

09:00 – 09:30

**Covestro Deutschland
DE-Leverkusen**



Dr. Christoph Thiebes*,
Wolfgang Arndt, Peter Kueker, Dirk Achten, Winfried Jeske

POLYURETHANE ADHESIVES FOR CONTACT BONDING APPLICATIONS

Despite some new developments in the past, polyurethane adhesives are still playing a niche role in contact bonding applications.

However, new market requirements and circumstances are constantly developing, creating a need for alternatives to the currently used technologies.

Hence, during this lecture we will evaluate the performance of polyurethane adhesives in contact bonding applications for different markets served today with alternative technologies.

Also, alternative application methods of contact adhesives will be presented.

09:30 – 10:00

**University of Alicante / Adhesion and Adhesives Laboratory
ES-Alicante**



José Miguel Martín-Martínez*, Mónica Fuensanta, Abbas Khoshnood

**DOES THE STAGE OF ADDITION OF THE INTERNAL EMULSIFIER IN
WATERBORNE POLY(URETHANE UREA)S SYNTHESIS DETERMINE THEIR
ADHESION PROPERTIES?**

Waterborne poly(urethane-urea) dispersions (PUDs) are colloidal systems consisting of hydrophobic poly(urethane-urea) (PU) particles dispersed in a continuous water phase. The stabilization of the particles is generally achieved by surface hydrophilic moieties of short internal emulsifier covalently bonded in the PU chains, the most common is 2,2-bis(hydroxymethyl)propionic or dimethylolpropionic acid (DMPA). DMPA contains two hydroxyls and one carboxylic group. During PUD synthesis, the two hydroxyls groups react with the di-isocyanate during prepolymer formation producing hard segments and, later, the carboxylic group is de-protonated by reacting with tertiary amine.

The structure of the PUD particles consists in soft and hard domains, and ionic interactions. The hard domains are produced by reacting isocyanate with DMPA, polyol and low molecular weight amine chain extender, and the soft segments correspond to the interactions between polyol chains; the ionic interactions are due to anionic carboxylate groups on the PUD particles and the quaternary ammonium cations in the water phase.

The most of previous studies have proposed the addition of DMPA before prepolymer formation, i.e., DMPA was mixed with the polyol and, later, the di-isocyanate was added. However, the stage at which DMPA is added, i.e., before, during or after prepolymer formation will change the structure of the PUD, but this aspect has been very scarcely studied, particularly its influence on the adhesion properties. Therefore, in this study, DMPA was added before, during and after prepolymer formation during the synthesis of PUDs, and, in order to assess their structure-properties relationships, their structural, thermal, rheological, viscoelastic and, particularly, the adhesion properties have been compared.

Materials and experimental techniques.

The PUDs were synthesized by using MEK (methyl ethyl ketone) prepolymer method, an NCO/OH ratio of 1.5 was used. The reactants were isophorone diisocyanate (IPDI), polyadipate of 1,6-hexanediol of molecular weight 2000 Da, 5 wt.% DMPA internal emulsifier, trimethylamine neutralization agent, dibutyltin dilaurate catalyst, and hydrazine chain extender.

The PUDs were characterized by pH, viscosity and particle size measurements, and the structure of the PU films was assessed by infra-red spectroscopy, differential scanning calorimetry, X-ray diffraction, thermal gravimetric analysis, plate-plate rheology and dynamic mechanical thermal analysis. The adhesion properties of the PUDs were measured by cross-hatch adhesion and T-peel test.

Results and discussion:

The stage of the synthesis at which DMPA is added should produce structural dissimilarities in the PUDs. Thus, the addition of DMPA before and after prepolymer formation (i.e., the reaction of the isocyanate and the polyol) should produce ordered DMPA-isocyanate hard segments as well as

polyol-isocyanate hard segments, but the distribution and length of the hard segments will be different. However, the addition of DMPA during prepolymer formation will produce random DMPA-isocyanate and polyol-isocyanate hard segments. Thus, depending on the stage of the synthesis at which DMPA is added, the structure of the hard segments and the degree of micro-phase separation of the PU will be different, the properties should be different too.

