



ADVANCED POLYMER DESIGN FOR ADHESIVE TAPES

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1. Introduction

Acrylate-based polymers have long been used to manufacture pressure-sensitive adhesives. Typical applications are adhesive tapes, labels and graphic films. The technical requirements for a pressure-sensitive adhesive can be very challenging, especially in the area of adhesive tapes. But this does not apply equally to all tapes. It makes sense to segment the adhesive tape sector into different applications. A possible breakdown is into masking tapes, home & office tapes, packaging tapes and specialty tapes (see Fig. 1).

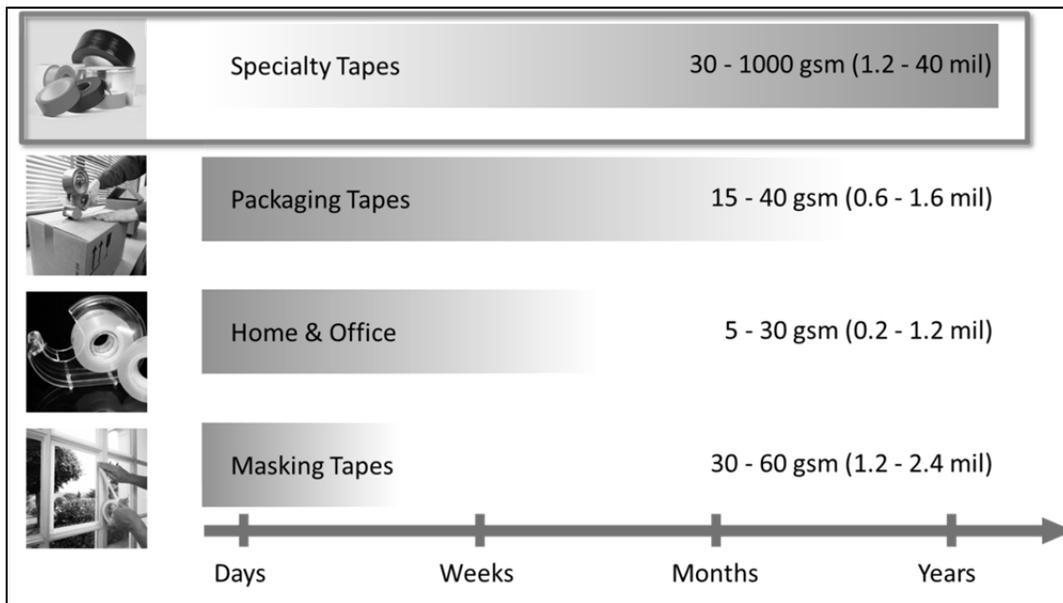


Figure 1. Segmentation of adhesive tapes by bond life

The requirements for bond durability and coat weight can vary considerably, depending on the application. The two criteria reach maximum values particularly in the specialty tapes segment. Specialty tapes are often used to create a permanent bond between very different materials, e.g. in the automotive, furniture and construction industries. The bond life is therefore determined by the life of the final article, e.g. vehicle or item of furniture, so that a bond is often required to last for years. High coat weights can help to achieve good adhesive effects even under adverse conditions (e.g. dust, rough surfaces and different substrates).

Despite the many different types of specialty tapes, the developer of pressure-sensitive adhesives regularly confronts the same essential problem of achieving a balance between the adhesive power (adhesion) and load-bearing capacity (cohesion) of the bond. A pressure-sensitive adhesive can attract considerable interest if it provides both high adhesion – especially on poorly wettable surfaces such as open-porous foams – and high bond strength. Further desirable technical properties that should not be overlooked are the stability of the bond at elevated or high temperatures and the resistance to weathering (water resistance) (see Fig. 2).

