

Sticks.

Polychloroprene for contact adhesives with high initial strength at low process temperatures

Baypren[®]

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1. Baypren® Description



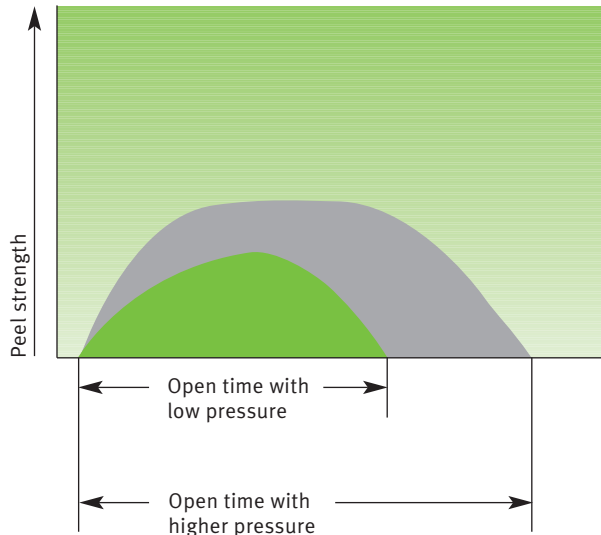
Baypren® is a 2-chloro-butadiene-(1,3) polymer (polychloroprene) produced by state-of-the-art processes.

Its excellent solubility in many organic solvents and its high rate of crystallizing make it ideal for the production of contact adhesives.

2. Baypren® Range of properties

Initial bond strength

Fig. 1: Initial strength as a function of open time and applied pressure

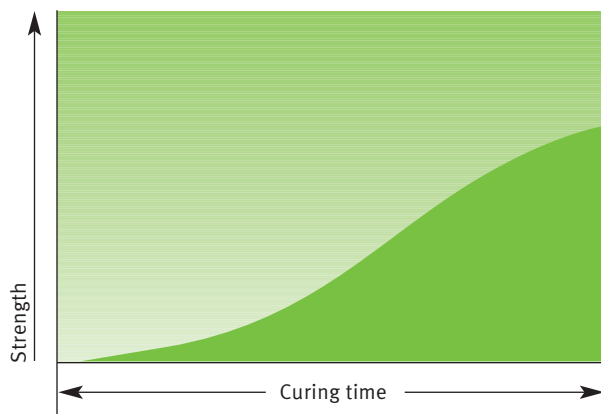


Baypren® adhesives are used widely all over the world, the main reason for their popularity being that, after brief surface drying, they are able during their open time to produce a bond of immediately measurable strength (Fig. 1).

Following momentary adhesion, the polychloroprene begins immediately to crystallize, with the result that the bond cures rapidly and its strength rises accordingly (Fig. 2).

The demand for contact adhesives based on Baypren® is particularly high in the shoe industry, in furniture production, in the construction and automotive industries and in the do-it-yourself sector. Apart from their simple, economical processing, these products are distinguished by their excellent adhesion to a wide range of materials and guarantee outstanding results.

Fig. 2: Increase in strength through crystallization



3. Baypren® Product range

To satisfy the varied demands arising in industrial practice, Baypren® is supplied with varying crystallization rates, viscosities and chip sizes (Table 1).

Table 1: Baypren® adhesive grades

Fast crystallizing Baypren® grades			Medium crystallizing Baypren® grades		
Grade	Chip-size [mm]	Viscosity [mPa·s] 10 % solution in Toluene	Grade	Chip-size [mm]	Viscosity [mPa·s] 10 % solution in Toluene
Standard grades			Standard grades		
310-1	2.5 – 3.0	70 – 220	213-1	2.5 – 3.0	70 – 220
310-2	2.5 – 3.0	220 – 380	213-2	2.5 – 3.0	220 – 380
320-1	2.5 – 3.0	350 – 550	223-1	2.5 – 3.0	350 – 550
320-2	2.5 – 3.0	550 – 810	223-2	2.5 – 3.0	550 – 810
330-1	2.5 – 3.0	700 – 1,000	233-1	2.5 – 3.0	700 – 1,000
330-2	2.5 – 3.0	900 – 1,400	233-2	2.5 – 3.0	900 – 1,400
340-1	2.5 – 3.0	1,130 – 1,800	243-1	2.5 – 3.0	1,130 – 1,800
340-2	2.5 – 3.0	1,800 – 2,500	243-2	2.5 – 3.0	1,600 – 2,500
350-1	1.5 – 2.0	2,200 – 4,000	253-1	1.5 – 2.0	2,200 – 4,000
350-2	1.5 – 2.0	2,500 – 5,300	253-2	1.5 – 2.0	2,500 – 5,300
TETD modified grades					
321-1	2.5 – 3.0	350 – 550			
321-2	2.5 – 3.0	550 – 810			
331-1	2.5 – 3.0	700 – 1,000			
331-2	2.5 – 3.0	900 – 1,400			
Special grades (MMA grafting)					
320-1p	2.5 – 3.0	350 – 550			
320-2p	2.5 – 3.0	550 – 810			

The meaning of the suffix is shown in Table 2.

