SPI

Symposium on Polyurethane Innovation 2023

Book of Abstracts

University of Miskolc

*Advanced Materials and Intelligent Technologies Higher Education and Industrial Cooperation Centre (**HEICC**)*

Institute of Chemistry

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FOREWORD

The Symposium on Polyurethane Innovation (SPI) was held in 2023 on 24th of August. The purpose of SPI 2023 was to discuss the latest developments in polyurethane raw materials, equipment, manufacturing technologies, and other related innovations. International companies, invited speakers, and young researchers presented their innovative solutions in polyurethane chemistry. The event took place in a hybrid format with fifteen presentations. Abstracts of the presentations are published within this booklet. In view of the great interest shown, we have decided to publish additional short papers about other research projects conducted at the Institute of Chemistry and the Advanced Materials and Intelligent Technologies Higher Education and Industrial Cooperation Centre (HEICC). Some of these may not closely related to polyurethanes but show the wide range of research being carried out at the University of Miskolc. We hope that these collections will further strengthen cooperation and initiate new research topics.

Kind regards,

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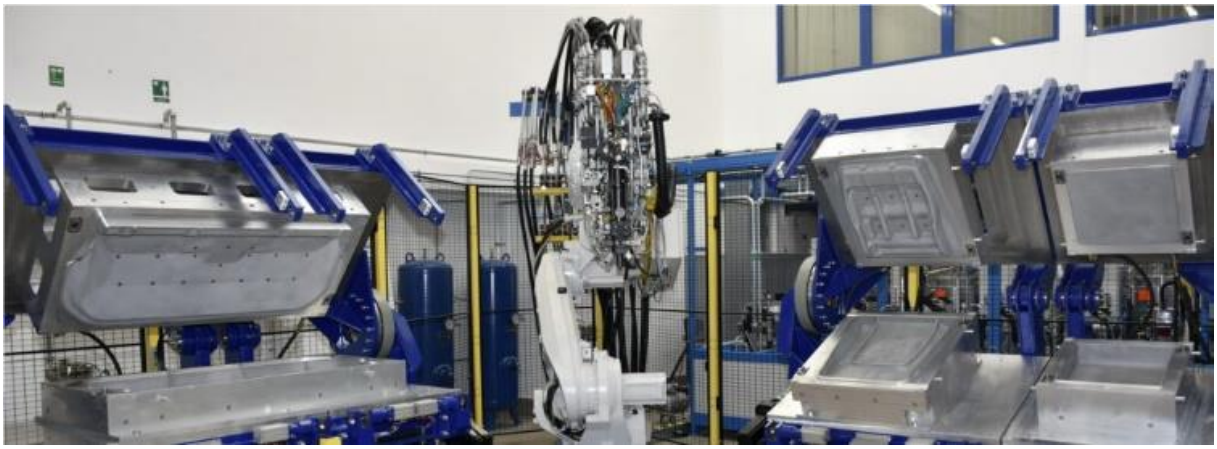

CONFERENCE PROGRAM

Symposium on Polyurethane Innovation (SPI) 2023

Timeframe	Speaker	LECTURE TITLE, ORGANIZATION
9:00 – 9:15	**Prof. Dr. Béla Viskolcz**	**Opening lecture, *University of Miskolc***
9:15 – 9:30	Enikő Hornyák-Mester	Low emission additives in polyurethane flexible foams; *UoM*
9:30 – 9:45	Hadeer Waleed	A computational study of the catalytic effect on urethane formation; *UoM (online)*
9:45 – 10:00	Lilla Márta Sőrés-Tölli	Algae coloured polyurethane foams; UoM
10:00 – 10:30	**Kitti Bartha-Lengyel**	**Study possibilities of recycling plastic products; *Wanhua-BorsodChem***
10:30 – 10:45	**BREAK**	
10:45 – 11:15	**Péter Simon**	**Development of insulating foams at Wellis; Wellis Hungary**
11:15 – 11:30	Miklós Varga	Development of polyurethane composites doped with carbon black; *UoM*
11:30 – 11:45	Julie Mallouhi	Toxicity tests of polyurethane foams using different organisms; *UoM*
11:45 – 12:00	Péter Koska	Genes, enzymes, microbes in the degradation of low molecular weight urethane compounds; UoM
12:00 – 13:00	**LUNCH BREAK**	
13:00 – 13:30	**Babak Minofar**	**Novel insights into polymer-biomolecule interactions via molecular simulations; University of South Bohemia (online)**
13:30 – 13:45	Tamás Horváth	Energetic perspectives of urethane linkage termination for sustainable polyurethane development; *UoM*
13:45 – 14:00	Anikó Jordán	Microbial lipase and esterase detection; *UoM*
14:00 – 14:15	**BREAK**	
14:15 – 14:45	**Péter Tóth**	**Investigating the efficiency of chemical equipment using numerical and statistical methods; Wanhua-BorsodChem**
14:45 – 15:00	Alpár Ferencz Hatvani-Nagy	Effect of clay minerals in polyurethane foam composites; *UoM*
15:00 – 15:15	Dalal K. Thbayh	A theoretical study of the applicability of natural antioxidant additives with polymers; UoM (online)
15:15	**CLOSING CEREMONY**	