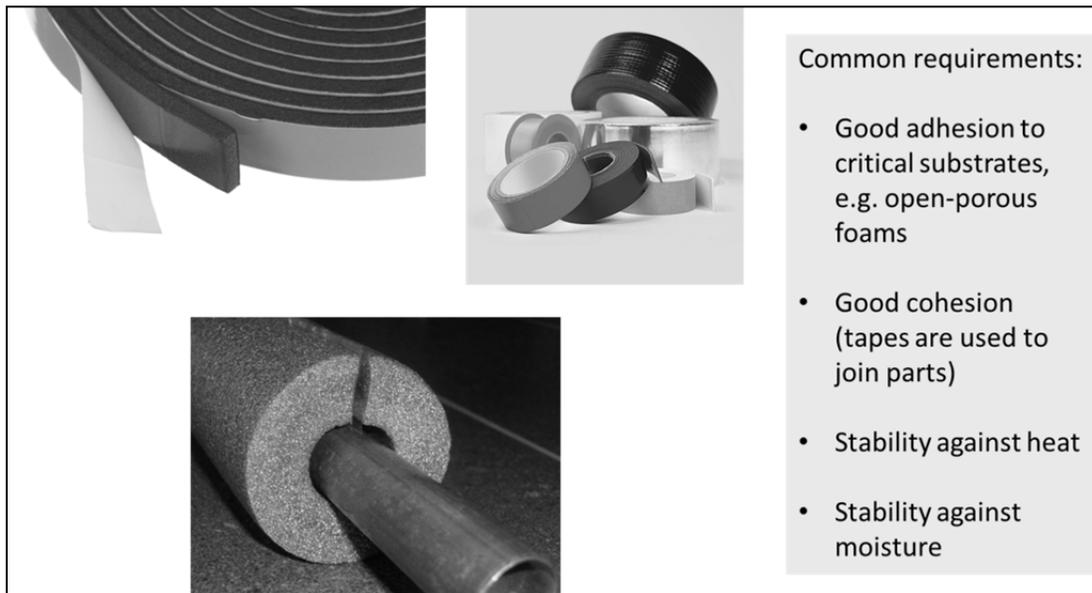


Figure 2. Examples of specialty tapes and typical requirements

Pressure-sensitive adhesives consist essentially of polymers synthesized through emulsion or solution polymerization or in bulk. The most common polymer classes are acrylates, styrene-diene copolymers, polyisoprene and their derivatives. However, pressure-sensitive adhesives are generally classed not by how they are produced, but by their supply form. Accordingly, they are subdivided into dispersions, solvent-based systems and hotmelts (see Fig. 3). Within these segments, of course, adhesives can also be differentiated according to their chemical nature.

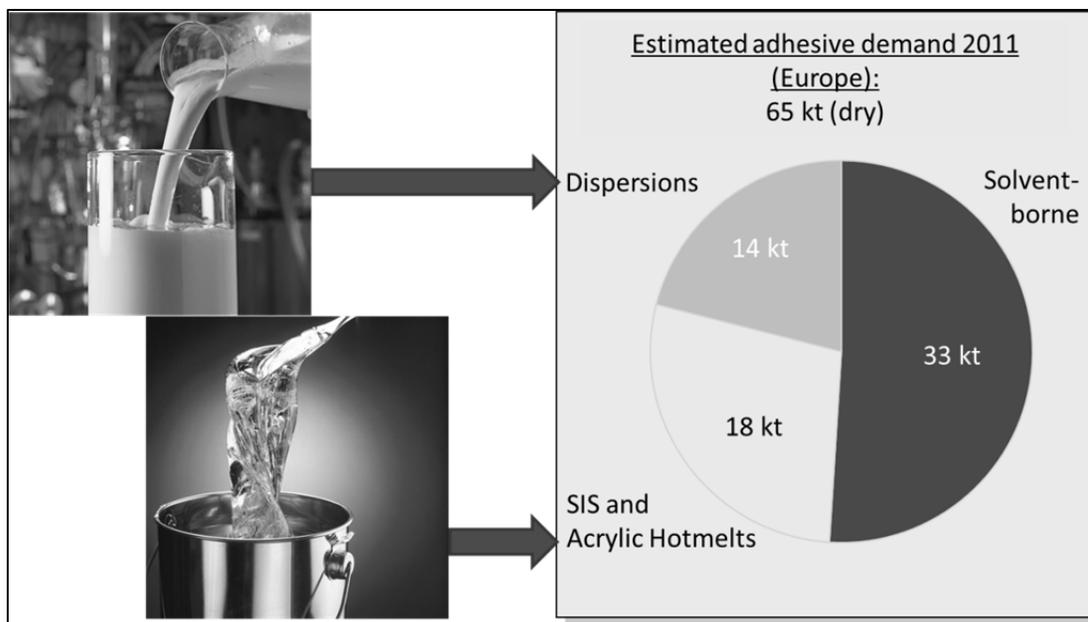


Figure 3. Segmentation of adhesive tapes by technology

While other applications for pressure-sensitive adhesives, such as adhesive labels, are dominated by dispersions and hotmelts because of their economic and ecological advantages, what is striking about specialty tapes is the large market share represented by solvent-based systems. Indeed, the most exacting technical requirements in terms of adhesion/cohesion balance and stability to heat and weathering are still matched by solvent-based systems. And since it is these applications that are of particular economic interest, it is attractive to develop dispersions for them.

It should be noted that the adhesive properties are not determined by either the polymer solution or the dispersion, but by the coated, dried polymer film. Intrinsic differences between films, derived from either solutions or dispersions are emphasized in the next section. They provide a starting point for the successful development of products based on acrylate dispersions.