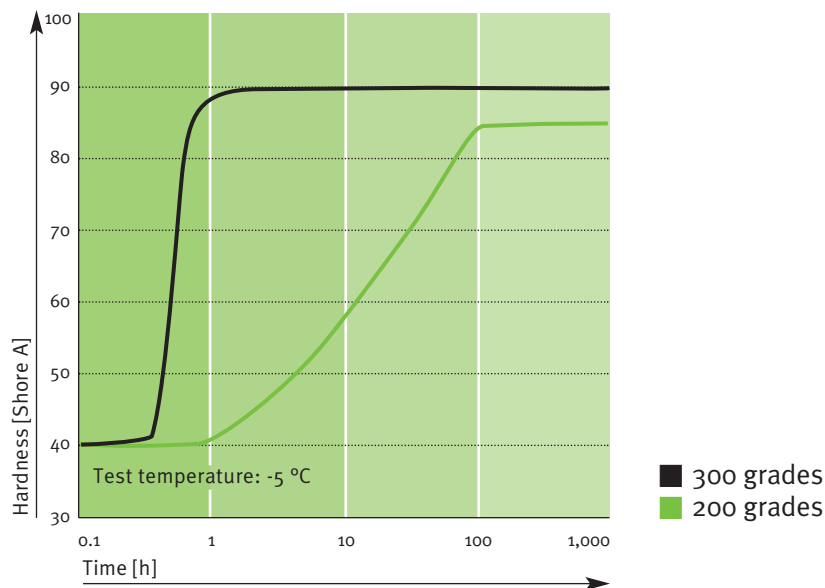
Table 2: Nomenclature of the Baypren® adhesive grades

First digit: Indication of the crystallization rate	
2	= medium
3	= rapid
Second digit: Indication of the viscosity	
1	= low
2 + 3	= medium
4	= high
5	= very high
Third digit: Indication of special properties	
0	= standard grade
1	= thiuram-based
3	= special grade in terms of crystallization
p	= special grade for “grafting”

4. Baypren® Formulation of adhesives

4.1 Selection of the Baypren® grades

Fig. 3: Crystallization



For adhesive production, use is made predominantly of Baypren® grades with a higher rate of crystallization (B 310 to 350). Adhesives formulated with them give bonds with high initial strength that cure very quickly indeed.

Thiuram grades for easier mastication

Baypren® 321 and 331 differ from the other Baypren® grades in that they are modified with thiuram disulfide. This additive makes mastication easier, increases compatibility with many other adhesive components (resins, for example) and extends the storage stability of the adhesives.

Thiuram-free grades for light-colored materials

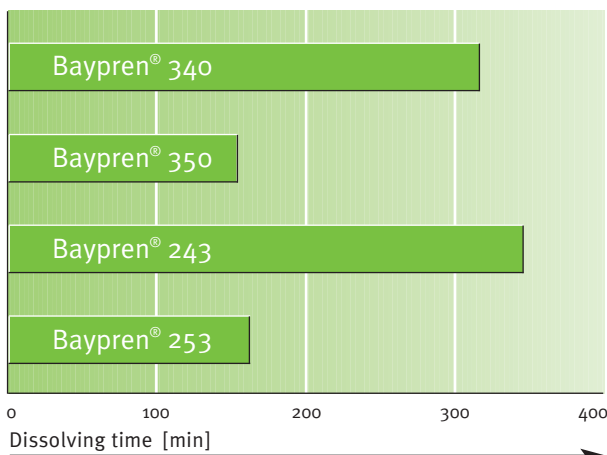
When bonding sensitive, light-colored materials such as white leather or PVC film, it is advisable to use the thiuram-free Baypren® grades. Under unfavorable conditions, e.g. in the presence of certain leather greases or plasticizers, there is a danger with light-colored materials that the thiuram contained in the Baypren® may migrate out of the adhesive film onto the surface of the material and produce a yellowish discoloration. It must also be taken into account that Baypren® adhesives containing thiuram can become discolored on contact with iron, copper or brass due to the thiuram in them.

Fig. 4: Dissolving time in relation to chip thickness



Baypren® 310, 320, 330, 340
(approx. 2 mm)

Baypren® 350 (approx. 1 mm)



In cases where high initial bond strength is not needed, use can be made of the medium crystallizing Baypren® grades of the 200 range. They are cheaper and prolong the open time of the adhesives – a factor that also enhances processing reliability.

The medium crystallizing Baypren® grades can be used both on their own and in combination with rapidly crystallizing Baypren® grades.

Because there is nowadays an increasing demand for high-viscosity polychloroprene for economic reasons, we have extended our range of rapidly and medium crystallizing grades. Baypren® 350 and 253 are two new products that can be used in combination with low-viscosity Baypren®. To align the longer dissolving time of high-viscosity Baypren® grades with the dissolving time of low-viscosity grades, Baypren® 350 and Baypren® 253 are produced in the form of extremely thin chips.

