Good news for your business

magazine

06/2020 DECEMBER/JANUARY

Interview: CPI personnel

African furniture market

Dry demoulding

Chemical recycling trends

Low VOC from PU foam

POLYURETHANES MAGAZINE INTERNATIONAL

Dr. Gupta Verlag

www.pu-magazine.com

Dry demoulding – practical demonstration of a mould coating with long service life

Sustainable thinking and acting is a constant driver of innovation in the polyurethane processing industry and is inherently applied in the development and implementation of future-oriented material and process technologies. Understandably, new technologies can succeed when they do not represent a step backwards in terms of robustness, flexibility and cost-effectiveness. In a German IGF cooperation (Industrial Collective Research) project at the Institute for Plastics Processing (IKV), Aachen, and the Fraunhofer Institute for Manufacturing Technology and Advanced Materials (IFAM), Bremen, the pilot plant readiness of a permanent release coating on a steel mould has now been demonstrated by consecutively demoulding more than 1,200 PU parts at constant low forces.

Prof. Dr.-Ing. Christian Hopmann[1]
Head of the Institute for Plastics Processing

Philipp Surray, M.Sc.[1]
Composites and Polyurethane Technology/ Research Associate
philipp.surray@ikv.rwth-aachen.de

Daniel Schneider, M.Sc.[1]
Composites and Polyurethane Technology/ Head of department

Dr. Peter Bitomsky[2]
Adhesives and Polymer Chemistry/ Research Associate

Dr. Michael Noeske[2]
Adhesion and Interface Research/ Research Associate

Dr. Klaus Vissing[2]
Plasma Technology and Surfaces/ Head of ND-Plasma Technology

[1] Institute for Plastics Processing at RWTH Aachen University Aachen, Germany
www.ikv-aachen.de

[2] Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM
Bremen, Germany
www.ifam.fraunhofer.de

All figures and tables, unless otherwise stated, have been kindly provided by the authors.

1 Introduction

In discontinuous polyurethane (PU) processing, demoulding of the cured components is a decisive process step, which, among other process parameters, determines the product quality. According to the current state of the art, an adequate selection of the release agent used is decisive for non-destructive demoulding of PU parts. Both external and internal release agents are used and, more rarely, thermoplastic inserts [1 – 3]. The systems ensure not only easy and non-destructive demoulding but also enable a high surface quality and increase process reliability, which guarantees a trouble-free process flow. However, these benefits are offset by various ecological and economic drawbacks. Non-permanent release agent films lose their effectiveness after just a few demoulding processes and must be reapplied [3]. In addition, upon film removal the release agent remains deposited on the component surface and contributes to a so-called mould build-up, a mixture of PU with release agent residues. This deposit accumulates on the mould surface over several component cycles and makes regular cleaning of the mould necessary, which is costly, time-consuming and energy-intensive [4]. In the production of high-quality components from visual surface applications mould cleaning is particularly frequent in order to ensure optically high-quality finishes.

On this basis, release agent-free demoulding with permanent release coatings represents a promising alternative to conventional demoulding technologies, because non-destructive and smooth component removal can be implemented permanently without the need for additional application or cleaning intervals. In an IGF joint research project that was successfully completed in July 2020 the

▼ ***Tab. 1:*** *Release behaviour of PU systems with different catalysts in ten consecutive demouldings*

Catalyst		Number of demouldings									
Type	Parts by weight	1	2	3	4	5	6	7	8	9	10
DBTDA, Dibutyltindiacetate (Sn)	0.05	3	3	3	5	6					
DBTL, Dibutyltindilaurate (Sn)	0.35	2	2	3	3	6					
Dibutyltindichloride (Sn)	0.2	1	2	4	4	3	5	6			
Dimethyltin mercaptide (Sn)	0.04	2	2	3	3	4	6				
Dimethyltindineodecanoate (Sn)	0.03	2	2	3	2	5	6				
Dimethyltindioleate (Sn)	0.03	2	2	3	4	6					
Dioctyltin dithioglycolate (Sn)	0.16	2	1	1	1	2	1	2	2	3	6
System: Bismuth tris(2-ethylhexanoate) (Bi), Zinc bis(2-ethylhexanoate) (Zn)	0.04	2	1	1	1	1	1	1	1	1	2
Zirconium chelate (Zr)	2.90	2	2	2	4	4	4	4	4	5	5
Aluminium chelate (Al)	5.90	1	1	1	1	1	1	1	1	1	2
Potassium ethylhexanoate (K)	0.69	1	1	1	1	1	2	1	1	1	1
Potassium acetate (K)	0.48	2	2	2	2	2	2	5	5	6	
Release behaviour from very good (1) to very bad (6)	non-destructive release with no effort / non-destructive release with little effort	non-destructive release with moderate effort			destructive release, few residues		destructive release, many residues			no release	

