

Self-Adhesive Roofing Felts: Mass Production or Made to Measure

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Abstract

In the roofing industry, modified bitumen membranes are generally applied by torching with an open flame or mopping with hot bitumen or asphalt and cold adhesive. These methods can ensure a strong and watertight seam of overlapping membranes. However, mopping creates health and odor concerns while torching carries the risk of fire. Use of cold-applied, solvent-based adhesives is growing rapidly but there are still limitations associated with volatile organic compound (VOC) issues and longer curing times than torched or mopped systems.

A growing demand for self-adhesive roof membranes, driven in part by insurance companies and legislation to increase the safety of the installation workers, stimulates the development of suitable formulations to improve the quality and expand the scope of these products.

Although there are regional differences, premium self-adhesive roofing compounds are generally composed of multiple ingredients: bitumen/asphalt, a mixture of SBS and SIS block copolymers, SB di-block polymer, tackifying resin, naphthenic oil, oxidised bitumen and filler. The mix of included ingredients is determined partly by the requirements for the final product. However, most importantly, this is strongly influenced by the kind of bitumen or asphalt that is used. In addition to the same high-temperature performance requirements of conventional membranes, self-adhesive compounds have the additional requirement of being tacky at the lowest application temperature. This more stringent requirement of performance over a wide temperature range usually necessitates more complex formulations.

The three most important characteristics required in self-adhesive compounds are: flow resistance, low temperature tack and resistance to disbonding. The first two are primarily rheology requirements while the latter is characterised by adhesive and cohesive strength. Rheological models exist for standard nonbituminous compounds, but with asphalt being the major component, the models no longer apply. Recent developments are focused on simplifying the composition of the compound and thereby easing the manufacture of the self-adhesive compound. Experimental isoprene- and butadiene-based block copolymers to be used as single polymers have been developed. They balance the various requirements for self-adhesive roofing felts.

Although the production may be simplified by the use of a single polymer combining sufficient viscous and elastic behaviour in a single SBS or SIS block copolymer

dedicated for this application, fine tuning may still be required depending on the nature of the bitumen/asphalt composition.

Author biography

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After graduating (Chemical Engineer) in 1986, I was employed by 'Shell Exploration and Production' for 2 years, modelling oil recovery profiles. After this period I was employed by 'Shell KRATON Elastomers' at the 'Royal Shell Laboratory Amsterdam'. In the first assignment the focus was on process engineering issues for the manufacture of KRATON D (SBS, SIS) polymers in the European production facilities. A second assignment focused on the start-up of the KRATON G (SEBS, SEPS) polymer production facility in Berre, France. After study Management Accounting a new role was taken up in KRATON Polymers. In my current assignment I am responsible for R&D programmes and Technical Support for KRATON Polymers in bitumen for industrial applications in EU/AF/ME. Member of the BWA (Bitumen Waterproofing Association) - Technical Committee (Europe).

1. Introduction

Mainly driven by health, safety and environmental (HSE) reasons, insurance companies and authorities promote the use of self-adhesive, bituminous roofing membranes that can be applied without torching, hot bitumen or solvent-based cold adhesives.

An adhesive may be defined as a material which, when applied to surfaces of materials, can join them together and resist separation. The term adhesion is used when referring to the attraction between the surfaces. The four main mechanisms of adhesion - the various intrinsic forces that may operate across the adhesive/substrate interface - are considered to be: mechanical interlocking, diffusion, electron transfer and adsorption.^{1,2}

It is evident that, depending on the circumstances, any of the four main mechanisms of adhesion may be responsible for the intrinsic adhesion which enables an interface to resist separation under the influence of an applied stress. Analogous to pressure-sensitive adhesives (polymer, resin and oil), the relevant mechanisms for a self-adhesive roofing felt would be: inter-diffusion of polymer chains across the interface [polymer entanglement, which requires that the adhesive and substrate are mutually soluble [compatible] and the macromolecules or chain segments have sufficient mobility], as well as interatomic and intermolecular forces between the surfaces of the adhesive and substrate (van der Waals forces).