Graft adhesive with outstanding resistance to discoloration

4.2 Choice of solvent

Baypren® 320-p is a polychloroprene which is suitable as a starting material for the grafting reaction with methylmethacrylate (MMA). These graft adhesives are commonly used in the shoe industry for bonding plasticized PVC and other substrates that are otherwise difficult to bond, such as EVA (ethylene-vinyl acetate copolymer) and SBS (styrene-butadiene-styrene block copolymer).

Baypren® adhesive raw materials are soluble in many organic solvents and solvent mixtures.

The solvent or solvent mixture used to produce the adhesive is chosen according to both economic and technical considerations. It has to be taken into account, for example, that the solvent can have a considerable influence on:

- the viscosity of the adhesive,
- the compatibility of the adhesive with an added crosslinking agent,
- the behavior of the adhesive during storage at low temperatures,
- the occurrence of phase separation during the storage of resin-containing adhesives
- the wetting of the adhesive surface,
- the drying of the adhesive film,
- the open time of the adhesive film,
- the curing rate of the bond.

Apart from the influence on the technical properties of the adhesives, the physiological effect of the solvents also has to be considered.

The use of certain solvents is subject to restrictions or is completely banned in some countries. Furthermore, attention must be paid to the flammability of many solvents and their ability to form explosive mixtures with air.

4.3 Higher bond stability with metal oxides

Fig. 5: Bayoxide® Z aktiv



4.4 Addition of resins for faster curing

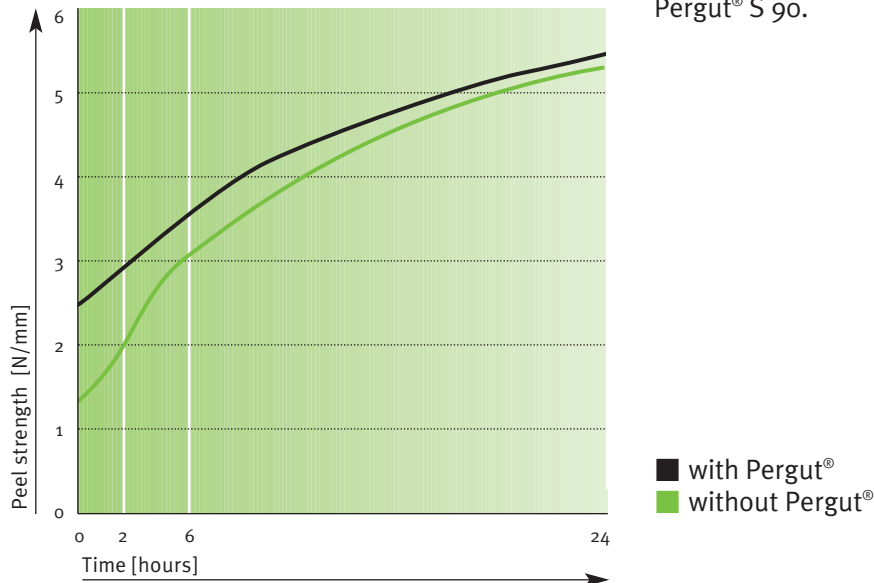
As a rule, magnesium oxide and zinc oxide are added to Baypren® adhesives. The presence of the metal oxides has a favorable effect on the storage stability of the adhesive and the stability of the bonds. This is because the polychloroprene splits off traces of hydrogen chloride over the course of time and the metal oxides serve as acceptors for them. The very fine-particle zinc oxides, Bayoxide® Z aktiv and Bayoxide® Z transparent, are ideal for use with Baypren® adhesives.

Resins are an excellent way of improving the adhesive properties of the Baypren® solutions. Through the addition of a resin, the open time can be adjusted over a broad range and curing can be accelerated. The final crystallization state of the Baypren® is barely affected by the resins, with the result that the adhesive films retain a high level of cohesive strength. However, these valuable properties can only be attained if the right quantity of the right resin is added, depending on the particular application.

Heat-activated alkyl-phenol resins or high-melting rosin esters are preferred whenever rapid curing of the bonds is needed. To prolong the open time, formulators generally use terpene-phenolic resins, coumarone-indene resins, or low-melting rosin esters.

4.5 Chlorinated rubber for improved initial strength

Fig. 6: Influence of Pergut® on the strength increase of Baypren® bonds



Through the addition of chlorinated rubber, the initial strength of the bonds can be significantly increased. Chlorinated rubber of medium solution viscosity is generally used, e.g. Pergut® S 40 or Pergut® S 90.

4.6 Addition of fillers

All kinds of fillers can be added to Baypren® adhesives. Typical examples are chalk, heavy spar and silica.

