Surface phenomena after the application of release agents

The properties of release agents

Release agents are generally regarded as the *Bête Noire* of plastics processing. Nevertheless, today's plastics processing industries are unimaginable without them because in addition to their real function, which is to remove a moulding easily and without damage, their task is to exert an effect on surfaces. They can improve the handle or touch of a moulding and can affect surface gloss or matt finish. In the case of soft foams in particular, release agents are partly responsible for the cellular character of the surfaces. Experience with these systems shows that the interaction of the foam and the release agent on one another must be matched together, because the effect on the surface is not always predictable [1, 2, 3].

Problems caused by release agents

Release agents are always a relevant factor when there is a need to carry out further processing of surfaces. This affects procedures such as painting and adhesive bonding in particular. The classical active ingredients of release agents such as waxes, silicones, paraffins and oils cause interference [1], with the result that expressions such as 'paraffin plague' or silicone plague' have become proverbial among processors.

Physical principles

The fundamental basis for the activity of release agents, adhesives and paints is the interplay between cohesion and adhesion. In this respect the forces that act in an intermolecular way, such as the Van-der-Waals force, electrostatic interaction or even chemical bonds, are responsible for the development of adsorption between two boundary surfaces. A pre-condition for adsorption onto a substrate is the wettability of the boundary surface, which also depends on the surface structure of the substrate, among other things. This can be observed macroscopically via the development of the surface tension or interfacial tension [4].

A physical explanation of surface tension is provided by looking into a water-filled capillary (Figure 1). The meniscus that forms, i.e. the wetting of the solid boundary surface, is described by the interaction between the liquid and the solid via the surface tension or interfacial tension on the basis of Young's equation:

$\sigma_{solid\,/\,liquid} - \sigma_{solid} = \sigma_{liquid} \cos\Theta$

$\sigma_{solid\,/\,liquid}$ is the interfacial tension between the liquid and the solid.

σ_{solid} is the surface tension of the liquid

σ_{liquid} is the surface tension of the substrate.

$\cos\Theta$ is the contact wetting angle that forms when a liquid/air surface is adjacent to a solid wall.

$\sigma_{solid\,/\,liquid} - \sigma_{solid}$ is defined as what is known as the adhesive tension [6]. A substance with a contact wetting angle < 90° will wet a surface because the adhesive tension is negative and releases energy to the surroundings during wetting. A contact wetting angle > 90 ° causes the adhesive tension to have positive values. Thus energy must be expended (work done) in order to cause a substance to wet.

The action of release agents

The activity of release agents can be attributed to a variety of mechanisms of action. First of all the release action can be described as an incompatibility between materials. This phenomenon can be attributed to, among other things, the differences in the polarity of the substrate and the release agent. Incompatibilities in the liquid/solid interactions lead to repulsion of the kind that are known, for example, in hydrophobing by waxes and silicones or in oleophobing by fluorine compounds.

These effects can also be explained by dividing the surface tension into a polar and a disperse component, whereby as a rule the polar component plays a decisive part in the adhesion. If the forces act exclusively dispersively, wetting of the surfaces is largely excluded and thus the pre-condition for adhesion is reduced. It can be concluded from this that for optimum activity a release agent must be configured in such a way that no wetting of the substrate or of the mould surface must take place, (Figure 2). In this case the contact wetting angle of the liquid increases to a maximum of 180°. The $\cos\Theta$ value then becomes negative. This is always achievable if $\sigma_{solid} < \sigma_{solid/liquid}$. The resulting adhesive tension becomes positive, i.e. work must be performed (energy expended) in order to achieve wetting. In this situation the release action now depends only on the adhesion and the material pressure.

A series of methods is known in the plastics processing industry for this purpose, in which an increase in the contact wetting angle is used to create the release effect. For example the activity of semi-permanent release layers based on silicone resins or even Teflonising relies on this process. As a rule components are easy to unmould if the adhesion values are considerably smaller than the cohesion values, so that there is no need to stretch the moulding irreversibly or to tear it. This holds true for example for highly compacted systems such as RIM (Reaction Injection Moulding) or elastomer components with a corresponding modulus of elasticity.

