

CONTROLLED ADHESION IN REACTIVE SOLUTION ACRYLIC PSAs

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Introduction

Henkel continued during the last year to investigate the features given by the RRP-Technology (Reactive Resistant Polymer). This technology provides a platform for the formulation of adhesives given by the flexibility to incorporate high levels of crosslinking monomers in a stable, 1-part system beneath the broad range of acrylic esters of different Tg.

The new development builds a bridge between removable adhesives showing a low adhesion on various substrates and “direct” adhesives, those with immediate high bond strength. The new grade delivers a slow build up of bond strength for a period of time until the level of full high bond strength is reached, a property often needed in graphic and tape application. This behavior results from a combination of functional and nonfunctional monomers together with a special designed crosslinking behavior. We looked into this behavior with standard performance tests as well as with different analytical methods.

Chemistry

Crosslinking of acrylic PSAs are possible with different chemical mechanisms. Two of them are mostly used:

Complex formation (e.g. metal chelates (fig. 1) like aluminum or titanium), where crosslinking takes place between the carboxylic acid groups of the polymer and leads to a 1-part system

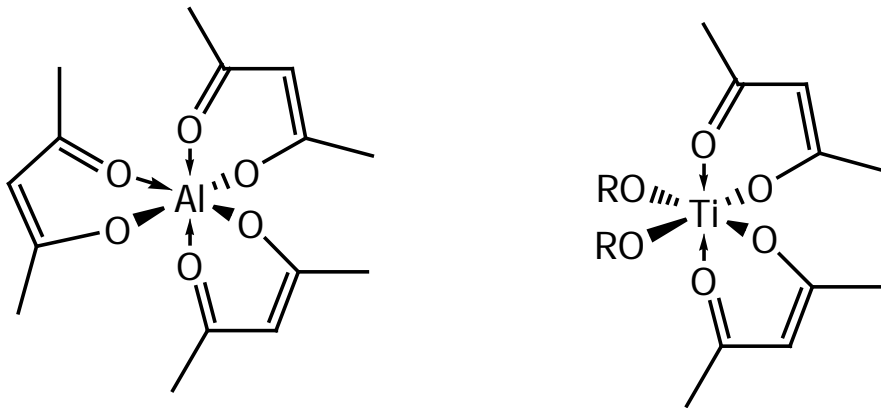


Figure 1. Aluminum tris(acetylacetonate) and Titanium dialkoxide bis(acetylacetonate)

2-part systems, where the chemical reaction of a diisocyanate, typically MDI, with hydroxyl groups of the polymer (fig. 2) form a covalent bond between two polymer chains

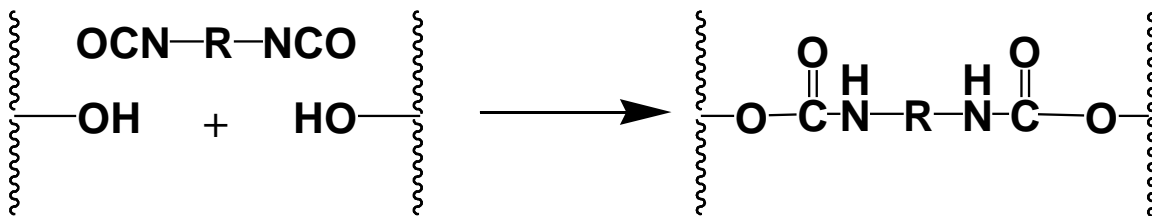


Figure 2. Example of hydroxyl functional PSA reacting with a diisocyanate

The RRP-technology developed by HENKEL KGaA uses the formation of a covalent bond to gain the advantages of higher cohesion at elevated temperatures, but implemented it in a 1-part system by using the crosslinking behavior of carboxylic acids with epoxy functional groups (fig. 3) like glycidyl methacrylate¹.

