Relationship of pressure sensitive properties and UV-crosslinking technology

PAUL L. GEISS, WALTER BROCKMAN, AND BERND MEYER-ROSCHER

ABSTRACT

Adhesive properties of UV-crosslinkable hot melt pressure sensitive adhesives are the result of reaction of the adhesive to the parameters of the irradiation process. Adjustable processing conditions offer the unique opportunity to produce pressure sensitive products with different characteristics using a single adhesive without the need to formulate or otherwise add additional materials. UV crosslinking also allows creating patterns of high or low irradiated areas in the adhesive coating using masks, grids, or templates. The functional separation of high tack and high shear resistance areas of adhesives can create new products with varying features. The experimental part of the paper compares tack, peel, and shear data of acrylic UV-crosslinkable hot melt pressure sensitive adhesives in standard and pattern processing.

Application:

Using a UV-crosslinkable acrylic pressure sensitive adhesive with a mask to provide a pattern of cure can result in a balance of tack, adhesive strength, and shear resistance.

HOT MELT PRESSURE SENSITIVE adhesives (HMPSA) have wide use for adhesive tapes because of their compliance with solvent emission regulations and their high productivity rate. With styrene block copolymers, balancing low temperature tack with high temperature cohesive force is difficult because the base polymer requires blending with tackifier resins and oils. In contrast, acrylic polymers offer resistance to bleeding and good weathering characteristics.

UV-crosslinking of pressure sensitive adhesives offers alternate approaches to HMPSA manufacture. When compared with solvent coating and thermal drying processes and even with standard HMPSA, UV crosslinking offers true pollution prevention combined with savings of energy. UV units are inexpensive capital items that easily fit in existing coating lines. Medium pressure mercury lamps are electrically efficient in converting electrical power to usable UV light. They are now available with a maximum electrical power of 200 W/cm.

UV acrylic hot melt polymers are especially suitable for labels in specialized applications where they can offer important technical advantages. This includes closures, removable labels, heat and moisture resistant labels *(1)*, and textile and tire labels requiring higher coating weights. Additional uses are possible in the field of adhesive tapes where solvented adhesives with high cohesion and high coating weights dominate. Mounting tapes for the automotive industry where good resistance to heat and shear are necessary is an important area.

Other fields of application are mounting, masking films in graphical applications, and splicing tapes. Medical applications comprise another large sector. Self-adhesive articles for industrial intermediates include sound dampening products and abrasive papers. For both these applications, the coated products must withstand very high temperatures. For sound dampening products, the adhesives must meet specifications of the automotive industry *(2)*.

