

CRAY VALLEY

HYDROCARBON SPECIALTY CHEMICALS

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NORSOLENE HYDROCARBON RESINS IN POLYCHLOROPRENE BASED CONTACT GLUES AND ADHESIVES



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1. Introduction

Contact glues and adhesives developed from polychloroprene elastomers occupy an important place among all methods ever developed.

The application of polychloroprene requires addition of metallic oxides (zinc oxides, in the presence of magnesium oxides if required).

But the most important constituent, apart from the polymer itself, is the system of resins.

Different types of resins are used in polychloroprene glues and adhesives. They give tack, cohesion and help in the development of specific adhesion. The basic resins used in glues and polychloroprene adhesives are phenolic reactive resins, that is, resol type alkyl-phenol resins, obtained by the reaction of tertiary p-alkyl phenols with an excess of formaldehyde. They provide a strong cohesion, in cold as well as hot state.

Aromatic hydrocarbon resins are used in medium concentration to provide tack, and in stronger concentrations in pressure sensitive adhesives (PSA) and mastics

Terpene phenolic resins, obtained from the reaction of beta-pinene and phenol, provide greater flexibility and residual tack as compared to alkyl phenol resins. They are mainly used in bi-component adhesives and glues.

The Norsolene resins, hydrocarbon resins with aromatic base, compatible with the polychloroprenes, are used, alone or in mixtures, in the formulations for polychloroprene adhesives and glues.

Norsolene resins in polychloroprene adhesives and gums in solution

1/ General properties

The resins typically used in the Norsolene are resins of the S series.

These are aromatic hydrocarbon resins, obtained from polymerisation of petroleum fractions. Light coloured, soluble in most industrial solvents, they have good thermal and chemical stability due to their very low olefinic insaturation and the absence of reactive chemical function.

Compatible with polychloroprenes, the S series Norsolene resins are commercially available in a large range of softening points (RB from 90°C to 155°C), offering large possibilities to formulators of glues and adhesives.

2/ Translucent formulations

In these formulations, the colour and thermal stability of the colour are important.

The Norsolene S resins and in particular Norsolene S 155 e, have an initial low colour and show a resistance to yellowing greater than that of a Terpene Phenolic resin and practically identical to that of a hydrogenated rosin ester.

If necessary, the adhesive thermal resistance can be improved by blending with better quality but more expensive resins (hydrogenated rosin esters, pure monomer resins with high softening point)

3/ Characteristics of Norsolene S resins

Specifications

NORSOLENE	S 95 e	S 105 e	S 1051 e improved odour	S 115 e	S 125 e	S 135 e	S 145 e	S 155 e
Softening point: °C R.B ISO 4625	88-98	99-109	99-109	110-120	120-130	130-140	140-150	150-160
Gardner Colour (50% in Toluene; ISO 4630)	4-7	4-7	4 - 7	4-7	4-7	4-7	3-6	3-6

Typical values

Iodine index: Iodine g /100g resin (WIJS ASTM D 1959)	< 25
Acid index: mg KOH/g resin (DIN 51559)	<0.1
Saponification index: mg KOH/g resin (DIN 51559)	< 3
Density at 20°C: (DIN 51757)	1.06 - 1.08
Ash content % : (ASTM D 2415)	<0.1

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Examples of solubility of Norsolene S
The solubilities are estimated at 25°C

S = Soluble
I = Insoluble

Only the results of S 95 e, S 105 e, S 125 e and S 155 e are shown here; the solubilities of S 115 e, S 135 e and S 145 e are comparable to adjacent categories.