Abstracts of Oral Presentations

The authors of the abstracts bear the full responsibility for the scientific and linguistic content.

Low Emission Additives in Polyurethane Flexible Foams

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ABSTRACT

In today's trends in environmental consciousness and regulatory demands, governments and automotive manufacturers across the globe are constantly challenged to uphold strict emission standards and minimize the release of harmful substances. From within vehicles most of these standards target volatile organic compounds (VOCs), as these can propose significant health and environmental risks. VOCs have gained adverse reputation as major contributors to gaseous air pollution, directly impacting human comfort and health.

To address these concerns, car manufacturers have made devoted commitments to the ongoing development of technologies and materials of polyurethanes aimed at reducing the emission of these volatile substances from the interior of vehicles. Key strategies include the utilization of recycled materials and low-VOC content materials, both of which have proven to be effective in improving indoor air quality and controlling the release of hazardous compounds.

One central aspect of this sustainability is the constant refinement and improvement of catalysts used in the automotive industry. Two catalysts used in polyurethane foam production, in particular, have undergone significant conversions: triethylenediamine (TEDA/DABCO) and bis(2-dimethylaminoethyl)ether (BDMAEE). The replacement of these catalysts plays a crucial role in the reduction of emissions from vehicle interiors. One method is when the original molecules of TEDA and BDMAEE are altered in a way that involves the replacement of some functional groups within their chemical structures with a more reactive substitute, such as hydroxyl-group. This replacement process aims to enhance their effectiveness in reducing emissions by connecting to the polymer molecule. As a result, the catalyst is not emitted as easily when subjected to heat as with the original mechanism.

A Computational Study of the Catalytic Effect on Urethane Formation

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ABSTRACT

A theoretical investigation of urethane formation through the reaction of phenyl isocyanate and methanol without and in the presence of a 1,4-diazabicyclo[2.2. 2]octane (DABCO) was carried out by using the density functional theory method in the acetonitrile solvent. The reaction mechanisms have been explored, and the corresponding thermodynamic properties have been computed. The reaction in the presence of the catalyst largely differs from the catalyst-free case. It was found that the barrier height of the reaction decreased significantly (ΔE_0 > 100 kJ/mol) in the presence of DABCO, which proves the importance of catalysts in (poly)urethane synthesis.

Study Recycling Possibilities of Plastic Products

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ABSTRACT

Plastics products have become indispensable or very difficult to replace in many areas of our daily lives, however those materials which are no longer used can become hazardous waste over a long period of time. As a major producer of plastic raw materials, we are committed to produce more sustainable plastic products.

Advantage of producing polymer blends at industrial level is that we can create new products with widespread properties. The compatibility of different polymers, such as thermoplastic polyurethane (TPU) and polyvinyl chloride (PVC), has been extensively tested to determine the properties of the blends.

The polymer blends were produced by mechanical melt mixing on extruder. TPU and PVC partially miscible, the increasing ratio of TPU changes the behaviour of blends.

In the spirit of sustainable development, we want to open up new directions by creating bio-based and biodegradable polymers, like polylactic acid and PVC blends. In addition to measuring the mechanical properties of the blends, the composition has been investigated by thermoanalytical methods (DMA, DSC) and the morphology by scanning electron microscopy (SEM).

Waste resins from PVC production have different properties such as colour, moisture content, and morphology. Studies have been carried out to explore of waste PVC resins from production and their potential use as plastic components. The waste resin slightly alters the mechanical properties of the plastic, but is suitable for the production of lower quality products.