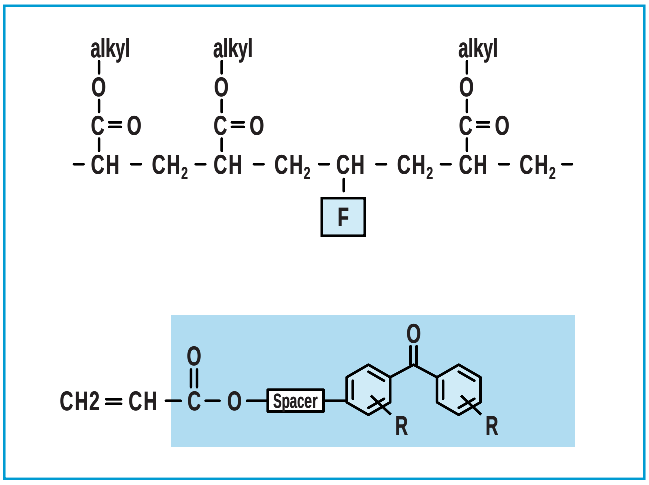
BACKGROUND

UV-crosslinking acrylic pressure sensitive adhesives

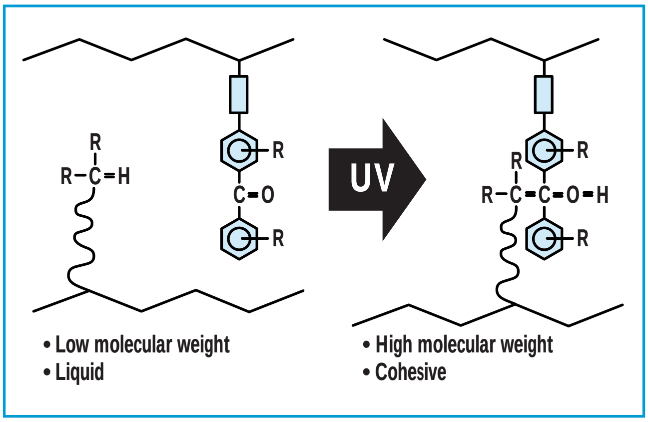
Standard HMPSA materials have a low viscosity suitable for application as a homogeneous thin layer when heated. These polymers achieve their adhesive strength during subsequent cooling on the base material. The absence of solvent gives this group of adhesives a high economic and ecological significance. In practice, this advantage leads to lower investment costs, lower space requirements, lower energy costs, and emission free processing.

Significant limiting factors for the application of hot melts do exist. A disadvantage is the restriction to a very narrow choice of polymers. Only very few polymers achieve the sharply defined viscosity change or jump between application temperature and temperature of use. Styrene-isoprene-styrene (SIS) and styrene-butadiene-styrene (SBS) are common block copolymers with major importance for hot melt applications.

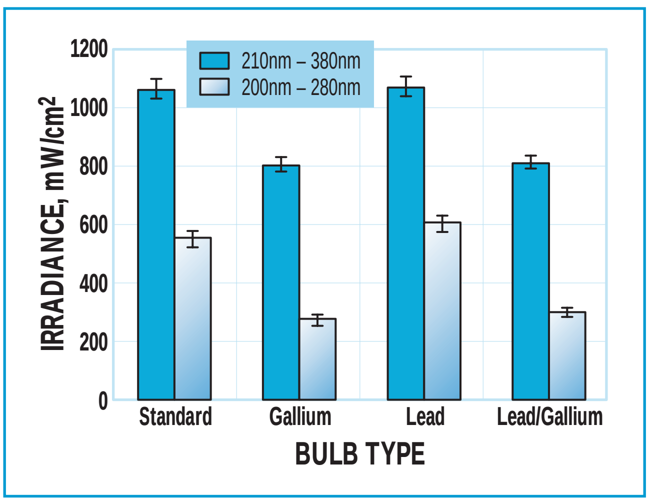
Polyacrylates that have proven their worth as high quality adhesives unfortunately have completely different flow behavior. Their temperature curve does not show any viscosity jump. Because the application of polyacrylates as a pressure sensitive adhesive requires high molecular weight, pure thermoplastic behavior—ability to flow at high temperature—is not possible. Acrylic HMPSA materials available commercially since 1996 use a completely new technology that avoids this disadvantage and brings many benefits.



1. *Structure of UV-crosslinkable acrylic pressure sensitive adhesives*



2. *Crosslinking reaction*



3. *Emission characteristic of different bulb types*

These polymers consist of common acrylic ester monomers used for adhesive synthesis such as butyl acrylate, ethyl hexyl acrylate, or acrylic acid and a copolymerizable photoinitiator as **Fig. 1** shows.

The polyacrylates can have molecular weights of 100,000–300,000 g/mol. The melt viscosities of such polymers at 120°C are approximately 3 x 104 mPa. This allows processing with conventional hot melt coaters.

The most important component of these new polymers is the copolymerizable photoinitiator. It is another monomer that forms part of the polymer chain as **Fig. 2** shows. This means it cannot migrate. UV exposure causes the photoinitiator to react with a C-H bond via a photo reduction to form a benzhydrole system.