Norsolene S /solvent (mass)	S 95 e		S 105 e		S 125 e		S 155 e	
	3/1	1/3	3/1	1/3	3/1	1/3	3/1	1/3
<u>Hydrocarbons</u>								
- White spirit with -5% aromatic	S	S	S	S	S	S	S	I
- Isooctane	S	I	S	I	I	I	I	I
- Cyclopentane and Cyclohexane	S	S	S	S	S	S	S	S
- Methylcyclohexane	S	S	S	S	S	S	S	S
- Dipentene	S	S	S	S	S	S	S	S
- Turpentine	S	S	S	S	S	S	S	S
- Aromatic hydrocarbons (160°C - 240°C)	S	S	S	S	S	S	S	S
- Toluene	S	S	S	S	S	S	S	S
- Xylene	S	S	S	S	S	S	S	S
<u>Cetones</u>								
- Cyclohexanone	S	S	S	S	S	S	S	I
- Methyl-ethyl-cetone (MEK)	S	S	S	S	S	S	S	S
- Methyl-isobutyl-cetone (MIBK)	S	S	S	S	S	S	S	S
<u>Esters</u>								
- Butyl phthalate	S	S	S	S	S	S	S	S
- Cyclohexyl acetate	S	S	S	S	S	S	S	S
- Butyl acetate	S	S	S	S	S	S	S	S
<u>Ethers</u>								
Propylene glycol monomethylic ether	S	S	S	S	S	S	S	S
<u>Chlorinated solvents</u>								
- Trichlorethane 1.1.1	S	S	S	S	S	S	S	S
<u>Alcohol</u>								
- Methanol	I	I	I	I	I	I	I	I
- Ethanol	I	I	I	I	I	I	I	I

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Compatibility with polychloroprenes.

Resin/Elastomer (mass)	NORSOLENE S 95 e			NORSOLENE S 115 e			NORSOLENE S 145 e		
	1/1	1/3	1/19	1/1	1/3	1/19	1/1	1/3	1/19
Neoprene WRT	C	C	C	C	C	C	C	C	C
NEOPRENE AD 20	C	C	C	C	C	C	C	C	C
Baypren 233	C	C	C	C	C	C	C	C	C

This table is not limited. The results of other compatibility tests show that all Norsolene S resins are compatible with commercial polychloroprenes routinely used in glues and adhesives.

4/ Materials, implementation, tests.

4-1- Materials

4.1.1. Resins

- Norsolene S resins.
- Phenolic terpene resins.
- Alkyl phenolic resins (1 and 2).
- Hydrogenated rosin ester.

4.1.2. Polychloroprenes

- Baypren 233, 320, and 321.
- Neoprene AD 20.
- Butachlor MA 424.

4.1.3. Solvents

- Toluene, gasoline C and ethyl acetate in mixture 1/1/1.
- MEK, ethyl acetate, cyclohexane, gasoline 60/95.

4.1.4. Substrates

- Rubber.
- Cotton.

4-2- Implementation = Baypren, Neoprene

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Formulas

- A
- 50 parts masticated polychloroprene (+ MgO and ZnO).
 - 50 parts pre-masticated polychloroprene.
 - 30-50-70 parts resin.
 - X parts solvent mixture.

Non-volatile matter: 25%

- B
- 100 parts of crude polychloroprene
 - 30-50-70 parts of resin
 - 5 parts of calcinated magnesia
 - 4 parts of active zinc oxide
 - X parts of solvent mixture

Solids content : 20%

Mastication of polychloroprene

The polychloroprene is masticated for 14 minutes on double cylinder with 5 parts of calcinated magnesium oxide and 4 parts of active zinc oxide for 100 parts of polychloroprene.

4.2.1 Solution preparation

Dissolution of the polychloroprene in the solvent, or mixture of solvents, then addition of resin or mixture of resins, followed by its dissolution by stirring.

