Technical Articles

Permanent release coatings – new strategies for demoulding reactive polyurethanes

The use of traditional release agents for processing PU materials has a number of disadvantages. For this reason, new strategies are being pursued to develop permanent release coatings for a wide variety of applications. Significantly reduced demoulding forces can be achieved by adapting the PU formulations and in particular by the customized use of additives in reaction mixtures. Optimal adaptation of PUR formulations results in no PU deposits or additive residues on the coated mould surface.

Introduction

Reactive polyurethanes have a high tendency to adhere to metallic surfaces. For batch production, release agents must therefore be used to guarantee an efficient process. Release agents are needed in order to remove moulded PU parts from metal moulds efficiently, quickly, and without damaging the surfaces. In industry, internal and external release agents are generally employed. However, this often results in the transfer and adhesion of release agents to the mould and component surfaces. This means extra work steps and higher production costs. For example, prior to coating or bonding, the PU parts have to be thoroughly cleaned to remove release agent residues. In addition, release agent residues build up on the surfaces of moulds during the course of several demoulding cycles, leading to increasingly poor demoulding. To ensure high product quality, the moulds must be cleaned at regular intervals.

In order to avoid these drawbacks, a variety of permanent release films having different molecular structures and applied in different ways have been developed in recent years [AHR01]. The low surface energy and non-polar character of these films mean they should theoretically have very good release properties [HM10]. In practice, however, the currently available release coatings have inadequate release properties and long-term stability and cleaning and recoating of the moulds is still required. Permanent release coatings that are currently available still have drawbacks for PU processing and their industrial use is not widespread.

Failure mechanisms for permanent release films

It has been demonstrated that the demoulding properties of reactive polyurethanes on permanent release films are highly dependent on the PU formulation being used. Failure of the release effect is due to nano-sized deposits on the release film surface. These build up over the course of just a few demoulding cycles and increase the adhesion forces. The deposits form during demoulding due to the fact that besides the desired adhesive fracture (between the component and mold surface) there is also cohesive fracture (in the interphase - the near-surface boundary layer) (Figure 1).

This interphase arises because the curing of reactive polymers is influenced by the boundary to the metal substrate [DBFP04, Weh08]. The mobility of the molecules in the non-cured state is restricted: Attractive or repellent interactions, for example due to polar or apolar groups, change the composition and reduce the reactivity. The chemical structure and molecular dynamics in the interphase are ultimately dictated by a complex interplay of various, and in some cases competing, physical and chemical processes.

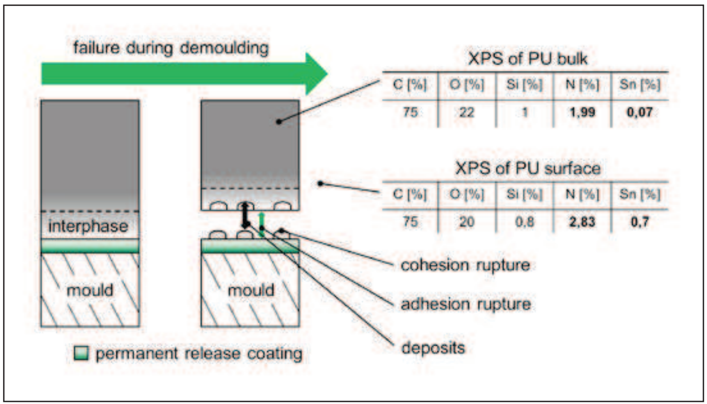

Figure 1: Effect of the interphase on failure of the release film

It has been demonstrated by x-ray photoelectron spectroscopy (XPS) that PU formulations in particular develop an interphase at the component surface that has a different chemical composition to the component bulk (Figure 1) [Mic11]. Also the rate of curing in the interphase and in the component bulk differs. Of particular relevance for PU processing is that the demoulding forces depend on the degree of curing of the interphase. It is generally desired to demould the component as soon as possible, meaning the degree of curing near the surface is often unknown.