The lowest pH value and the highest mean particle size were found in the PUD made by adding DMPA after prepolymer formation. The highest viscosity and noticeable shear thinning were obtained in the PUD made by adding DMPA during prepolymer formation. Depending on the stage of addition of DMPA, the length of the prepolymer varied and the PU films showed different degree of micro-phase separation. Because the shortest prepolymer was formed in the PU made with DMPA added before prepolymer, this PU showed the lowest storage moduli and early melting indicating higher degree of micro-phase separation. The highest storage modulus, later melting, higher temperature and lower modulus at the cross between the storage and loss moduli corresponded to the PU made by adding DMPA after prepolymer formation, because the longer prepolymer produced during synthesis. The lowest thermal stability corresponds to the PU made by adding DMPA during prepolymer formation and the structures of all PU films were dominated by the soft domains, the main structural differences derived from the hard domains. Whereas DMPA-IPDI, urethane and urea hard domains were created in the PU made by adding DMPA during prepolymer formation, the other PUs showed DMPA-IPDI, polyester-IPDI and two different DMPA-IPDI-polyester hard domains. Finally, the adhesion properties of all PUDs and PU coatings were excellent and they were not determined by the structural differences caused by adding DMPA in different stages of the synthesis.

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10:00 – 10:30

Croda – Smart Materials

NL-Gouda

Tina Arbatan PhD



FUTURE HIGH-PERFORMANCE SOLUTIONS FOR ADHESIVES

In modern society the demand of smart and multi-functional adhesives is becoming continuously more important. Adhesives are an extremely versatile in use and suitable for high-demand applications as automotive and electronic industry.

But today the market is also requesting solutions that can reduce the carbon footprint and have a concrete sustainability benefit. Finding a reliable raw material able to provide performance and sustainability in one single solution is a major challenge.

Croda is a leading global solution provider of high-performance bio-based building blocks that provide a variety of smart effects and benefits in a wide range of polymer types and applications. Croda has a broad portfolio of 100% bio-based diacids and diols, polyols up to 100% bio-based and 100% bio-based dimer diamines. Among these, Pripol 2043 is the latest innovation Croda brought to the market: a higher functionality dimer diol for PU adhesive to help our customers to tackle this challenge.

The use of these products can support the formulators to modify adhesive systems, offering flexibility, extreme hydrophobicity, improved flow and low moisture absorption. Furthermore, a unique combination of improved adhesion to various substrates, including low-polarity substrates.

With our innovations we offer formulation freedom to the adhesive market, enabling new and exciting high-end applications for example in electronics, automotive and sportswear.

10:30 – 11:00

Bostik

Fr-Venette

Jean-Francois Chartrel*, Stefano Gherardi



NEW CRACKLESS PROCESS FOR CYANOACRYLATES PRODUCTION

For more than seventy years, Cyanoacrylates and particularly Methyl and Ethyl-Cyanoacrylate monomers have been produced via a process of condensation, cracking and distillation, following the Knoevenagel route.

With the “**New Crackless Process**” (Patent W0/2015/150882), Bostik has changed the game by creating a one step process, offering improvements in **Productivity** (*fast reactions, high yields, cost effective, ...*), **Quality** (*monomer purity, reactivity, stability, reliability with high a level of automation*

and process control,...) and **Sustainability** (low waste, no solvents, low energy consumption, lower CO₂ footprint).

Without aggressive thermal cracking, the new process gives access to an array of Specialty CA monomers and adhesives, allowing for:

Higher molecular weights (up to C18, proven as of today (solid product), but without real limit) resulting in **lower vapor pressures** (low odor and blooming) **More sophisticated structures offering specific properties** (flexibility, hydrophobicity, adhesion on low surface energy materials, crosslinkable with multifunctional CAs (ex: BisCA) ...) and **added functions** vs. standard CAs.

An enlarged product portfolio has been created with **new differentiated monomers** (formulation precursors for Cyanoacrylate(s), Acrylate Hybrids, Epoxy Hybrids, Silicone Hybrids, etc...) , **adhesives and coatings**, serving both standard and high-end markets: Electronic, Medical, Optical. These new formulations are adaptable to different processes & functionalities (1K, 2K, UV, dual cure), offering **friendly labelled products** and introduce **debonding behaviors** for recycling (*Tunable thermal debonding*).