4.7 Antioxidants

Baypren® itself is considerably more resistant to aging than many of the resins used for adhesive production. Rosin esters, coumarone resins and terpenephénolic resins, being unsaturated compounds, are prone to oxidation over the course of time. This phenomenon starts with embrittlement or softening of the adhesive layer in the outer edges of the bond, and can finally lead to its complete destruction.

The aging of Baypren® bonds can be countered by the addition of suitable antioxidants.

The ideal antioxidants for resin-based Baypren® adhesives are sterically hindered phenols such as Vulkanox® BHT, Vulkanox® DS and Vulkanox® BKF (Lanxess AG).

4.8 Addition of Desmodur® to improve the bonding properties

Fig. 7: Colors of the various Desmodur® R-grades

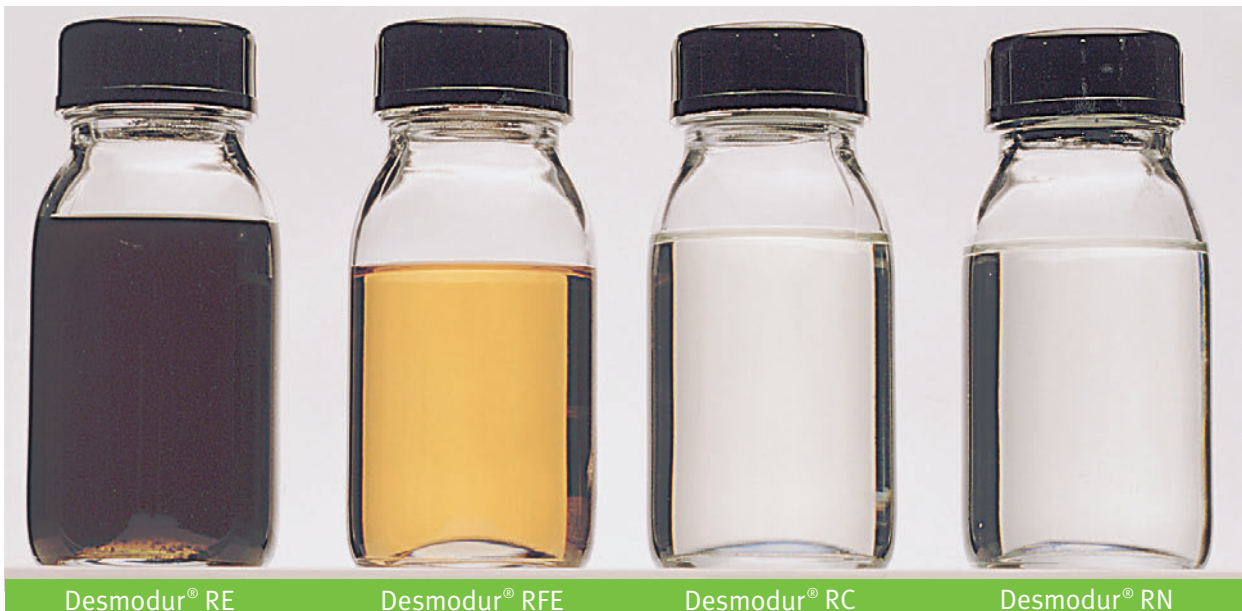
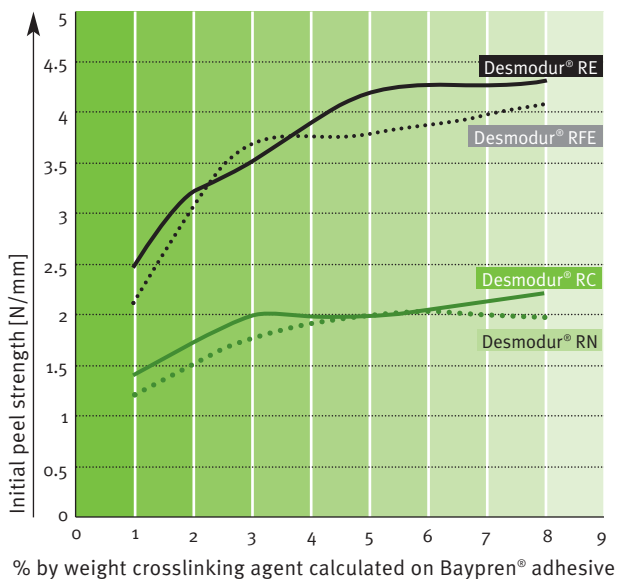


Fig. 8: Initial strength of the bonds after storage in heat (30 min/50 °C), substrate: Nora rubber



Although for many applications completely satisfactory strength characteristics are obtained with one-component Baypren® adhesives, the addition of Desmodur® (polyisocyanate), e.g. Desmodur® RE, RFE, RC or RN, can significantly improve the bonding properties, in particular the

- heat resistance of the bonds,
- initial strength of the bonds,
- resistance of the bonds to grease and oil,
- adhesion to critical materials.

Desmodur® RE and Desmodur® RFE have the highest peel strength.