2. Discussion

2.1.1 Comparison of emulsion and solution polymers

To produce emulsion polymers, the latex particles must be dispersed in water and sufficiently stabilized for production and processing operations. As a rule, this involves functionalizing the surface of the latex particles with suitable comonomers, e.g. by incorporating acid groups or amphiphilic protective colloids. In addition, emulsifiers are generally added during or after polymerization. Emulsion polymers usually also contain salts, which are introduced when the initiator is added and the pH is adjusted. They therefore contain significant quantities of hydrophilic components.

The polymer film with its adhesive properties is formed as the water is gradually evaporated. Different phases of film formation are distinguished. The latex particles first pack closely and fuse together. The latter phase, known as coalescence, is an interdiffusion process in which

polymers from each latex particle diffuse into adjacent particles and form a solid polymer film. The film is nevertheless heterogeneous, leaving the original structure of the latex particles largely visible. One reason is the presence of the hydrophilic components, which accumulate on the interfaces and in the voids between the latex particles. Furthermore, the latex particles generally inhibit gel. This gel content also promotes the formation of a heterogeneous polymer film.

Solution polymers, on the other hand, do not contain particles but are polymers dissolved in organic solvents. Stabilization with hydrophilic components is unnecessary. Film formation produces a homogeneous polymer film (see Fig. 4).

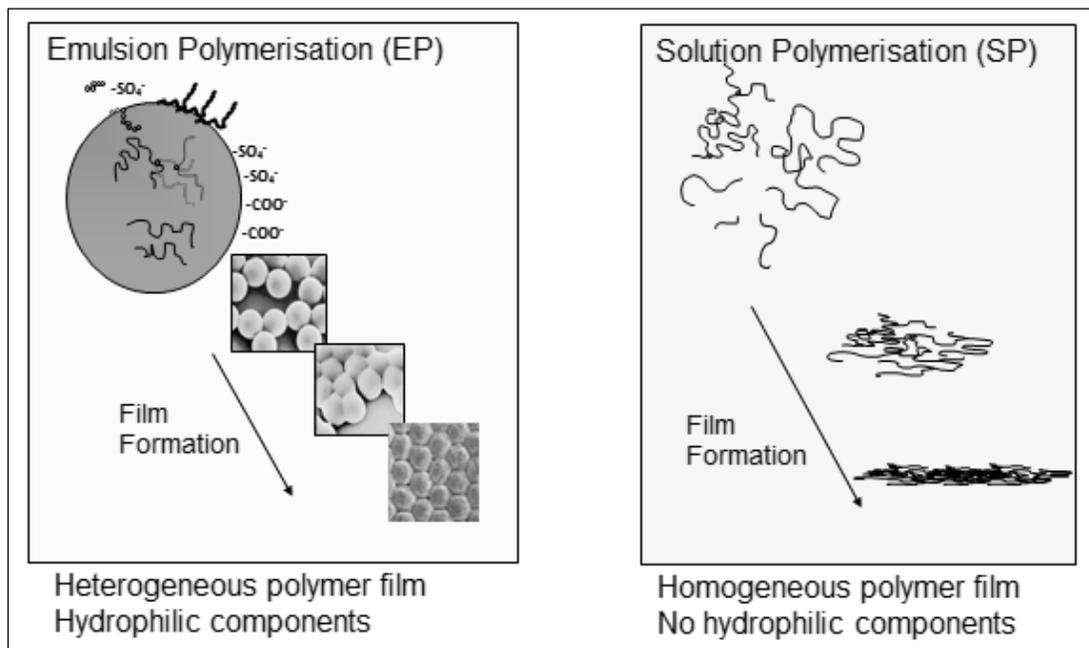


Figure 4. Intrinsic differences between emulsion and solution polymers

The concept of reproducing the beneficial properties of solution polymers by emulsion polymerization is thus partly based on controlling the hydrophilic components and producing a polymer film that is as homogeneous as possible.

2.1.2 Sensitivity to water and drying rate

The requirement for controlling the hydrophilic components was met by carefully selecting the monomers and emulsifier system used. The sensitivity to water (see section 2.2.1 for technical results) and drying rate were considerably improved.