Acknowledgements: *Authors are thankful for opportunity provided by Wanhua-BorsodChem to conduct this study and to Tamás Purzsa, Vice President and Chief General Engineer of Wanhua-BorsodChem for his support.*

Development of Polyurethane Composites Doped with Carbon Black

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ABSTRACT

I investigated the effect of nanoparticles in foam composites. I investigated the mechanical and thermal conductivity properties. Mechanical tests showed that the addition of carbon black to the foam resulted in a softer foam compared to the reference at NCO indices between 0.8 and 1.0, while a stronger structure was obtained at NCO indices between 1.1 and 1.2. The density of soot-supplemented foams with NCO indices between 1.1 and 1.2 was higher compared to the reference foam. The results of the thermal conductivity coefficient measurements showed that the addition of carbon black slightly improved the insulation properties of the foams.

Toxicity Tests of Polyurethane Foams Using Different Organisms

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ABSTRACT

Polyurethanes (PUs) represent a distinct category of polymeric materials that exhibit notable differences from most other plastic types in various aspects. This polymer continues to grow at a rapid pace throughout the world, and because of its good properties, it is used in many applications. Environmental pollution released from various materials, which can be harmful to both humans and the environment, is a significant concern. Many methods are available for the ecotoxicological assessment of PU. In this study, two methods have been used to investigate potentially hazardous substances that can arise during the degradation and aging of PU materials. The first method involves utilizing Sinapis alba (White mustard) seeds for testing liquid samples, such as the dilution water used for soaking PU foam. The second test is based on bacterial toxicity, where a piece of PU foam is directly immersed in the growth medium for bacteria. In our study, polyurethane foam was used, as it represents the most commonly used type of PU, with different polyol: isocyanate ratios (0.8, 0.9, 1.0, 1.1, and 1.2). All in all, two toxicity tests were developed successfully, and both are applicable in the ecotoxicological assessment of PU foams.

Genes, Enzymes, Microbes in the Degradation of Low Molecular Weight Urethane Compounds

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ABSTRACT

Hydrolysis of urethane compounds are a hot spot in environmental sciences. Aryl-carbamates are the major components of polyurethane, several types of herbicides, and pharmaceuticals. Aryl carbamates may have a risk to the environment due to its toxicity, poor solubility in water and recalcitrant feature. The enzymes which can hydrolyse aryl-carbamate compounds have been characterised only in the last decades. It can be distinguished markedly two types of aryl carbamate hydrolase by its substrate such as N-aryl carbamate hydrolases, and O-aryl carbamate hydrolases. The former is a special type of esterase which encoded in mibile genetic elements plasmids and even transposons. They have substrate specificity but can be characterised some degree of promiscuity.

N-aryl amidases are belonged to the metal dependent amidase family. As polyurethane hard segment constituent toluene-dicarbamate and bis-phenyl-dicarbamate can be regarded as N-aryl carbamates, the deeper knowledge of N-aryl amidases may help to find solution to biodegradation of polyurethane.

These amidases in structure and function significantly differ from the conventional proteases and amidases which take part in central metabolic pathways of microbes.

Energetic Perspectives of Urethane Linkage Termination for Sustainable Polyurethane Development

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ABSTRACT

The urgency to find viable recycling methods for the waste generated from the growing polyurethane production is increasing, supporting sustainable development. The stability of the urethane linkage is a major issue in the recycling of polyurethane-based plastics. To evaluate the energetic profile of potential transformation pathways of the urethane bond, research has focused on the reactions of a model urethane molecule, methyl N-phenyl carbamate (MPC), using the G3MP2B3 composite quantum chemical method. Energetics of hydrogenation, hydrolysis, methanolysis, peroxidation, glycolysis, ammonolysis, reduction with methylamine and dimethyl phosphite reactions had been explored in both gas and condensed phases. Out of these reactions, reactions with H2, H2O2 and CH3NH2 revealed promising results, especially in water solvation. The products obtained from these reactions are also relevant in the industry, as they can be reused in polymer technologies, offering a potential pathway to a circular economy. As further potential transformations, several ionizations of MPC had also been examined. including electron capture and detachment, protonation/deprotonation, and reactions with OH-. Notably, the reactivity of OH- against the model urethane MPC suggests a promising breakdown due to a relatively low activation barrier. In an ideal case, the transformation of the urethane bond could be enzymatic process, therefore potential enzymes had also been investigated for the catalysis of the most favorable chemical re-actions including hydrogenation and peroxidation.