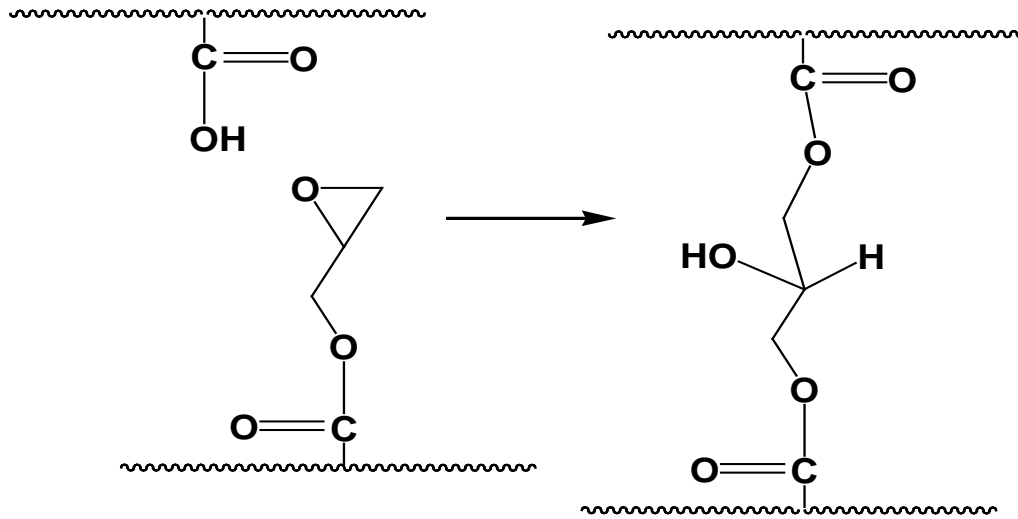


Figure 3. Acid and epoxy reaction

The amount of reactive units needed to form a strong enough network for the desired cohesion would be normally too high to guarantee a stable formulation without early crosslinking during manufacturing or later coating and drying. HENKEL KGaA developed a method to overcome these difficulties: the implementation of a monomer M with a bulky side chain and a generic formula like in fig. 4 is able to stabilize the polymer.²

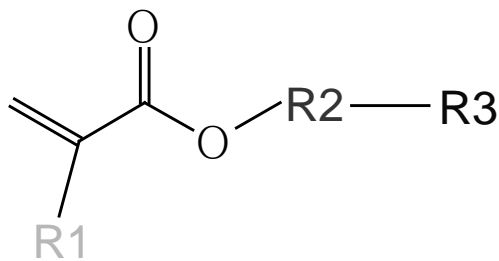


Figure 4. Generic formula of monomer M; R1= H or CH₃, R2 is a spacer with a length of 0 to 5 atoms (pure aliphatic or an ether chain), R3 is a bulky group (fig. 5)

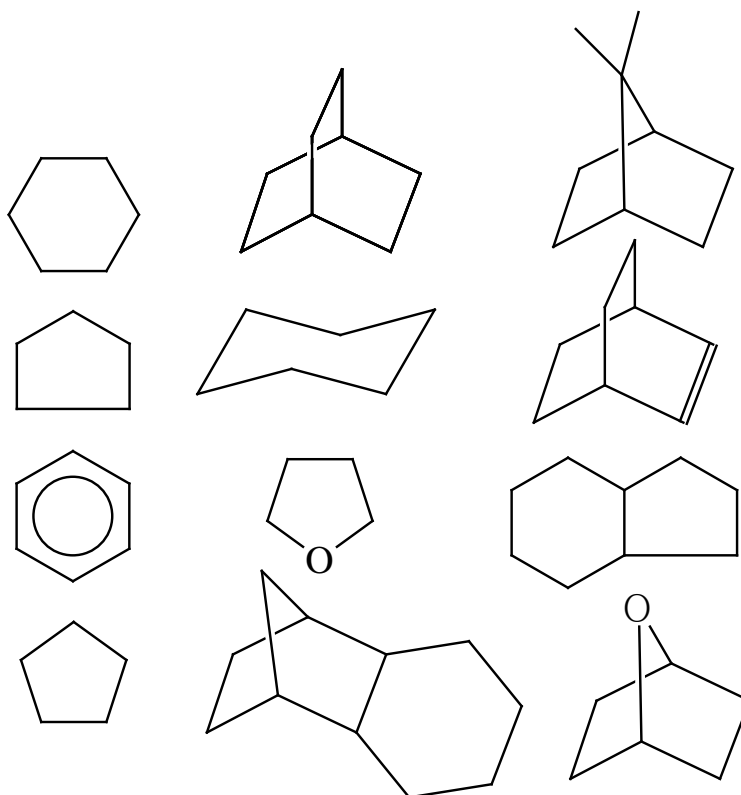


Figure 5. Possibilities for R3 (fig.4)