release behaviour of a plasma polymer release coating for PU processing developed at Fraunhofer IFAM was investigated, primarily assessing impacts of the curing catalyst used in the PU system.

A first set of project results focusing on demoulding behaviour and a mould technology adapted to release agent free production of PU parts was presented in a previous issue of this magazine [5]. It was highlighted that organic amine catalysts are highly compatible with the release coating in terms of low release forces. In contrast, the interim results using the example of dibutyltin dilaurate (DBTL) raised the question of whether the new mould coating under consideration is generally incompatible with tin-containing and possibly other organometallic catalysts. Based on the presented project contents, this article deals with validating further catalysts with regard to a positive demoulding behaviour and with establishing a laboratory method to qualify the compatibility with the mould coating. Moreover, durability of the latter using three commercial PU systems in a production-related mould technology adapted for this purpose was investigated. In addition to the required demoulding forces, the detailed forming of microstructured mould surfaces was used as a quality criterion for permanently good demoulding.

2 Experimental

2.1 Influence of organometallic catalysts on the demoulding behaviour

In order to classify the previously mentioned incompatibility of DBTL with the permanent release coating, additional organometallic catalysts were investigated **(tab. 1).** The selected organometallic tin catalysts vary in their activity upon driving the curing reaction that yields the finished PU system. This graded performance is interesting with regard to a possibly differential interaction with the release coating. In order to clarify whether other organometallic catalysts prove to be incompatible, the scope of testing was extended to include bismuth, zirconium, aluminium and potassium catalysts.

Laboratory-scale detachment tests involving PU systems with the different additives were carried out by adding one of the catalysts to a catalyst-free basic PU system for completing the formulation. The composition of the formulations is shown in **table 2.**

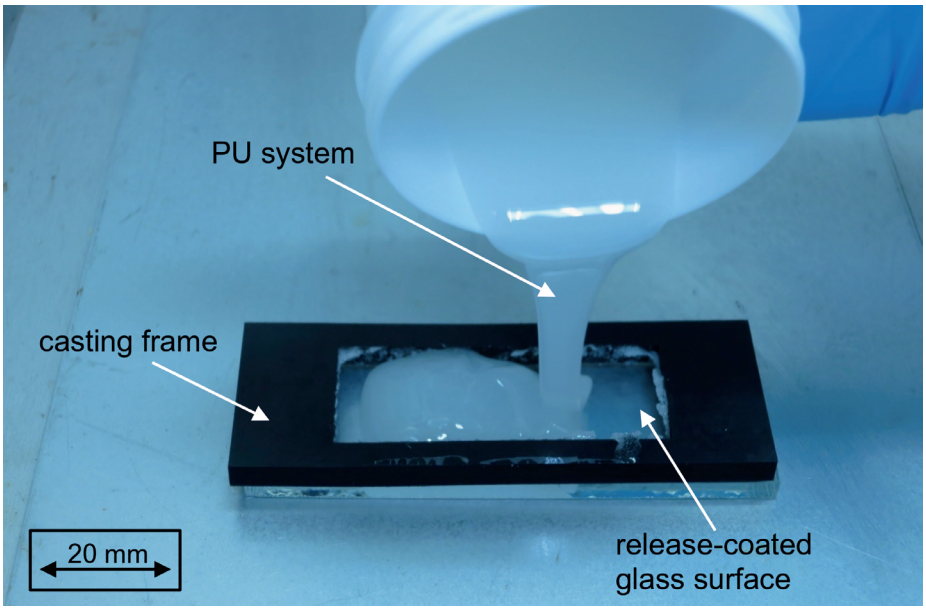
▼ ***Tab. 2:*** *Basic PU system for testing the suitability of different catalysts*