11:00 – 14:00 NETWORKING

14:00 – 14:30

Fracture Analytics

A-Mörbisch am See

Dr. Martin Brandtner-Hafner



A NOVEL HOLISTIC EVALUATION SYSTEM FOR RATING ADHESIVE BOND SAFETY AND PERFORMANCE

Adhesives are already in use in the most diverse industries. Their flexibility allows them to occupy ever newer areas of joining technology. However, a look at industrial practice shows that there are no holistic evaluation methods available to assess the failure behavior of adhesive composites authentically. Furthermore, there is an almost unmanageable mix of possible external parameters that could be considered influencing bond performance and safety. To handle such challenges, a specially developed mathematical evaluation algorithm was utilized. It incorporates the relative performance of a distinct set of adhesives under consideration by a predetermined set of inputs and outputs. With that, a novel adhesive performance index (API) was created to focus comprehensive informational value for adhesive evaluation into one single metric. Next, comparable peer groups were formed from which an authentic adhesive rating was derived. Finally, a case study on different adhesive systems from SIKA and MUREXIN demonstrated the efficacy of this novel rating technique. Decision-makers are thus given the opportunity to optimize their choice of adhesives under different conditions and boundaries.

Keywords:

Evaluation System, Adhesive Bond Safety, Adhesive Bond Performance, Adhesive Performance Index, Bonding Process, Adhesive Rating, Selection Support

14:30 – 15:00

M&M Network-ING

DE-Mainz

Dr. Michael A. Kraus*, Dr. Michael Drass



SEMI-PROBABILISTIC DESIGN OF SILICONE ADHESIVE JOINTS USING NOVEL FAILURE CRITERIA AND A MESH-INDEPENDENT FEM APPROACH

This presentation deals with the semi-probabilistic design of structural silicone sealants acc. to EN 1990 (Eurocode 0) and introduces a new Eurocode-conform design concept for verification of silicone bondings for a stretch-based limit state equation. A short repetition section delivers background on semi-probabilistic modelling and the general framework for deriving partial material safety factors at a level I stage for structural sealants. Afterwards, the new concept is compared to the current international (ETAG002) legal situation for designing with structural silicone sealants in façades. Then

the specific material partial safety factor (MPSF) for DOWSIL 993 silicone using existing experimental data, obtained under the ETAG 002 testing protocol, is determined for a stretch-based failure criterion. A subsequent section deals with the specific requirements of a finite element based static verification of design limit states analysis using the MPSF within a semi-probabilistic design to reach a mesh-independent structural verification computation. A Structural Sealant Glazing (SSG) example illustrates the new concept and enables comparison of different design approaches. This research found, that the correct level I calibration of a MPSF for structural silicones leads to significantly lower MPSF values compared to currently existing estimates. This allows for a great optimization of structural sealant design situations with potentially high economical as well as ecological / sustainability gains in the future. As this is a reliability- and mechanics-based approach, the methodology can easily be transferred to the automotive industry.

15:00 – 15:30



University of Kaiserslautern / AWOK-Workgroup

DE-Kaiserslautern

Franziska Zajonz*, Paul L. Geiss

USING HAND-HELD SPECTROSCOPIC ANALYSIS DEVICES FOR QUALITY ASSURANCE OF ADHESIVE BONDING PROCESSES

Glass is used in a wide variety of industrial sectors: In the automotive industry, in architecture (including photovoltaic/solar thermal or facade construction), in rail vehicle construction, in shipbuilding and in the furniture industry. Glass surfaces to be bonded have their own specific requirements for the adhesive and the surface pre-treatment. For safety-relevant bonded glass assemblies, clean surfaces and pre-treatment processes are crucial for the long-term durability of bonded joints. Therefore, there is a high demand for economical, process-integrated surface analysis methods that enable technical quality assurance and quality documentation of bonded glass joints. Surface analysis of glass for in-line and non-destructive quality assurance of cleaning and treatment processes are missed until now. With this background, the project aim is to provide a cross-industry quality assurance concept for glass bonding and validation of in-line capable surface-sensitive inspection methods. Hand-held spectroscopic analysis enables fail-safe resistant glass bonding by ensuring that the bonding surfaces are sufficiently free of contamination after cleaning and by detecting the effectiveness of adhesion promoters and primers.

15:30 – 16:00



IGB-tech GmbH

DE-Friedelsheim

Dr. Stefanie Wellmann

Abstract

Coming soon!