5. Mastication or direct-dissolve process

Fig. 9: Adhesive application of viscous and visco-elastic solutions

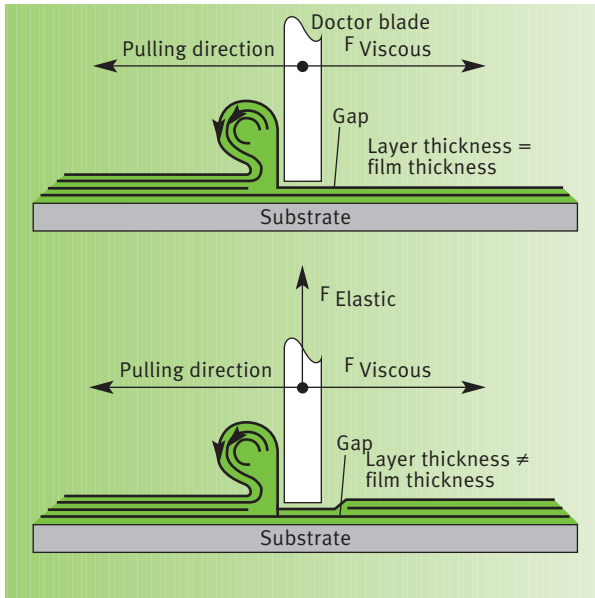
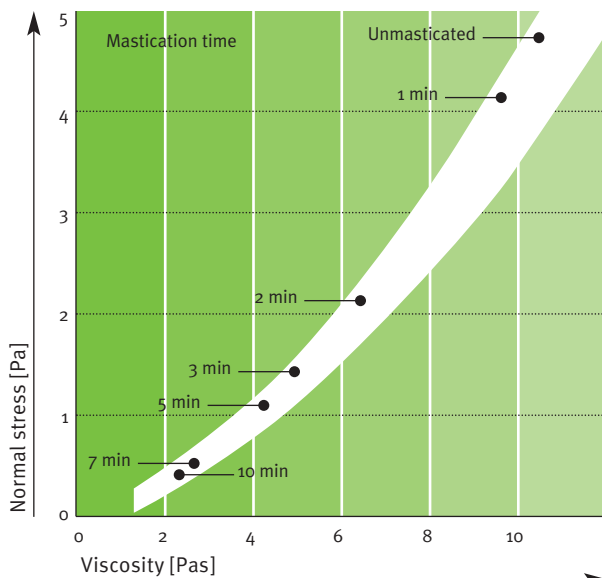


Fig. 10: Viscosity and normal stress after mastication of Baypren® 330



Formerly, mastication of the polychloroprene before dissolving was an integral part of the formulation procedure in the adhesives industry. It also enabled adhesives with acceptable properties to be produced from polychloroprene raw materials of average quality.

As a result of continuing research, it has now become possible to guarantee consistent polychloroprene quality. Contact adhesives based on Baypren® can therefore be formulated without previous mastication using the so-called direct-dissolve process. Polychloroprene solutions also have elastic characteristics in addition to their purely viscous properties. These elastic properties mean that extra force is needed to apply the solution to the substrate (Fig. 9).

Studies carried out on solutions of the Baypren® 300 grades show that the level of elasticity, measured as normal stress, is dependent on the viscosity of the Baypren® solution. With increasing viscosity of the solution, the normal stress rises (at constant solids concentration) (Fig. 10).

The mastication of Baypren® results in products with lower viscosities and normal stresses. However, the pairs of values lie within the normal stress/viscosity band that applies to the unmasticated Baypren® 300 grades, i.e. although the values for masticated Baypren® 330 are lower, they do not differ from the normal stress/viscosity data of an unmasticated Baypren® 320 of equal viscosity. Bonding tests on formulated adhesives produce the same bonding data for masticated as for unmasticated Baypren® of the same viscosity.

Baypren® can thus be used for formulating adhesives with optimum rheological and bonding properties even without the time and cost-intensive procedure of mastication prior to dissolving.

6. Formulation examples

Table 3 shows typical formulation examples for Baypren® contact adhesives.

By adding more of the given solvent mixture, the solution viscosity of the adhesives can be set to the desired level.

With the adhesive prepared according to formulation no. 3, 10 pbw Desmodur® RE or RFE can be added as a crosslinking agent to 100 pbw adhesive immediately before application.

Table 3: Formulation examples for Baypren® contact adhesives

Formulation no.	#1	# 2	# 3	# 4	# 5
Baypren® 320	100	100	100	100	—
Baypren® 233	—	—	—	—	100
Magnesium oxide	4	4	4	4	4
Bayoxide® Z aktiv	4	4	4	4	4
Pergut® S 40	—	—	—	var	—
Heat-reactive alkyl-phenolic resin (SPF 121H*)	30	30	—	var	var
Terpene-phenolic resin (SP 553*)	—	—	30	var	—
Ethyl acetate	120	35	35	35	35
White spirit (boiling range 65–95 °C)	120	70	70	70	70
Toluene	120	—	—	—	—
Cyclohexane	—	140	140	140	140
Methylethylketone	—	105	105	105	105

* Schenectady Europe S.A., Bethune, France

High initial strength

It frequently happens that a bond is subjected to a high level of stress at a very early stage – for example when bonding curved soles in the shoe industry or curved surfaces of wood or plastic in furniture production. In such cases, high initial strength and rapid curing are essential. This is no problem for adhesives formulated with the rapidly crystallizing Baypren® grades.