Ingredient	Parts by weight	Remark
Baygal K55	100.00	polypropylene glycol (trifunctional polyol)
Sylosiv A 300	4.00	zeolite (drying agent)
Catalyst	0.03 to 5.9	
Desmodur VP 20RE10	86.30	aromatic polyisocyanate (MDI-based)

Since the catalysts are differently active, the proportions added for completing the basic PU system vary. In preliminary tests, they are determined in accordance with the thread-pulling time in order to raise the reactivity of the formulations to a comparable level. The target time lies between one and three minutes. The determined catalyst portions are usually added to the polyol component and premixed at room temperature. In contrast, the zirconium catalyst is added to the polyisocyanate component. Subsequently, hardener and resin are mixed at room temperature and then poured onto a release-coated glass plate (4 x 8 cm^2) the temperature of which was adjusted to approx. 80 °C using a heating plate. **Figure 1** shows a test setup designed for this purpose. In addition to the release-coated glass plate, this setup comprises a loosely mounted rubber profile that serves as a frame and, having a height of 5 mm, defines the maximum sample volume.

After a dwell time of 10 min, the hardened PU specimen is manually separated from the coated glass. The force required for this detachment is subjectively evaluated and classified following a score that ranges from "(1), very easily detaching" to "(6), not removable". Casting, curing, detachment and evaluation are repeated ten times on the same release-coated glass surface, unless the test specimen has turned out not to be removable. To ensure that a poor peel-off result is not due to insufficient curing going along with a significant surface stickiness of the test specimen, the degree of curing is monitored by infrared (IR) vibration spectroscopy. If necessary, the test series must be repeated at longer dwell times or higher interface temperatures until a sufficiently high reactive conversion is achieved. For each test series and catalyst, a maximum of ten PU test specimens and the corresponding release-coated glass sample are available for further surface analytical in-

▼ ***Fig. 1:*** *Test setup for manual evaluation of catalyst influence on PU demoulding behaviour*



vestigations with regard to different surface species using X-ray photoelectron spectroscopy (XPS). **Table 1** shows the results of the individual test series, which include up to ten separation steps.

In addition to dibutyltin dilaurate (DBTL), all other tin catalysts also show a negative separation behaviour going along with a high effort for releasing the cured PU part. The results also correlate with the detection of tin species on the corresponding interface surfaces by surface analytical XPS investigations. However, a general incompatibility of organometallic catalysts with the interface is not observed, especially since a catalyst system comprising bismuth and zinc compounds did not show any negative effect. Positive separation results were also obtained with an aluminium catalyst, while the potassium types described above repeatedly showed an indifferent behaviour. The molecular cause for this finding has not yet been clarified.

to a small extent within the release layer [6]. By comparison with the tin coverage obtained when immersing surfaces with a defined and high silanol content, such as quartz glass, the binding via silanol groups could be established. In contrast to the low surface concentration of 0.05 atomic percent (at %) tin detected on the release layer, the chemisorption of 0.48 at % tin on quartz glass is significantly higher. The presented results help to improve the understanding of the different catalyst influences on the release behaviour from the coating. On this basis, we infer that further optimizing the release coating may prospectively facilitate that even tin-organic systems can be easily demoulded permanently.

2.2 Mould technology and pilot plant runs

Based on the initial laboratory tests, the use of permanent release coatings was validated for approved PU systems under process-related conditions. The main objective was to characterize the durability of the coating for exemplary commercial PU systems. In order to demonstrate the release agent-free component production for a variety of PU applications, a PU clear coat, a compact casting system and a water-blown flexible foam formulation were selected. For the investigations, the commercially used catalysis of the systems was used and is shown in **table 3.**