The results were partly derived from physical characterizations. A very helpful method in this regard was confocal laser scanning microscopy (CLSM), which can be used to visualize film formation and trace the drying kinetics. The samples were marked with a fluorescent dye, whose fluorescence slowly vanishes during drying dependent on the amount of water present. When excited by laser light, the aqueous phase fluoresces (light grey in Fig. 5), while the latex particles appear black. Particles, which are smaller than 200nm in diameter, are not detectable but

concealed by the fluorescent aqueous phase. In a typical experiment, a dispersion droplet of approx. 100 μ l is dried on a coverglass at room temperature. Samples were compared by adjusting them to a common solids content (SC) of 56%. Film formation can be visualized as an online video sequence. Up to a solids content of approx. 70%, the Brownian motion of the particles can be clearly observed. As expected, the small particles (approx. 150-300nm in Fig. 5) move faster than the big ones (approx. 800nm in Fig. 5). The amount of water of the polymer film falls steadily as it dries. At the same time, the fluorescence decreases in intensity until finally no detectable fluorescence signal is produced by the dry polymer film. The disappearance of the fluorescence signal can also be used as an indicator for the drying time. Compared with a standard pressure-sensitive adhesive product, the new product approximately dries twice as fast. The validity of the laboratory results was verified by trials at our in-house pilot coating plant (see section 2.2.2).

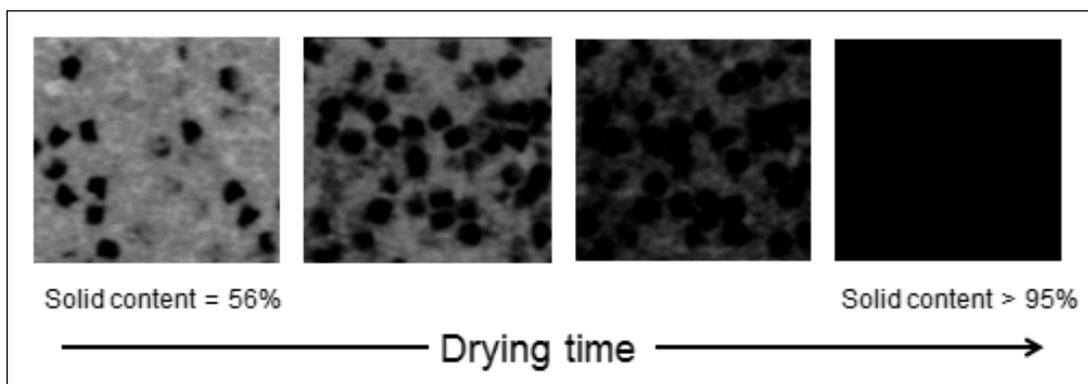


Figure 5. Confocal laser scanning microscopy for visualizing film formation by emulsion polymers. The fluorescence signal decreases as the film dries (color code: grey: strong fluorescence to black: no fluorescence). Image size approx. 7 x 7 μ m.

2.1.3 High heat resistance and cohesion

A comparison of emulsion polymers and solution polymers leads to the further requirement that the polymer films be as homogeneous as possible and yield a good wetting of the substrate to be bonded. A logical step in this direction would be to reduce the gel content and the molecular weight of the polymer. But such positive steps in terms of adhesion are very counterproductive in terms of heat resistance and cohesion. A successful concept for new product development is to incorporate temporary crosslinking points in the adhesive in the form of strong dipole-dipole interactions or hydrogen bonds (see Fig. 6). Like a hook-and-loop fastener, such cohesion-improving bonds can open and close and so not only produce good wetting and adhesion, but also effectively increase the heat resistance and cohesion. This mechanism is not possible with permanent crosslinking points, e.g. by chemical crosslinking.

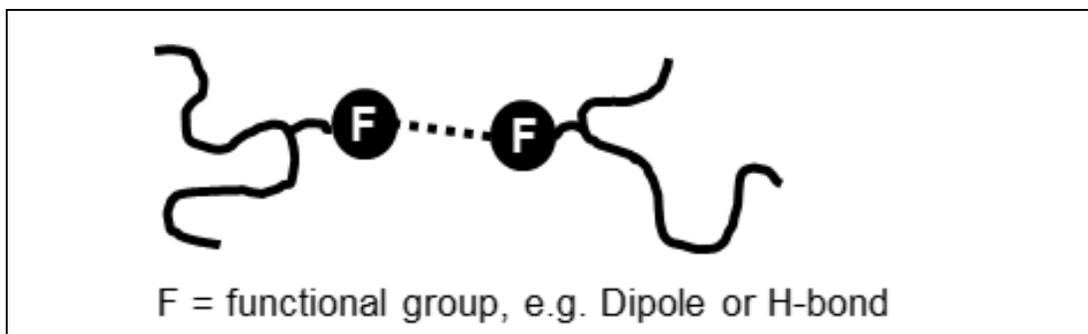


Figure 6. Temporary crosslinking by dipole-dipole interactions or hydrogen bonds

Using functional comonomers allows the concept described above to be tested and implemented (see Fig. 7). Selected acrylate monomers (amount < 5%) were copolymerized with the adhesive polymer and the resulting products compared. Comonomers with NH- (amine or amide) and OH- (hydroxyl) groups were used to examine the effect of strong dipole functionality. The effect of hydrogen bonds was also investigated by derivatizing the NH- group in an acrylate monomer to form an NCH₃- group or replacing the NH group with oxygen (O). Since neither of these derivatives can act as a hydrogen bond donor, they allow the effect of hydrogen bonds to be estimated in comparison with dipole-dipole interactions. In addition, the acrylate monomer containing oxygen (O) is a monomer with weak dipole functionality, so that the effect of this incremental difference on the technical properties could also be studied.