Varying the initial and final strength

Figs. 11–14 show how the initial strength of the bonds can be adjusted by varying the Pergut® content, resin content and open time. The highest initial strength is obtained in resin-free formulations containing Pergut® (formulation no. 4). On the other hand, Pergut® has no influence whatsoever on the final strength of the bonds. Here, the addition of resins has a positive effect.

Fig. 11: Influence of Pergut® on the initial strength in a formulation without resin (no. 4)

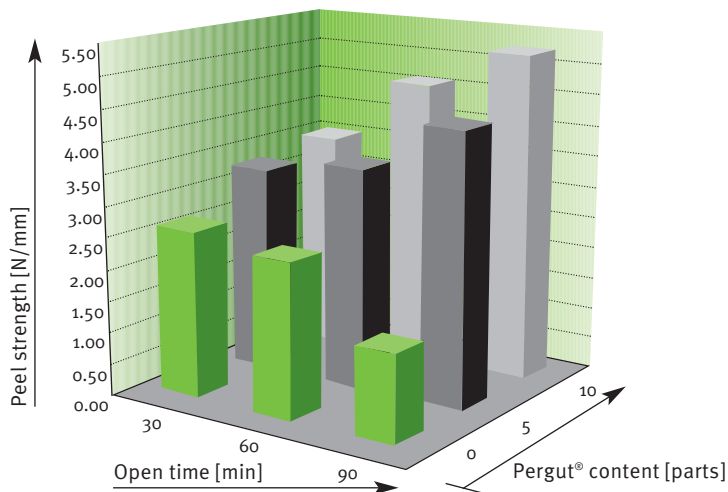


Fig. 12: Influence of Pergut® on the initial strength with the addition of various resins (no. 4, open time 60 min)

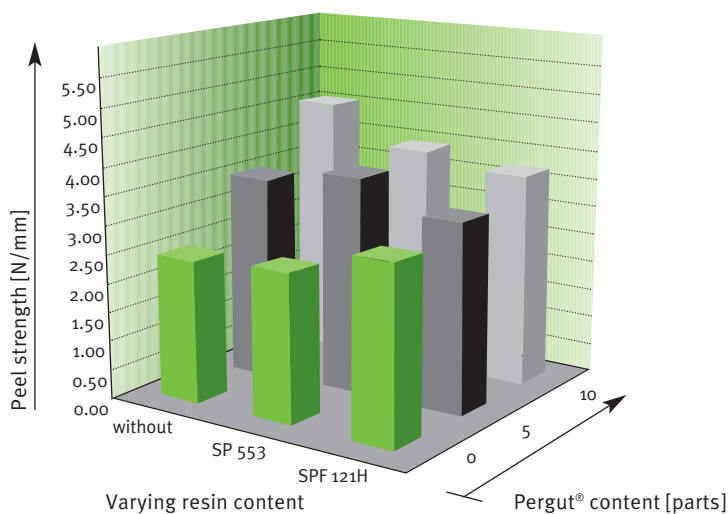


Fig. 13: Influence of Pergut on the final strength after 9 days with the addition of various resins (no. 4, open time 60 min)