Another area of application involves plastics with a corresponding shrinkage, because the hardened plastic component can eliminate the adhesion forces at the boundary surface. In the case of processes that press the plastic to the surface of the mould, wetting of the mould surface is facilitated by the resulting pressures. The plastic that is to be moulded is at least mechanically anchored to the surface. The substrate will adhere to the separation surface in spite of a low wettability, and the application of additional force in order to unmould is to be expected. The extent to which surfaces can also be influenced by this method is not immediately predictable. However, it is clear that any alteration in the surface of the separation layer also changes the moulding surface that is to be configured.

To solve these difficult problems, a search was made for other alternative ways to achieve easy unmoulding with a constant surface quality. The release agent must form a completely closed layer both on the mould surface and also on the plastic that is to be unmoulded. A pre-condition for this is that the release agent wets both the mould surface and the surface of the moulded component. This is feasible only if the surface tension of the release agent is smaller than that of the mould surface and also smaller than that of the plastic. This fact is an absolutely essential pre-condition for any kind of release agents that work well, and also for adhesives.

However, the effectiveness of the two systems is quite dissimilar. For an adhesive, good wetting and thus good adhesion means good anchorage to the surface of the moulded component. The adhesive has high cohesive values and is removable only by destroying the plastic. In the case of a release agent, the break within the fluid phase is really ideal. Cohesion is low because of the molecular movement in liquid systems, and amounts to about 40 kJ/mole depending on the viscosity. Thus the following must hold true for the release agent: cohesive fracture at low viscosities in the liquid phase leads to low forces being exerted during unmoulding. Of course this contrasts with the action of adhesives, which must have high cohesion values as well as good adhesion to the boundary surface.

Further processing

Since release agents require the same pre-conditions as adhesives in order to act in an optimum way, it is always necessary to expect release agent contamination on a surface that is to be adhesive-bonded. The consequence of this is that the surface tension of the moulding is reduced by the release agent and an adhesive can no longer wet it. Justifiably, therefore, the requirement is: removal of the release agent to allow subsequent processing, or match all of the parameters to the subsequent processing [5]. The fact that this works is shown by, among other things, the manufacture of 2-density shoes. In this case a second PUR sole is foamed onto the surface of the first sole after separation and without the need to clean the component beforehand. This process was made possible by the following measures:

- The operating steps in fabrication are optimised to such an extent that the time delay between the foamings is so small that the residual activity of the PUR surface remains sufficiently high for it to bond to the second layer.
- Application of an optimised amount of release agent, approx. 1g per sole.
- Partial solubility of the release agent in the foam.

The physical property values showed that without removing the release agent, the cohesive break is situated inside the lower density foam.

It should also be possible to achieve good adhesion results or painting results for other PUR foams in spite of the use of release agents. The following alternative options are available for this at the present time:

1. Removing the release agent by washing processes
   This process guarantees a surface that is free from release agent, but the process entails an additional operating step.
2. Solubility promoters

The release agent layer is absorbed into the paint or adhesive by means of solvents or solubility promoters.

3. Increasing the polar component of the plastic surface
   Activation by radiation, chemical activators and/or reactive groups.
   Utilising the residual activity of the foam.
4. Increasing the polarity of the release agent
   Development of release agents that are friendly to subsequent processing.

Conclusions

Release agents and adhesives only operate under the same pre-conditions: wetting of the corresponding substrate. Whereas an adhesive holds the two phases together by cohesion, a good release agent operates by cohesive fracture. There are various possible ways of incorporating the release agent as an integral part of the subsequent processing. However, this is possible only if the parameters of the foam, release agent, paint and/or adhesive are matched to one another. This is confirmed by practical experience.