Experimental

Repositionable adhesive A was prepared using standard free radical polymerization and was compared by different methods with other adhesives, produced in the same way, showing either directly full bond strength (adhesive B and C) or long term removable properties (adhesive D).

Dynamic viscoelastic properties were determined using a Physica UDS 200 (Paar-Physica) in a parallel plate mode using 25-mm diameter plate. The temperature was scanned at 2 °C/min at a constant frequency of 10 rads/sec.

The build up of adhesion was measured by time dependent peel measurements (according to FINAT method) at 23°C and 50% humidity.

We investigated the pure surface of polymer A and B as well as the interface bonded to a glass plate (observation over a period of time). We have used light microscopy (LM) and atomic force microscopy (AFM) to get an image of the structure of the surfaces over time.

All samples were transfer coated from release liner or directly coated on PET (50µm) (drying conditions: 5min@120°C). The coating weight varied from 25g/m² to 100g/m². All laminates were prepared using the same release liners.

Results and Discussion

The general physical properties of the investigated adhesives are listed in table 1 below. These adhesives vary by composition (T_g) and crosslinking system. Adhesives B, C (standard acrylics) and D (removable acrylic) are not based on RRP polymer crosslinking. They all have comparable molecular weight.

Table 1. General physical properties of investigated adhesives.

	A	B	C	D

Solids, %	34.6	50.8	40.8	44.8
Brookfield visc., mPa.s	1600	5200	3500	3300
Tg	high	low	medium	low

1. Rheology

The rheological profiles of Adhesives A, C and D are given in figure 6 in a temperature range from 25°C to 150°C. For these measurements an uncured film of 100µm thickness (dried at ambient temperature for at least 12h) was used to monitor the curing behavior of the samples. While the rheological behavior of the long term removable adhesive D seems less temperature dependent, A and C show comparable behavior. Each product is fully crosslinked as seen by the rheology measurements.