Dynamic mechanical analysis (DMA) of polymer films, in which the storage modulus E' was measured against temperature, gave unambiguous results (see Fig. 7). A strong dipole-dipole interaction is clearly reflected in the E' modulus curve at temperatures above 180°F. Derivatives with pronounced dipole-dipole interactions maintain a higher E' modulus level than samples with weak interactions. Thus the E' modulus of the acrylate derivative with the oxygen group (O) fell significantly. The effect of hydrogen bonds on such measurements is less marked, as the comparison between the derivatives with NH- and NCH₃- groups shows.

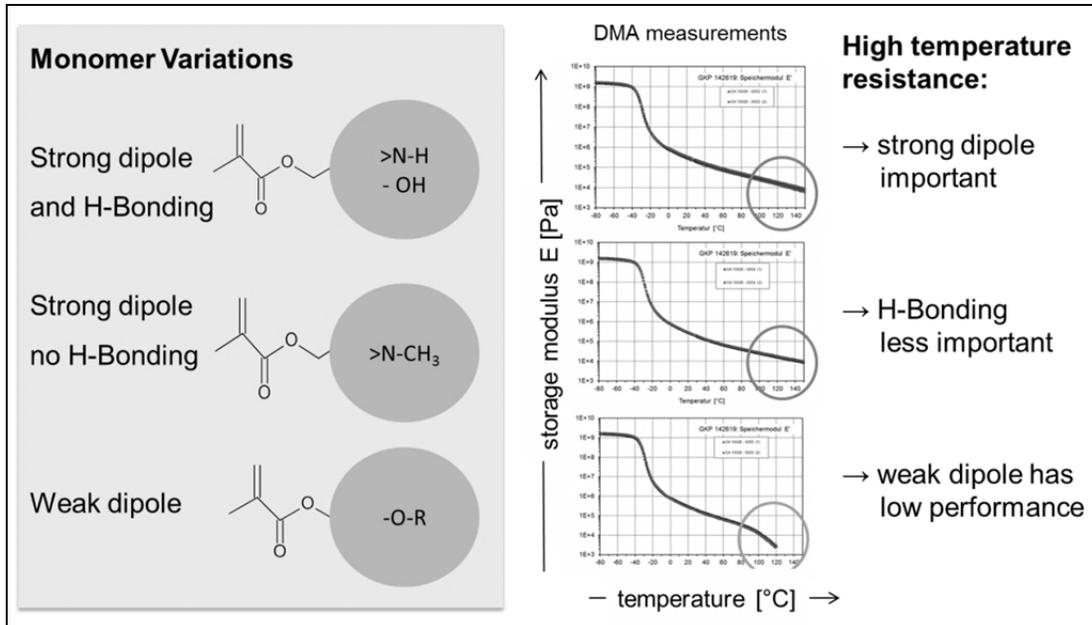


Figure 7. Effect of dipole-dipole interactions and hydrogen bonds on temperature resistance

These results are corroborated by stress-strain experiments on polymer films (see Fig. 8). The comonomers with strong dipole-dipole interactions showed high stress, while in the case of the acrylate derivative containing the oxygen group (O) it was several times lower. At the same time, the maximum strain decreased from 1400% to 1200%.