The three most important characteristics required in self-adhesive compounds are: flow resistance, low temperature tack and resistance to disbonding. The first two are primarily rheology requirements while the latter is characterised by adhesive and cohesive strength. One challenge is to satisfy these conflicting requirements of the visco-elastic compound. Rheological models have been developed for nonbituminous compounds. However, even if complying with the rheological models, the performance

of bituminous compounds may not fulfil the requirements, and additives may have to be used to obtain the desired final properties.

Although there are regional differences, premium self-adhesive roofing compounds are generally composed of multiple ingredients: bitumen/asphalt, a mixture of SBS and SIS block copolymers, SB di-block polymer, tackifying resin, naphthenic oil, oxidised bitumen and filler. The mix of included ingredients is determined partly by the requirements for the final product. However, most importantly, this is strongly influenced by the kind of bitumen or asphalt that is used. In addition to the same high-temperature performance requirements of conventional membranes, self-adhesive compounds have the additional requirement of being tacky at the lowest application temperature. This more stringent requirement of performance over a wide temperature range usually necessitates more complex formulations.

Recent developments are focused on simplifying the composition of the compound and thereby easing the manufacture of the self-adhesive compound. In this paper, the influence of the various ingredients is described and the development of new, experimental styrene-butadiene- and styrene-isoprene-based block copolymers to be used as single polymers in this application are highlighted.

2. Experimental

To scrutinise the influence of multiple ingredients on the rheological and adhesive properties of a self-adhesive compound, the following compositional effects have been examined:

- **Influence of type of polymer (mixtures)**

Evaluations were carried out in a 200 pen reference bitumen (approximately AC3 or PG 52) comprising compounds with a standard radial SBS, high-vinyl radial SBS¹, linear SIS, SB di-block and mixtures thereof. Polymer [A] and Polymer [B] are used as single polymers to achieve the desired properties.

Polymer [A] and Polymer [B] are experimental isoprene and butadiene- based styrenic block co-polymers (SBC), respectively, especially designed for self-adhesive applications.

- **Influence of tackifying resin**

The effect of the addition of a tackifying resin to compounds for self-adhesion was determined. A modified aliphatic resin commonly used for these applications was added to the compounds.

¹) High-vinyl (1,2-butadiene) Styrenic block co-polymers are available from KRATON Polymers under the trademark "IPD". For reasons of simplicity, the grade is referred to as IPD in this document.

- **Influence of bitumen**

Various commercially available types of asphalt/bitumen were used to produce self-adhesive compounds. The influence of the bitumen (composition) on the rheological and adhesive properties of various blends was determined.

2.1 Polymer modified blends

Blends were made with a Silverson L4R high shear mixer. The bitumen was heated to 160°C and subsequently the polymer(s) and/or other additives were added. Upon blending, the temperature increased to 180°C caused by the energy input from the mixer. Blending at this temperature was continued until a homogeneous blend was obtained, as determined by fluorescence microscopy.

2.2 Specimens for adhesion testing

The roofing sheets for adhesion testing (T-Peel ASTM D1876-93) were prepared by pouring 55 grams of the compound in a 230 mm by 160 mm by 1.5 mm spacer and covering it with a polyester carrier. Covered with silicon paper, the sample was placed in a hydraulic press and pressed for five minutes with a load of 15,000 pounds at 140°C. After a cooling period of 10 minutes, a second spacer was placed on the other side of the carrier and filled with an additional 55 grams of compound. Pressing again created an artificial roofing sheet 3 mm thick. The roofing sheet created was cut from its spacers. Specimens for T-peel testing measuring 25 mm by 200 mm were cut from the sheet.