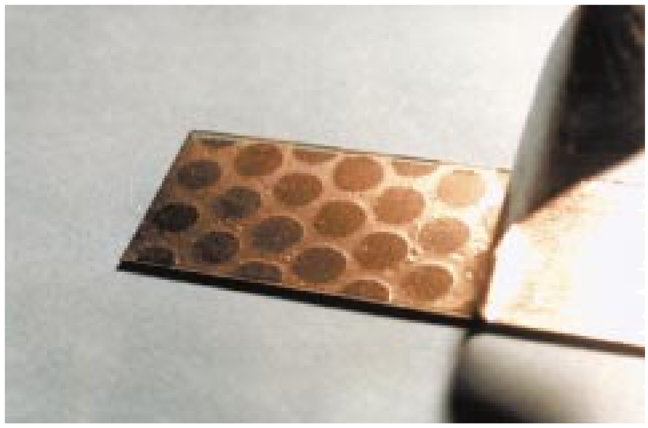
The outstanding characteristics of the crosslinking principle are the following:

- The reaction proceeds using any hydrogen atom, i.e., no specially activated C-H bond or double bonds are necessary.
- Oxygen does not inhibit the reaction, i.e., UV exposure does not require an inert plant atmosphere.
- No byproducts form during the crosslinking reaction such as with UV curing involving added photoinitiators.
- Crosslinking proceeds as long as UV light is present. Photocrosslinking is therefore very rapid. The UV dose controls the degree of crosslinking. This means it also controls the adhesive properties.

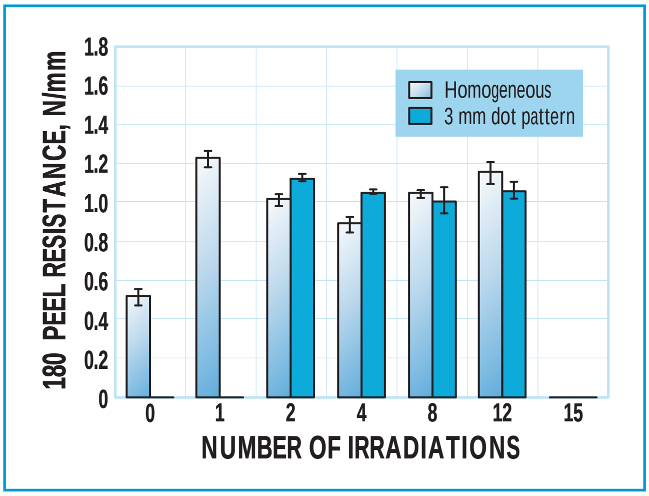
The products have high tack but low cohesion before crosslinking and possess marked cold flow properties. The pressure sensitive properties of the adhesives are the result of defined UV exposure from conventional UV lamps such as used with printing inks and coatings—medium pressure mercury vapor lamps—shining directly on the coated substrate. Depending on the UV exposure, the failure mechanism can change from cohesive to adhesive. UV exposure is the result of the number, type, and output of the lamps and the speed of the web. Varying the degree of crosslinking can adjust the adhesive properties. This gives the processor an additional degree of freedom to develop products. This allows making different products with properties ranging from high cohesion and little adhesion to high adhesion and low cohesion using only one raw material.

The UV acrylics meet all the current requirements for environmental and working safety. They cause no problems in processing and produce almost no emissions. The resulting products are toxicologically safe as shown by comprehensive studies involved in obtaining approval for food packaging and in determining skin irritation and cytotoxicity.