Objective and approach

The objective of this work is to improve understanding of the factors that affect interphase formation and to customize this to develop lasting and effective release properties for PU formulations. There is a need to avoid the mixed fractures (adhesive fracture and cohesive fracture) that commonly occur in the interphase when using the currently available release systems. These lead to a build-up of deposits on the mould surface and consequent impairment of the release properties. The demoulding properties must be customized such that there is pure adhesive fracture between the PU component and a permanent, low-energy release coating on the mould.

In order to achieve this objective, a joint research project was undertaken by the Institute for Plastics Processing (IKV) at RWTH Aachen University (Aachen) and the Fraunhofer Institute for Manufacturing technology and Advanced Materials IFAM (Bremen). Two different approaches were pursued to improve the demoulding properties of a permanent release coating (ReleasePLAS developed by Fraunhofer IFAM). The first approach involved evaluating the effect of the PU formulation on the interphase by systematically varying the polyol, isocyanate, and catalyst contents. The second approach involved modifying the interphase of the PU component using surfactants to provide a sufficiently high cohesive strength for the demoulding process.

The experiments were first of all carried out under laboratory conditions. This involved applying a reaction mixture, using a manual moulding procedure, to a coated silicon wafer for curing. After demoulding, the almost ideally smooth wafer and PU surfaces allow the release behaviour to be characterized using surface analysis techniques. Following the laboratory experiments, selected PU formulations were evaluated under practical conditions using high-pressure dosing equipment. The test mold was equipped with integrated technology to measure the adhesion between the component and release film surface by means of moveable stamps (Figure 2). The spherical front of the stamps that comes into contact with the PUR material has a diameter of 30 mm and a surface area of 707 mm^2.

Effect of the formulation composition

As the chemical structure of PU has a major influence on the adhesion between the component and coated mould, additive-free model systems of known composition were selected based on systems used in practice. Exclusively compact systems were used. This meant there were no undesired side-reactions due to foaming. Also, the effect of surface-migrating substances could be seen with compact systems. Based on a simple model formulation of just polyol, isocyanate, catalyst, and drying agent, the nature and concentration of the components were systematically varied. Due to the large number of formulations that were tested, only the following summarizing statements are given here:

The use of polyols of high equivalent weight improves the demoulding properties. A high equivalent weight requires a relatively small amount of isocyanate in the formulation, leading to a low urethane concentration in the component, which lowers the adhesion. The use of polyols with primary OH groups as opposed to polyols that contain

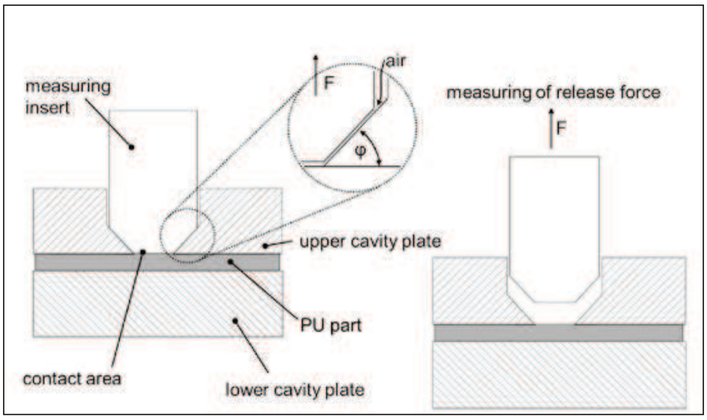

Figure 2: Quantitative adhesion measurement for molds

some secondary OH groups also considerably improves the reactivity and demoulding properties. Conversely, increasing the functionality of structurally similar isocyanates (trifunctional instead of bifunctional) leads to poorer demoulding properties. It is assumed that this is due to steric hindrance and to the poorer reactivity of trifunctional, polymeric isocyanates compared to bifunctional, monomeric isocyanates. The catalyst has a significant effect on the demoulding properties, even though no general statements can be made here.

These findings were then verified under near-industrial processing conditions by quantitative measurement of the adhesion forces. Customized formulations based on bifunctional MDI, trifunctional polyether polyols, an amine catalyst, and a molecular sieve had excellent demoulding properties that did not worsen even after several demoulding cycles. The adhesion (demoulding) force of model formulation 1 was in the range of ca. 10 – 30 N (0.014 – 0.042 MPa). The effect of the polyol on the demoulding properties is clear from the results for model formulation 2. Using a polyol with a higher share of secondary OH groups considerably increased the demoulding forces to values over 400 N (0.566 MPa), with the values tending to become larger with the number of demoulding cycles (Figure 3).

