl měly PS a ABS, kde zdrojem byla bílá technika, později i PC/ABS.

Kde byla zdrojem stará auta, tam je k dispozici, PP, PE a ABS, PC/ABS.

Můžeme např. vysledovat výrobce, kde je hlavním zdrojem suroviny PP(copo) tělo klasických autobaterií, jiný je specializován na zpracování nárazníků (různé varianty PP + EPDM)

Většina recyklačních firem měla vznik jako malé startupy, často s podporou lokálních práv, dotací z EU apod. (Rakousko)

V posledních pěti letech odchází k akvizicím menších firem velkými výrobci z oblasti chemie, podobně jako jsme to viděli předtím v oblasti energetiky a jako to nyní vidíme v pivovarnictví.

Krátký přehled aktuálně známých recyklačních a eko technologií, alespoň na velikosti pilotních projektů (poloprovoz) :

Mechanické přepracování - post consumer odpad a post industrial odpad

Depolymerace – rozklad na výchozí monomer

Pyrolýza – rozklad na směs chemikálii, převod na výchozí monomer

Technologie polymerace bez ropného základu surovin:

Biologické suroviny – přepracování organických odpadů, dřevních odpadů

Obnovitelné suroviny – třtina, kukuřice, atd.

U této technologie se používá k deklaraci ekologického přínosu tzv. hmotnostní bilance – Mass balance approach

Pohyb cen

Trh byl poslední roky navyklý na měsíční pohyb cen u komoditních materiálů (PS, ABS, polyolefiny)

Existovala zde jistá návaznost na pohyb cen výchozích surovin, nutných pro výrobu daného polymeru.

Cena RECY materiálů se řídí ale jinými pravidly. S rostoucím zájmem trhu, je stále problematictější přístup k surovinám, ze kterých se pak vyrábí výsledný produkt. Faktorem určujícím cenu je zde nabídka – poptávka. Faktorem určujícím existenci RECY materiálů je energie – její dostupnost a cena...

Dostupnost, disponibilita materiálů

Jednoduše řečeno, dostupnost surovin je aktuálně rozhodujícím faktorem o úspěchu na trhu. S rostoucím zájmem trhu o EKO materiály (opět s podporou legislativy, reklamy a politikou firem užívajících EKO materiály ve svých výrobcích) se významně zhoršila dostupnost EKO materiálů a významně narostla jejich cena. Původní očekávání zákazníků, že EKO materiály budou levnější vzala velmi rychle za své. Dnes lze říci, že se nabídka materiálů pohybuje cenově pod primárním materiálem (např. mechanicky přepracovaný PP + minerál) i vysoko nad primárním materiálem (např. PP vyrobený ne z ropy, nebo R PET).

Závěrem

Dostalo se nám téměř fyzického poučení, že jistého není nic a předpověď zítřka je komplikovaná. Přesto náš obor funguje zatím vcelku dobře a věříme, že to bude tak i nadále.

Ve vývoji recyklace polymerů, myslím, bude dalším krokem výstavba větších výrobních jednotek, spíše s technologií na bázi depolymerace (např. u PS) či termického rozkladu.

Vývoj polymerů vyráběných ze surovin mimo ropu je technologicky zvládnutý, úzkým hrdlem je zde dostupnost surovin pro polymeraci.

Samozřejmě, veškeré technologické kroky jsou energeticky náročné. A jsme na počátku úvahy – máme energii na tyto účely a máme peníze na tuto energii?

Naše snahy a úvahy se odehrávají na relativně malém území EU, populační explozí postižená Asie a Afrika nemá naše ambice.

PROCES ZPRACOVÁNÍ PLASTŮ – UDRŽITELNOST A UHLÍKOVÁ STOPA

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ABSTRAKT

Udržitelnost je pojem, který se hluboce dotýká také plastikářského průmyslu. Evropská unie si vytyčila ekologické cíle a ty jsou postupně zapracovávány i do legislativy. Jak zpracovatelé plastů, tak dodavatelé technologií do zpracovatelského průmyslu musí tyto cíle nejen respektovat, ale také svými řešeními být konkurence schopni. Do dnešní doby se téměř veškeré úsilí průmyslové výroby soustředilo na ekonomickou efektivitu, tzn. vyrábět co nejvíce s co nejmenšími náklady. Nyní se k tomuto přidává další zásadní a ekonomicky protichůdný parametr - vyrábět šetrně k životnímu prostředí.

Příspěvek přináší příklady obecného přístupu výrobce vstřikovacích strojů ARBURG k tématice udržitelnosti a také výsledky měření dopadů průmyslové výroby pomocí parametru uhlíkové stopy. Firmy západní Evropy prokazují svou výrobní uhlíkovou stopu pomocí metodiky CDP (mezinárodní nezisková organizace), která zohledňuje 14 environmentálních kategorií včetně využívaného energetického mixu. Tyto firmy zároveň hodnotí své produkty z pohledu environmentální náročnosti při jejich vzniku (Cradle to Gate) a následného používání (Gate to Grave). Metodikou technické normy ISO 14067:2018 společnost ARBURG deklaruje uhlíkovou stopu svých vstřikovacích strojů ALLROUNDER 370 H až 570 H v rozmezí 6 530 – 16 430 kg ekvivalentu CO₂.

Měření a deklarování environmentálního dopadu svých produktů bude pro firmy závazné. Je životní nutností pro české podnikatelské subjekty tento standard co nejdříve zavést a svou výrobu v případě negativních výsledků optimalizovat. Stejně tak spotřebitelské produkty – zboží pro koncové spotřebitele – musí v poměrně krátké době odpovídat požadavkům legislativy. S tím se pojí přístup „Reduce-Reuse-Recycle. Velkým úkolem pro zpracovatele plastů bude zvládnout proces s vysokým poměrem recyklátu. Společnost ARBURG i další dodavatelé technologií přináší technická řešení pro stabilizaci procesu zpracování recyklátu díky využití inteligentních sw asistentů integrovaných do řízení stroje.

Příspěvek se věnuje všem výše uvedeným tématům s ukázkou příkladů řešení. Jeho cílem je ukázat účastníkům konference jakožto odborné plastikářské veřejnosti trendy v západoevropských firmách, na které jsou české podniky životně navázány a jejichž pravidla hry musí dodržovat.

LIBS TECHNOLOGY ROLE IN RECYCLING PROCESSES

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ABSTRACT

Amount of plastic materials used in modern society is increasing rapidly for several decades. Plastic waste, however, is a huge concern nowadays with increasing level of pollution of even the most remote environments. To reduce the dangers of pollution by plastics of all kinds, modern society started to recycle bigger and bigger amounts of plastic waste. To efficiently reuse or recycle plastic waste, its plastic type must be recognized with high accuracy. Furthermore, to reduce dangers to environment, producers of polymers must control levels of dangerous or toxic additives efficiently in reused or newly produced articles. For control of toxicity levels, samples are sent to techniques with long sample preparation times such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS). However, this technique uses acids and other chemicals and its direct implementation in industrial processes is impossible.

Laser Induced Breakdown Spectroscopy (LIBS) allows effortless qualitative and quantitative elemental analysis. Due to its instrumental robustness and simplicity, it can be deployed in off-line and even on-line system. LIBS has already demonstrated its benefits and potential in recycling and sorting metal waste [1] Its popularity is also rising in several industrial fields. The biggest advantages of LIBS are: none or minimal sample preparation, in-situ measurements possibilities, little to none damage to sample and immediate results of measurements. In respect to plastic samples, apart from possibility to classify plastic samples, LIBS can be used as reliable indicator of dangerous elements like lead (Pb), cadmium (Cd), chromium (Cr), or even mercury (Hg) in samples. These measurements can be done quickly on large scale maps with additional information of element distribution in the sample.

In this work we introduce a way to utilize LIBS correctly to control levels of potentially dangerous elements like lead (Pb). By acquiring a large sample set of plastic pre-processed samples from industrial field, we possess a high quality and high variety data set to construct a highly accurate model for Pb content identification. By referencing the Pb content by

Inductively coupled plasma mass spectrometry (ICP-MS), we are able to predict Pb content in new samples measured by LIBS alone with minimal error.

[1] Chamradová, P. Pořízka, and J. Kaiser, “Laser-Induced Breakdown Spectroscopy analysis of polymers in three different atmospheres”, *Polymer Testing*, vol. 96, 2021.