▼ ***Tab. 3*** *Overview of commercial PU systems used in pilot plant runs*

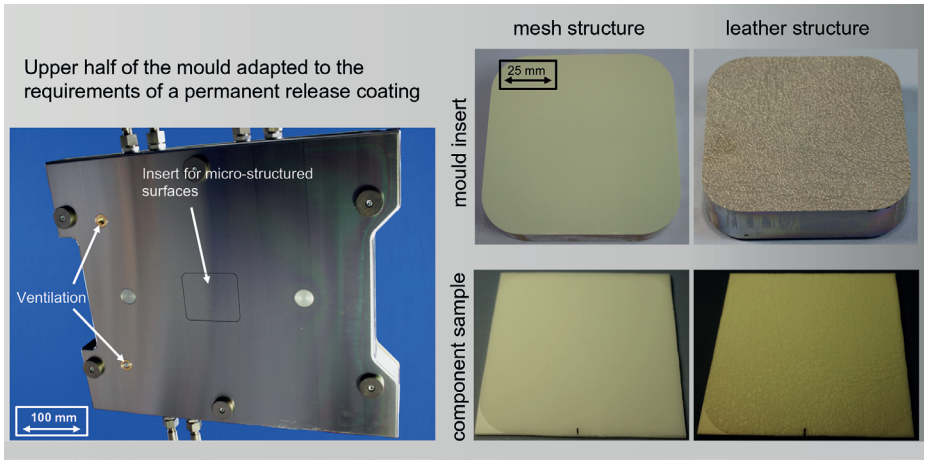
Material	Supplier	Application	Catalyst base
Clear coat	Votteler Lackfabrik GmbH & Co. KG	RIM-coating of wooden and plastic parts	Approved bismuth system [tab. 2]
Casting system	Plixxent GmbH & Co. KG	Non-cellular RIM-applications (e.g. furniture)	Approved amine system [5]
Flexible foam (waterblown)	Rühl Purometer GmbH	Sound-insulating PU-components	Approved amine system [5]

The interaction of a mould surface with tin catalysts, on the other hand, could exemplarily be elucidated for DBTL by performing submersion tests of release-coated glass substrates in solutions of the catalyst. The tin species detected later on adhered to the coated glass in the form of stoichiometric chemisorbates and could not be removed by solvent extraction. The differentiation between physical and chemical interaction is relevant, because chemisorbates bond tightly to surfaces and make them resistant to cleaning. In case of immobilised PU catalysts, they form undesirable back bonds towards the PU material and cause an adhesion-promoting effect. The reason for the surface bonding is considered to be a specific interaction between tin catalysts and silanol (Si-OH) groups, which are present

For the investigations, a mould adapted to the requirements of release agent-free component production was used [5]. The mould is characterized by an opening mechanism that provides a peel geometry and reduces reduces the demoulding stress on the component and coating. All components contacting PU, including the employed profile seal, were supplied with the plasma polymer coating before the tests were started. An exchangeable insert cantered in the upper half of the mould allows different surface structures to be tested. In addition to a coarse leather texture with a maximum structure height of 250 µm, which is in demand for automotive applications, a fine and regular mesh structure was used. The mesh structure consists of a uniform arrangement of homogeneous pins with a pin diameter of 250 µm and a height of 125 µm. The centres of consecutive pins are 250 µm apart **(fig. 3).** On the base of an unstructured withdrawable insert, the durable integrity of the coating surface was monitored by microscopic examinations. The surface analyses were carried out with a laser scanning microscope (LSM). **Figure 2** shows the inserts used and their position in the upper half of the mould.

For the systematic evaluation of the durability of the release coating, which was flexibly contacted with approved compatible PU systems, and for the analysis of the surface structures, PU plates with a thickness of 2 mm were produced from both the clear coat and the compact casting system and then demoulded. While the mould insert was exchanged at a time after performing additional 100 demouldings for being inspected the surrounding mould surface was not changed during the overall demoulding series. For the production of flexible foam plates, the height of the mould cavity was increased to 10 mm by replacing the base plate. At a time after having realized another 50 demouldings, two test specimens with an area of 10 x 10 cm^2 were removed from the PU-plates. Using these test specimens, the component surfaces were examined by means of LSM at the position of the mould insert and at an adjacent, unstructured position. For all samples, three images were taken at 200-fold magnification in an area of 500 x 705 μm^2. The use of a coordinate system ensures that the images were always taken in the same surface region. Comparison among the LSM images obtained in the course of the demoulding test series is devised to identify potential microscopic material build-up caused by local failure of the

▼ ***Fig. 2:*** *Upper mould section (left) and different microstructured mould inserts (right)*



