NOVEL UV-PSA for MEDICAL APPLICATIONS

Dr. Volker Erb, Manager PSA Platform, Henkel AG & KGaA, Düsseldorf, Germany
Cynthia Cain, Senior Development Chemist, Henkel Corporation, Bridgewater, NJ, USA

1. Introduction

Henkel introduces their newly developed radiation curable PSA class. The polymer base can be described as UV-Polyurethane-Acrylate and can be applied without solvents at low viscosities at temperatures below 100°C. The modular pre-polymer system has a very low non-polymer content, as well as an extraordinary property profile.

Additional outstanding characteristics include suitable adhesion to various surfaces, its conformity to ISO 10993 for medical devices and the exceptionally good processability in a variety of applications.

In processes and applications used in the medical market, the products have to fulfill many functional as well as legislative requirements, so the qualification of an alternative product is difficult and time consuming. The paper reports from a new UV-PU-Acrylate adhesive for medical devices, where the water vapor transmission rate is one key parameter in the area of the modern wound management. Further the adhesive has to have a very well controlled adhesive strength, so that the removal of the wound covering causes the least pain possible for the patient and provides a low-trauma-function.

In this context the new UV-PU-Acrylate adhesive system provides new opportunities, where current adhesives are limited in their performance.

2. Modern Wound Management

The days when plasters for wound dressing were accepted to cause skin irritation, pain when they are removed and leave dark sticky residuals on the skin around the wound are numbered. These are still found in the low performance (cost) range of the Traditional Wound Management environment.

Modern Wound Management is needed, where chronic wounds, serious large injured or inflamed skin areas are affected. The wound dressing is not to compare with the traditional plaster, as it usually combines the need for covering a wound with the therapy to close it. The common causes of these chronic wounds are diabetics (feet), decubitus (bedsore) and Ulcus cruris (ulcers).

To support the optimum recovery, the dressing – and so the adhesive used to affix it – needs to fulfill a number of requirements reaching from toxicological and dermatological clearance to functional must-haves like a high moisture vapor transmission rate (MVTR), adapted adhesion to skin, drug storage and release properties, as well as the compatibility with various substrates.

The main issue with chronic wounds is the change of cover material. If the wrong material had been chosen, tremendous pain is the consequence. Therefore the challenge in this application is the balance of adhesion to a very complicated substrate called human skin and the gentle removability.
In general, the adhesion to skin can not be simulated in all aspects. Even if corpse skin is used, the adhesion values can not be compared to skin of living persons. Even if tested on a living person, the adhesion can vary from day to day, from person to person, and also from different parts of the body.

3. Adhesive Performance

3.1 Adhesion Properties Testing

The new UV-PU-Acrylate was evaluated using standard PSA test methods, backed with PET and bonded to stainless steel. Tack was measured according to FINAT test method #9, “Loop-tack”. Peel strength was measured according to FINAT method #1, “Peel Strength (180°) 300 mm/min”. Static shear strength was determined according to FINAT method #8 “Shear Strength on Standard Surface”, modified by using polished stainless steel instead of float glass. The shear test was stopped at 100 hours.
While standard testing with PET backing is useful for industrial PSAs, it has much less relevance for medical applications. Testing on alternate substrates and with more flexible backings can be revealing. Figure 3 and 4 refer to polyethylene foam backed adhesive.

**Figure 3.** Loop Tack: 40 gsm, 60mJ/cm$^2$ UV-C on PE-Foam backed with 23 µm PET

Mechanical tack testing is better able to differentiate between tack levels compared to physiological testing on human skin and has a better repeatability. The general trend can be seen however, that initial tack on skin is increased for the high tack adhesive, as is the loop tack from steel and glass.

**Figure 4.** Peel development over time: medium tack adhesive, 40 gsm, 60mJ/cm$^2$ on PE-Foam backed with 23 µm PET
The peel adhesion values should represent the long term adhesion performance. The peel force of the UV-PU-Acrylate is much higher on steel compared to low surface energy substrates, as expected. Peel build on S.S. over time is shown in Figure 4, where it consistently builds to the level of foam tear, thus no longer representing the strength of the adhesive. There is no significant peel build on LDPE or PP.