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HANDSHAKE – DESIGNOVÝ NÁVRH VOLEJBALOVÉHO MÍČE

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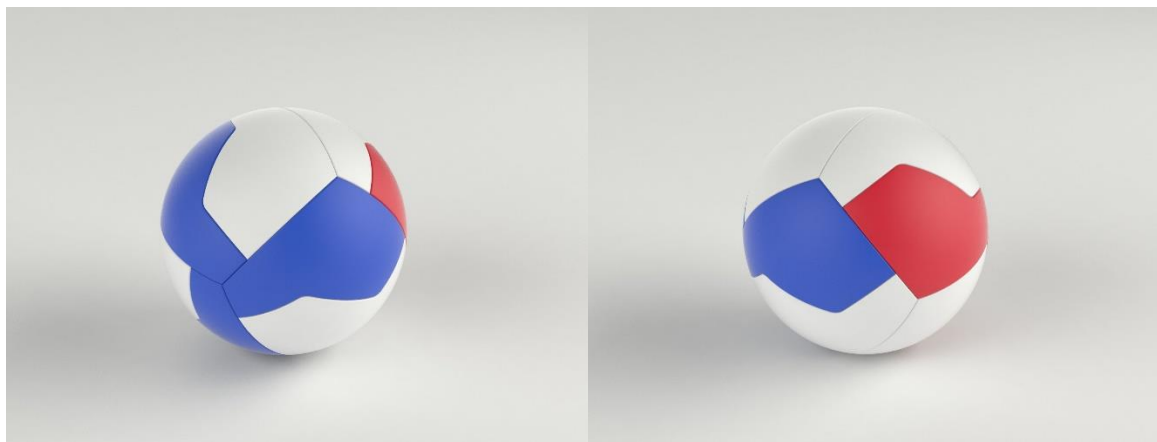
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ABSTRAKT

V rámci projektu TP01010006 Komercializace na Univerzitě Tomáše Bati ve Zlíně II podpořeného TAČR bylo navrženo nové konstrukční a vzhledové řešení lepeného volejbalového míče. Cílem bylo navrhnout novou konstrukci míčových dílů pro lepenou výrobní technologii tak, aby výsledný produkt splňoval podmínky dané FIVB (Mezinárodní volejbalovou federací). Mezi tyto podmínky mimo jiné patří také velikost míče (obvod 66.0 ± 1.0 cm), počet míčových polí (8 -18), počet barev (dvě nebo tři). Během projektu byla nejprve 3D tiskem vytvořena pozitivní poloviční maketa míče s konstrukční sítí pro možnost snímání povrchu míčových polí. Následně byly vytvořeny ideové návrhy ve 3D zobrazení pro lepší zhodnocení konstrukčních a vzhledových vlastností. Z připravených schématických 3D návrhů byl vybrán jeden jako základ pro konstrukci míče. S využitím zhotovené makety a konstrukčního softwaru byl sejmout navržený tvar míčových polí. Následovalo převedení segmentů koule do rovinné podoby a korekce o technologické a materiálové přídatky. S pomocí takto získaných šablon byly vytvořeny ověřovací modely a následně byly znovu korigovány šablony. Upravené šablony byly využity pro přípravu míčových polí při výrobě funkčního vzorku. Vzniklé řešení je dvanáctidílné, přičemž všechna míčová pole mají stejný tvar. To je dobré jednak pro snížení rizika deformace míče při jeho používání, jednak je to velmi výhodné pro výrobu, protože stačí jeden tvarový vysekávací nůž. Tvar dílce navíc umožňuje rovnoměrné rozložení spojů po povrchu míče, a to zaručuje stejnoměrné letové vlastnosti při různých natočeních míče po jeho odehrání. Název designového návrhu „Handshake“, přímo koresponduje se vzhledem míčem, kde si červená a modrá pole „podávají ruce“, a odkazuje na

fair play ve sportu. Tento míč byl na soutěži German Innovation Awards 2021 v příslušné kategorii oceněn titulem „Winner“.



Obr. 1. Digitální zpracování konečného návrhu míče ze dvou úhlů pohledu.



Obr. 2. Vytvořený funkční vzorek lepeného volejbalového míče..

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KOMPOZITY KYSELINY POLYMLÉČNÉ S ROSTLINNÝMI VLÁKNY PRO APLIKACE V BALICÍM PRŮMYSLU

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ABSTRAKT

České firmy SYNPO, akciová společnost, a SPA 2000 s.r.o. ve spolupráci s vědci z Univerzity Azory, Portugalsko, a z Univerzity Oviedo, Španělsko, se podílejí na vývoji nového typu biologicky rozložitelného polymerního kompozitu využitelného jako obalový materiál, především v potravinářském průmyslu. Tento kompozit se skládá z biodegradabilního polymeru vyztuženého rostlinnými vlákny a obsahujícího antibakteriální sklo. Použitá rostlinná vlákna, poskytnutá pracovištěm Azorské Univerzity, jsou získávána z rostlin druhu *Hedychium gardnerarium*. Tato vysoce invazivní rostlina představuje značný problém pro životní prostředí Azorských ostrovů, a proto musí být likvidována. Komerční využití vláken z této rostliny by tak snížilo finanční náročnost této likvidace. Vývoj nového obalového materiálu tak umožní nahradit obalové materiály vyráběné z ropných derivátů a využít odpadní materiál z likvidace invazních rostlin a antibakteriálního skla z recyklované suroviny. Vyvíjený materiál je kompostovatelný, a tak má nižší vliv na životní prostředí než dosud používané obalové materiály.

SUSTAINABLE BIO-BASED PLA/LIGNOCELLULOSE WASTE COMPOSITE MATERIAL FOR IMPROVING WATER RETENTION CAPACITY OF SOIL

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ABSTRACT

One of the most promising strategies for conserving water in agriculture is the use of water biopolymeric absorbent polymers. This work reports the preparation and characterization of absorbent material based on low molecular weight poly(lactic acid) (PLA) and residual biomass from the agriculture and wood industry (wheat straw and wood sawdust) cross-linked with carboxylic citric acid for improvement of the water retention capacity of the soil (*Fig. 1*). The mechanical and structural properties of the material was characterized using differential scanning calorimetry, thermo-gravimetric analysis, Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy techniques (SEM). The swelling properties of the absorption material as well as its efficiency to retain water in the soil was also investigated using water retention study. The rate of biodegradation in the soil and the changes in chemical and morphological properties of the crosslinked material during biodegradation was monitored by gas chromatography, gel permeation chromatography, FTIR and SEM techniques. The results of this study show that water retention capacity of the soil may be increased by almost 20% after application of 1% w/w PLA/lignocellulose waste material to the soil. The crosslinked structure of the material is capable to swell/de-swell water many times indicating its good reusability.

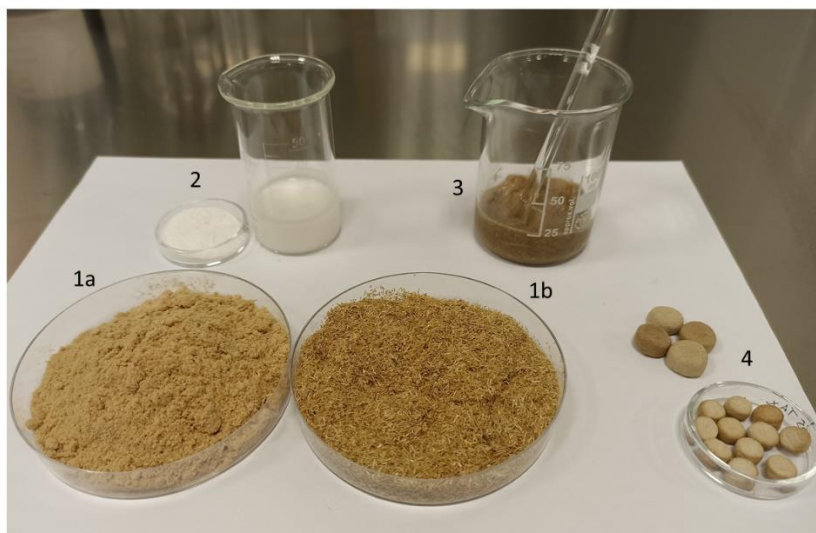


Fig. 1. Preparation of the samples. 1a) wood sawdust, 1b) milled wheat straw, 2) dissolution of PLA in acetone, 3) addition of the relevant amount of the residual biomass to 10% w/v PLA/citric acid solution, 4) PLA/lignocellulose waste samples obtained after curing at 90°C.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Agriculture of the Czech Republic (Project No. QK1910392), and the Ministry of Education, Youth and Sports of the Czech Republic (Grant No. RP/CPS/2020/002).

POLYOLEFINS SOLVENT BASED RECYCLING: BACK TO NASCENT POLYOLEFIN

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ABSTRACT

Plastic waste accumulation is the world-wide issue and despite of that PET is the only polymer material which is now feasibly recycled. Polyethylene (PE) and polypropylene (PP) dominate plastic and waste production since they constitute half of the world production of synthetic polymers but also half of the world plastic waste. Despite of PE and PP fraction in polymer waste we can mark PE and PP as environmentally friendly materials considering their chemical composition. Unfortunately, they contain number of additives causing difficulties in recycling, such as pigments and additives with sulfur, halogens, nitrogen and certain organic chemicals. The removal of additives is the aim of this contribution where we focus on solvent-based purification and refining of PE and PP.

Our first experiments were conducted to probe possibilities of creating polymer solutions and handling them with extraction apparatus. Assembled stirred pilot apparatus is designed to set various experimental conditions (pressure up to 30 bar and temperature up to 150 °C). Apparatus is equipped with three glass windows for visual control, instrumental check of polymer-solvent dissolution or determining its cloud point.

Pilot experiments were conducted with commercial plastic waste of PP ice cream box. We have followed experiment from literature [1] for system glycerin-cyclohexane-PP or glycerin-limonene-PP and we have also successfully cleared the batch to visually pure PP.

To conduct systematic study of additives removal from polymer matrix we employed the colored nascent PE and PP. The removal of colorant by solvent-based processes was analyzed by Raman spectroscopy.

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TRIBOELECTRIC SEPARATION OF PLASTIC WASTE: ADVANTAGES AND CHALLENGES

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ABSTRACT

The separation of plastic materials is crucial for their material or energy-content recycling, i.e., for making a positive economic value from useless waste. None of the separation methods for plastics can be used universally. We are focusing on efficiency improvement of triboelectric separation of plastics because this method is low cost and can be automated, utilizes no chemicals, and can separate even black-pigmented plastics.