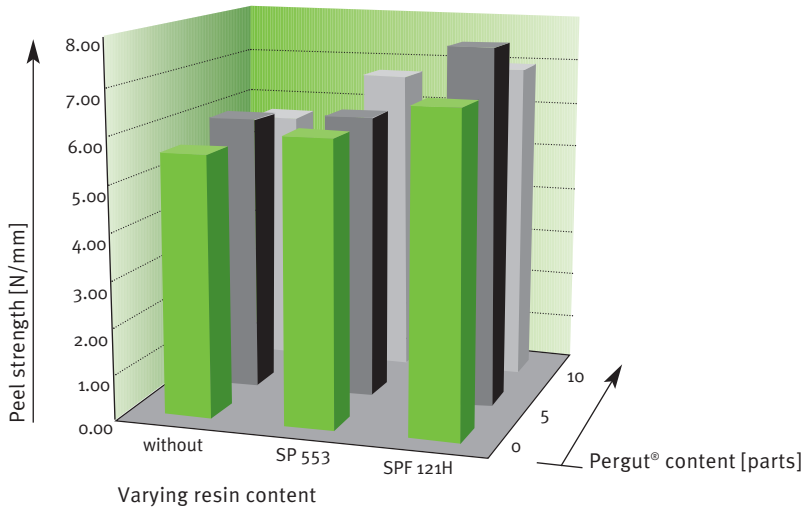
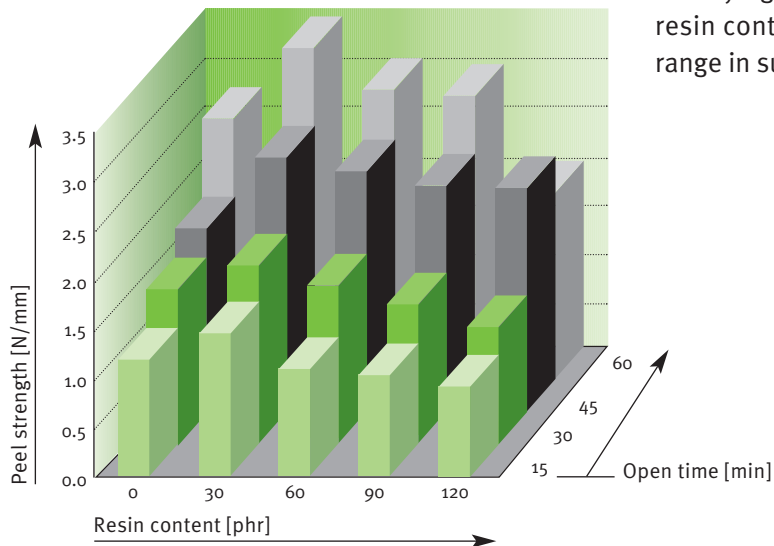


Fig. 14: Initial strength when using medium crystallizing grades (no. 5, with heat-reactive alkyl-phenolic resin [SPF 121H*])



If high initial bond strength is not absolutely essential, medium crystallizing grades can also be used (for example, for laying flexible floorcoverings). The resin content can be varied over a wide range in such formulations.

* Schenectady Europe S.A., Bethune, France

Peel strength of toluene-free formulations

Because of the negative physiological effect of toluene, its use is subject to restrictions or is banned entirely as an adhesives solvent in many countries. If we look at formulations 1 (Fig. 15) and 2 (Fig. 16), it can be seen that comparable bond strength can also be attained with toluene-free Baypren® adhesives.

Fig. 15: Formulation 1, peel strength with a toluene-based adhesive

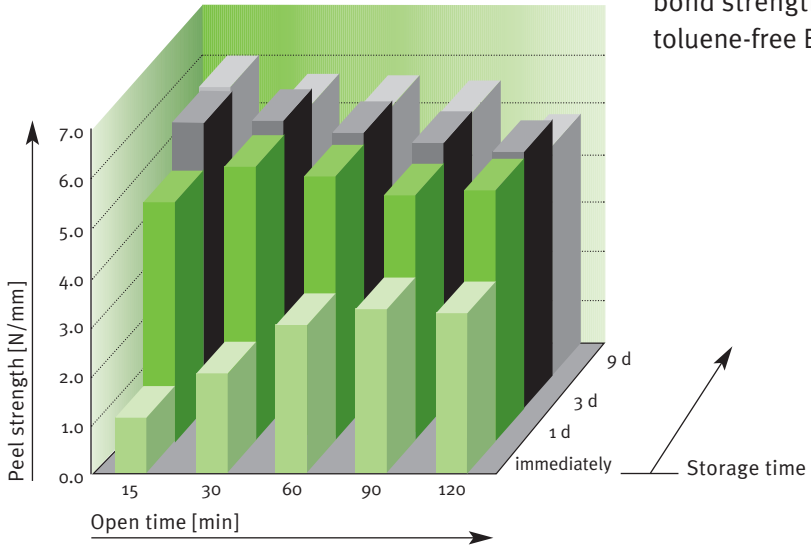
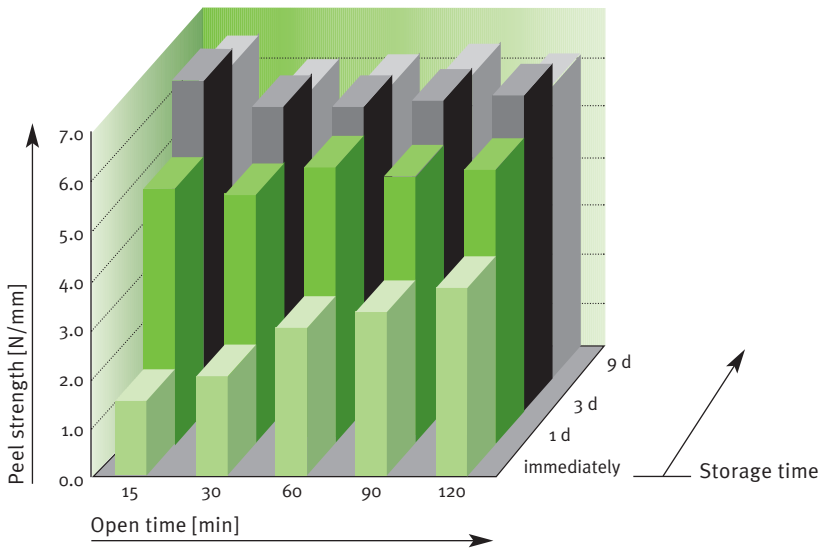
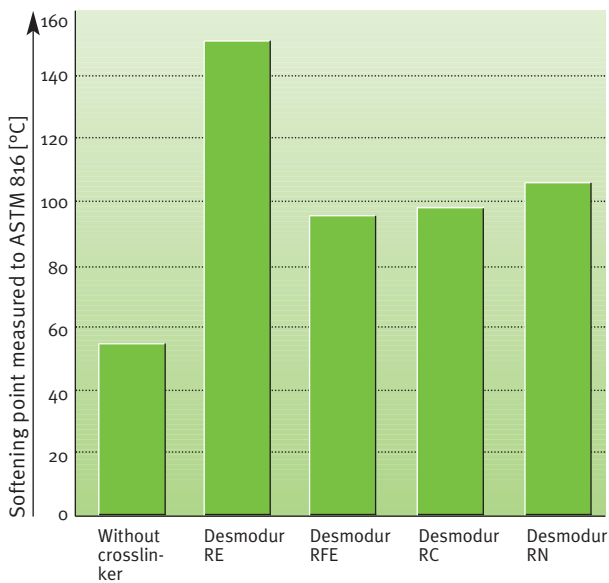


