The bonding model of pressure sensitive adhesives (PSAs) was used in the search for new tackifying materials which show superior peroxide compatibility compared to commercially available resins. As future developments, e.g. in belts, are directed towards higher temperature resistance combined with good dynamic properties, the request for new systems is often directed towards the chemists. Sulfur systems, which were predominately used in the past, are becoming more and more obsolete. How to increase building tack, however, is a question that still remains to be solved. New polymeric tackifiers based on Levapren® VP KA 8896 were therefore designed using the bonding model first described by Chang [1]. This polymer shows excellent peroxide compatibility with superior tack efficiency compared to the C5 naphtha stream derived resin described in the last chapter.

### Theory of adhesive and cohesive bonding

The term pressure sensitive (or sometimes self adhesive) is used to designate a distinct category of adhesives. They are permanently tacky in the dry form (solvent-free) at room temperature and firmly adhere to a variety of dissimilar surfaces. This definition is aimed at excluding solvent-active adhesives which require solvent to introduce tackiness, hot melts which are tacky at elevated temperatures but not at room temperatures, and contact adhesives which adhere to themselves but not to other surfaces [3].

In order for a PSA material to form a physical bond, two requirements must be met: the bond formation must be thermodynamically favorable, and the contact area must be established using light pressure within a reasonably short time.

The first requirement is based on the intrinsic surface activity, which is the result of thermodynamic interactions such as dispersion forces and polar interactions. These interactions control the development of a contact interface between the components.

The second requirement, the bonding term B, is a kinetic process and depends largely on how easily a PSA material can flow under pressure. Consider $A_0$ to be the total area available for the adhesive material to make a contact, and A is the actual contact area established during the time t. The bonding term B is proportional to the ratio $A/A_0$, which is related to the creep compliance $J(t)$, given by the following equations:

$$B \sim A/A_0 = 1 - e^{-J(t)} \quad (1)$$

$$J(t) = 1/G'((\omega)) \cdot 1/(1 + \tan^2(\omega)) \quad (2)$$

In the above equations, $G'$ is the dynamic storage modulus measured at the bonding frequency $\omega$, and $\tan \delta$ is the ratio $G''/G'$ in which $G''$ is the dynamic loss modulus measured at the same frequency [2, 3]. Another important attribute of PSAs is the energy of separation (de-bonding). De-bonding is a measure of the energy dissipation upon deformation. The energy of deformation can be related to dynamic loss modulus $G''$, measured at the de-bonding frequency. The viscoelastic window concept as published by Chang [1, 2] was used for the interpretation of the data gained from dynamical measurements of the storage $G'$ and loss $G''$ modulus. This methodology allows determination of the application areas of PSAs as measurements at 0.01 Hz reflect bonding and 100 Hz reflect the de-bonding stages of PSAs. These frequencies are chosen because the range covers most of the time scales corresponding to the uses of PSAs at different application rates in performance tests (Fig. 1).

The viscoelastic window concept based on $G'$ and $G''$ at different frequencies was experienced by Chang [1, 2]. He found that for most PSAs the range of $G'$ and $G''$ at room temperature falls between $10^3$ and $10^6$ Pa. The bonding frequencies of 0.01 Hz (bonding) and 100 Hz (de-bonding) in conjunction with $G'$ and $G''$ gives therefore the concept shown in Figure 2:

This model allows identification of the adhesive performance of the PSA according to the position of the viscoelastic window (with reference to $\tan \delta = 1$).
Dahlquist criteria line refers to the critical value of the elastic modulus $G'$ [4, 5]. The Dahlquist criteria lines are an important reference as they indicate whether a material would be contact efficient (PSA) or deficient (non PSA). All established PSAs have a bonding modulus $G'_0$ well below the upper Dahlquist criteria, which means good conformability. Viscoelastic windows above the lower Dahlquist criteria, on the other hand, correlate with sufficient bonding strength. (the lower limit is shown in figure 5) All HS PSA (high shear pressure sensitive adhesives) viscoelastic windows are placed above the upper limit. In other words, by comparing the base of the window with the Dahlquist criteria, we know immediately whether the material is a PSA and what PSA category.