Triboelectric separation is based on the phenomenon that each plastic material obtains a different electrostatic charge by friction contact with a proper counter-material. The selection of a counter-material is the most challenging task of designing a triboelectric separator, as it plays a crucial role in controlling the charge obtained by individual plastic pieces. The tribocharging of insulators is not well understood yet, although some theoretical or empirical concepts correspond well with experimental results.

Our self-constructed charging apparatus enables the following contacting approaches: contact during rotational or vibrational motion and charging via corona discharge. The average charge in a sample is measured by a Faraday pail connected to the electrometer. The charge distribution in the heterogeneous sample is characterized using the self-constructed free-fall separator in which pieces are separated according to their charge/mass ratio.

We apply the results of our systematic investigation of counter-materials to the separation of 3-component mixtures, aiming for the successful separation of halogenated material – PVC from the mixture. In three simple separation steps, we managed to sort out the PVC with purity up to 91 % at 88% recovery; we obtained a fraction of PET of 77% purity and 64% recovery and completely PVC-free, and PP of 75% purity and 80% recovery with approx. 3 % of PVC. In the newest experiments, we focus on the effect of an external electric field on fine-tuning and speeding up the charging of plastic particles during tribocharging.

EFFECTS OF NATURAL RUBBER BLENDS ON MECHANICAL PROPERTIES OF POLYLACTIC ACID

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ABSTRACT

Poly(lactic acid) (PLA) has gained significant interest because of its biodegradable properties. However, a relatively high glass transition temperature of 58 °C makes the material brittle and thus limits its application. Furthermore, PLA polymers have very low crystallinity, as PLA crystallization proceeds extremely slowly. To overcome these weaknesses the modification of PLA needs to be considered. This paper is focused on an approach to improve the mechanical properties of PLA by melt-blending with natural rubber (NR). As a part of this study, a series of PLA/NR samples at various compositions were prepared. Subsequently, the effect of natural rubber on poly(lactic acid) was evaluated in terms of mechanical properties. The thermal properties of the sample were measured by the differential scanning calorimetry method. The tensile test investigated properties such as tensile stress, elongation at break, and tensile modulus. The amount of energy absorbed by a material during fracture was measured by the Charpy impact test, and the resistance of a material to the penetration of a needle was examined by the Shore D hardness test.

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HOT-MELT ADHESIVES BASED ON METALLOCENE POLYOLEFIN

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ABSTRACT

Metallocene ethylene–octene random copolymer Resinex PE RXP 1502 (RXP), was grafted with acrylic acid to increase the RXP's polarity and adhesion to cellulose-based substrates. The most effective procedure was to graft RXP with acrylic acid in the melt. The heat-fail temperature resistance of adhesive joint in peel of RXP grafted with acrylic acid increased by more than 10 °C, while the heat-fail temperature resistance the same adhesive joints in shear were similar.

INTRODUCTION

Hot-melt adhesives (HMAs) are a tacky when hot, and solidify in a few seconds to one minute. HMAs can also be applied by dipping or spraying. HMAs provide several advantages over solvent-based adhesives [1] Volatile organic compounds as well as, and the drying or curing procedures are eliminated. HMAs having a long shelf life usually can be disposed of without special precautions. Some of HMAs disadvantages involve thermal load of the substrate, and loss of bond strength at higher temperatures, up to complete melting of the adhesive. Metallocene polyolefin (MePO) was selected as a basis for hot-melt adhesives with improved performance [2] The non-polar chains of MePO interact well with non-polar surfaces [3] Nevertheless efforts to adjusting the HMAs application parameters, especially regarding increased adhesion to polar surfaces, focus either to basic polyolefin chains polarity increase, or polar polymers addition to the adhesive compositions. The reason is that more polar compositions owing to the higher surface energy lead to higher adhesive peel and shear strength [4, 5] An increase of HMAs polarity has been frequently achieved by addition of polar components to an adhesive polymer composition [6, 7]

In the contribution paper we report on the experiments consisting in the modification of MePO with the aim to increase of polarity of the polymer. Acrylic acid (AA) was grafted on polymer activated with mixture of oxygen and ozone. The created graft copolymer was used as an additive to formulate HMAs with increased adhesive properties.

EXPERIMENTAL

Metallocene ethylene-octene random copolymer Resinex PE RXP 1502 (RXP) ($T_m = 70\text{ }^\circ\text{C}$, $\rho = 0.874\text{ g/cm}^3$) was used for HMAs preparation as a basic component as well as the adhesive additive after modification by grafting. Acrylic acid (AA, Aldrich) monomer, 99 % purity).

RXP powder was treated in the flow of $\text{O}_2 + \text{O}_3$ gas produced in an atmospheric plasma generator, power = 300 W (Masaryk University, Czech Republic), input O_2 flow 5L/min. The modification of the activated RXP powder proceeded in Brabender Plasticorder in 30 mL chamber at $110\text{ }^\circ\text{C}$ for 30 minutes. Filling the chamber with polymer and homogenization polymer melt with sodium dodecyl sulphate (wetting agent) starts the grafting procedure and takes 5 minutes at $80\text{ }^\circ\text{C}$.

The presence of grafted poly (acrylic acid) (PAA) in grafted RXP copolymer (RXP-g-AA) was proved by FTIR analysis. The spectrometer Nicolet 8700TM in the attenuated total reflectance spectroscopy mood was used. Based on contact angle measurements the hydrophilicity changes of RXP-g-AA surfaces were evaluated. The Surface Energy Evaluation (SEE) system with CCD camera (Advex Instruments, Czech Republic) was used for experiments and a sessile drop technique was applied. The temperature resistance of the adhesive joints was evaluated by measuring the strength of the adhesive joints in peeling (shear) on the laminated paper with biaxially oriented polypropylene (BOPP) foil used in the packaging industry. The adhesion was evaluated by testing the adhesive joints in peel by ASTM-D-4498 (Peel Adhesion Failure Temperature (PAFT)) and in shear by ASTM D-4498 (Shear Adhesion Failure Temperature (SAFT)).

RESULTS AND DISCUSSION

The presence of grafted PAA in RXP-g-AA was proved by FTIR analysis. For all samples prepared in this study the valence bands have been observed pertaining to CH deformation vibration (region of $2800 - 3000\text{ cm}^{-1}$), typical for PE. The bands for C-O and C-O-C (1715 and 1170 cm^{-1} , respectively) indicate the presence of PAA chains. The ratio of the FTIR absorbance intensities for acid carbonyl compounds at 1715 cm^{-1} and the reference band at 1464 cm^{-1} serves for the PAA concentration determination in grafted copolymer. Changes in FTIR absorbance

of these bands in samples 1, 2 and 3 (Table 1) prepared in polymer melt and with a various amounts of AA are shown in Figure 1.

Tab. 1. Batch components concentration and grafting efficiency for RXP grafted in melt. Polymer activated 3 hours with ozone-oxygen mixture.

Sample	sample 1	sample 2	sample 3
Activated RXP [g]	24.7	22.2	19.7
Monomer AA [ml]	2.5	5	7,5
AA in sample [%]	9.2	18.4	27.6
NaLS [g]	0.12	0.21	0.30
Grafted PAA in sample [%]	8.7	14.1	26.8
Grafting efficiency	0.88	0.77	0.97

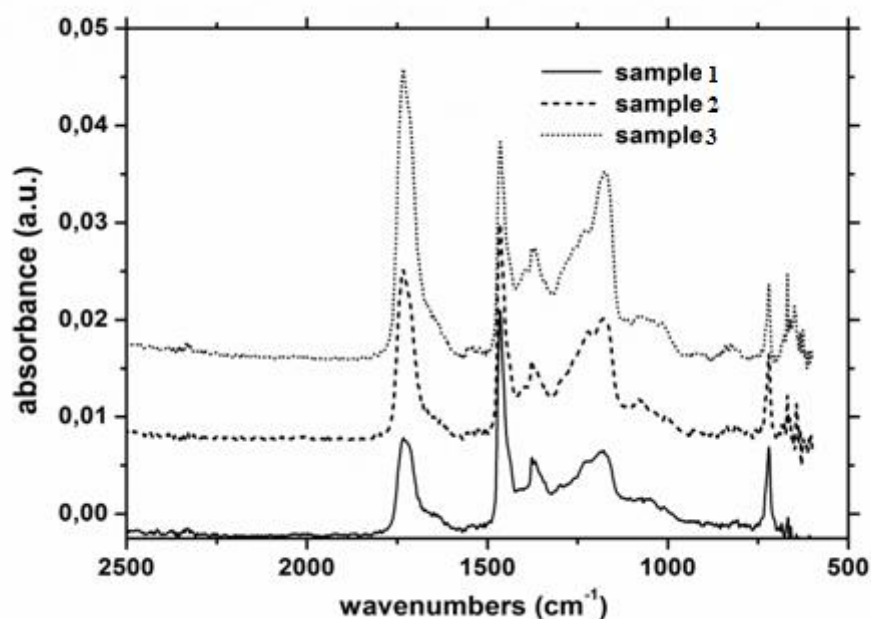


Fig. 1. FTIR spectra for RXP grafted with AA in polymer melt prepared in Brabender Plasticorder: Sample 1 – 9.2 % AA, Sample 2 – 18.4 % AA, Sample 3 – 27.6 % AA.