3.2 Variables that May Effect Adhesion

UV Dose
UV dose is an important parameter to control when working with UV-curable PSAs. Figure 5 shows the influence of UV dose on S.S. peel. The higher peel value at 30 mJ/cm² of UV-C signifies the adhesive is less cured than at the higher UV doses. The similar peel values for 60 and 90 mJ/cm² of UV-C show that the cure has leveled off and that this adhesive is not sensitive to UV doses above 60 mJ/cm². The same trend was seen for loop tack values of adhesive cured with different UV doses.

![Figure 5. Effect of UV dose on 24h peel: high tack adhesive, 35 gsm on 50 µm PET](image)

Coat Weight and Formulation
Two common ways to increase adhesion are by increasing coat weight and through formulation. Figure 6 shows loop tack results for three tackification levels at two different coat weights. While the tack is clearly higher for 100 gsm coatings compared to 50 gsm coatings, the influence of formulation is more pronounced. For the lowest tack level, coating thickness does not play a role. Tackifier has a greater effect on tack at higher coat weight.
Increasing coat weight and tackifier content also results in an increase in peel force, as shown in Figure 7. While formulation is a factor in peel on all substrates and for both coat weights, it is most obvious at higher coat weights and on more polar surfaces. Coat weight influence is more pronounced for non-polar substrates and most likely is caused by better surface wetting.

Through factors such as backing, UV dose, coat weight and formulation, the new UV-PU-Acrylate can be tailored to the optimal levels of adhesion for specific medical applications.
3.3 Gel Content

A hint on the efficiency of the UV-crosslinking is the gel content. It is the fraction of adhesive, which cannot be dissolved under specific conditions (80µm mesh size filter for 24 h in ethyl acetate). The decrease in gel content versus the film thickness is remarkably low.

![Gel Content vs. Coating Weight](image)

In summary it can be concluded that the new UV-PU-Acrylate is an excellent candidate for very thick adhesive film coatings with excellent robust curing properties. This is an important point for Modern Wound Management as it had been proven, that thick adhesive films cause less pain on sensible skin than thin films.

4. Application Performance in Modern Woundcare

4.1 Moisture Vapor Transmission

One of the most interesting properties of an adhesive used for medical application is its capability to provide a controlled environment for the wound and the skin around the wound. There are several test methods for evaluating MVTR (ASTM D1653 - 03(2008)). In one method the water is in a cup and in direct contact to the film for 24 h at a climate of 25% relative humidity and approximately 40°C. Then weight loss is measured as water evaporates from the cup. This method is called “Wet Inverted Cup” method. The other common method is called “Dry Upright Cup” method. A cup filled with an absorbent and covered with adhesive film is placed in a climate of 90% relative humidity at 40°C. The MVTR is calculated by measuring the weight increase of the cup by the absorbed water vapor diffusion through the film.
Using the Wet Inverted Cup method, the new UV-PU-Acrylate has the same or higher MVTR than a commercial solution acrylic product designed for very high breathability. The standard solution acrylic PSA for medical applications has a much lower capability to provide the right environment for modern wound management. The rubber based PSA, which is used in lower performance medical products, is mentioned to demonstrate the development of new materials over the past 15-20 years.

Additional data achieved by Dry Upright Cup method confirms the trend. The performance difference between a common medical grade acrylic UV-PSA and the new UV-PU-Acrylate PSA is even higher with this method, while the influence of the different tackifier levels used with the UV-PU-Acrylate base polymer is not as significant as with the Inverted Cup method.

4.2 Toxicological and Physiological Testing

The testing of the adhesive is a multiple step process. In the actual case, the polymer base is completely new, so that the toxicity plays a major role.

4.2.1 Chemical Assessment

The first step is a chemical assessment, where the data from different analytical methods like GPC, HPLC, etc. is evaluated. In addition to this the complete preparation procedure is simulated in a so called “virtual reaction pot” in order to get additional information on potential new side products. If all components are identified and potential toxic substances could have been excluded, the adhesive is a candidate for the biological tests.
4.2.2 Toxicological Approval

Before a new adhesive base material can be tested on volunteers, the adhesive has to pass the Toxicological approval after ISO 10993-5 procedure. In this test the influence on the cell vitality with and without the adhesive is compared with a positive chemical (0.01% SDS, Sodium dodecylsulfate).