The presence of residues on the surface of the release coatings after ten demoulding cycles is the reason for this trend. Atomic force microscopy (AFM) showed that the extent of the nano-sized residues depends on the PU formulation that is used (Figure 4). Effective release systems require a pure adhesive fracture between the PU surface and release film surface, with no residues on the surfaces. It is only possible to confirm this on ideally smooth substrates (coated silicon wafers), because the roughness of metal substrates makes the detection of nano-sized residues impossible.

Based on these findings, an industrial system was formulated by Bayer MaterialScience AG, Leverkusen (Polyol: BAYDUR 80IK28/DO, Isocyanate: Desmodur SWE). The raw materials used were comparable to those used for model formulation 1, with the PU system meeting commercial requirements. Even after 50 demoulding cycles the adhesion force was low at a value of ca. 10-30 N (0.014–0.042 MPa) (Figure 3). As such, a long mould service life can be assumed. This showed that the laboratory results were also applicable for real industrial moulds and PU formulations.

Customized use of additives

Due to the fact that not all the formulations showed effective demoulding properties, additives were evaluated for their effect on the interphase. A screening was undertaken using surface-active compounds of differing chemical structure. Surfactants based on siloxanes with polar hydroxypolyether side chains were shown to give very good demoulding, even when present in low concentration (0.1 wt.-%), in