4.2.2 The different tests were based on DIN 5327 specifications

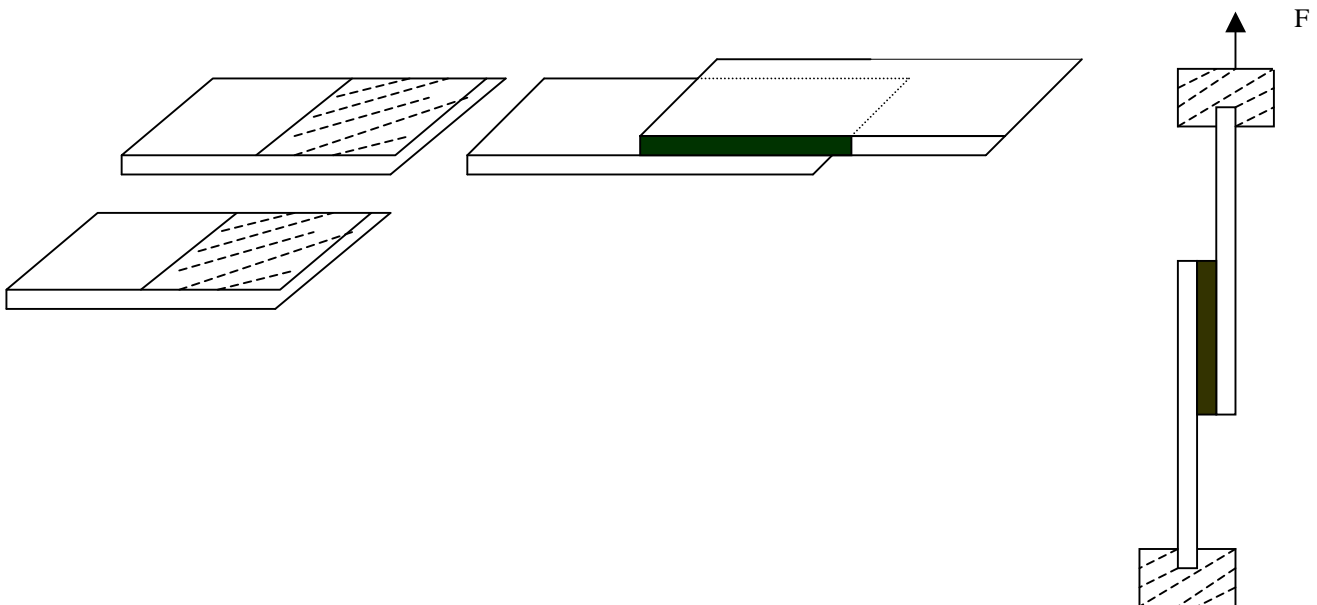
Viscosity

The Rotovisko HAAKE mobile MV1 apparatus is used

Shear resistance (30° and 50°C)

Rubber strips (100 x 20 mm) are pasted with a brush, in two successive layers, over an area of 4 cm² at one of their extremities.

After 30 minutes of drying, the two strips are pasted one over the other and subjected to around 1 kg/cm² pressure for 30 seconds

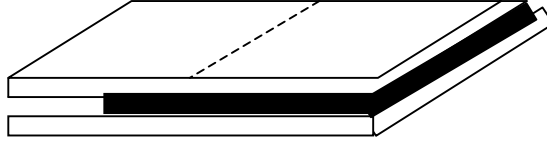


On the 5 test pieces thus pasted, the breaking stress is measured after three days with the help of a dynamometer. The results are expressed in kg/4cm²

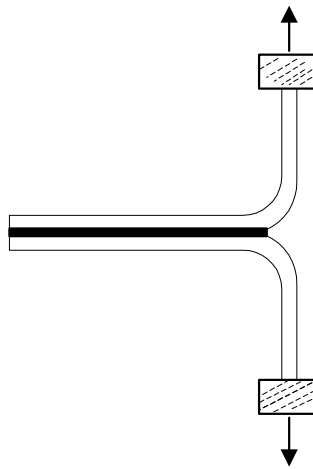
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Peel resistance

Two strips of rubber (100 x 20 mm) are pasted together (according to the same procedure as above) on a 10 cm² area.



The tearing is done by peeling as shown in the diagram below.



The results are expressed in kg/2cm

Thermal Resistance (SAFT)

Pasting over a 4 cm² area (see rupture in shearing) is subjected to a static stress (500g) in an enclosure whose temperature rises by 1°C /minute. The temperature is noted at the time of ungluing.

Measurement accuracy

- Shear resistance : 15% max
- Shear resistance : 7% max
- Heat resistance : 10 max

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5/ Baypren 331 base formulations

Formulation : 50 parts of masticated polychloroprene
 50 parts of pre-masticated polychloroprene
 30-50-70 parts of resin for hundred parts of polychloroprene
 X parts of solvent mixture