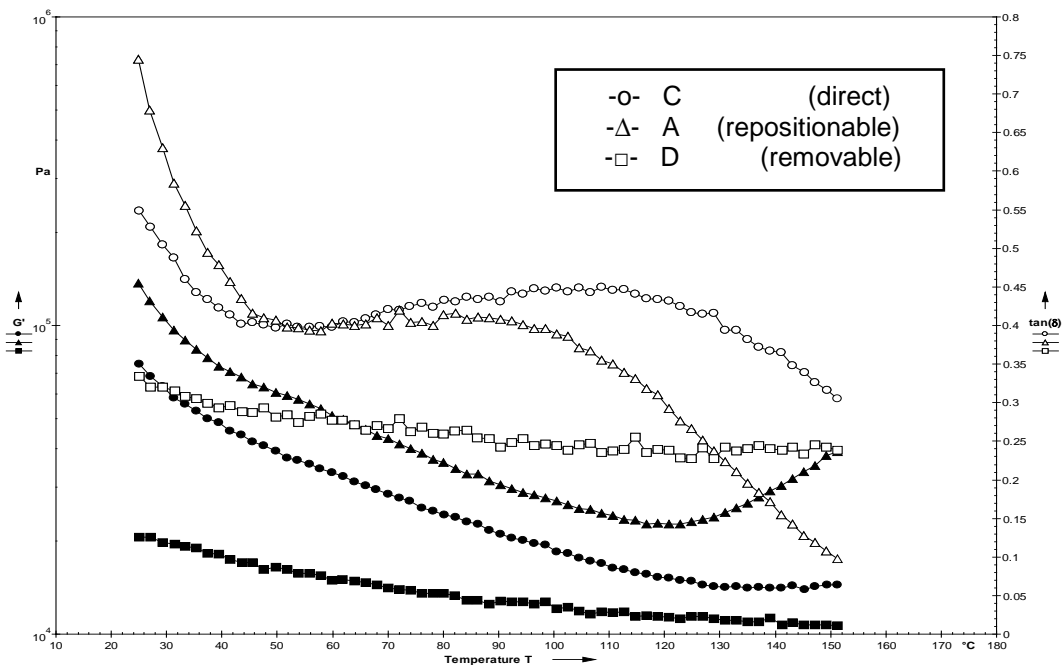


Figure 6. Rheological profiles of A, C and D

2. PSA performance data

The following graphs (figures 7-9) show time dependent performance data of the adhesives A, B, C and D on different substrates.

180° Peel on SS with 60gsm on PET

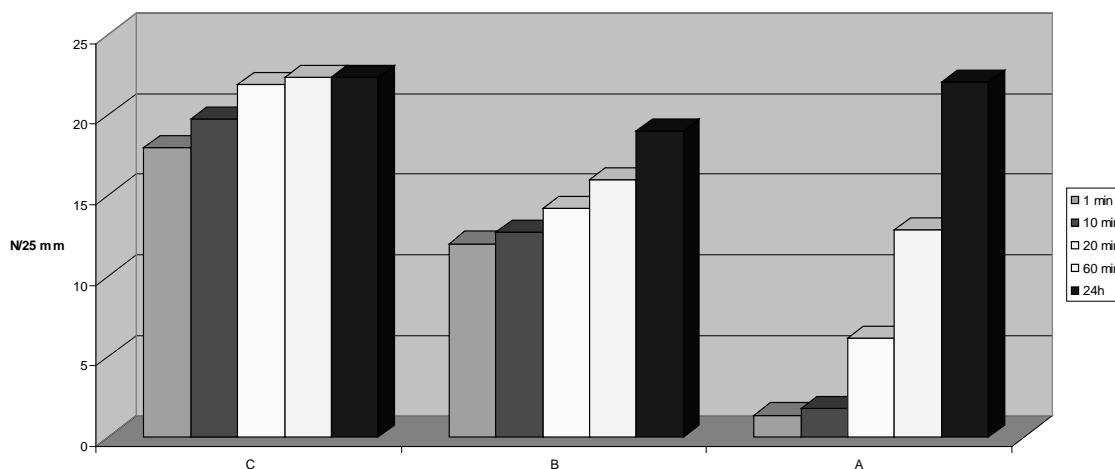


Figure 7. Time dependent peel of A, B and C on stainless steel. 60gsm on 50µm PET.

The standard grades B and C use aluminium metal chelate chemistry for crosslinking, grade A uses the same as additional crosslinker.

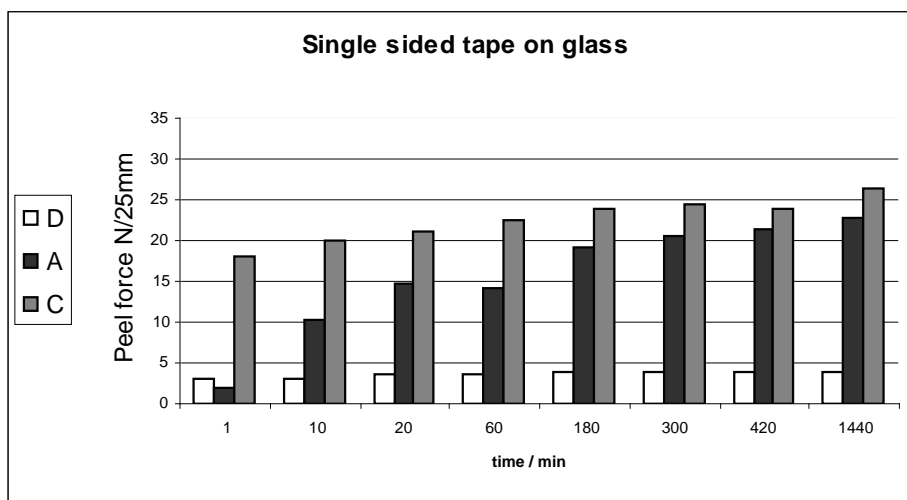


Figure 8. Time dependent peel of adhesives A, C and D; 26gsm on monomeric PVC.