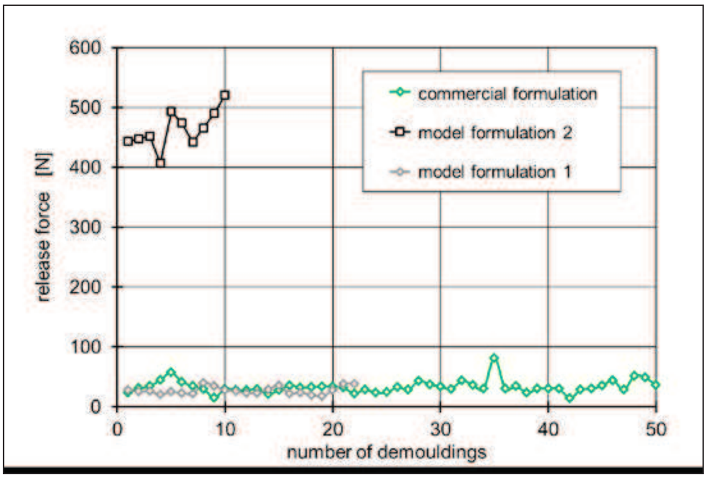

Figure 3: Effect of formulation composition on demoulding behavior

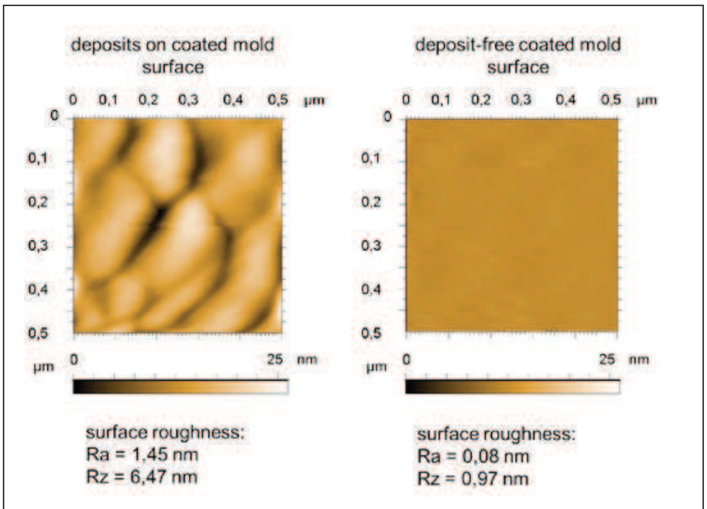

Figure 4: Release film surface after 10 demoulding cycles

the presence of the ReleasePLAS coating. This effect was even evident for formulations that could not be effectively demoulded without the use of these additives. As the additives increase the cohesion within the interphase, fully wet the component surface, and do not transfer to the release film, these additives fulfil all the requirements for improved demoulding behaviour. Additives without ambiphilic character, possessing solely apolar properties, did not have the same effect. In order to clarify whether the additives that gave positive results also function without release films, relevant blank samples were tested. The results were negative, indicating there is a synergy between the release film and the additive. An important result was that no transfer of the interphase or additive to the release film was detected using surface-analytical methods. This is due to chemical incorporation into the polymer network of the component.

The effect of the additives under near-practical processing conditions was then tested using model formulation 2. The addition of 3 wt.-% additive significantly lowered the adhesion force from ca. 430 N (0.608 MPa) to ca. 15 N (0.021 MPa), namely to ca. 4 % of the original value (Figure 5). It is noteworthy that the adhesion force of model formulation 2 with additive is even slightly less than the values achieved using external release agents on an uncoated surface (ca. 45 N or 0.064 MPa). Testing the additives with a commercial system (Polyol: EP 3417, Isocyanate: puronate 980; manufactured by Rühl Puromer GmbH, Friedrichsdorf) also showed that considerably lower amounts (0.1 wt.-%) suffice to improve the demoulding behaviour (Figure 5).

Release coating

In order to allow release agent free and transfer free production, the release coating must meet specific requirements. The key requirements of release films are as follows:
- High cohesion strength within the release film
- High adhesion of the release film to different substrates
- Low surface energy and a low polar fraction of the surface energy
- High thermal and chemical stability

Low film thickness (< 2 µm), high imaging precision of surface contours, and avoidance of blasting methods to improve adhesion are also very important.

ReleasePLAS coatings are suitable for release agent free PU production, provided their surface energy remains below 25 mN/m and the polar fraction of the surface energy is less than 1.5 mN/m.

Summary and outlook

Suitable PU formulations were selected and their formulations systemically varied in order to determine the effect on demoulding behaviour. Analysis of the release film surfaces showed that effective demoulding leaves a clean release film, with no deposits that can increase adhesion in subsequent demoulding cycles. It is assumed that a significantly more stable interphase forms.

An additive was also identified that improves the release behaviour of the tested PU formulations on ReleasePLASrelease film for difficult-

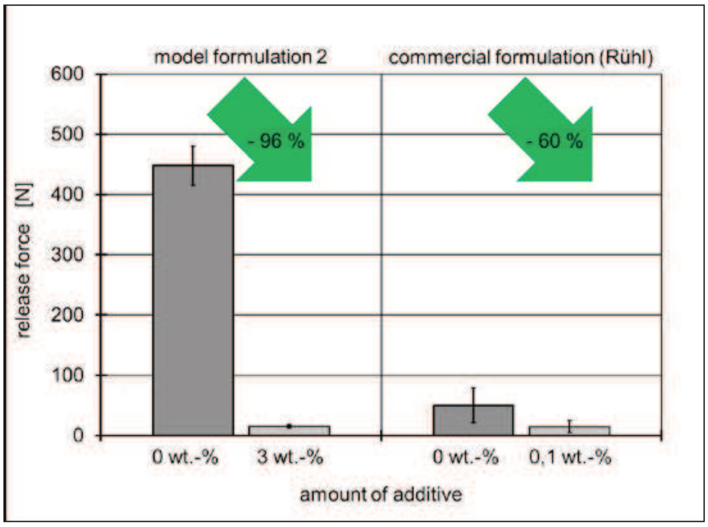

Figure 5: Effect of additives on demoulding behavior

to-release systems. The additive acts by concentrating in the interphase. It does not act like a conventional internal release agent because, according to current knowledge, it does not migrate out of the component. Rather, it becomes incorporated into the PU structure and it is thus assumed that its use would lead to considerably longer service lives for moulds.

Future projects will investigate the extent to which the new release systems can be used for PU materials in industrial practice. They have potential applications for the production of ready-to-coat surfaces and for the demoulding of microstructures.

Acknowledgment

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