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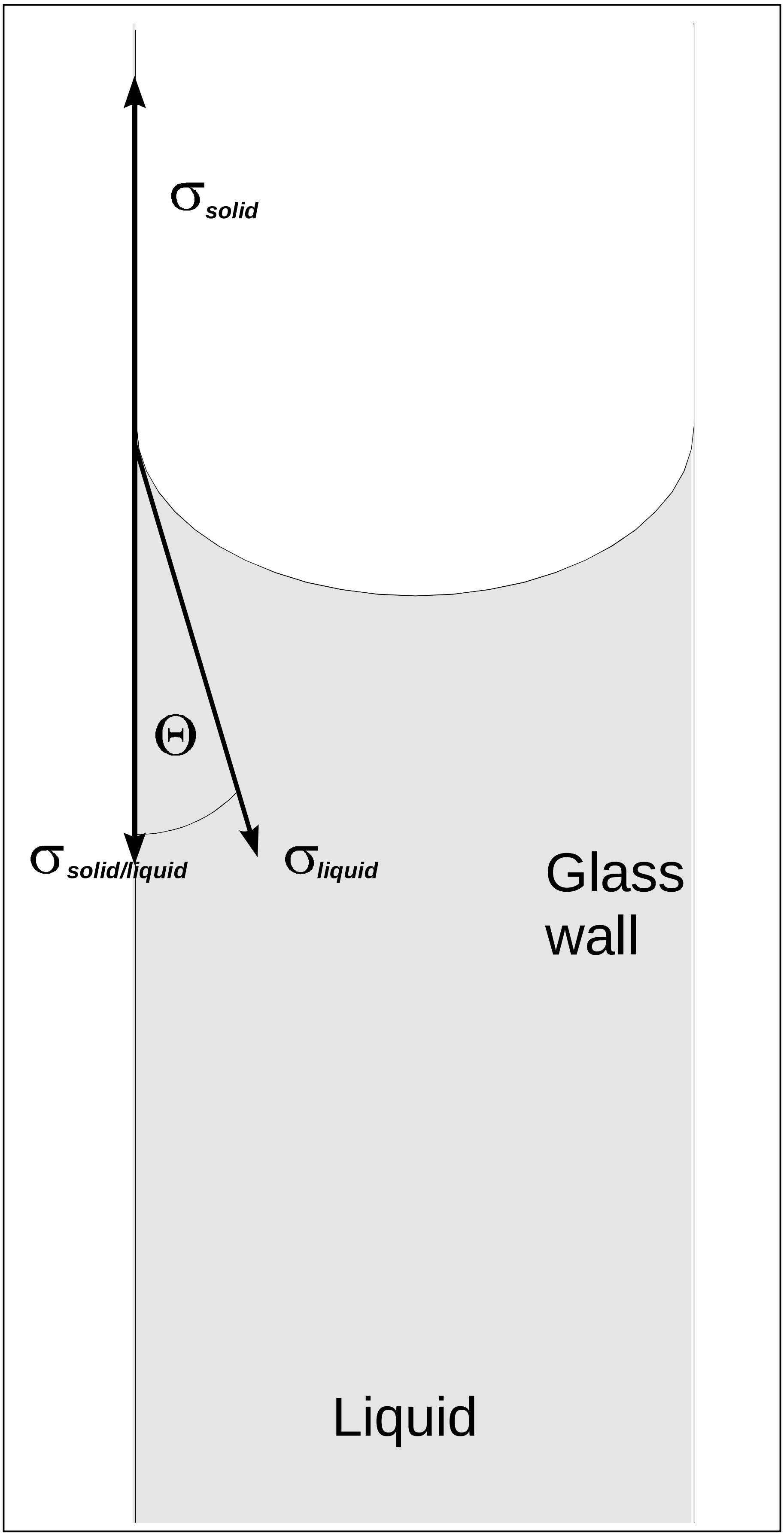

Figure 1: Wetting of a glass capillary by a liquid.