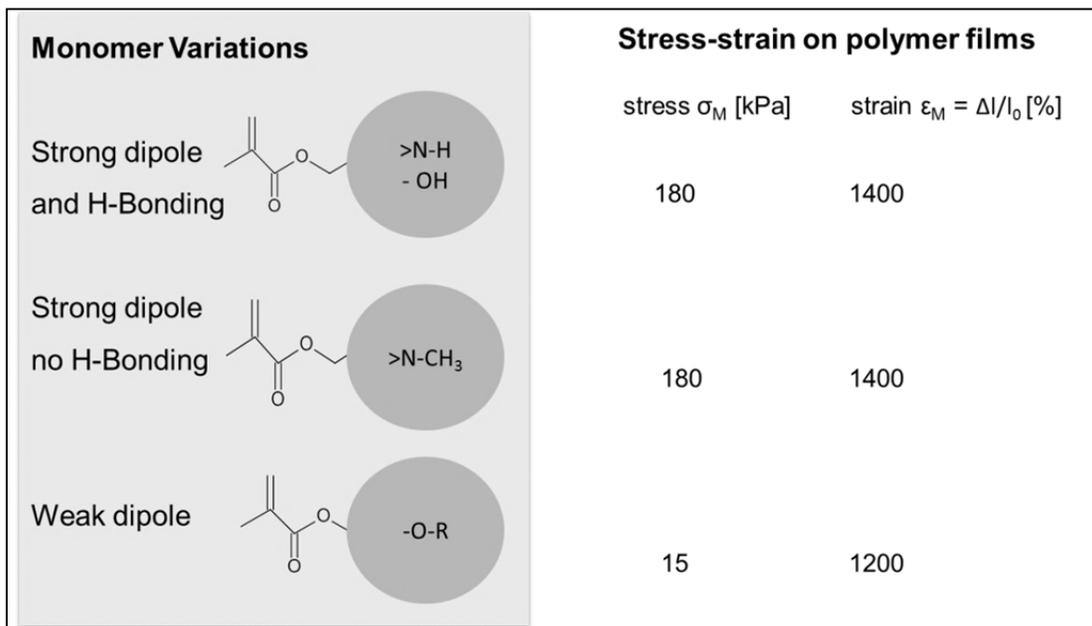


Figure 8. Effect of dipole-dipole interactions and hydrogen bonds on stress-strain of polymer films

Δl = change in length of polymer film, l_0 = initial length of polymer film

Application tests to determine peel values, cohesion and heat resistance confirm the results of the physical characterizations (see section 2.2.1).

2.2 Correlation with application properties

In a matrix with adhesive power (adhesion) on one axis and internal strength (cohesion) on the other, commercially available dispersions are all found within a zone in which there is a certain balance between the two properties (see Fig. 9).

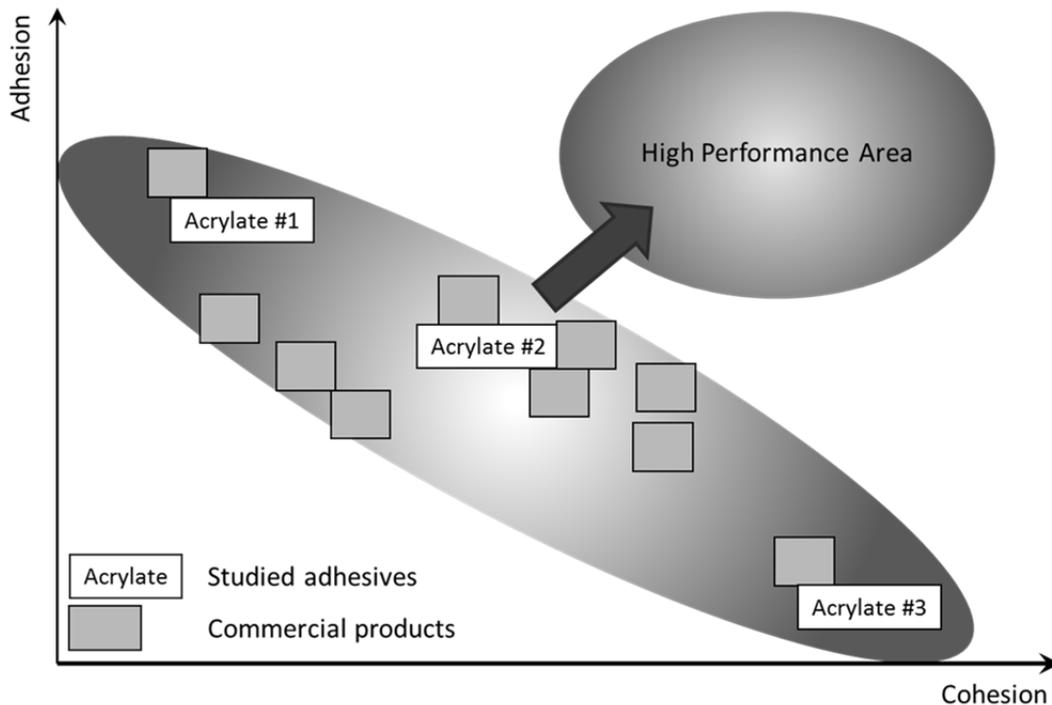


Figure 9: Adhesive properties of commercially available dispersions

The range includes products with high adhesion and moderate cohesion (top left of the diagram), cohesive products with moderate adhesion (bottom right of the diagram) and formulations in between. The aim of a new development is to move away from this balance zone towards greater cohesion or adhesion (or both) without compromising the other property.

The axis labels 'adhesion' and 'cohesion' may seem somewhat unspecific, but they are based on measured technical values. A qualitative estimate of adhesion is obtained by measuring peel strength values on steel and polyethylene after an adhesion period of 24 h. The cohesion evaluation involved measuring cohesion values at room temperature and 160°F and the so-called shear adhesion failure temperature (SAFT), the temperature at which a bond fails when heated.