2.3 Test methods

A standard evaluation on the blends was carried out - the determination of the penetration at 25°C, softening point, viscosity, DIN flow resistance and cold bend.³

T-peel testing: The adhesive performance of a formulation for self-adhesion was determined by welding two membranes of equal composition and subsequently separating them in a T-geometry with a tensile tester. The force (N/25 mm) necessary to separate the membranes is a measure of the adhesive bond strength.

The adhesive bond strength of the various compounds was determined at 5°C and 21°C. Conditioning at 5°C was achieved by placing the membranes in a refrigerator for at least 12 hours and welding immediately when taken from the refrigerator, followed by immediate T-peel testing. Specimens welded at ambient temperature were stored for at least 12 hours before peel testing. The welding at both temperatures was established by rolling a 1.0 kg weight 10 times over the membranes. Adhesion was prevented over a length of 50 mm by covering the ends of the membranes with silicon paper.

T-peel tests were carried out with an Instron 4501 tensile tester. The free ends were clamped in the grips and then separated at a constant rate of displacement of 254 mm/min according to ASTM D1876-93.⁴

Tack of the membranes is an important product parameter for quick bonding, especially at low welding temperatures (<10°C). In this investigation, the tack was not analysed quantitatively. It was determined qualitatively using a well-calibrated thumb. Tack may be quantified by standardised adhesive tests such as Polyken probe and loop tack.

SARA (Saturates Aromatics Resins Asphaltenes) analysis determines in broad sense the chemical composition of the bitumen. With the SARA method, the asphaltenes present in the bitumen were first separated from the maltenes by precipitation in n-heptane. Subsequently, the asphaltenes content was determined gravimetrically. The resins, aromatics and saturates remaining in the maltenes fraction were separated and quantified by means of High Pressure Liquid Chromatography (HPLC).⁵

3. Results

3.1 Adhesive performance of commercial felts

In Figure 1 a limited overview is given of the adhesive performance of multiple commercially available roofing felts for self-adhesive application. The adhesive properties are specified by the T-peel strength of the welded membranes as conditioned and determined at the two temperatures.

Although the substrate of each membrane is its own self-adhesive compound, the tests were carried out similarly for each product, resulting in a representative comparison. Obviously, the differences in adhesive performance found for the commercial coatings are apparent. However, it must be noted that products with excellent adhesive properties do not necessarily excel in high temperature flow resistance. Although self-adhesive roofing felts often are composed of standard felts used to provide the flow resistance and are coated completely or partially with a thin layer of an adhesive coating, the adhesive should also have resistance to flow when applied on inclined roof surfaces.