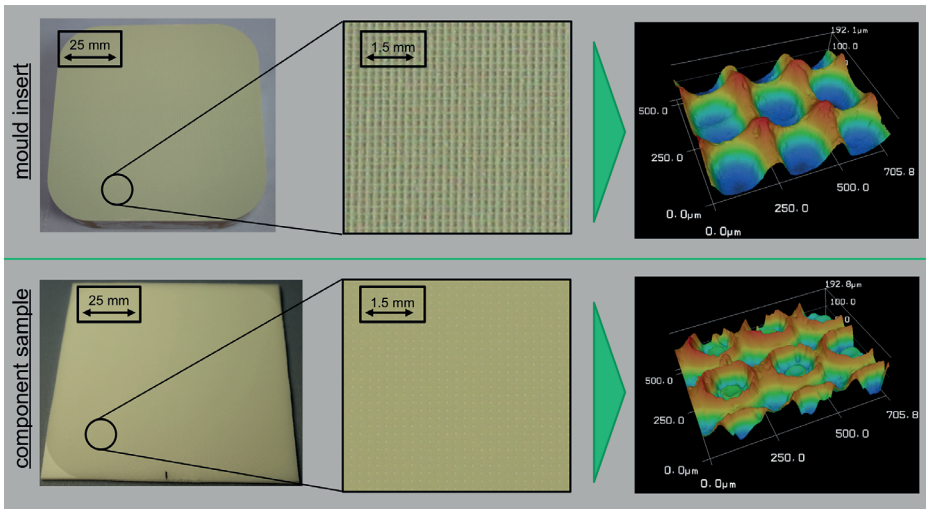
release coating function and leading to a topographic change of the surfaces. In this way, the service life of the coating can be recorded systematically and traceably.

2.3 Application of the mould coating under industrial conditions

During the demoulding runs in the project, a total of 1,200 plates were produced with a single coating. Initially, 500 plates were made with the clear coat PU formulation, then 500 plates with the compact casting system and finally 200 parts with the flexible foam system. During and after the 1,200 demouldings, no perceivable reduction of the release performance was observed based on the demoulding behaviour. Subsequently, the analyses for the two compact PU systems are discussed. The surfaces of the flexible foam plates are not considered further at this point because their properties are strongly influenced by the pin structure due to the thin foam skin and the findings are therefore not comparable with those of the compact systems.

By means of the comparably fine mesh structure, the limits of the impression behaviour are investigated using the permanent release coating. The comparison of the insert with the texture of an exemplary PU component specimen after 200 demouldings shows that the pin structure is reproduced in the micrometer range **(fig. 3).** The moulded pins show a similar geometry compared to the insert structure with a pin diameter of 250 µm. With the mould filling strategy applied, sinks result on the upper side of the pins with a depth of 30 µm to 50 µm. The shape of this reproducible sink pattern can be controlled by varying the cavity pressure, which allows the haptic impression to be adjusted. Similar results were obtained for the comparably coarse leather structure. The structure was reproducibly moulded in detail over 200 demouldings. In the course of the investigations, no change in the release behaviour was observed here either. The performed investigations show that both coarse structures with haptic features and fine structures with a pin diameter of 250 µm can be permanently reproduced by means of a permanent release coating. Thus, a transfer to large-scale technical applications is feasible.