The efficiency of the measures for optimizing acrylate dispersions was tested on the product 'Acrylate new'. This product was characterized by comparison with representative acrylate dispersions. As can be seen in Fig. 9, the two commercially available dispersions Acrylate #1 and

Acrylate #2 are appropriate for this purpose. The conditions under which the technical tests were carried out can be found in the appendices.

Transfer coatings were performed on polyester film (Hostaphan® RN 36*) with an average coat weight of 75g/cm² (3 mil). The final dispersion film was produced by drying for 5min at 200°F. The measurements were made in a standard climate of 73°F (R.T.) and 50% relative humidity.

2.2.1 Comparison of adhesive properties

The newly developed acrylate dispersion ('Acrylate new') is compared with the two commercial products (Acrylate #1 and #2) in Fig. 10.

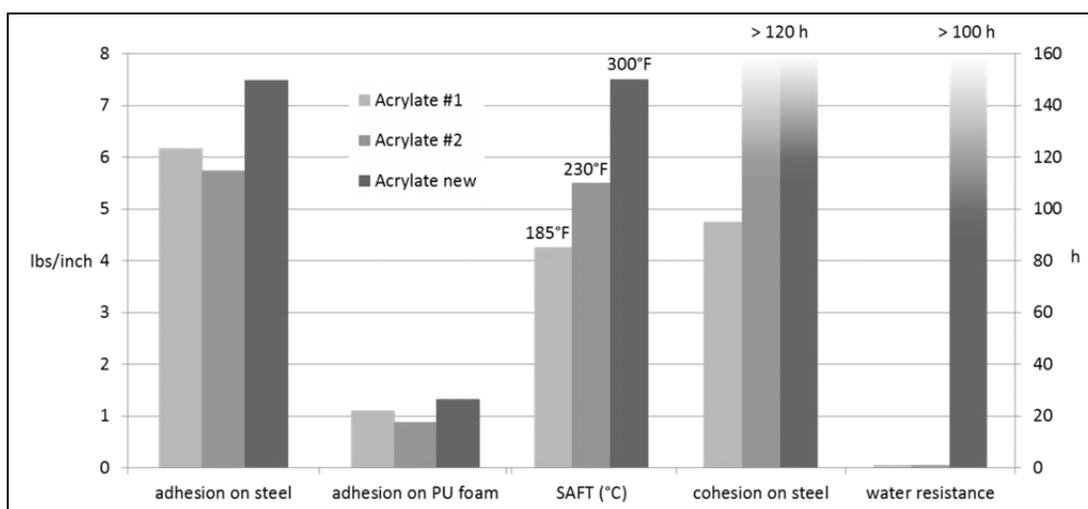


Figure 10. Technical tests on Acrylate #1, Acrylate #2 and 'Acrylate new'

A comparison of Acrylate #1 and Acrylate #2 reveals the above-mentioned disparity between adhesive and cohesive strength. It is clear that Acrylate #1 exhibits higher peel strengths (adhesion) on steel and – although less pronounced – also on open-porous foam than Acrylate #2. The greater adhesive power of Acrylate #1 is obtained at the price of lower bond strength and somewhat poorer heat resistance. This is evident in the comparison of the cohesion (on steel) and SAFT values of Acrylate #1 and Acrylate #2.

'Acrylate new' shows superior adhesion with respect to the two commercial Acrylate products. Optimizing the wetting power of the dispersion was clearly successful. However, the steps for achieving greater adhesion mentioned in section 2.1.3 tend to conflict with the development of high cohesion. To compensate for this, 'Acrylate new' was provided with monomer units that form hydrogen bonds and produce dipole interactions. The effect is seen in the cohesion (on steel), which is superior to that of Acrylate #1 and approximately equal to that of Acrylate #2. In addition, 'Acrylate new' has the highest heat resistance values (SAFT) achieved in the study.

As described in section 2.1.1, dispersions, unlike solvent-based products, must contain hydrophilic substances such as emulsifiers, protective colloids and salts. These substances generally do not contribute positively to the technical properties of the final polymer film. Rather, they may have an adverse effect on some properties, e.g. the film's water resistance.

Although it is not possible to completely dispense with hydrophilic substances, it is worthwhile to optimize them in the synthesis (see section 2.1.2). This becomes clear when the water resistance of Acrylate #1 and Acrylate #2 is compared with that of 'Acrylate new'. Polymer films of Acrylate #1 and Acrylate #2 loose anchorage on aluminum foil after approx. one hour of immersion in water, while the bond of 'Acrylate new' with aluminum foil remains intact even after being immersed for four days.