In addition Franck experienced in practice that tan delta correlates well to the cohesive strength of an adhesive for $\tan \delta < 1$ [6].

From major regions or quadrants plus a central region PSA application windows can be identified as shown in figure 3:

High shear PSAs occupy the top right hand corner which means that they exhibit high modulus $G'$ and high dissipation $G''$ within the application frequencies. GPSSAs, general purpose PSAs are located in the central region overlapping part of all four quadrants, illustrating the general purpose nature of this type of adhesive.

**Ethylene Vinyl-Acetate copolymers: Thermoplastic EVA and EVM rubbers**

In the thermoplastics industry, ethylene vinyl-acetate copolymers (EVA) with a VA content typically from 19–28 weight % are well known. This is due to the large consumption of this classical hot melt material in various applications, ranging from construction to book binding for example [3]. In contrast to the thermoplastic EVA, Levapren® grades can be classified as EVM.

The VA content of these grades range from 40–80 weight %. With a VA content below 40 weight %, severe crystalinity of the polyethylene moieties is observed, thus restricting these grades for low temperature applications. On the other hand, the Levapren® grades from 50–80
weight % VA content show no signs of crystallinity. The Tg of the 800 grade is shifted towards thermoplastic regions around 0°C. This restricts this grade for adhesive applications which involve high dynamic loads (figure 5).

The product range includes grades of different VA content and Mooney viscosities or MFI. In addition to the standard grades, new pre-crosslinked grades are available with 50±70 weight % VA (table 1).

Results and discussion

All Levapren® grades were examined applying the Chang method described in the introductory chapter using a Bohlin rheometer VOR with a frequency sweep method with constant deformation at room temperature and at 40°C.

The EVM grades were primarily found in quadrant 2 (upper right hand side, high $G''$ high $G''''$) which reflects high energy dissipation $G''''$ throughout the adhesion process and high modulus $G'$. Shear is high because of the high $G' = high cohesive strength of the material (figure 6).

Two significant observations were made:
- Levapren® 800 HV shows only a very narrow viscoelastic window, as the Tg plays a dominant role at higher frequencies.
- Levapren® VP KA 8896 = Baymod® L.2418 (here indicated as Levapren® 2418) shows the largest viscous area in the application quadrant explaining the excessive cold flow properties of this grade.

Influence of the molecular weight

Within the Levapren® 450–456 series the MW is varied as demonstrated by the melt flow index. MFI values of the respective EVM grades are given in brackets (MFI measured at 190°C):450 (3–5) < 452 (5–15) < 456 (15–30). The influence of the MW on the positioning of the quadrants is shown in figure 7.

As can be seen from figure 6, a higher MFI (which correlates with a lower molecular weight) yields to more general purpose PSA qualities. (GPPSA) It is therefore possible to tailor-make PSAs as a function of MW. The lower the MW (Levapren® 456), the lower the resulting bonding strength at room temperature. Levapren 456 can therefore be classified as a GPPSA.
Influence of the VA content

The lower the vinyl acetate content of the EVM and the higher the ethylene content, the closer the thermoplastic PE border. Within the Levapren® 800 HV – Levapren® 500 HV series the tendency to more nonbonding materials can be clearly observed. In contrast, Levapren® 700 HV and Levapren® 800 HV show optimum HS PSA quadrant fit (figure 8).

Influence of the lack of crystallinity

The Dahlquist criteria with \( \tan \delta = 1 \) reflects an equal proportion of the resulting bonding energy, which can be described by the elastic modulus \( G' \), and the dissipation of the energy throughout the bonding process, which can be described by the loss modulus \( G'' \). It was assumed that within a nonvulcanized rubber – rubber surface contact the physical entanglements should be most favored by a material which exhibits a relatively high viscous part. These properties were found with the Levapren® VP KA 8896 which has a VA of 68 % and an MFI of 15–35. From the MW point of view, it is therefore similar to Levapren® 456. With the 456 grade, however, stronger crystallizing effects yield a quadrant placement with a very small \( G'' \) proportion. (see figure 7 and compare with figure 9).