After kneading the activated RXP-AA reaction mixture in a Brabender chamber, the resulting polymer contains more than 70 % AA grafted to RXP. Table 1 summarizes the batch component

concentration and the grafting efficiency in the molten state. Moreover, as presented in Table 2, sample 4 (the AA feed content is the same as for sample 2 in Table 1) was tested for reproducibility. The graft efficiency equal to 0.75 ± 0.06 confirms the very good reproducibility.

Tab. 2. Batch components concentration and grafting efficiency of RXP grafting in molten state. Polymer activated 2 hours with ozone-oxygen mixture.

Sample 4	a	b	c	d
Activated RXP [g]	37			
Monomer AA [ml]	8.33			
AA in sample [%]	18.4			
NaLS [g]	0.35			
Individual experiments	14.1	13.3	14.5	13.1
Grafted PAA [%], average	13.75			
Average grafting efficiency	0.75 ± 0.06			

The grafted PAA in the obtained polymer product (RXP-g-AA) is proportional to the AA monomer used in the batch. Since the RXP was activated to equal peroxide concentration, the identical grafting initiation rate was ensured, and the longer branches are supposed to be grafted in systems with higher AA concentrations.

Tab. 3. Water contact angle, surface energy and its polar components of RXP-g-AA films.

Sample	WCA ($^{\circ}$)	Total SFE (mJ.m^{-2})	PC SFE (mJ.m^{-2})
RXP initial	$106.4 \pm 2.4^{\circ}$	29.2	2.3
AA 8.7 %	$105.0 \pm 1.8^{\circ}$	29.8	2.5
AA 14.1 %	$99.0 \pm 2.0^{\circ}$	30.2	3.6
AA 26.8 %	$87.0 \pm 3.2^{\circ}$	30.0	3.8

WCA = water contact angle, PC of the SFE = polar component of the surface energy.

The water contact angle (WCA) of initial RXP (106.4°) after grafting by AA decreased (Table 4). This decrease depends on the amount of grafted AA (RXP with AA 14.1% - WCA = 99°, RXP with AA 26.8 % - WCA = 87°). The increase of hydrophilicity of the grafted RXP samples reflects the growth of PC of SFE. PC of SFE for initial RXP reached the value 2.3 mJ/m² and after grafting with AA 14.1 % PC of SFE increased to 3.6 mJ/m² and/or 3.9 mJ/m² (AA 26.8 %).

The temperature resistance in peel as well as in shear of the adhesives based on RXP polymer is summarized in Table 5. The temperature resistance in peel for unmodified RXP is PAFT = 64 °C, but for RXP-g-AA is temperature resistance higher: with AA 14.1 % is PAFT = 77 °C and with AA 26.8 % is PAFT = 78 °C.

Tab. 4. Temperature resistance of adhesive joints using peel (PAFT) and shear (SAFT) tests for RXP-g-AA samples.

Sample	Grafted PAA (%)	PAFT (°C)	SAFT (°C)
1	8.7	75	90
2	14.1	77	92
3	26.8	78	95
RXP initial	0	64	93

CONCLUSION

The grafting proceeds in medium with high viscosity $10^2 - 10^5$ Pa.s affects the individual polymerization steps involved in grafting. The determined grafting efficiency is high and varies between 0.77 and 0.97. The water contact angle on RXP surface grafted with PAA or PCA decreases at least of 15 % or more and the surface energy and its polar component increased 1.1 – 1.7 times. The temperature resistance of adhesive joints in peel of RXP-g-PAA in peel increased 1.3 times, and the values of temperature resistance of adhesive joints in shear are similar.

ACKNOWLEDGEMENTS

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MODIFIED SMART COLLAGEN BIO-COMPOSITES AND ADHESIVES

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ABSTRACT

One of the substances applicable for preparation of biologically degradable polymer composites is collagen. It belongs among the most technically important fibrous proteins. Characteristic structure of collagen with high degree of internal organization of molecules is the main aspect determining the mechanical properties of this tissue. Unmodified native collagen is relatively difficult to process for intended applications. This work presents potential application possibilities of modified collagen biopolymer for biodegradable foils and adhesive applications. Modification of the properties and processability of collagen is possible plasticizing and compounding with suitable types of polymers. For this study copolymer of ethylene-vinyl acetate (EVAc) as the polymer matrix which was modified with biopolymer collagen was tested. The obtained results are perspective mainly from the point of view of controlled biodegradation.

Another technical application is focused on the preparation of non-formaldehyde collagen thermoplastic adhesive with required quality for gluing of books or wood veneered materials.

INTRODUCTION

Many types of synthetic plastics do not decompose naturally, which has caused serious environmental pollution from the waste polymers. Biodegradable polymers are polymers which can completely degrade under the action of biological organisms and environmental weather conditions.

There is an effort to improve existing products and find new options for their application and processing. Many possibilities of effective and ecologic processing and application of leather wastes into different products have already been analyzed [1, 2, 3] Collagen is the main component of animal tissue mostly of leather, bones, tendons and belongs among the most important fibrous proteins [4] In this work [5] has modified polyethylene (MPE) with protein

collagen hydrolysate. As was noted C-H bonds of collagen easily blends with MPE, but like other biopolymers, it also has effects on the original mechanical properties of the MPE. The addition of collagen in the blends significantly increases the biodegradation rate. 53% biodegradation is observed when the polymer is blended with 5% collagen and about 63% biodegradation was detected in the case of polymer blended with 20% collagen. Although MPE/C-H thermoplastic film with 40% content of collagen has shown the best biodegradation, the mechanical strength properties were the worst in this case. For the development of new collagen-based materials, one possible solution is the production of a plastic matrix with a component which is able of gradual degradation under external conditions. The combination of bio- and synthetic polymers gives space to achieve a favorable economic, commercial, and environmental performance – biodegradable component is originating from raw materials from leather and food industry. One of the ways to modify properties and processability of collagen is plasticization and compounding by suitable types of polymers. Films were made using blow extrusion technology from prepared granules and their parameters and optimal concentrations of modifying agents were tested [6] Thermoplastic adhesive was prepared by collagen modification and tested with high strength and flexibility of the adhesive bonds. This paper investigates the possibility of modified collagen to reduce formaldehyde emissions in wood-based products bonded with urea-formaldehyde (UF) resin. Previous results of laboratory tests have confirmed that collagen is a suitable modifier for the treatment of condensation time, viscosity, reducing formaldehyde emissions and increasing of the strength of the bond [7] Lifetime and condensation time of UF resin were tested and studied by determining the kinetics of condensation reactions of di-methylolurea with urea and aldehyde [8]

EXPERIMENTAL

Biodegradable polymer foils

Collagen to be chemically modified for its further application. Copolymers of ethylene vinyl-acetate were used as the polymer matrix for collagen modification. Individual compounds were homogenized during the compounding process. Prepared granules were tested at the foil production by blowing technology. Physical and mechanical parameters of foils were evaluated as strength, elongation, permeability to water vapor and biodegradability. FTIR spectra were measured on a NICOLET 8700™ instrument by Thermo-Scientific (Madison, WI, USA) and scanning electron microscope (SEM) images were taken at VEGA II LMU by Tescan.

Used materials:

- EVAc – ethylene vinyl acetate copolymer Evatane 24-03,

- Collagen – laboratory prepared hydrolysate of collagen,
- Modifier I – based on polyvalent amines in granular form,
- Modifier II – based on polyvalent alcohols.

Collagen based hot-melt adhesive

This investigation was focused on the research and preparation of non-formaldehyde thermoplastic hot melt adhesive based on collagen biopolymer. Parameters of adhesive can be varied by selecting the appropriate modifying additive, e.g., elongation of the film, hydrophilicity, hydrophobicity, viscosity, melting and solidification points etc.

Collagen as modifier of UF adhesive mixtures

Natural modifiers of UF adhesives were raw collagen materials produced from waste from the leather industry. To modify the collagen hydrolysate were applied:

Marking of collagen samples:

- *Collagen No. 1 – collagen hydrolysate modified with urea and glutaraldehyde,*
- *Collagen No. 2 – collagen hydrolysate modified with urea,*
- Collagen No. 3 – collagen hydrolysate, prepared from waste from leather industry.

In the experimental research, there were applied:

- UF resin KRONORES CB 1639F,
- hardener RODA M 210 pH = 7.4, overall nitrogen as N weight 21.5 %, amidic nitrogen weight 4.5 % (Duslo Šaľa, Slovakia).

Rotary-cut veneer sheets of beech wood (*Fagus Sylvatica* L.) free of defects with dimensions of 300 × 300 mm, thickness of 1.7 mm, and moisture content of approximately 6% were used for the experiments. Formaldehyde emissions from five-layer plywood of beech were tested according to the test method JIS A 1460 “Building boards. Determination of formaldehyde emission. Desiccator method” according to following conditions:

- volume of desiccator: 9-11 dm³,
- loading coefficient: 1800 cm²,
- temperature of 20 ± 0.5 °C,
- test duration 24 h,

The concentration of formaldehyde absorbed in distilled water was evaluated by acetyl-acetone method with spectrophotometric evaluation using the ultraviolet spectrophotometer UviLine SI 5000 at 412 nm wavelength.

RESULTS AND DISCUSSION

Biodegradable polymer foils

Experiments were focused on the preparation of polymer composites based on ethylene vinyl acetate with the collagen biopolymer. The impact of these components on the physical and mechanical properties and biodegradation of polymer foils was investigated. Series of samples were prepared with the content of collagen and modifier from 20 to 60% with vinyl acetate content of 24 %.