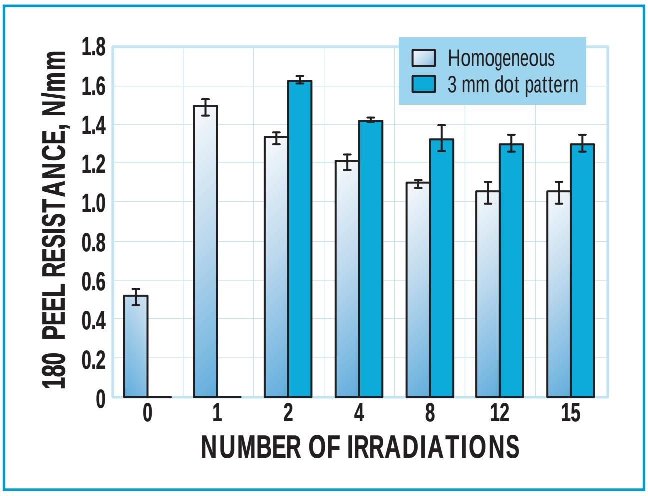
4. *Cohesive failure*



5. *Mixed cohesive and adhesive failure due to selective crosslinking*



6. *Standard medium pressure mercury bulb results*



7. *Gallium doped medium pressure mercury bulb results*

UV technology

Medium pressure mercury UV units are common. A clear fused quartz tubing encloses the mercury vapor and a starting gas. When the lamp receives power, the voltage between the electrodes at either end increases until ionization of the starting gas occurs. As the lamp warms, the plasma changes from that of the starting gas to a constricted mercury arc. The output energy of standard lamps is characteristic of mercury emission spectra. The dose in energy per unit area received by a surface moving under a UV lamp is inversely proportional to its linear speed and proportional to the time integrated irradiance—the area under the peak width curve. Several instruments allow determination of the UV irradiance available. One source for deviations between instruments of various manufacturers is the different valuation of the direct and transverse parts of the UV radiation.

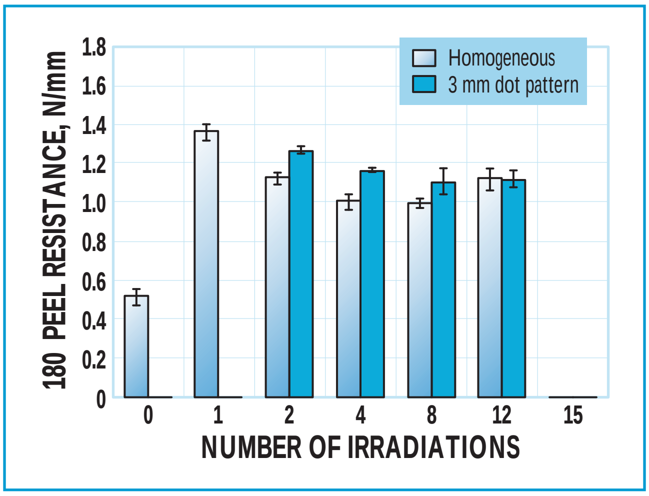
The reflector system focuses about 30% of the radiant energy to the exposed surface. Using special so-called “cold mirror” reflector materials can eliminate the infrared share of the spectra to reduce the thermal stress of the irradiated substrate significantly. This allows application of higher peak UV doses without thermally damaging the adhesive. Safely processing heat sensitive materials is also possible.

Use of specific filling gases and temperature and pressure can influence the wavelengths emitted and their relative energies. Additives such as metal halides as small quantities in the filling modify the emission spectra. Short wavelength energy emitted by the mercury interacts with molecules of the additive material to re-emit light at longer wavelengths. This fluorescence enriches the spectral output in the longer UV wavelengths and is the basic principle of special UV bulbs. The composition of the quartz bulb material can also change the emission spectra in the region of short wavelengths. UV radiation below 240 nm is especially responsible for ozone generation. Ozone free UV bulbs often use a special quartz tubing that absorbs this part of the mercury emission spectra.

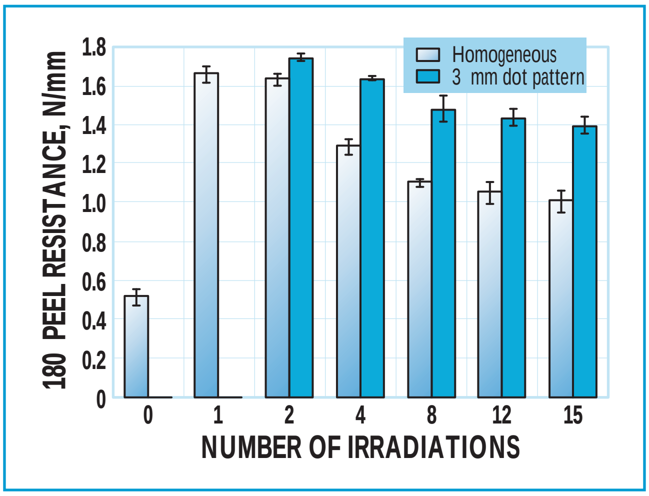
Selection of UV spectra can produce different results in the crosslinked adhesive such as depth of cure and adhesion.