A comparison of A, C and D, here (figure 8) on monomeric PVC on glass, shows a large difference in build up of adhesion during time, caused by different polymer architecture of the grades. While the peel values of grade D stay on a low level over the entire time and peel of C already starts on a relatively high level in the first minute of bonding, one can see clearly the slow built up of adhesion of A over the first observed hour.

The repositionable character of grade A is not only given in case of fresh material. This property persists even when the coatings are stored for 1 week at 70°C before application (figure 9).

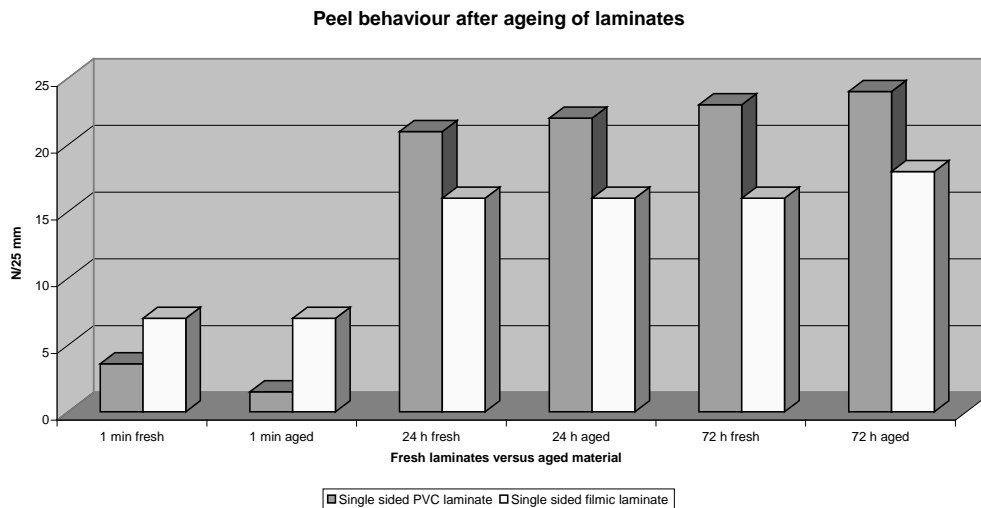


Figure 9. Time dependent peel behavior after storage of coatings. Adhesive A (26gsm), tape on glass

3. LM (light microscopy)

LM was used to get a deeper in look in the possible reasons of repositionable behavior. A free film of adhesive A (26gsm on release paper) was transferred to a glass plate (same conditions like preparing peel tests according to FINAT). The first measurement was started directly after application and monitored until no changes could be observed any longer. The pictures show the status of wetting with a fresh bonding and again after 18h and 65h.