Based on obtained results, it was found that composites based on EVAc polymer matrix containing 30 to 50% of a mixture of collagen and modifier 80:20 can be processed by blow extrusion technology. The Fig. 1 presents the sample of 50% EVAc copolymer + 50% modified collagen with the thickness of 0.09 mm.

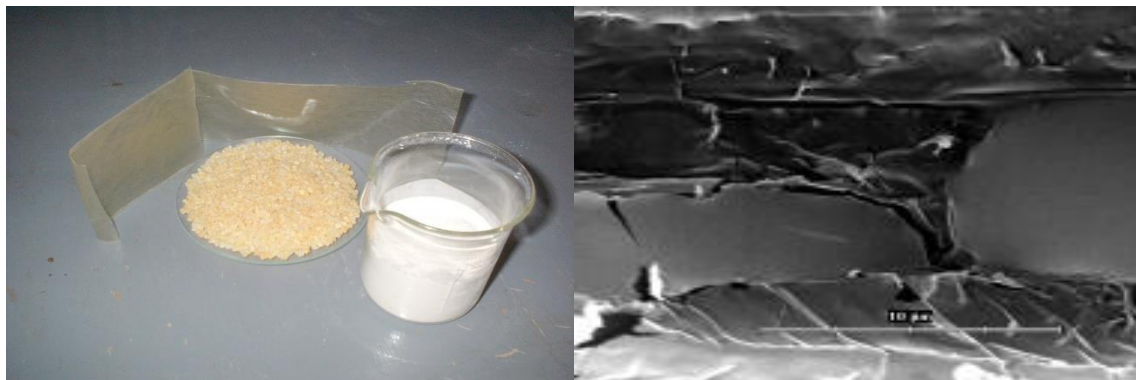


Fig. 1. Collagen powder and Granules (EVAc + collagen) and EVAc foil modified by collagen and scanned by SEM

Biodegradation of polymer bio composites

Prepared foil sheets based on EVAc and collagen were placed into the soil and the effect of soil culture and water on the degradation of the material was investigated. Fig. 2 presents the biodegradability of foils and the process of their chemical decomposition.

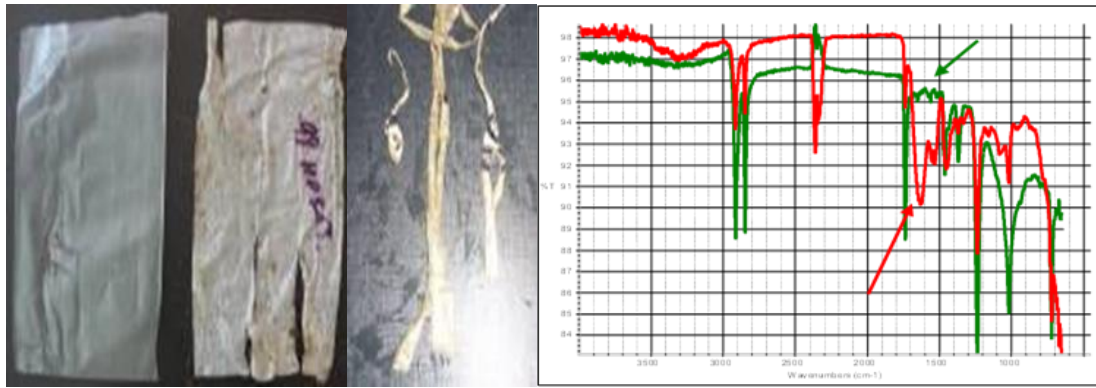


Fig. 2. EVAc foil with collagen and testing its degradation after 24 hours and 45 days in the soil. FTIR spectra of EVAc foil degraded after 24 h – red curve and foil tested after 45 days of degradation in the soil – green curve.

As indicated by FTIR spectra, the action of soil and/or water degraded the collagen from the foil – within the wavelength range of nitrogen compounds from 1550 to 1650 cm^{-1} , there are no peaks present (green line), which would correspond to the presence of collagen in the material. For implementation, there have been proposed polymer composites and films with the content of vinyl acetate and modified collagen:

- foil EVAc + 20% of modified collagen,
- foil EVAc + 40% of modified collagen.

Parameters of the foils prepared by blowing extrusion technology are shown in Table 1.

Table 1 Technical parameters of prepared foils

Sampling	Tensile strength at break [MPa]	Relative elongation at break [%]	Permeability to water vapor [$\text{g}\cdot\text{m}^{-2}\cdot 24\text{h}^{-1}$]
Foil EVAc + col 20%	10.5	462.1	10.2
Foil EVAc + col 40%	7.6	74.7	16.1

Collagen based hot-melt adhesive

The investigation was oriented on the research and preparation of non-formaldehyde thermoplastic hot-melt adhesive based on collagen biopolymer. Biopolymers of animal origin (e.g., technical leather glue, gelatin etc.) were specified by laboratory tests as suitable raw materials for preparation of thermoplastic collagen adhesives, with possible use for book sheets bonding as can be seen on Fig. 3.



Fig. 3. Thermoplastic collagen adhesive used for gluing of book hard covers

The infrared spectrum of the plasticized collagen sample was measured on a NICOLET 8700™ instrument by Thermo-Scientific (Madison, WI, USA) in the mid-infrared region (4000-650 cm⁻¹) using an ATR attachment with a Ge crystal in reflection mode, shown in Fig. 4.

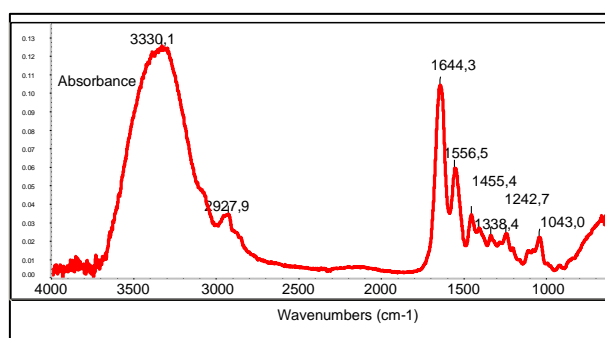


Fig. 4. The infrared spectrum of the plasticized collagen sample

In the FTIR spectrum, observable absorption bands are typical for functional groups of protein-type materials (bands corresponding to bonds 3330.1 cm⁻¹ for –OH groups; 1644.3 cm⁻¹ for amides of group I; 1556.5 cm⁻¹ for amides of group II ; 1455.4 cm⁻¹ for terminal –CH₃ groups; 1338.4 cm⁻¹ for N-H groups; 1242.7 cm⁻¹ for N-H groups; 1043.0 cm⁻¹ for C-O and C-O-C groups).

Qualitative parameters of the model collagen thermoplastic dispersion at 60 °C: pH: 6.5 ± 0.5, viscosity: 1500-2500 mPa.s, refractive value: 55-60% - dry matter, open drying time: short, surface adhesiveness of the glue: immediate, shelf life: min. 6 months at room temperature, melting point 50-55 °C and solidification point 30-35 °C - depends on the concentration of collagen and modifying additives, pH, time, and temperature of hydrolysis.

The influence of collagen on formaldehyde emission from UF adhesive mixtures

The effect of the addition of collagen modifications No. 1, 2 and 3 on the formaldehyde (fd) content was tested in UF adhesive mixtures hardened at 100 °C during the time of 20 minutes. The measured values show that collagen is a suitable modifier for the reduction of formaldehyde in UF cured adhesive compositions. Collagen No. 1 most significantly reduces emissions of fd, and this effect is increasing with increasing concentration. The content of formaldehyde in reference sample was 0.35 mg/g and in the modified resin only 0.25 mg/g as can be seen from Fig. 5.

Formaldehyde emissions from five-layer plywood of beech were tested according to the test method JIS A 1460 "Building boards. Determination of formaldehyde emission.

These results were confirmed on plywood testing formaldehyde was lowered down to 50 % in comparison with the reference sample.

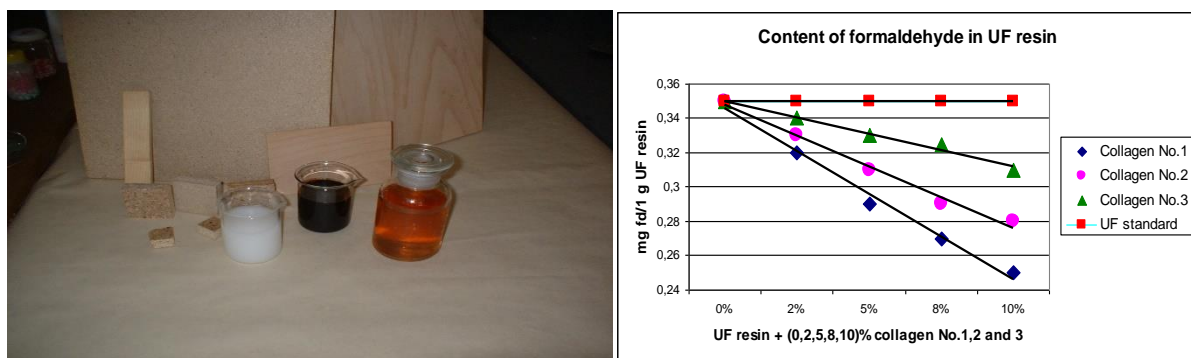


Fig. 5. UF resins modified with collagen applied for plywood bonding and influence of different modifications on the lowering of formaldehyde emission

CONCLUSION

Copolymer of ethylene vinyl acetate and collagen hydrolysate were specified for preparation of polymeric bio-composites. Polymer bio-composites and foils with controlled biodegradation were prepared by combining the components of mixtures, with defined physical and mechanical properties.