The high cold flow which is observed with VP KA 8896 correlates very well with the positioning of the visco-elastic window.

Influence of the operating temperature

The \( \tan \delta \) measurements at room temperature reveal a value of 0.3–0.7 depending on the grade of Levapren® investigated. The exception is Levapren® 800 HV, which shows a very high increase in \( \tan \delta \) due to the shift of the \( T_g \) of the polymer. A \( \tan \delta \) drift to higher values of 0.3–0.9 is observed when the operating temperature is increased to 40°C. Again it is very significant to note that Levapren® VP KA 8896 shows the highest viscous properties. This is clearly seen in the high \( \tan \delta \) values over the entire frequency range. At higher frequency, a slight increase in the \( \tan \delta \) value of Levapren® 800 HV is observed, but not as significant as measured before at room temperature. At 40°C it was found that the Chang visco-elastic windows of all Levapren® grades are shifted towards lower \( G' \) and higher \( G'' \) ranges.

Comparison of Levapren® grades versus resin tackifiers

Tack measurements of Peroxide-Accelerated EPDM batches

The intended properties for a new polymeric tackifier were directed towards the following requirements:
- increasing building tack in technical rubber goods construction (high adhesion for both first contact and permanent contact once adjusted, higher cohesion for immediate separation without cohesive failures)
- peroxide compatibility
- easy to handle and mix
- no disadvantageous effects on physical properties of the finished product.

An EPDM (Buna® EP-G 3850) test recipe was chosen for first comparison studies (table 2). In addition, tack measurements were performed using the tack meter set up shown in figure 10.
Mixing procedure:
A GK 1.5 E mixer was used with the following mixing sequence: (filling level 70%, 60 rpm)
- 60" polymer
- 60" black, ZnO, AO, 1/2 oil
- 60" 1/2 oil
- 60" degassing
- 60" or max 150°C

Accelerators were added on the open mill.
The nonvulcanized batches were pressed onto cotton fabric (Baumwollkreuzkörper-Gewebe Fa. Walraf) to give 25x25x0.1 plates in Teflon film at 105°C with the following sequence:
- 5 min: 20 bar
- 5 min: 200 bar
- 10 min cooling.

This sample preparation was intended to simulate the construction of a e.g. belt fabric and it’s subsequent contact to a e.g. cord compound. For tack measurements the plates were immediately covered in Teflon film and stored for 1 day at room temperature (apart from those samples which were additionally stored at elevated temperatures for long-term tack measurements).

The sample geometry which was used for the measurements with the tack machine shown in figure 10 is a plane-to-plane contact of a round rubber surfaces approximately 1 cm in diameter. One rubber sample is glued onto a metal cylinder and is pressed with a constant pressure of 5 bars for 10 sec onto a fixed rectangular rubber slab. The force which is required to separate both samples is measured over the period of 6 min.

In comparison to the Buna® EP G 3850 control batch, Levapren® 600 HV showed an increase in the first peak, which was ascribed to the adhesive de-bonding

Table 2. EPDM test recipe with EVM tackifiers

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Fig. 9. Levapren VP KA 8896 (here Levapren 2418); the potential rubber tackifier

Fig. 10. Tack measure set up
force. In addition, Levapren® 700 HV was also found to yield an increase in the maximum of the first adhesive peak. The VA range for an optimum adhesive material was therefore assumed to be between 60–70 weight % (figure 11).

A further request in tackifier design is to allow adjustment of the rubber-rubber contact. This implies that the overlapping slabs will have to be separated and rejoined in an optimum position. A decrease in cohesive strength (inner reinforcement) would ultimately lead to cohesive failure, hence leading to inherent failure of the finished article.

A reduction in the cohesive de-bonding force, however, implies an increase in cohesive bonding in the polymer network. This effect is predominantly influenced by the batch viscosity, as shown below (e.g. TRIM = batch 1, see also red graph in figure 11 shows no cohesive peak) (table 3).

In order to compare the tack efficiency of the standard Levapren® grades with commercially available tackifier resins, the following recipe was used.