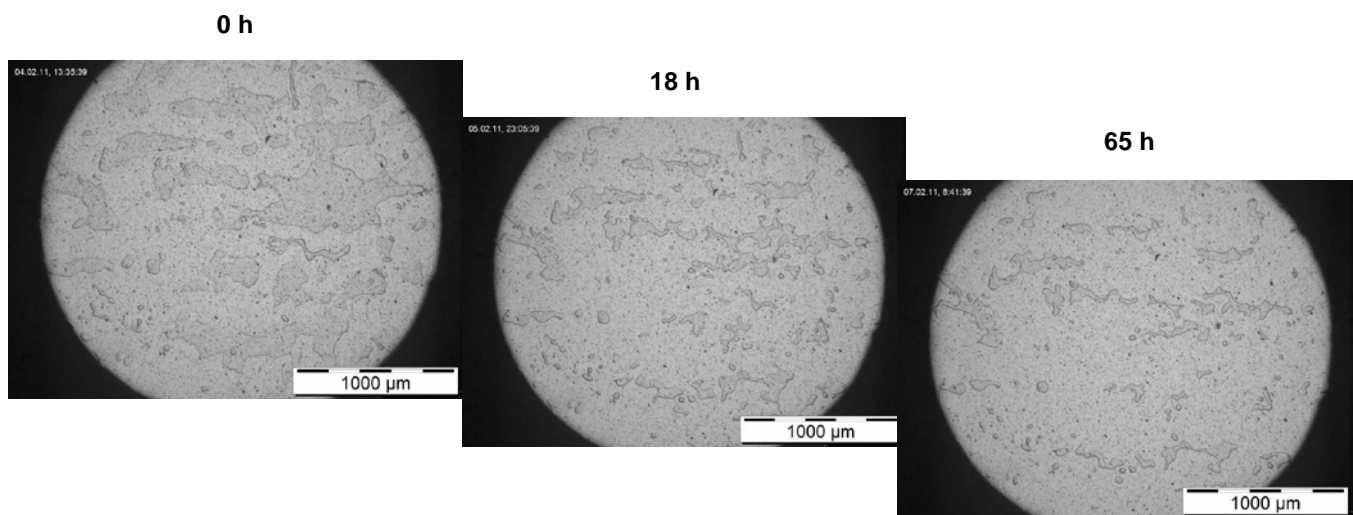


Figure 10. Time dependent wetting behavior of adhesive A on glass, done by LM

The investigations show large non wetted areas when measured directly after application. The size of the *wetted* areas increases over time (figure 10.)

Adhesive B demonstrates a totally different behavior: nearly the entire area of the glass plate was wetted by B from the first moment of application. A further increase of the wetted areas could not be seen over time (figure 11.)

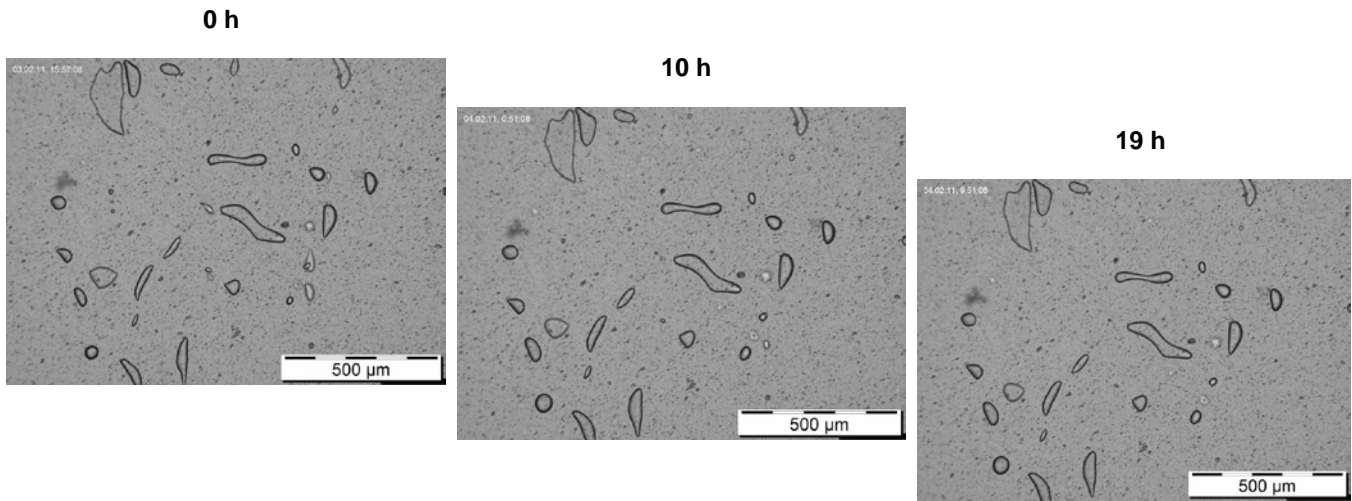


Figure 11. Time dependent wetting behavior of adhesive B on glass, done by LM. Visible dots are identified as air bubbles.