Obtained results confirmed the possibility to use the modified biopolymer collagen for preparation of ecologic and thermoplastic adhesives. Glued joint displayed high strength and flexibility after application of modification plasticization agents based on collagen.

Presented research proved the possibility of lowering the formaldehyde emission from wood products glued with urea-formaldehyde adhesive. Results of laboratory tests confirmed that collagen prepared from leather waste is a suitable additive for lowering of formaldehyde

emission from wood products glued with UF adhesive. Tests confirmed the decrease of formaldehyde content in plywood in comparison with the reference sample down to 50 %.

AKNOWLEDGEMENT

This work was supported by the Slovak Research and Development Agency under the contracts No. APVV-18-0378, APVV-19-0269 and APVV- 21-051.

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NANOTECHNOLOGICAL MODIFICATION OF POLY(ETHYLENE TEREPHTHALATE) BY COLD PLASMA

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ABSTRACT

Poly(ethylene terephthalate) (PET) surface was pre-treated by cold plasma to improve its adhesive properties. The surface energy as well as the peel strength of the adhesive joints of PET, modified by cold plasma to polyacrylate, increased significantly. A correlation between adhesion of polyester modified by cold plasma to polyacrylate and its surface energy was found.

Keywords: cold plasma; peel strength of adhesive joint; PET; surface energy.

INTRODUCTION

Poly (ethylterephthalate) (PET) is one of the most important polymers that are frequently used in many industrial applications, e.g. in the automotive industry for cars construction, due to its excellent properties. The surface energy of PET is insufficient in some applications, e.g. bonding, printing, etc. Several efficient methods have been used to improve the surface and adhesive properties of polymers [1, 2] The application of cold plasmas for pre-treatment of polymeric surfaces [3, 4] is a dry, ecological method of modification, which can tailor polymers in order to modify their surface energy and adhesion to other materials. However, for preparation of strong adhesive joints, modification of PET by diffuse surface barrier discharge (DSBD) plasma is essential [6, 7]

EXPERIMENTAL

The modification of the PET foils by a diffuse surface barrier discharge (DSBD) plasma was performed in a laboratory plasma source at atmospheric pressure in medium of N₂ or O₂ gases of technical purity. The DSBD plasma generator consists of electrodes separated by an alumina dielectric plate. The voltage of the DSBD source was 100 V, current intensity 1 A, and

frequency 6 kHz. The power used for the modification by DSBD plasma in N₂ or O₂ was 100 W.

The surface energy of PET was determined by measurements of the contact angles of a set of testing liquids with a SEE (Surface Energy Evaluation) system (Advex, Czech Republic).

The ATR-FTIR spectroscopy measurements of the PET foils were performed with a Nicolet Impact 400 FTIR spectrometer (Nicolet, USA) having a resolution of 4 cm⁻¹, a scan range was 4000 – 400 cm⁻¹.

The peel strength of the adhesive joint (P_{peel}) of the plasma modified PET foil to polyacrylate was determined by peeling of the adhesive joint (peel tests) at a 90° angle using a 5 kN universal testing machine Instron 4301 (Instron, England). The adhesive joints were fixed in the aluminum peeling circle.

RESULTS AND DISCUSSION

The surface energy of the PET modified by DSBD in O₂ and N₂ plasma at atmospheric pressure vs. the activation time is shown in Figure 1. The surface energy of PET during modification by DSBD plasma in O₂ and N₂ (Figure 1, plot a, b).

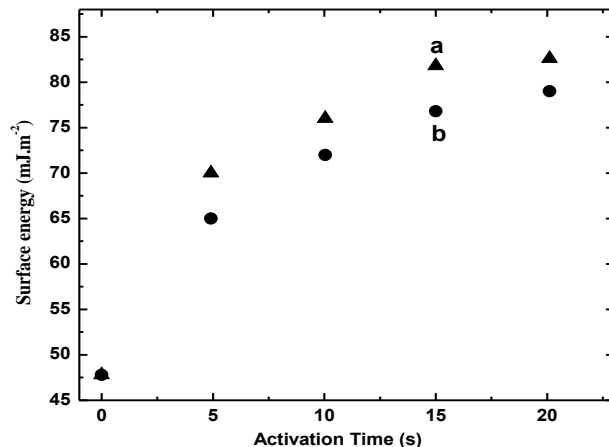


Fig. 1. Surface energy of PET foil modified by DSBD plasma: in O₂ (a) and in N₂ (b) vs. activation time.

significantly increased in comparison with untreated polymer. Figure 1, plot a shows that the surface energy of PET modified by DSBD plasma in O₂ increases from an initial value of 47.8 mJ.m⁻² for untreated PET to 82.6 J.m⁻² for 20 s of plasma modification. Figure 1, plot b shows the surface energy of PET modified by DSBD plasma in N₂. These values are lower than those of PET modified by the same method in O₂.

The peel strength of the adhesive joints of PET foils, modified by DSBD plasma (Fig. 4) in nitrogen (Figure 2, plot b), in oxygen (Figure 2, plot b) to polyacrylate vs. time of activation is shown in Figure 2. The peel strengths of PET to polyacrylate after modification by DSBD plasma significantly increased, and these increases were higher for the samples modified in oxygen. The peel strength of the adhesive joint increased from 77 N.m⁻¹ (pristine PET) to 180 N.m⁻¹ (DSBD, 10 s, N₂), and 237 N.m⁻¹ (DSBD, 10 s, O₂). These results clearly indicate that plasma irradiation considerably improves the adhesive properties of PET for DSBD plasma.

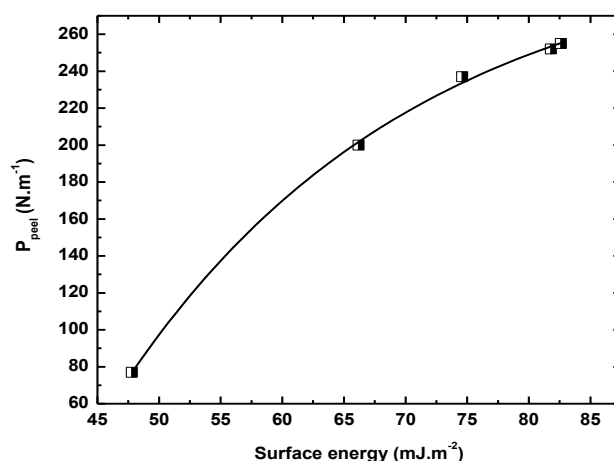


Fig. 2. Relation between peel strength of adhesive joint of PET modified by DSBD plasma in O₂ to polyacrylate vs. PET surface energy.

Figure 2 shows the relation between peel strength of the adhesive joint of PET, modified by DSBD plasma in O₂, to polyacrylate and the surface energy of polymer. A 1st order exponential decay was found for modification of PET in O₂ plasma in Figure 2. For this processing gas the relation between peel strength of the adhesive joint O₂ plasma-treated PET-polyacrylate and surface energy is given by the following relation: $P_{\text{peel}} = 309.5 - 1719.8 \cdot \exp(-SE/23.9)$ (SE = surface energy).

CONCLUSION

The surface energy of PET modified by DSBD plasma significantly increased, and this increase was higher for oxygen compared to nitrogen. The peel strength of PET, modified by DSBD plasma or RFD plasma, to polyacrylate significantly increased, and this value was higher in the case of oxygen than in the case of nitrogen. A correlation between the peel strength of the

adhesive joint of PET, modified by DSBD plasma in O₂ to polyacrylate and PET surface energy by the following relation: $P_{\text{peel}} = 309.5 - 1719.8 \cdot \exp(-\text{SFE}/23.9)$ was found.

ACKNOWLEDGEMENTS

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PREPARATION OF POLYMER FOAMS AND POROUS STRUCTURES

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ABSTRACT

Polymeric foams offer number of advantages attending their applications. Behind modifications of well-known utility properties – acoustic, thermal, and electric insulation; weight reduction, transport protection, economical benefits guaranteeing material costs savings, or ecological initiatives as material and energy consumption reduction could be put on and highlighted.

During our recent research and development activities, we were involved in several industry driven cooperations focused on establishment and modification of batch as well as continuous foaming processes employing chemical and physical type of foaming agents. Polymers up to now employed for foam production included polylactide (PLA), polypropylene (PP), polyethylene (PE), polyurethane (PU). PP foams were extruded using CO₂ and N₂ as additional environmentally positive aspect, PLA uncrosslinked and partially crosslinked foams were produced via foaming with CO₂ and N₂ using pressurized cell, PE recipe was modified to increase creep resistance as well as influence porosity density. For defined controlling of porous structure growth, blending of suitable polymers, addition of nucleation agents based on inorganic and polymeric particles, modification via crosslinking agents, as well as optimisation of processing conditions were involved and studied.

In order to acquire desired utility properties of foamed products, prepared porous structures were characterised using optical microscopy, computer tomography analysis, scanning electron microscopy, porosimetry, mechanical testing, thermal analysis.