Fig. 16: Formulation 2, peel strength with a toluene-free adhesive



Crosslinking with Desmodur

Fig. 17: Heat resistance of Baypren®/Desmodur® bonds – adhesive formulation based on Baypren® 320/terpene-phenolic resin + 5 % crosslinking agent, substrate: SBR rubber



Baypren® adhesives to which Desmodur® is added before application to increase the heat resistance are extremely valuable, for example, in floorcoverings near a radiator or for table-tops that need to withstand hot dishes and plates.

The adhesion-improving effect of Desmodur® additives is utilized, among other things, in shoe production for bonding rubber materials that are otherwise difficult to bond.

7. Supply form

Baypren® adhesives are supplied in the form of flat chips. To ensure consistent pourability, the chips and the granules are powdered with talc (max. 1 %).

8. Packaging

For transport purposes, the Baypren® grades are packed in sacks of 25 kg. The sacks are made of multi-ply kraft paper lined inside with polyethylene. Each sack is labeled clearly with details of the grade. 35 such sacks are stacked on a one-trip pallet and the pallet is then shrink-wrapped with polyethylene film.

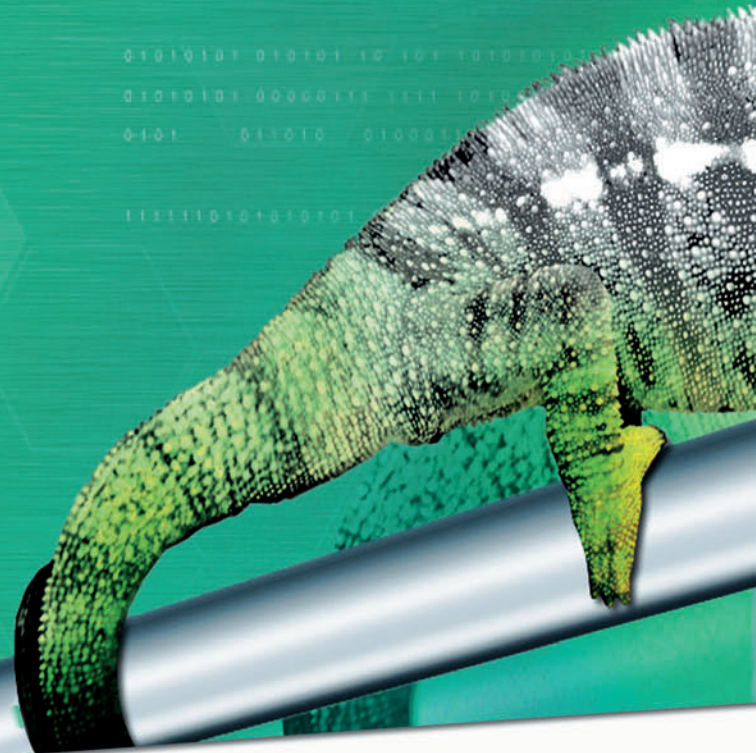
9. Storage

All Baypren® adhesives have excellent storage stability if stored under the proper conditions (i.e. 25 °C and 50 % relative humidity). To maintain perfect solubility, the product must be protected from heat and direct sunlight.

In isolated cases, the Baypren® chips in the bottom sacks of pallet may stick together due to the dead load of the product. The chips can be separated by lightly shaking the sacks. Baypren® chips tend to clump if stored improperly. the chips can then no longer be separated by shaking.

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