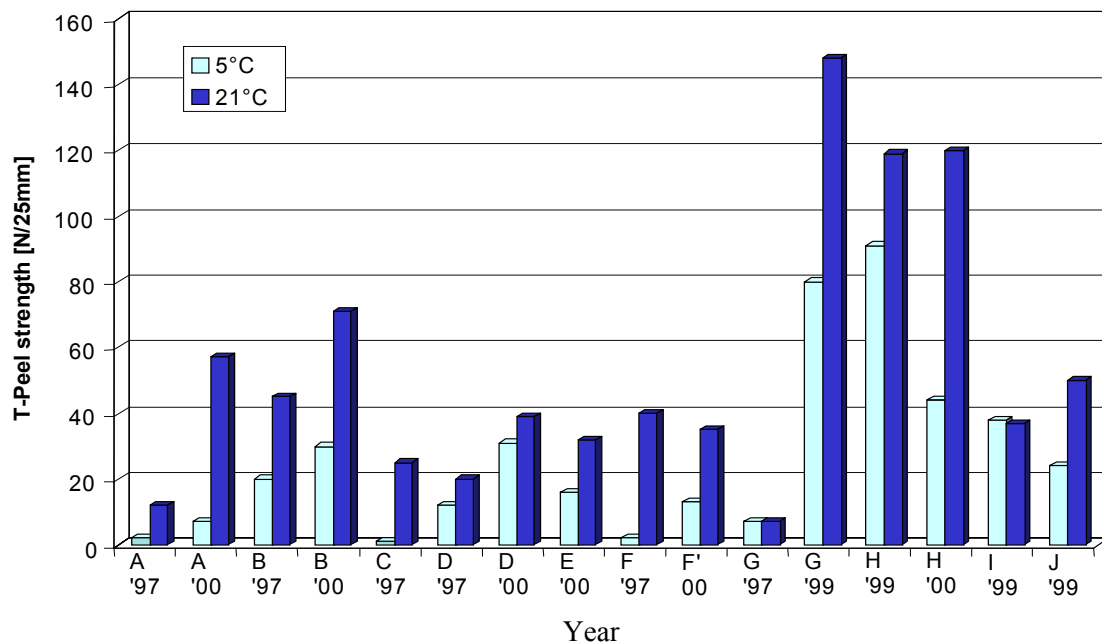


Figure 1. Adhesive performance of commercially available self-adhesive roofing felts.

3.2 Polymer ingredients for Self-Adhesive Membranes

As noted in the introduction, compounds or coatings for premium self-adhesive products can be relatively complex. They typically require more ingredients than a standard bituminous compound for modified bitumen membranes. Each of these ingredients plays an important role in combining the required performance characteristics. The challenge is to simultaneously obtain sufficient resistance to high temperatures (nonflow) and sufficient viscous behavior and mobility of molecules to create entanglements at low temperatures (flow) in one compound.

Styrenic Block Co-polymers (SBCs) can play a vital role in enhancing the desired properties. Currently a variety of different SBS, SIS and SB polymers in linear, radial and full sequential architectures are produced, as presented in Figure 2.

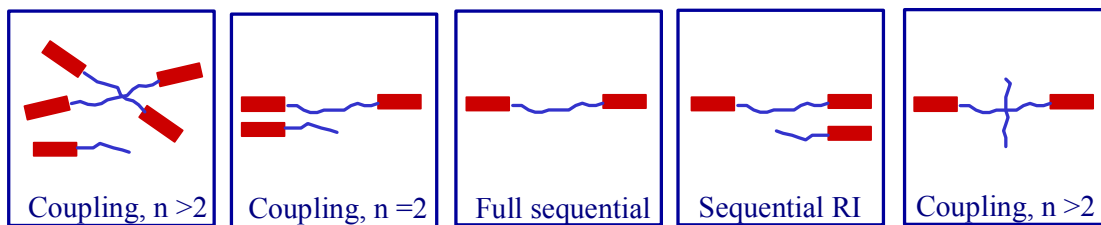


Figure 2. Type of Styrenic Block Co-polymers commercially available for self-adhesive applications.

The required properties set for a self-adhesive membrane compound is similar to that of a pressure-sensitive adhesive (PSA). The same formulation strategy can be used to obtain desired properties. Formulations for PSAs are usually well-defined.⁶ Their adhesive and processing properties are determined not only by the SBCs' types but also by the nature and concentration of the various ingredients, such as tackifying resins, and by their interaction with the two-phase structure of the polymer. Components such as resins will normally concentrate in one phase of the polymer, the mid-block or the end-block. Mid-block compatible resins modify the low temperature glass transition temperature (T_g) and modulus. End-block compatible resins modify the high temperature T_g and flow resistance. Decreasing the elastic modulus is in this case the route to adhesion. In other words: provide a compatible environment and soften the compound.

3.3 Balancing adhesion and rheological properties

A coating for self-adhesion should have both good tack and adhesive strength so one can "put it down and forget it", especially at lower temperatures. However, the SBCs available that provide these properties are by nature smaller molecules that provide insufficient flow resistance for typical roofing applications.

To obtain a better understanding of the possibilities with SBCs' in bitumen for coatings for self-adhesive, evaluations were carried out in the 200 pen reference bitumen. These evaluations show the influence of the types of polymers and mixtures thereof on the adhesive and rheological properties, i.e. softening point R&B, DIN flow resistance and cold bend. The results are presented in Figure 3.