Microbial Lipase and Esterase Detection

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ABSTRACT

Polyurethane (PU) and other plastics are integral to our daily lives, with PU foam being widely used in various products, resulting in its accumulation as environmental waste, notably in water and soil. While multiple waste management approaches exist, one of the less explored methods is biological degradation. This process offers the advantage of minimal energy input requirements and the potential for complete plastic mineralization. However, it carries the drawback of potential toxic compound formation during degradation and premature polymer decomposition. Extensive research has investigated the biodegradability of polyurethanes with the involvement of microorganisms. Microbes, in general, play a role in breaking down different polymers, including polyurethane. The most studied bacteria in polyurethane biodegradation belong to the *Pseudomonadaceae, Enterococcaceae, Corynebacteriaceae,* and *Comemonadaceae* families. Microorganisms' degradation capabilities stem from their long-term adaptation to polymers as an energy source. To use polyurethane as an energy source, microorganisms require specific enzymes. The literature identifies three primary enzyme types: lipase, urease, and esterase, with esterase playing a predominant role. In the research was gather all available bacterial esterase sequences, determine their homology using BLASTp and MSA programs, and mathematically analyze the implications of this similarity. Then it was evaluated the microorganisms identified during the similarity search and map the bacterial strains available in the university collection, including those known from the literature and those exhibiting homology. Subsequently, based on the analyses, was demonstrate lipase and esterase activities using microbiological methods with Triybutirin and Impranil DLN SD substrates.

Investigating the Efficiency of Chemical Equipment with Numerical and Statistical Methods

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ABSTRACT

Adaption to the changing climate is becoming more and more relevant to the chemical industry as it has a notable influence on the water and energy consumption on chemical manufacturers. One of the key climate conditions which can influence the operation of chemical companies are times of droughts as it limits the available water used for production. For the above reason analysing the different possibilities for water saving is crucial for every aspect of the industry to maintain a steady and sustainable production. The authors of this work had been using numerical methods to determine the possible hybridization of wet-, cross-flow cooling tower to reduce the evaporated quantity of water and plume abatement. Thus, a Python script has been constructed to offer solution to the above-mentioned optimization problem.

The program calculates the thermodynamic properties and flowrates of a given packed wet cooling tower. The equations governing the mass and heat flow of a given counter-flow, wet cooling tower are Ordinary Differential Equations with unknown boundary conditions on both sides of the cooling tower which was solved using the Runge-Kutta numerical method. The maximum and minimum of these boundary conditions are guessed and followed with a binary search with which the program determines the outflow of water and the influx of air which will satisfy the problem determined by the governing differential equations. For determining the annually evaporated water the relevant weather data is also required.

On the other-hand BorsodChem is keen on utilizing statistical tools and approaches for uncovering bottle-necks in the production and to predict product quality by analysing and finding the most significant correlations amongst the tremendous amount of data arriving from the control systems and analytical measurements. The above publication will demonstrate a case study for such a statistical analysis.

Acknowledgements: *Authors are thankful for opportunity provided by Wanhua-BorsodChem to conduct this study.*

Effect of Clay Minerals in Polyurethane Foam Composites

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ABSTRACT

The aim of the present research is to produce PUR composites that allow the use of a higher percentage of natural materials, with mechanical properties at least equal or better than the starting polyurethane. A general characterisation of the starting and composite materials is given, with particular emphasis on the interactions between layered silicates and plastics. The interactions of polyols with various minerals have been studied, characterizing the mixtures from a rheological point of view. Polyurethane foam composites were synthesized with these minerals and the parameters of foam formation, reaction kinetics and concentration-dependence were measured.

A Theoretical Study of the Applicability of Natural Antioxidant Additives with Polymers

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ABSTRACT

Oxidative stress is a physiological condition that occurs when there is an imbalance between the production of reactive oxygen species (ROS) or free radicals and the body's ability to detoxify them or repair the resulting damage. Antioxidants additives are molecules that can neutralize ROS and prevent or repair cellular damage. They include vitamins (e.g., vitamin C and vitamin E), enzymes (e.g., superoxide dismutase and catalase), and other compounds found in a healthy diet, such as flavonoids and polyphenols in fruits and vegetables. Vitamin C or L-ascorbic acid (Asc) is one of the most well-known natural antioxidants of all time. The antioxidant potential and thus, the applicability of Asc as natural antioxidant additive was studied through using the computational tools. Hydrogen atom transfer (HAT) mechanism was considered to know the antioxidant potential for the structure. The geometries of Asc, and the corresponding radicals, radical cations, and anions were optimized through employing the M05-2X functional in combination with the 6-311++G(2d,2p) basis set. From the results, we can see that the O-H bonds are more potent to donate H-atoms to free radicals than C-H bonds. The lower BDE, the higher the antioxidant potential. Asc can be applied to safeguard common polymers and prohibit oxidative stress-induced material deterioration.

University of Miskolc

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