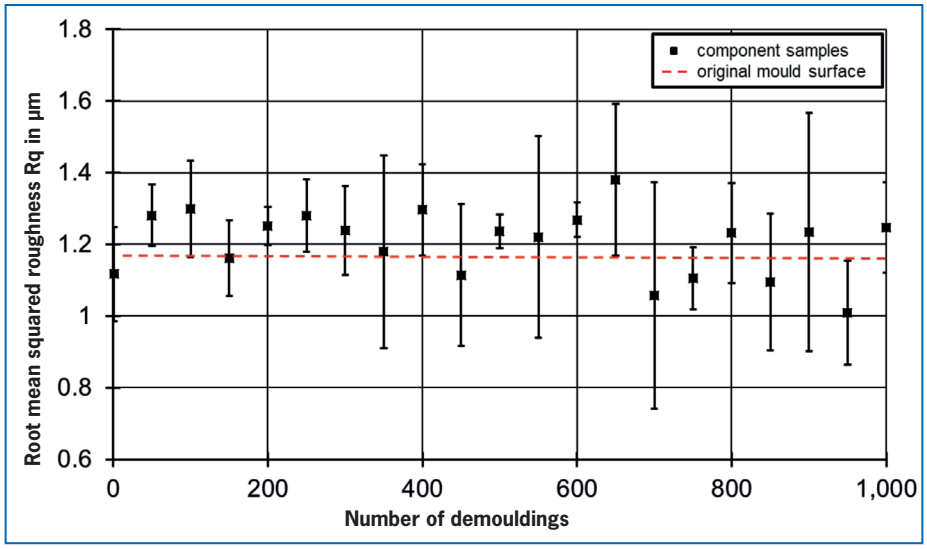
▼ ***Fig. 3:*** *Photo, detailed view and LSM image of a mould insert and a demoulded component sample with a fine-mesh surface structure*



The structured mould inserts were exchanged at regular intervals, so that a quantitative analysis of the durability of the release coating was carried out by comparing the unstructured mould surface with the corresponding surfaces of 20 PU components in the course of 1,000 demouldings. As a comparative parameter for monitoring the durability, the root mean squared roughness Rq providing the average amplitude in height direction was chosen. The development of the surface roughness of the PU components in the course of 1,000 demouldings compared to the pristine mould surface is shown in **figure 4.**

The dashed characteristic line at Rq = 1.16 µm in **figure 4** indicates the root mean squared roughness of the smoothened unstructured mould insert after its coating. As can be seen from the graph, the Rq roughness value is always close to the dashed characteristic line for all measured component samples and corresponds to the roughness of the pristine mould surface. Furthermore, the roughness does not increase during the demoulding tests, while an increase would indicate microscopic material residues on the mould surface. It is concluded that, as already observed on the macroscopic level, there is no failure of the release coating on the microscopic level neither. For assessing the influence of the flexible foam system on the re-

▼ ***Fig. 4:*** *Root mean squared roughness Rq of the unstructured mould surface and the component surfaces in the course of 1,000 demouldings*



lease coating as well all foam plates were produced with the unstructured insert and the mould surface was examined at the end of the tests. No material residues whatever were detected and the average roughness did not change significantly with a value of 1.19 µm.

2.4 Economic and ecologic factors of an industrial mould coating

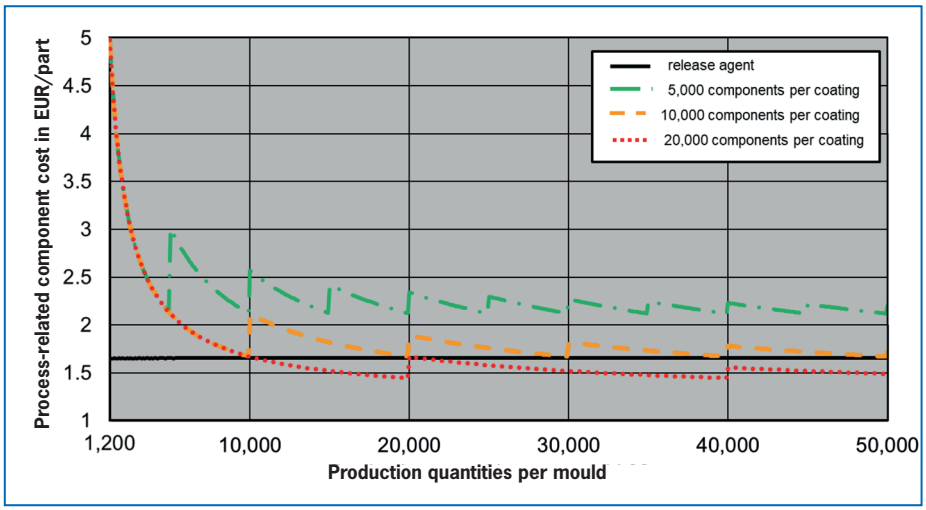
Permanent release coatings have been investigated in polyurethane processing for many years. Permanent solutions and the elimination of release agents allow a significant increase in process efficiency. For instance, expenditures like regular release agent applications, both mould and component cleaning or even safety devices for emission control when using release agents become obsolete. In this way, all pillars making up a sustainable process are covered and fortified. The elimination of energy-intensive cleaning steps supports a significant reduction of CO_2 emissions.