4. AFM (atomic force microscopy)

Atomic force microscopy was used to receive an image from the “pure” surface of the adhesives A and B. Figure 12 gives an excellent impression about the differences between both: The surface of grade B appears absolutely smooth in the chosen resolution, whereas the image of grade A indicates a rough surface.

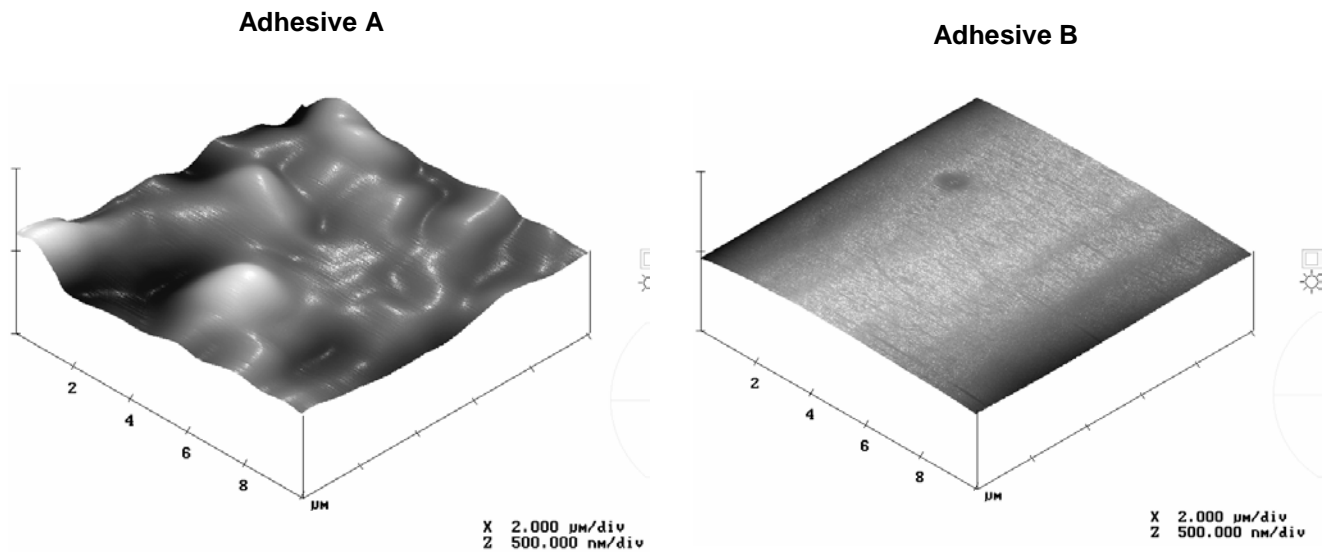


Figure 12. Roughness of surfaces of adhesive A and B, done by AFM

Conclusions

The adhesion behavior of the four different pressure sensitive adhesives shown above is influenced by the choice of monomers, polymer Tg and crosslinking system.

The right balance of monomer composition and crosslinking system leads to the unique adhesion behavior of adhesive A described above. The repositionable character seems to be a consequence of less contact area at the beginning of the application to the substrate due to the micro structure of the surface

of the formulation. Adhesive A shows increased wetting time as seen in the time dependent measurements. After extended time adhesive A reaches full wetting, similar to standard formulations. Ageing experiments could show that the micro structure which is causing this repositionability is not affected by high temperature storage of the coatings

Additional microscopy measurements are planned to compare removable adhesive D.

These results we have so far give an inside into the physical reason of the repositionable behavior.

Further studies have to be done to get an impression of the chemical structure behind.

Acknowledgements

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1. Silverberg, Eric (2009), "New solution acrylic PSA's for transfer tape applications", Contribution to PSTC TECH 32.
2. van Wijk, K., et al. (2007) Pressure sensitive adhesive composition as well as a method of applying it and a method for the preparation thereof, European Patent EP1858999