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PREPARATION OF FIBERS AND NONWOVENS BY MELT SPINNING TECHNOLOGY

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ABSTRACT

Melt spinning process is one of the most cost-efficient ways of producing fabrics at an industrial scale, mainly due to the simplicity of the process, which does not require solvents, there are no toxic by-products and the production speed is high. This area of research is very promising as nonwoven fabrics offer various application possibilities in many market segments (hygiene, medical, construction, automotive, filtration, food and beverage, agriculture, ...). During our recent research and development activities we have been involved in the preparation of fiber structures and nonwovens by melt spinning technologies meltblown and spunbond. Due to the possibilities of the melt spinning laboratory line, attention was focused on the preparation of mono- as well as bicomponent fibers in different configurations (sheath/core, islands in the sea, segment pie). An integral part of the melt spinning process is also the characterization of the flow behavior and viscoelastic properties of the input polymer materials and their mixtures. Polymers up to now employed for preparation of fiber structures and nonwovens included various types of polypropylene (PP), polyethylene (PE), polystyrene (PS), polyethylene terephthalate (PET) and polyamide (PA) as well as biodegradable materials based on polylactide (PLA), polybutylene adipate terephthalate (PBAT), polybutylene succinate (PBS) and polyvinyl alcohol (PVOH). Prepared fibers and nonwovens were characterized using optical microscopy, scanning electron microscopy, mechanical testing, thermal analysis, spectroscopy, assessment of breathability, filtration efficiency and surface properties.

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FIRE RETARDANTS IN POLYMERS: PARTICLE DISTRIBUTION WITHIN THE MATRIX WITH CASE STUDIES

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ABSTRACT

To plastic materials fire retardants are commonly added to suppress their flammability and thus to fulfil often very high demands on their properties. Due to enormous legislative restrictions and pressure on environment and sustainability, new fire retardants are being developed or a combination of more kind of fire retardants in order to find synergistic effect giving rise to enhanced reduction in flammability, lowering the price of fire retardant systems or their loading in the systems, *etc.*, is commonly used. Such systems are then with benefits used for example in automotive industry, airplanes, trains, power and communication cables.

This contribution introduces fire retardants that can be used even to provide an additional application property, such as thermal or electrical conductivity, for the polymer matrix beyond enhancing its fire resistance. Furthermore, some ideas how to determine a quality of particle distribution within the system after processing process using rotational rheometry and help of a Cole-Cole plot are introduced. In this study polypropylene served as a polymer matrix and various fire retardants possessing different flame retardant mechanism were used. The prepared samples were analysed through a rotational rheometer and were put in contrast with scanning electron microscopy.

In addition, solutions in some case studies for systems based on wood flour composites or for seat backside part, where lowering flammability of the composite was the main goal, are present.

ACKNOWLEDGEMENT

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CHEMICKÁ RECYKLACE ODPADNÍCH POLYMERŮ (PE, PP, PS)

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ABSTRAKT

Rozsáhlé používání plastových materiálů vytváří celosvětově velké množství odpadu, který kvůli nízké míře recyklace končí na skládkách nebo v přírodě. Rostoucí množství plastového odpadu tak představuje vážné riziko pro životní prostředí i zdraví člověka a zvířat. Podpora recyklace plastů může tato rizika snížit a zároveň podpořit oběhové hospodářství plastů. Proces chemické recyklace (známý také jako terciární recyklace nebo surovinová recyklace) může přeměnit plastový odpad na různé chemické látky, které lze použít jako buď suroviny pro výrobu nových polymerů, nebo dalších cenných chemických látek a paliv. Chemická recyklace má tedy potenciál přispět k zachování zdrojů i k minimalizaci odpadu. Jedním ze slibných procesů chemické recyklace odpadních plastů může být katalytická pyrolýza. Při katalytické pyrolýze dochází k termochemickému rozkladu polymeru s využitím katalyzátoru pro úpravu selektivity požadovaných produktů.

Část práce je zaměřena na katalytickou pyrolýzou polyolefinů na zeolitových katalyzátorech (typu HZSM-5). Zeolity s jedinečnou architekturou pórů a laditelnými texturními i kyselými vlastnostmi jsou pro takové aplikace zajímavými katalytickými materiály. V tomto ohledu se naše práce zabývá katalytickou konverzí čistého a odpadního polyethylenu (HDPE) či polypropylenu (PP) v jedноступňových a dvoustупňových zařízeních na zeolitech HZSM-5 s různým poměrem křemíku a hliníku, a tudíž s různou hustotou kyselých míst. Při jedноступňovém procesu (pyrolýza in-situ) se ukázalo, že zeolitový katalyzátor HZSM-5 s vyšší hustotou kyselých míst podporuje aromatizaci, při níž v kapalně fázi vznikají především sloučeniny BTEX (benzen, toluen, ethylbenzen, xyleny). Na druhé straně katalyzátor s nízkou hustotou kyselých míst podporuje tvorbu lehkých (C₂-C₄) olefinů v plynné fázi. Při nekatalytické pyrolýze vznikaly v pyrolýzním oleji téměř výhradně alifatické uhlovodíky a v plynné fázi byly výtěžky lehkých olefinů relativně nižší. Dále bylo prokázáno, že dvoustупňový

proces (tj. katalytické krakování ex-situ a aromatizace) může zlepšit obsah BTEX v pyrolýzním oleji za předpokladu, že se použije zeolitový katalyzátor s vysokou hustotou kyselých míst [1]. Druhá část této práce se zabývá katalytickou pyrolýzou odpadního polystyrenu (PS). Plastový odpad z materiálů na bázi PS může být dobrým zdrojem styrenu a monoaromatických sloučenin BTEX (benzen, toluen, ethylbenzen, xyleny). V tomto ohledu se naše práce zaměřila na provedení katalytické pyrolýzy různých vstupních surovin z odpadního polystyrenu (WPS) na kyselých a bazických katalyzátorech použitých v režimech ex-situ a in-situ. Hlavním cílem bylo porovnat složení pyrolýzních produktů získaných při změně vstupních surovin, katalyzátorů a provozních režimů. Bylo prokázáno, že expandovaný polystyren poskytuje velmi podobné rozložení produktů ve srovnání s čistým PS ($M_r = 190\ 000$), přičemž oba poskytují vysoký obsah styrenu. Vysoký obsah styrenu poskytují i obalové materiály na bázi houževnatého polystyrenu (HIPS), liší se ale množstvím produkovaných BTEX a oligomerů. Ukázalo se, že bazické katalyzátory ovlivňují složení produktů pyrolýzy jen nepatrně ve srovnání s termickým rozkladem. Naopak kyselý katalyzátor vykázal významný vliv na složení produktů pyrolýzy ve srovnání s nekatalytickou pyrolýzou, zejména z pohledu produkce benzenu, který termickým rozkladem nevzniká [2].

Tyto výsledky mohou poskytnout nové poznatky pro chemickou recyklaci plastových odpadů.

PODĚKOVÁNÍ

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POLY (VINYLIDINE FLUORIDE) ELECTROSPUN MEMBRANE WITH PIEZOELECTRIC PROPERTIES APPLIED AS PRESSURE SENSORS, ENERGY HARVESTING AND ELECTROSTRICTION

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ABSTRACT

The most promising piezoelectric polymer for applications like self-powered sensors, actuators or energy harvesting is polyvinylidene fluoride (PVDF). Piezoelectric properties are due to the beta crystalline face of PVDF where the dipolar orientation of this covalent crystal is given by a proper arrangement of positive hydrogen and negative fluorine atoms. In the present study, jet electrospinning technology was used to prepare PVDF nanofibers collected on polymeric substrate, leading to non-woven membrane like structure. The nanofiber and membrane structures were characterized using scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) analysis. Then three types of experimental setups with the incorporated PVDF electrospun membrane were prepared. They were capable of generating electrical voltage in response to pressure stimuli like pressure pulse (unit of volt) or sound wave (unit of millivolt). The generated charge can be harvested to a capacitor the efficiency of which was demonstrated through the discharging of reasonably high voltage and also the capability to light up three LED diodes connected in series. Finally, electrostriction detected with the help of the generated piezoelectric voltage by electrostrictive stimuli reached the maximum at around 77 mV.

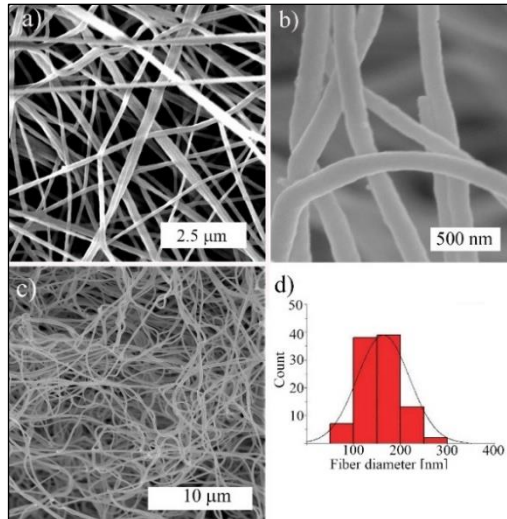


Fig. 1. This is a figure. Schemes follow the same formatting. SEM images of PVDF fibres non-woven structure a), b) detailed view of some PVDF nanofibers, c) cross section of PVDF membrane made of PVDF nanofibers, d) fibre diameter distribution of PVDF nanofiber network.