Different resins were compared using a 15 phr dosage rate which was intended to give compounds with similar hardness in comparison to the first Levapren® series. The sample preparation for the subsequent tack measurements was identical as described previously.

The highest adhesive de-bonding force (delta 0.2 N/mm²) was observed with the Exxon Mobil product. It is, however, not possible to differentiate between adhesive and cohesive de-bonding mode, as the adhesive peak is very broad. This, however, might indicate, that adhesion effects are far more dominant than cohesion effects. In summary, this was observed with most of the investigated resin systems. This might be due to the difference in molecular weight as most resins will range in between 3000–4500 g/mole, which is nowhere near a polymeric tackifier such as VP KA 8896.

Comparison of the influence of resin and Levapren® systems on crosslink density (XLD) and physical properties

The influence of both systems on the XLD (in dNm) is shown in figure 13:

In general resins reduce the XLD significantly (up to 90 %), the exceptions being batches 4 and 6 where approximately 50 % of the control XLD was achieved. In contrast, the standard Levapren® grades with a dosage of 10 phr show no influence on XLD. With increasing dosage rate, more polymer is available (or less peroxide) hence the XLD is reduced. As expected, the coagent TRIM increases the XLD.
The modulus 100 and hardness of the resin systems are therefore significantly reduced as shown in figure 14.

It was found that Rhenosin P6173 and Escorez 1102 systems exhibit the best overall tackifying performance. The big disadvantage, however, is the lack of peroxide compatibility.

In addition, it was assumed previously that an optimum Levapren® tackifier should exhibit a VA content of between 60–70 weight % (reflects adhesive mode) and a relatively low molecular weight = high MFI (reflects the cohesive mode).

Table 4. EPDM test recipe with Resin tackifier

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Rhenosin is a registered trademark of Rhein Chemie, Escorez is a registered trademark of Exxon Mobil Chemicals.

Fig. 13. Influence of tackifiers on cross-linking-density

Fig. 14. Physicals of EPDM vulcanisates
Comparison of a new polymeric tackifier Levapren\textsuperscript{\textregistered} VP KA 8896 vs. Escorez\textsuperscript{\textregistered} 1102 with adjusted finished article hardness

Different dosage rates of Levapren\textsuperscript{\textregistered} VP KA 8896 (68 weight \% VA content, MFI \textasciitilde 15\textpm30 at 190 °C) were compared in a 3rd series with Escorez 1102 using 8 phr of peroxide for batch 8 as shown in table 5.

In addition to the 1 day storage period for the cotton fabric sample, further aging at 40 °C in Teflon\textsuperscript{\textregistered} film (loose, not attached to the surface) was performed. The strength of the adhesive de-bonding force was measured with the Monsanto Tel Tack set up (figure 15). This investigation was performed with the high Mooney Buna\textsuperscript{\textregistered} EP G 6850 grade. Due to the change in polymer and the change in measuring device, a direct comparison of the control values as described in the previous chapters is therefore not possible.

A maximum tack value was observed with 5 phr of Levapren\textsuperscript{\textregistered} VP KA 8896. The value, however, decreases drastically upon aging. This identifies the new experimental grade as a short term tackifier.

Summary

The purpose of this investigation was to identify an alternative for classical resin tackifiers for peroxide cured EPDM applications. It was demonstrated, that Levapren\textsuperscript{\textregistered} VP KA 8896 enhances tack of the uncured batch without negative effect on the physicals of the vulcanisate. In addition, it was found that Levapren\textsuperscript{\textregistered} VP KA 8896 gives an immediate tack increase which declines after 1 day storing at 40 °C. It is therefore classified as "short-term" tackifier in EPDM peroxide cured systems.

Acknowledgement

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Literature


The authors:

Dr. Parg is employed as Technical Manager for Speciality Elastomers in the Rubber Business Group at the Bayer headquarters in Leverkusen, Germany. Within this appointment he is in charge of developing new applications for specialty elastomers such as HNBR, EVM and others in the automotive; construction / building and off-shore industry.

Corresponding author:

Dr. R. Parg
Geschäftsbereich Kautschuk Forschung und Entwicklung Bayer, AG 51368 Leverkusen