Pattern crosslinking

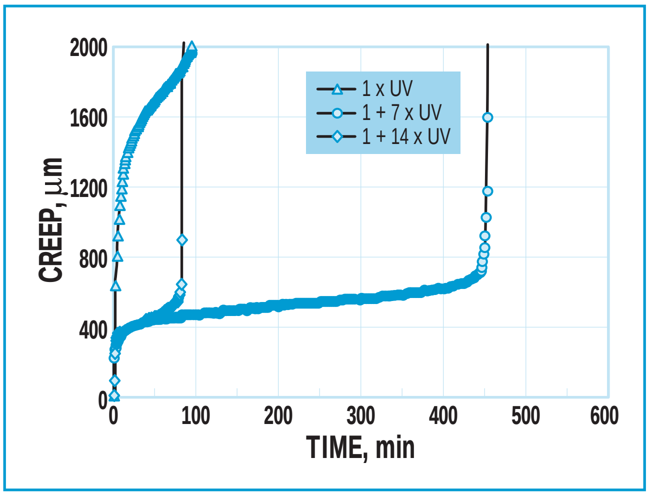
UV-crosslinkable HMPSA materials



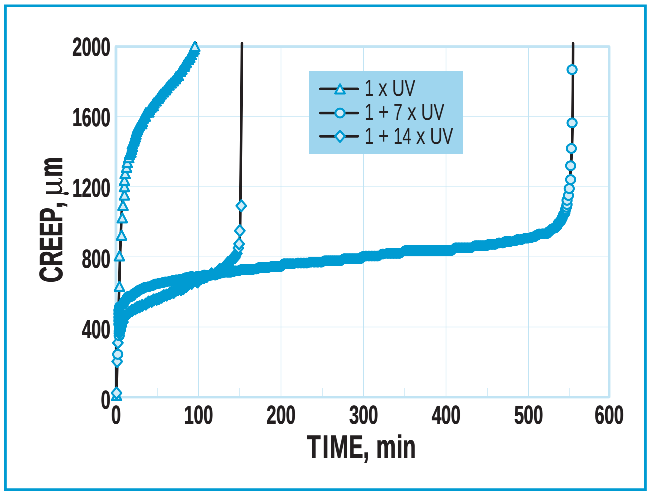
8: Lead doped medium pressure mercury bulb results