![Figure 10. Impact on Cell Vitality. The new UV-PU-Acrylate PSA has about the same effect as Aqua demineralis](image)

4.2.3 Dermatological Testing

The next step is the dermatological testing in a patch test, where volunteers are testing the adhesive on their skin for 24 hours. The Single Application 24h Patch Test according to COLIPA (The European Cosmetics Association) is an occlusive epicutaneous test method suitable to obtain experimental data for skin irritation of raw materials and/or formulations.

The irritation effects observed were recorded and documented 6, 24, 48 and 72 hours after removal of the plasters, separated to each of the parameters erythema, edema, scaling and fissuration according to the scale of Frosch (P.J. Frosch, A.M. Kligman: J Am Acad Dermatol 1, 1979, 35 - 41).

The resulting score values are evaluated numbers comprising the strength of the individual reaction. The individual score values were added over all recorded time points and divided by the number of volunteers. The resulting total irritation score was calculated for each test substance for the parameter erythema and for the parameter combination erythema + edema + scaling + fissuration.

As reference substances for this test method Texapon N70 1% AS (standard surfactant with good skin compatibility known), SDS 0.5% AS (sodium dodecyl sulfate), cosmetic alcohol and demineralized water were used.
Table 1. Calculated Total Irritation Score in % (number of volunteers n = 20) in comparison to the control substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>Total Irritation Score (all)</th>
<th>Total Irritation Score (Erythema)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% covered on Texapon</td>
<td>% covered on SDS</td>
</tr>
<tr>
<td>Demineralized water</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Cosmetic alcohol</td>
<td>23.7</td>
<td>16.4</td>
</tr>
<tr>
<td>SDS 0.5% AS</td>
<td>144.6</td>
<td>100.0</td>
</tr>
<tr>
<td>Texapon N70 1% AS</td>
<td>100.0</td>
<td>69.2</td>
</tr>
<tr>
<td>UV-PU-Acrylate formula, 110µm Film, undiluted</td>
<td>2.9</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The new UV-PU-Acrylate formula induced one slight and one medium erythema and one slight scaling reaction. Under these test conditions the skin compatibility of the new adhesive system was not significantly different compared to demineralized water.

4.2.4 Panel Test

Every time major changes are made in the formulation in order to adapt the functionality of the adhesive, the three first steps – Chemical Assessment, Toxicological Approval and Dermatological Testing – have to be done before the next Panel Test can be set up. The Panel test is the first time the adhesive is applied and tested mechanically on skin.

The major questions which have to be answered in a Panel Test regard the functionality, like initial tack, Adhesion after 24h, is the removal painful?, skin wetness after removal, and if the skin shows any kind of irritation (redness). As an example of the complexity of a wear study, Figure 11 shows a comparison between a commercial UV-acrylate used for traditional wound management and three variations of the new UV-PU-Acrylate adhesive cured at 90 mJ/cm² of UV-C.

On living human skin, the performance of the new UV-PU-Acrylate compounded with tackifier is comparable to the acrylate based UV-curable adhesive. It is important for modern wound management applications that the adhesion is matching exactly the needs. This means that it is not necessarily the highest peel which is wanted. With the new UV-PU-Acrylate the complete range of adhesion can be achieved.
Figure 11. Panel test on forearm of the new UV-PU-Acrylate vs. a standard UV-Acrylate on a breathable backing.