One example of use is the production of damping parts from a PU flexible foam on a rotary machine with ten moulds and a high-pressure dosing unit. The annual output is 160,000 parts with a cycle time of 450 s. The release agent formulation consumed per component amounts to 125 g. The costs for the release agent are 2.88 EUR/kg. Approximately 15 s are required for the application of release agent. The treated surface must then be ventilated for 60 s so that the solvents present in the formulation can evaporate. Due to the resulting build-up on the mould surface, the moulds are thoroughly cleaned with dry ice in intervals of four to five days. The costs for the cleaning agent and cleaning staff are 16.23 EUR/mould.

For the release agent-free process, the costs and process times for release agent application and mould cleaning are eliminated. However, the economic efficiency of a release coating is largely determined by its lifetime varying from application to application. When a decrease in release performance is observed, the moulds are disassembled and transported to a service provider for re-establishing the coating. Costs for transportation and coating are 4,490 EUR/mould and coating. Depreciation costs for equipment such as the dosing unit or moulds are identical for both production scenarios and are not considered any further in the subsequent comparing examination. A cleaning of the manufactured components from release agent residues, which in individual cases is necessary for subsequent processes and cost-effective, was not considered here. Based on the data presented, an economic comparison of the conventional release agent-loaded process and its release agent-free alternative is made for three different reestablishment intervals corresponding to three lifetime scenarios supposed for the mould coating. **Figure 5** shows the process-related component costs as a function of the production quantities of one mould in the rotary machine.

For the PU production scenario under consideration, the process-related component costs for the conventional process with release agent are slowly increasing from EUR 1.59 to EUR 1.65 due to the regular cleaning cycles for every 300 components produced. In contrast, the costs for the release agent-free process start from a high level and decrease asymptotically with increasing production quantities down to the limit of EUR 1.22 per part. The re-occurring costs for the mould coating lead to the formation of a sawtooth curve for the three reestablishment intervals under consideration. With increasing number of components produced with one coating the

▼ ***Fig. 5:*** *Economical comparison of conventional and release agent-free PU production in an exemplary scenario*



respective costs drop significantly. In **figure 5,** the break-even point is reached after 10,000 demouldings for a re-coating interval of at least 20,000 parts for the considered production scenario (red curve). Even though the calculative component costs increase again following the first re-coating, the calculated threshold is not exceeded anymore. In addition, it should be highlighted that the release agent-free process allows a higher annual output of 19,200 components per mould, compared to 16,200 components produced in the conventional production due to the increased process efficiency. The process-related component costs are thereby reduced by 12 % to EUR 1.45. This favourable economic balance comes along with the indicated ecological and sanitary benefits.

Nonetheless, in this exemplary scenario, at least 20,000 components must be reliably demoulded with a release coating in order to be used cost-effectively. Since a coating service life of at least 1,200 demouldings has already been determined on a pilot plant scale, the coating is expected to have a sufficient service life to enable sustainable PU production.

3 Conclusion and outlook

In the present work, pilot plant readiness was successfully demonstrated for a permanent release coating. A series comprising 1,200 demouldings was carried out with different PU systems without observing any deterioration of the release properties. The release coating is as effective as on the first day, no wear and tear was observed. The previous approval and selection of a suitable catalyst system proved to be ground-breaking for this success, as laboratory tests have shown that the adequately selected catalysts of the PU systems in particular are decisive for permanently good demoulding behaviour. A large number of different amines and organometallic catalysts are highly compatible with the release layer; they were approved by detachment tests in laboratory scale. However, a release of PU parts cured with organotin catalysts did not work, rather a negative release behaviour with high forces was observed. This is attributed to a specific interaction between the tin catalysts and trace amounts of silanol groups within the release coating of the mould in the pilot plant. The established understanding of this behaviour is an important prerequisite for the further optimization of the coating.