9. Lead/galium doped medium pressure mercury bulb results



10. Creep under static shear stress with lead/galium doped bulb and homogeneous irradiation

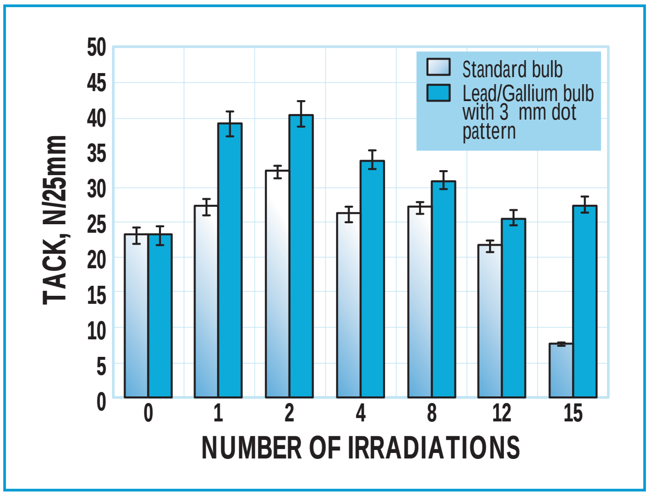


11. Creep under static shear stress with lead/galium doped bulb and pattern crosslinking

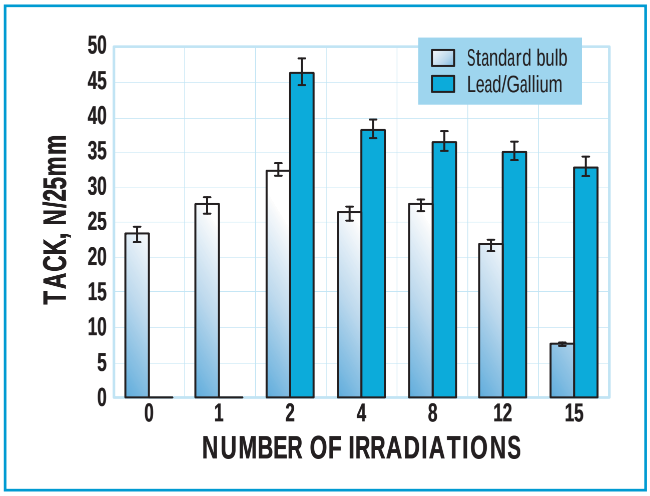
offer low melt viscosities during the coating process and excellent shear stability in the application after irradiation. Crosslinking has a strong influence on tack and peel resistance of the adhesive. For best pressure sensitive performance, finding process settings that lead to balanced values of tack, peel resistance, and shear resistance for the intended application is necessary. If satisfactory results are not possible with homogeneous UV crosslinking *(3)*, a functional separation of high tack and high shear resistance areas will result by using grids or masks between the UV lamp and the adhesive during irradiation.

EXPERIMENTAL

The results in this study used a commercially available acrylic adhesive. The product comes ready for use, and small portions are easily melted. Coating used a small, heated, table-like laboratory coater that can coat sheets of 0.3 m x 0.5 m with an accuracy in thickness of 5 µm. Coating thickness of the UV-crosslinkable acrylic adhesive was 60 µm. The UV crosslinking of all samples used a conveyor type, single lamp UV unit with a cold mirror reflector at a working distance of 100 mm and a line speed of 600 mm/min. The experiments compared four different UV bulbs—one with a standard mercury filling and three bulbs doped with different gallium and lead halides---to determine their effect on the adhesive performance in typical pressure sensitive tests. The grid to create a crosslinking pattern had holes of 3 mm diameter with a total shaded area of 3%. It was 5 mm from the surface of the adhesive. For the 180° peel tests, the adhesives were coated directly on a 0.15 mm alu-



12. Loop tack test for two different UV bulb types



13. Loop tack after standard processing compared with pattern crosslinking with a lead/galium doped bulb

minum foil. The sheets were cut into 25 mm wide strips and rolled twice on 1.5 mm $AlMg_3$ specimens 100 mm x 25 mm with a 4.5 kg rubber-covered roller. After 24 h, the samples were tested at 100 mm/min. The loop tack test used 175 mm long and 25 mm wide strips of 0.1 mm stainless steel foil on adhesive coated sheets of 1.5 mm $AlMg_3$. The contact time was 10 s, and separation speed was 100 mm/min. The creep results in this study used single lap shear samples of stainless steel and a bonding area of 25 mm x 25 mm at a load of 1 kg. Dwell time after joining was 24 h. All tests were at room temperature.

RESULTS AND DISCUSSION

UV measurements

Figure 3 shows the peak UV irradiance values of different bulb types for two different UV sensors. One sensor is sensitive in the entire UV spectra, and the other sensor only provides emissions of wavelengths from 200–280 nm. The readings of both sensors in Fig. 3 therefore give information about total energy emission and the reduced portion of the spectra.

180° peel test

The 180° peel test provides a numerical value of the adhesive strength and indicates the state of the adhesive by its failure mode. The uncrosslinked adhesive fails by cohesive separation with strong fibrillation during the peel test as **Fig. 4** shows. The viscous properties of the adhesive govern the peel strength. Strength is also very dependent on peel rate.