<table>
<thead>
<tr>
<th>Initial tack directly after application</th>
</tr>
</thead>
<tbody>
<tr>
<td>medium tack, UV-PU-Acrylate</td>
</tr>
<tr>
<td>full surface bonding</td>
</tr>
<tr>
<td>medium tack, UV-PU-Acrylate</td>
</tr>
<tr>
<td>completely sticking</td>
</tr>
<tr>
<td>Removal painful?</td>
</tr>
<tr>
<td>medium tack, UV-PU-Acrylate</td>
</tr>
<tr>
<td>painless</td>
</tr>
<tr>
<td>Wetness of plaster area, directly after removal:</td>
</tr>
<tr>
<td>medium tack, UV-PU-Acrylate</td>
</tr>
<tr>
<td>dry</td>
</tr>
<tr>
<td>Mechanical skin irritation or damage:</td>
</tr>
<tr>
<td>medium tack, UV-PU-Acrylate</td>
</tr>
<tr>
<td>no irritation</td>
</tr>
</tbody>
</table>
5. Processability

Viscosity is one of the key parameters when coating adhesive. The new UV-PU-Acrylate PSA is applied as a hot melt 100% solid material, which means, that no solvent or water has to be evaporated.

![Melt Viscosity range of tackified UV-PU-Acrylate PSA at elevated temperatures](image)

*Figure 12. Melt Viscosity range of tackified UV-PU-Acrylate PSA at elevated temperatures*

As shown, the viscosity at elevated temperatures is well below 5,000 mPas. Indeed the test coatings had been performed at 40°C on a lab coater. Thus, the new UV-PU-Acrylate PSA can be applied also on thermally sensitive substrates.

For processing and performance the viscosity and thermal characteristics are extremely important. It makes a difference if a new material can be used in common processes or if a new process has to be developed.

Because of the low temperature of the application, there is the opportunity to add sensitive components into the UV Acrylate formulation to make smart PSA adhesives.

Another process, where this new adhesive system works with success, is the transfer of adhesives with a metered roller applicator on a film, i.e. in a regular shape like a perpendicular line, on fast running machines. Usually this transfer of 100% solid PSA is only possible on very slow running applicators, because the melt has a tendency toward stringing. This new UV-PU-Acrylate makes an accurate transfer as the low viscosity and its high surface tension avoids the stringing effect.
6. Summary

A new UV-curable adhesive system was introduced. The technology is based on an advanced building block system which can be adapted and optimized especially in applications where highest technical and legislative demands have to be fulfilled.

Common in medical applications are adhesives made from acrylic copolymers or styrenic block copolymers, as solventborne or hot melt adhesive, UV or thermally-reactive or non-reactive. As mentioned above, one of the key-properties of an adhesive which is used in modern wound management is the moisture vapor transmission rate. The block builder UV-PU-Acrylate systems have MVTR values that are much higher than traditional solution acrylic adhesives and commercial UV acrylates and are infinitely superior to traditional SBC-based hot melts. This opens the door to new constructions.

The very low viscosity also opens process windows, which had been closed until now. Thermal sensitive substrates and fast accurate adhesive transfer are just first examples of what can be made.

The new UV- curable PU-Acrylate adhesive fulfills the ISO/DIN 10993 requirements and is entering the medical market for modern wound management.

In addition the VOC of the adhesive system is so low, that it fulfills the ISEGA compliance for food packaging without any limits and the ISO 10993 for medical products.

Acknowledgments

The authors would like to thank Melanie Lack for her dedication and personal efforts to make the mentioned adhesives work so fantastic. Further two teams headed by Peter Palasz, Kerstin van Wijk have contributed fantastic analytical and testing work, of which we were only able to show a small part.

Further we would like to thank Phenion GmbH & Co KG and their volunteers for the physiological testing.

Further we thank LOHMANN & RAUSCHER for authorizing the pictures demonstrating the field of Modern Wound Management used in the presentation.
Volker Erb, Ph.D., studied chemistry and polymer science at the University of Mainz, Germany and the University of Massachusetts, Amherst until 1993. He completed his masters’ degree and his Ph.D. at the Max-Planck Institute for Polymer Research at Mainz in the field of structured research on ultra thin films. After his Ph.D. in 1997, he joined the 3M Laboratories (Europe), where he was responsible for adhesive, coating and film development.

From 2000 to 2005, Dr. Erb worked for PolymerLatex, a former Bayer-Degussa Joint Venture, as product development manager and technical service manager for North and South America and later as technical marketing manager in the Middle East and Asian region with the Specialty Business Unit. Since 2006, he has managed Henkel KGaA’s Pressure Sensitive Adhesives Platform Adhesives Technology Platform in Düsseldorf.

He can be reached at volker.erb@henkel.com.