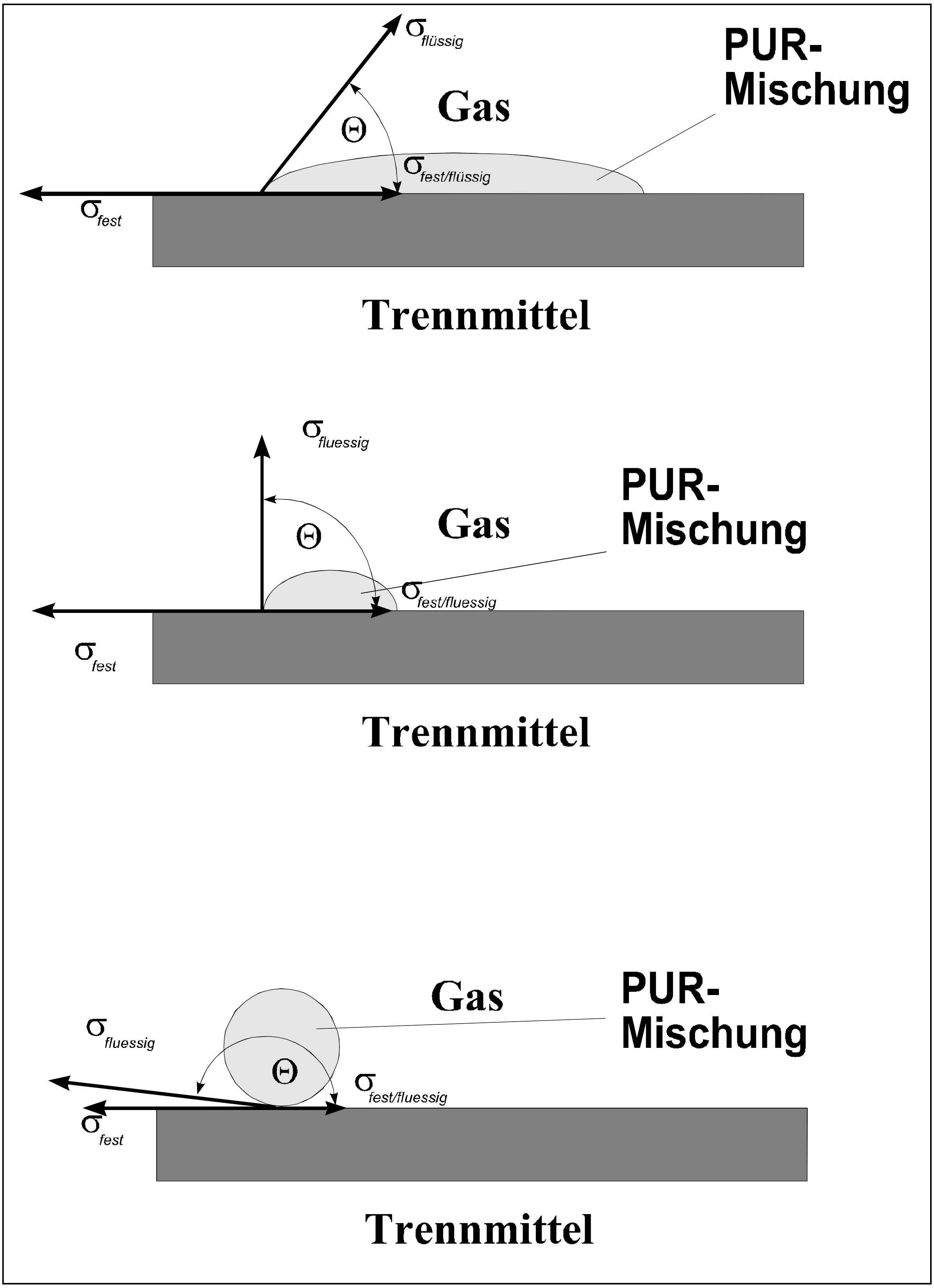

Figure 2: Force relationships at the PUR/release agent phase boundary

Information

Translations of the legends in Figure 2

German	**English**
PUR-Mischung	PUR (polyurethane) composition
fest	solid
flüssig / fluessig	liquid
Trennmittel	Release agent