The incompletely crosslinked adhesive coating separates in a mixed mode during peel with areas of cohesive and adhesive failure. These samples usually have the highest peel strength. Further crosslinking reduces the peel strength and finally leads to a purely adhesive separation of the specimens. The correct combination of high or low crosslinked areas in a single adhesive film that **Fig. 5** shows can cause a mixed failure and therefore increase the total peel strength over a wide temperature range. **Figures 6–9** display the peel strength for different bulb types with and without the pattern crosslinking technique for various UV doses. For the selective crosslinked samples, one pass through the UV unit did not use the grid to ensure a minimum crosslinking density in the shaded areas to avoid fibrillation in the peel test. The following irradiation passes used the 3 mm round hole grid.

The results show that the combination of selective pattern crosslinking and improved lamp technology can lead to a higher peel resistance compared with a standard bulb with homogeneous irradiation. This effect is especially obvious at high UV doses.

Creep test

Similar to the 180° peel test, the crosslinked adhesive behaves completely different from the uncrosslinked raw material. The untreated adhesive is a liquid polymer and therefore cannot support any static shear load. With increasing crosslinking density, the cohesive strength increases until adhesive failure leads to a premature failure under small deformations. Loss of adhesion is the cause for this behavior that was already obvious in the 180° peel specimens. **Figure 10** shows the creep measurements of 60 µm adhesive between stainless steel plates at a load of 1 kg per 25 mm x 25 mm for three different irradiance doses with the lead/gallium doped bulb.

The samples irradiated 15 times that show adhesive failure after 85 min especially demonstrate the negative effect of excessive crosslinking.

Using the 3 mm grid with the lead/gallium doped bulb in **Fig. 11** also has a positive effect on the time to failure in the creep experiment, although the total deformation of the adhesive due to the lower total crosslinking density is higher than with the homogeneously irradiated samples.

Tack test

The loop tack test in **Fig. 12** used uncoated strips of 0.1 mm stainless steel foil on sheets of 1.5 mm $AlMg_3$ with 60 µm adhesive. The advantage of this procedure is that the strips for the test loop are easier to cut and handle without adhesive coating.

Fig. 12 illustrates the gain in tack by using a UV source with reduced ozone generation compared with a standard medium pressure mercury lamp. **Figure 13** shows that an additional improvement in tack will result from the combination of the lead/gallium doped bulb with pattern crosslinking technology.

SUMMARY

Tuning the emission spectra of a UV source to match the needs of an adhesive crosslinking system can give an improvement in pressure sensitive properties. Superior peel resistance, shear strength, and tack are hard to combine in a homogeneous material. The solution to these contradictory demands is to create a radiation pattern by using a mask between the UV source and the adhesive. This can generate a micro structure of low and high crosslinked areas on the adhesive film and help combine apparently contradictory properties in a single adhesive layer of UV-crosslinkable pressure sensitive adhesive. The functional separation of high tack and high shear resistance areas leads to more reliable process conditions and allows tailoring the pressure sensitive properties by changing the UV dose and the size, distribution, and percentage of shaded and irradiated area. TJ

Geiss and Brockmann are research engineer and professor, respectively, at University of Kaiserslautern, Kaiserslautern, 67663 Germany, and Meyer-Roscher is research chemist at BASF AG, Ludwigshafen, 67056 Germany.

Received for review March 25, 1998.
Accepted May 1, 1998.

Presented at the TAPPI 1998 Hot Melt Symposium.

LITERATURE CITED

1. Brockmann, W and Geiss, P. L., *Proceedings of the International Pressure Sensitive Adhesive Technoforum*, The Adhesion Society of Japan, Tokyo, 1997, p. 1.
2. Barwich, J., Dusterwald, U., Meyer-Roscher, B., et al., *Adhesives Age* 40(4):22(1997).
3. Brockmann, W and Geiss, P. L., *TAPPI 1997 Hot Melt Symposium Proceedings*, TAPPI PRESS, Atlanta, p. 153.