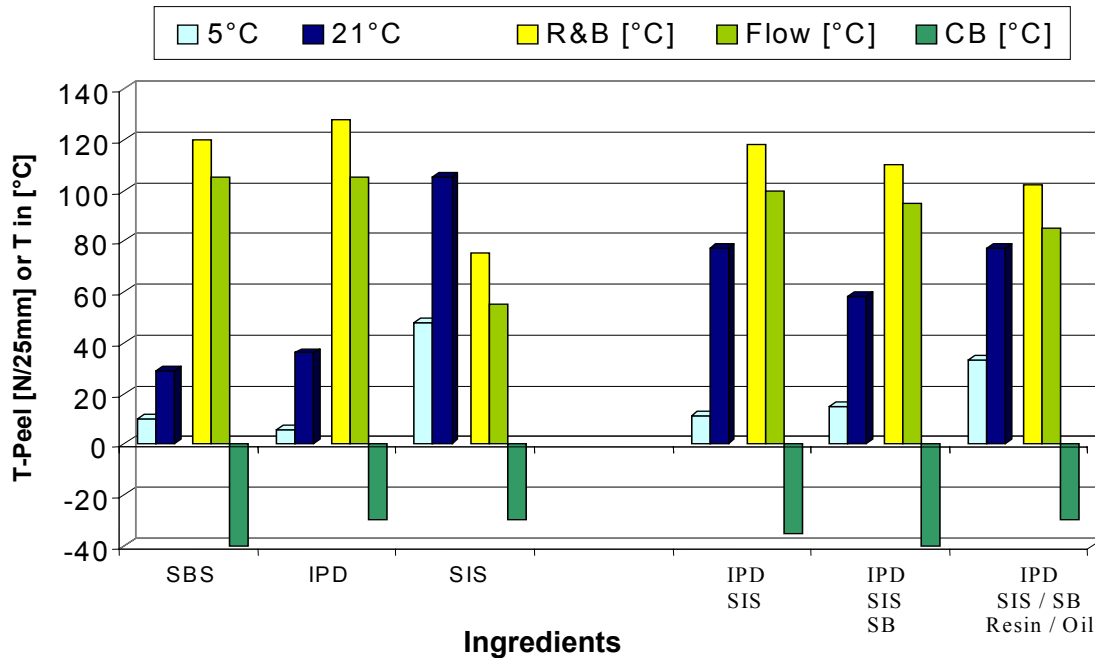


Figure 3. Adhesive and rheological properties of SBC modified asphalt (200 pen).

In this pragmatic approach, butadiene based SBCs', SBS and IPD typically used in roofing application only provide good rheological properties; the adhesive strength is rather poor, especially at low temperatures.

A typical SIS polymer gives excellent adhesion at low temperature. However, a flow resistance of 50°C is not sufficient for adequate performance.

Mixing SBS and SIS to combine the desired adhesion and rheological properties is a logical step. Indeed a better balance is obtained, however, in this case the adhesive strength at low temperatures has not significantly improved. Addition of SB di-block reduces the flow resistance and slightly improves the adhesion at low temperature.

The addition of naphthenic oil and tackifying resin increases adhesion for reasons described below. For this specific formulation a good balance in properties is obtained. Unfortunately, six different ingredients are required, which complicates production safety.

3.4 Effect of tackifying resin

Resins are commonly used ingredients in compounds for self-adhesives. There is a wide variety of commercially available resins, aliphatic and aromatic, that modify SBC mid-block, end-block or both, and in that sense consequent formulating principles apply. Unfortunately, the presence of asphalt frustrates those principles and expertise had to be built.

In a bituminous adhesive coating, such a resin should essentially improve compatibility of SBC and asphalt and change the mid-block T_g, allowing the adhesive strength to improve. Resins manufacturers in cooperation with the roofing industry have found that optimum improvement is obtained with resins compatible with both blocks. The latter is indeed the case as is presented in Table 1. However, including a resin in an adhesive compound also affects other typical properties.