2.2.2 Drying properties

The confocal laser scanning microscopy method introduced in section 2.1.2 impressively demonstrated the accelerated film formation of 'Acrylate new' compared with Acrylate #2. The practical significance of this result was investigated in a coating trial on a pilot coater (see Fig. 11).



Figure 11. Pilot coating plant

The two dispersions were adjusted to a common solids content of 60%. Various coat weights of the dispersion were transfer coated onto silicone paper (NSA 1350 White, product of Laufenberg GmbH) at a web speed of 100ft/min, dried, and then laminated to 36- μm (1.4 mil) polyester film. In each case, a well-anchored, uniform coating without wetting faults was obtained.

The drying properties were characterized by comparing the residual moisture levels of the 'Acrylate new' and Acrylate #2 coatings (see Fig. 12).

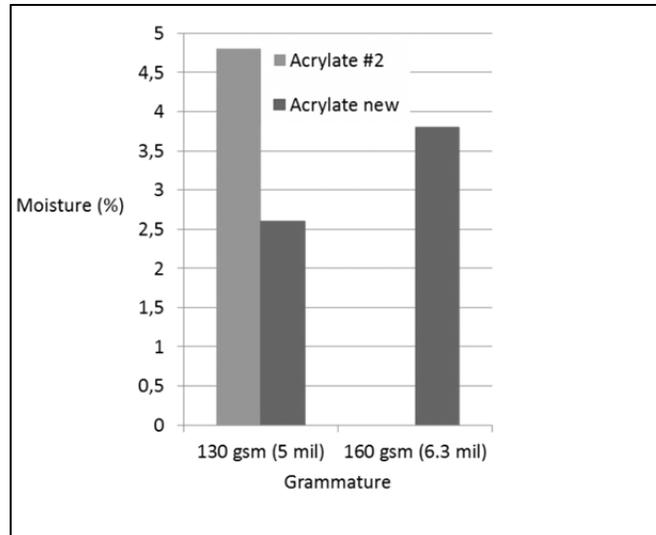


Figure 12. Residual moisture of Acrylate #2 and 'Acrylate new' at different coat weights

Good drying of dispersion films becomes more challenging with higher coat weights. The trials were therefore begun with a coat weight of 130g/m^2 (5 mil):

At a web speed of 100ft/min, Acrylate #2 showed a satisfactory residual moisture content of just under 5%. To achieve higher coat weights, however, the web speed would have to be reduced below 100ft/min.

Employing the same coating conditions (130g/m^2 (5 mil); 100ft/min), 'Acrylate new' had a residual moisture level of only 2.5%. The product could therefore either be coated faster than 100ft/min while maintaining the same coat weight, or higher coat weights could be applied at the same web speed. In fact, at a coat weight of 160g/m^2 (6.3 mil) and a web speed of 100ft/min, the residual moisture content was still only just under 4%.

3. Conclusion

By controlling the unavoidable hydrophilic components of dispersion products, on the one hand, and combining optimized gel content and molecular weight with temporary crosslinking points, on the other, a dispersion can be developed that combines conflicting properties:

Both physical characterizations and application tests showed that high adhesion values, internal strength, heat resistance, colloidal stability, rapid drying and high water resistance can be achieved in a single product.

Meticulous product development makes it possible to further extend the application range of acrylate dispersions.

4. Appendices

Adhesion on steel:

The test was conducted with a bond width of 1" and a peel-off speed of 12"/min (300mm/min) after 24h bonding to stainless steel. The measured values were reported in lbs/inch.

Adhesion on PU foam:

The test was conducted with a bond width of 1" and a peel-off speed of 12"/min (300mm/min) after 3 days' and at 140°F bonding to an open-porous PU foam (Bulapur® ES 30**). The measured values were reported in lbs/inch.

Cohesion on steel:

The test was conducted with an adhesive surface of 1" x 1" on stainless steel and a weight of 2.2 lbs (1kg). The static cohesion was determined, i.e. the time in hours until bond failure.

SAFT (°F):

Like the cohesion measurement, the test was conducted with an adhesive surface of 1" x 1" on stainless steel and a weight of 2.2 lbs (1kg). Unlike the cohesion measurement, the sample was heated at a rate of 0.9°F/min, beginning at 73°F. The temperature in °F was determined at which the bond failed.

Water resistance:

To determine the water resistance, the dispersion was applied directly on 30-µm (1.2 mil) aluminum foil at an average coat weight of 40g/m² (1.6 mil) and dried as described above. The entire coating was then immersed in a water bath and the time measured in hours until bond failure between dispersion film and foil.

* Hostaphan® is a registered trademark of Mitsubishi Plastics, Inc.

** Bulapur® is a registered trademark of Hutchinson SA

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