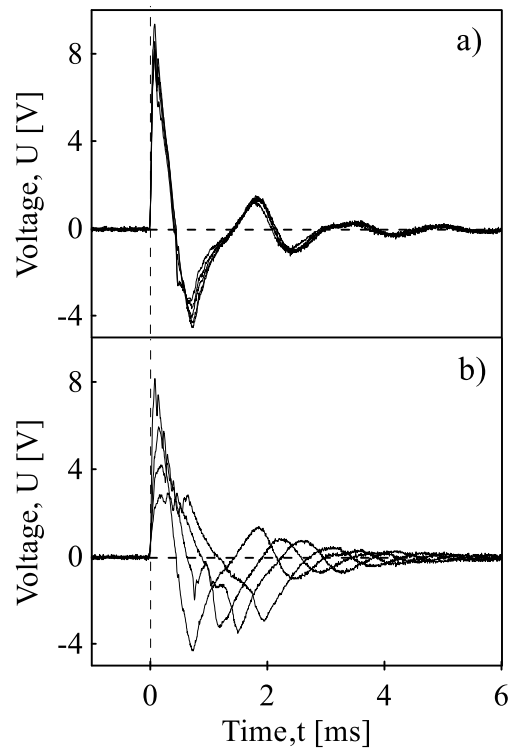


Fig. 2. Piezoelectric response to pressure pulse on the top surface of PVDF membrane pendulum impact; part a) for five impact with the same energy and part b) for impact of pendulum with bouncing to the pendulum impact dumping.

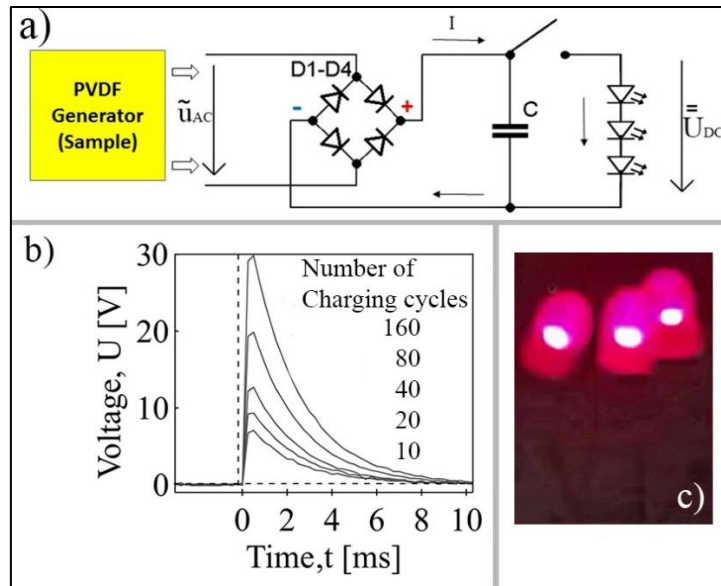


Fig. 3. Energy harvesting: part a) Graetz bridge with storage capacitor to direct generated piezoelectric response to charge capacitor, part b) Discharge of stored charge into capacitor for different number of impact cycles, part c) Light blink of the LED diodes connected in series after 20 impact cycles.

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MODIFICATION OF POLYMER SUBSTRATES FOR BIOMEDICAL APPLICATIONS BY MULTISTEP PHYSICO-CHEMICAL APPROACH

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ABSTRACT

Polymeric biomaterials that are intended for clinical use must have excellent mechanical properties, as well as adequate surface properties to ensure biocompatibility while interacting with living tissue. The current problem that can be encountered with biomaterials used for implants and other devices may be acute and chronic inflammatory responses, ultimately leading to fibrous capsule formation and thereby impairing normal tissue growth [1,2]. Furthermore, insufficient hemocompatibility due to surface-induced thrombosis or restenosis must be taken into account [3,4]. Further improvements of given materials rely on the precise control of cellular interactions in terms of cell adhesion and proliferation via modification of the biomaterial surface [5]. The surface modification of polymers consists of changes in surface energy, polarity, charge, topography, etc. [6,7].

Therefore, activation procedures have been carried out to make the polymer surface more hydrophilic and obtain specific features by introducing functional groups (carboxylic, hydroxyl, carbonyl, hydroperoxide, etc.) for further covalent bonding with selected agents [8]. The typical surface modification techniques used include chemical vapor deposition, wet chemical methods, UV light radiation, ozone-induced treatment and plasma exposure. Among the physical and chemical methods used to obtain required surfaces without affecting the bulk properties, plasma treatment is an appropriate and efficient technique [9,10,11]. In addition to the efficiency of immobilization, plasma treatment is able to enhance hydrophilicity and create a high density of functional groups on the surface without the use of toxic chemicals and heat processing. Thus, this method is suitable for many immobilization techniques with biologically active molecules and chemically unstable substrates (including polysaccharides) [12,13].

The plasma-treated polymer results in a negatively charged surface; therefore, subsequent immobilization of a potential anionic polysaccharide is challenging. The negative charge

prevents the formation of covalent bonds between the molecule interfaces and polymer surface embedded radicals due to electrostatic repulsive forces. The binding affinity can be increased by reducing the negative charge of the polymer surface. One promising solution might be introducing more positively charged groups through mediators, such as N-allylmethylamine (MAAM). This liquid chemical is able to graft onto a plasma-treated polymer surface by a copolymerization process to create a polymer brush structure with a high density of positively charged amino groups via a radical “surface from” reaction in the gaseous phase [14,15]. Such amine-rich coatings have been studied to control cell behavior, demonstrating a positive effect on cell adhesion, proliferation, and differentiation for different cell types, such as osteoblast-like cells and fibroblasts [16]. Moreover, the advantage of using these functional groups is the possibility of exploiting them for the immobilization of bioactive molecules [17,18,19].

This research is the first study dedicated to the description of various furcellaran applications in biomedicine. Moreover, to the best of our knowledge, no study using furcellaran as a polysaccharide film layer for PET functionalization has been reported. The objective of this study is to represent a method for immobilizing furcellaran onto PET surfaces. For this purpose, RF plasma discharge is applied onto the PET surface to create oxidative functional groups for further covalent binding with selected agents. First, MAAM is grafted onto plasma-treated PET to create a high-density polymer brush for improved adhesion interaction properties. Consequently, furcellaran immobilization on such a treated surface is performed. As-prepared substrates are subjected to various selected cell interactions. Namely, the antibacterial activity, anticoagulant activity, fibroblasts and stem cell cytocompatibility of the samples were investigated.

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CHARACTERIZATION OF STRUCTURE-PROPERTIES RELATION IN HETEROPHASE POLYMERS

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ABSTRACT

Heterophase polymers, their manufacturing and end-use application properties such as transport, optical and mechanical properties are closely related to their morphology. The knowledge of the relation between the morphology, structure and properties plays an important role in defining the polymer behaviour during its manufacturing as well as for achieving the desired polymer properties.

To obtain the overall information about the polymer morphology several imaging techniques need to be applied. Our combination of X-Ray microCT and atomic force microscopy (AFM) provides the visualization of heterophase morphology on the wide scale with the sufficient contrast between phases. Raman microscopy supplements the morphological study by the chemical composition mapping on microscale. Morphological features such as pores, rubber or other phases are characterized by advanced morphological descriptors.

This contribution presents the morphology-properties investigation on heterophase polyolefins such as (i) polyethylene (PE) with various densities and (ii) high impact polypropylene (hiPP) with rubbery domains incorporated in polypropylene matrix. In both cases, the distribution between crystalline and amorphous phase has a great impact on polymer thermodynamic behaviour and mechanical properties. Moreover, the quantitative models for estimation of local PE density and rubber composition in hiPP were created based on morphological and Raman spectra results.

Additionally, the morphology-structural investigation plays an important role also directly in industrial manufacturing as we demonstrate on searching the root causes of various defects in painted layers of industrially made materials affecting the visual appearance and properties of final commercial products.

THE INFLUENCE OF PROCESSING PARAMETERS ON POLYMORPHISM OF LONG CHAIN BRANCHED POLYPROPYLENE

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ABSTRACT

The influence of injection moulding processing parameters on structure of long-chain branched polypropylene (LCB-PP) Daploy WB130HMS supplied by Borealis Company Vienna, Austria was investigated. It is a propylene-based polymer that is produced by grafting monomer during radically controlled reactions of isotactic polypropylene with peroxides to form long chain branches. Examined material has the value of melt flow rate (230 °C, 2.16 kg, ISO 1133) of 2.1 g/10 min.

Long-chain branched polypropylene was injection moulded using four sets of processing parameters. In the P-set holding pressure was varied within a range of 30–70 MPa by 10 MPa, in T-set mould temperature was precisely controlled – increased from 40 to 120 °C in 20 °C step, while in S-set1 and S-set2, respectively injection speed increased from 20 to 140 mm/s in 30 mm/s step and the mould was held at temperature of 40 or 120 °C. Other parameters remained unchanged: temperatures of heating zones 190; 220; 230 °C, melt temperature (nozzle) 240 °C and holding pressure time 60 s.

The polymorphic composition of LCB-PP derived from wide-angle X-ray scattering showed a significant dependence on the processing technology and their parameters. Comparison of the morphology evolution through the injection-molded specimen cross-section brings an interesting observation – coexistence of α -, β - and γ - phases. The increase of holding pressure and mould temperature positively influenced the γ -phase content in both skin and core layers, in the case of mould temperature β -phase content increased as well. Higher injection speed led to increase of β -phase content, however, only in skin layer, independently on mould temperature.

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