In this example, a modified-aliphatic resin with a T_g of 43°C was used, giving a ring and ball softening point of 97°C. The T-peel strength is improved with the addition of the resin to this specific compound; however, at low temperatures no improvement was observed. Furthermore, it is clear from Table 1 that an optimum in resin content needs to be determined.

The T_g of the resin influences the cold bend of the total compound negatively. Although the softening point of the compound gradually decreases with increasing resin content, because of the softening of the polystyrene domains by the resin, the flow resistance is maintained at 95°C.

Blend no.	1	2	3	4
Polymer	IPD	IPD	IPD	IPD
Polymer	SIS	SIS	SIS	SIS
Bitumen	PX-200	PX-200	PX-200	PX-200
Resin, %wt	0	5	10	15
Pen at 25°C, dmm	65	53	45	40
R&B, °C	119	118	115	113
Viscosity at 180°C				
20 s ⁻¹ , Pa.s	2.7	3.1	3.0	3.3
100 s ⁻¹ , Pa.s	2.6	3.0	2.9	3.2
Cold bend, pass °C	-30	-25	-25	-20
DIN Flow, pass °C	95	95	95	95
T-peel at 5°C, N	8	1	1	4
T-peel at 21°C, N	55	80	98	99

Table 1. Effect of tackifying resin (content) on typical performance.

3.5 Developments in polymers for self-adhesive applications

Investigations intended to simplify the production of self-adhesive roofing compounds have led to the development of experimental polymers for this specific application - a single polymer to replace the multiple ingredients for a premium compound for self-

adhesive application. The ultimate challenge is to combine sufficient cohesive and adhesive properties in the final product by balancing viscous and elastic properties at the right temperature in one polymer.

This work resulted in polymer [A], an isoprene-based SBC, and polymer [B], a butadiene-based SBC. The results are presented in Figure 4, and the result of the mixture of components is also given for comparison reasons. The adhesive performances presented represents commercial felts as described in Figure 1.

With the single polymer [A] in bitumen, a satisfactory balance is obtained between the adhesive properties and typical rheological performance. The results observed easily match those of the compound with the multiple ingredients. However, with a single polymer the manufacturing process is greatly simplified.

With the single experimental butadiene SBC polymer [B] in bitumen, the low temperature adhesive performance might be considered insufficient. This directly demonstrates the difference between butadiene and isoprene in a SBC for adhesive purposes. Isoprene is intrinsically softer than butadiene and therefore better suited for adhesive applications.