Furthermore, the industrial relevance of the release layer performance was shown in comparison to conventional demoulding methods. In this context, especially the moulding of structured surfaces offers interesting application perspectives. Coarse patterns as well as very fine microstructures down to the micrometre range were reproducibly well implemented. Based on the results, it is expected that even high-gloss surfaces can be permanently reproduced in highest quality. Economic considerations implying miscellaneous industrial examples show that a coating life of ten thousand to a few hundred thousand demouldings justifies industrial use.

With the proof of long service life, low demoulding forces [7, 8] and versatile application possibilities in PU processing, the foundation has been laid for transferring release agent-free component manufacture to industrial series production. The application of this new technology represents a substantial and sensible intervention in the production chain. This innovation requires a lot of trust and long-term commitment from the companies, which is rewarded with economic, ecological and operational safety advantages promoting sustainable production.

4 Acknowledgments

The research project IGF 19967 N of Forschungsvereinigung Kunststoffverarbeitung and DECHEMA was sponsored as part of "Industrielle Gemeinschaftsforschung (IGF)" by the German Federal Ministry for Economic Affairs and Energy (BMWi) due to an enactment of the German Bundestag through the AiF. We would like to extend our thanks to all organizations mentioned.

5 References

[1] Kübler, M., 2010, Verfahrensentwicklung zur Herstellung gebrauchsbeständiger kleinstrukturierter Kunststoffbauteile, Berlin, Technische Universität Berlin.

[2] Heisler, P., Gick, S. G., Franke, J., 2018, 4th International Conference on Control, Automation and Robotics (ICCAR), Auckland, 2018, p. 116 – 120.

[3] Meyer, F., 2011, Schäumen ohne Trennmittel, FAPU, 69 (6), p. 36 – 38.

[4] Defonseka, C., 2013, Practical guide to flexible polyurethane foams. Shawbury: Smithers Rapra Technology Ltd, 1st edition.

[5] Hopmann, C., Surray, P., Schneider, D., Vissing, K., Noeske, M., Bitomsky, P., 2019, PU Magazine International, 16 (4), p. 232 – 235.

[6] Brenner, T., 2017, Struktureigenschaftsbeziehung von chemisch gleichartigen plasmapolymeren Trennschichten mit stark variierendem Elastizitätsmodul. Unpublished master thesis, University of Bremen.

[7] Schöldgen, R., Holz, C., Vissing, K., Bitomsky, P., 2014, Permanent trennend – neue Strategien zur Entformung reaktiver Polyurethane, FAPU, 85 (5), p. 35 – 38.

[8] Hopmann, C., 2014, Trennfreundliche PUR-Systeme durch Interphasenkontrolle. IKV, RWTH Aachen, Abschlussbericht zum IGF-Forschungsvorhaben Nr. 437 ZN.

Bundesministerium für Wirtschaft und Energie

Publication information & contacts

Dr. Gupta Verlags GmbH
Am Stadion 3b,
40878 Ratingen

CEO Hans Langohr

Amtsgericht Düsseldorf HRB 79922
VAT No. DE 314055034

Tel. +49 2102 9345-0
Fax +49 2102 9345-20

E-mail info@gupta-verlag.de

Internet www.pu-magazine.com

Editors
Dr. Wolfgang Friederichs (WF)
(Editor-in-Chief)
Dr. Isabella Kappner (IK)
(Deputy Editor-in-Chief)
Dipl.-Biol. Markus Linden (ML)
Robert Müller (RM)
Dr. Christine Rüdiger (CR)
Dr. Stephanie Waschbüsch (SW)

† Dr. Heinz B. P. Gupta

Freelancers
Angela Austin (AA)
Denis Hicks (DH)

Editorial office
info@gupta-verlag.de
Tel. +49 2102 9345-0

Advertising
ads@gupta-verlag.de
Tel. +49 2102 9345-12

Subscription
service@gupta-verlag.de
Tel. +49 2102 9345-12

Layout + Printing
D+L Printpartner,
Schlavenhorst 10, 46395 Bocholt,
Germany

Frequency of publication
6 issues / year
Post distribution no. 66226
ISSN 1864-5534

Bank accounts
Deutsche Bank
IBAN DE49 3007 0024 0729 0729 00
BIC DEUTDEDBDUE

Commerzbank
IBAN DE33 3004 0000 0859 3915 01
BIC COBADEFFXXX