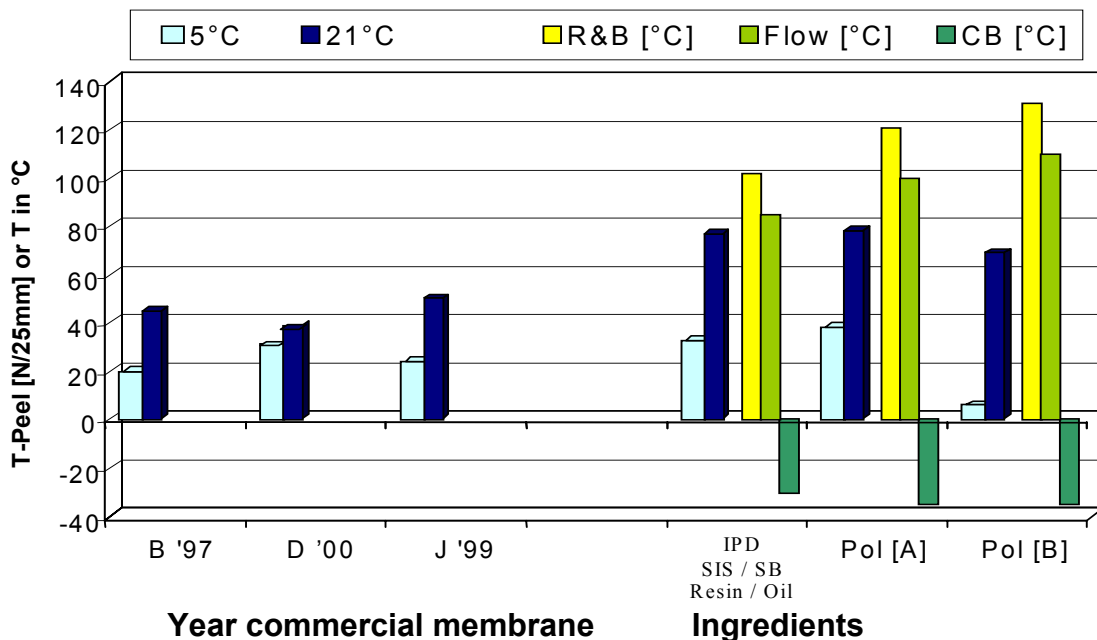


Figure 4. Performance of single polymers [A] and [B] in 200 pen reference bitumen.

3.6 Influence of asphalt in compounds for self-adhesive

As already mentioned in section 3.2, compounds for pressure-sensitive adhesives are mixtures of well-defined components. The primary component in a compound for self-adhesive roofing felts is the bitumen or asphalt. Although the components of the asphalt

can roughly be divided into saturates, aromatics, resins and asphaltenes (SARA), it is still a mixture of multiple molecules of various length, polarity and structure, depending in composition and consistency on the crude oil processing of the oil used. There are too many uncertain parameters to call it a well-defined ingredient in terms of composition.

An indication of the effect of the asphalt on the quality of a self-adhesive compound is shown in Table 2. The results show the adhesive properties, T-peel strength and tack of polymer [A] in various commercially available types of asphalt. Furthermore, SARA-analysis was carried out on the bitumens to obtain an indication of the composition.

Bitumen	A	B	C	D	E
Pen at 25°C, dmm	190	145	234	174	176
R&B, °C	39	43	40	42	41
Asphaltenes, %wt	6.0	9.0	6.8	11.2	7.9
Saturates, %wt	5.7	14.0	11.7	10.5	10.1
Aromatics, %wt	66.5	58.9	67.1	59.4	63.9
Resins, %wt	21.8	18.1	14.5	18.9	18.2
T-peel at 5°C, N	42	1	27	31	1
T-peel at 21°C, N	86	77	81	48	73
Tack at 5°C	very good	no	very good	good	no
Tack at 21°C	very good	poor	very good	very good	poor

Table 2. Influence of asphalt on adhesive performance – Polymer [A] incorporated

The effect of the asphalt on the tack and T-peel strength at low temperature is manifest. Unfortunately, the ratio and content of the components of the asphalt do not explain or clarify the differences found. There is no clear relationship between the asphaltene content or aromaticity and the adhesive properties of the blends with the various types of bitumen.

However, it must be noted that the results from the SARA-analysis do not give any information about the molecular weights and molecular weight distribution of the various components, which is an important factor with respect to the dissolving power and compatibility of the bitumen for polymer modification.

Furthermore, the above evaluations were carried out with the experimental polymer [A]. To exclude the potential fact that the above observed phenomena is only because of the use of the experimental polymer, evaluations were carried out with blends typical for a self-adhesive in bitumen E. The results of these evaluations are presented in Table 3.

Composition	Pol [A]	Pol [A] oil	IPD SIS	IPD SIS oil	IPD SIS SB Resin	IPD SIS SB Resin oil
T-peel at 5°C, N	1	34	1	10	0	49
T-peel at 21°C, N	84	34	106	63	111	61
Tack at 5°C	no	good	no	moderate	no	good
Tack at 21°C	poor	good	poor	good	poor	good

Table 3. Performance of compounds for self-adhesive in bitumen E.

The results demonstrate that the effect of the asphalt on the adhesive properties is not dependent on the types of SBC polymers used. This again confirms that the asphalt is one of the major determining factors for the quality of a compound for self-adhesive applications.

However, it also demonstrated that changing the environment for the polymers present by improving the solvency power and compatibility can result in intimate contact between the two surfaces. The latter suggests quick diffusion and entanglements. This is the result of a good SBC polymer surface distribution which is confirmed by the good tack and T-peel strength found.

4. Long-Term Storage

A common problem with self-adhering membranes is reduction in tackiness upon long-term storage. A suspected cause is transfer of silicone from the release film, but this has never been demonstrated. Other possible contributing factors include surface oxidation, migration of light ends from the surface and volatilisation of light ends from the surface. An experimental programme was undertaken to ascertain the mechanism of loss of tack. Samples of a commercial underlayment were stored for six months under a variety of conditions. The surface of the samples was then analysed by x-ray photoelectron spectroscopy (XPS) to quantify changes in the chemical composition of the surface. Samples were stored with and without the release film in place. The four storage conditions were:

- Ambient air
- Dark oven at 60°C
- Window glass filtered sunlight
- Nitrogen flushed dessicator

After six months, the samples were rated for tackiness as follows:

- ++ tacky
- + slight tack
- 0 no tack
- - rough, chalky surface

The results are shown in Table 4.

	With release in place	Without release
Ambient air	+	0
Dark oven at 60°C	-	-
Filtered sunlight	-	-
Nitrogen	++	++

Table 4. Tackiness rating of self-adhesive underlayment samples.

Surface analysis by XPS showed little change in silicon content relative to as manufactured membrane. However, there was significant increase in surface oxygen content in all but the nitrogen blanketed sample.

It is clear that in this case the primary culprit leading to loss of tack is surface oxidation. Loss of light ends may contribute, but that is not a major factor as the nitrogen stored sample retained nearly all of its tack. Silicone migration does not appear to be a factor.

5. Conclusions

Compounds or coatings for self-adhesive roofing applications are often relatively complex because of the multiple ingredients required. Each of these ingredients plays an important role in creating the required balance of performance characteristics, flow resistance, low temperature tack and resistance to disbonding. The challenge is to obtain in one compound sufficient resistance against molecule mobility (flow) at high temperatures while simultaneously maintaining sufficient viscous behaviour and mobility of molecules to create entanglements at low temperatures (adhesion).

The requirements of the final product are important in determining the mix of ingredients that should be introduced, but of greater significance is the nature of the bitumen or asphalt that is used. The self-adhesive compounds must be tailored precisely. Although production may be simplified by the use of a single polymer combining sufficient viscous and elastic behaviour in a single SBS or SIS block copolymer dedicated for this application, fine tuning is required on the basis of the variability of bitumen/asphalt composition.

Loss of tack upon long-term storage is probably because of surface oxidation. This is another factor to consider in the formulation of self-adhesive products and the choice of the release foil.

6. References

¹ A.J. Kinloch, *Adhesion and Adhesives: science and technology*, Department of Mechanical Engineering, University of London, 1987

² Cyprien Gay and Ludwik Leibler, "On Stickiness," *Physics Today*, November, 1999, p. 48.

³ F. de Bats, *Analysis of the DIN flow test and cold bending test for water proofing membranes*, "green cover" issue of Shell International Petroleum Company Limited.

⁴ Annual book of ASTM standards, Volume 15.06, *Standard test method for peel resistance of adhesives (T-peel test)*, ASTM D1876-93.

⁵ "Rapid Bitumen Analysis by High Pressure Chromatography," *Construction & Building Materials*, Vol. 6, No. 3, 1992.

⁶ S. Gun Chu, *Viscoelastic Properties of Pressure Sensitive Adhesives*, Handbook of Pressure Sensitive Technology, P-TR89129.