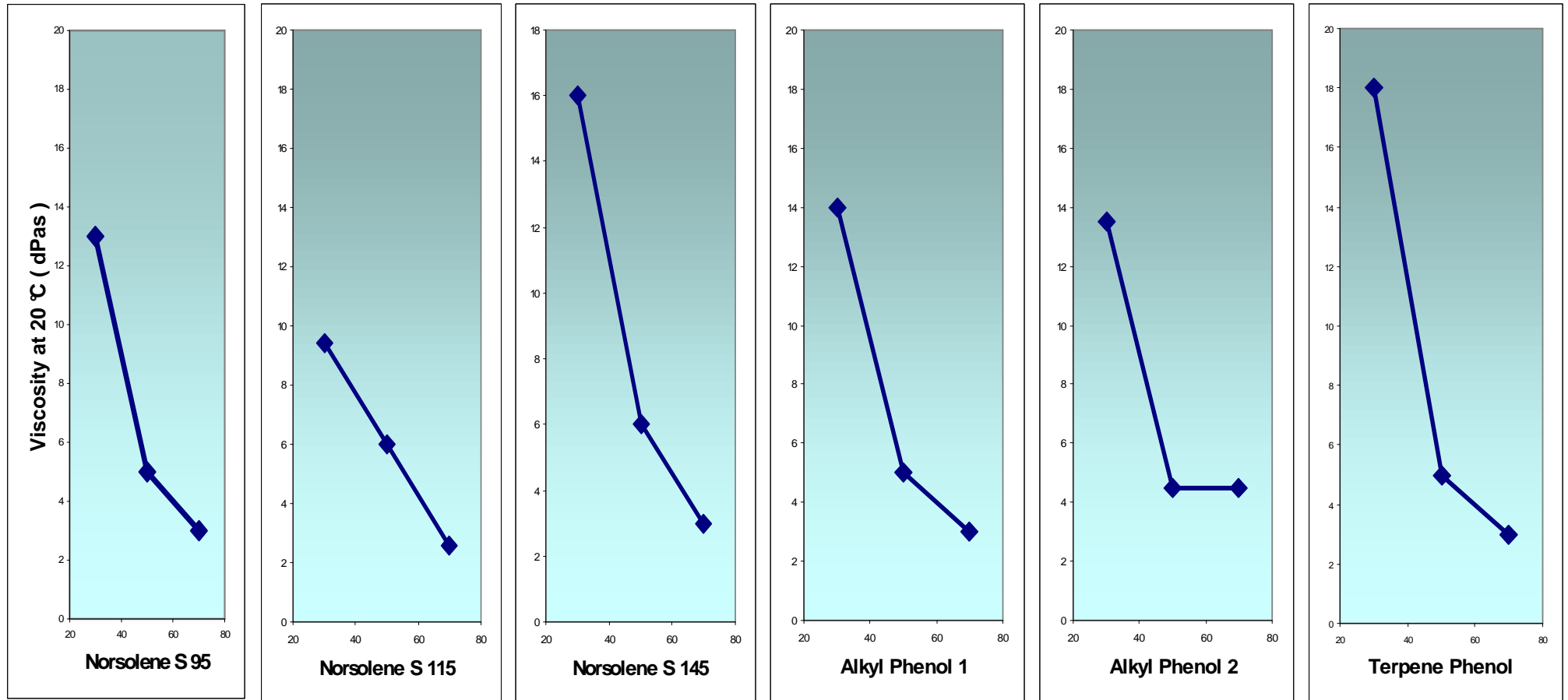
Solids content : 25%

5.1 Table of Results

Number of parts of resin for 100 parts of polychloroprene	PHR	Viscosity at 20°C dPas	Shear resistance kg/4cm ²		Peel resistance	Thermal resistance
			30°C	50°C	kg/2cm	°C
Norsolene S 95 e	30	13	33	7	3.4	68
	50	5	44	5	2.6	62
	70	3	39	5.4	7.4	70
Norsolene S 115 e	30	9.4	44	8.4	4.8	85
	50	6	43	5.6	6.2	75
	70	2.6	45	4	6	66
Norsolene S 145 e	30	16	< 46	9.1	6	73
	50	6	< 46	8	15	68
	70	3	< 44	6.4	18.6	65
Alkyl Phenol 1	30	14	42	32	3.2	88
	50	5	42	31	8	84
	70	3	44	25	3.2	82
Alkyl Phenol 2	30	13.5	39	19	1.7	76
	50	4.5	38	28	2.2	79
	70	4.5	37	22	1.8	81
Terpene Phenol	30	18	37	14	2.8	71
	50	5	38	13	2.2	71
	70	3	38	9	2.2	68

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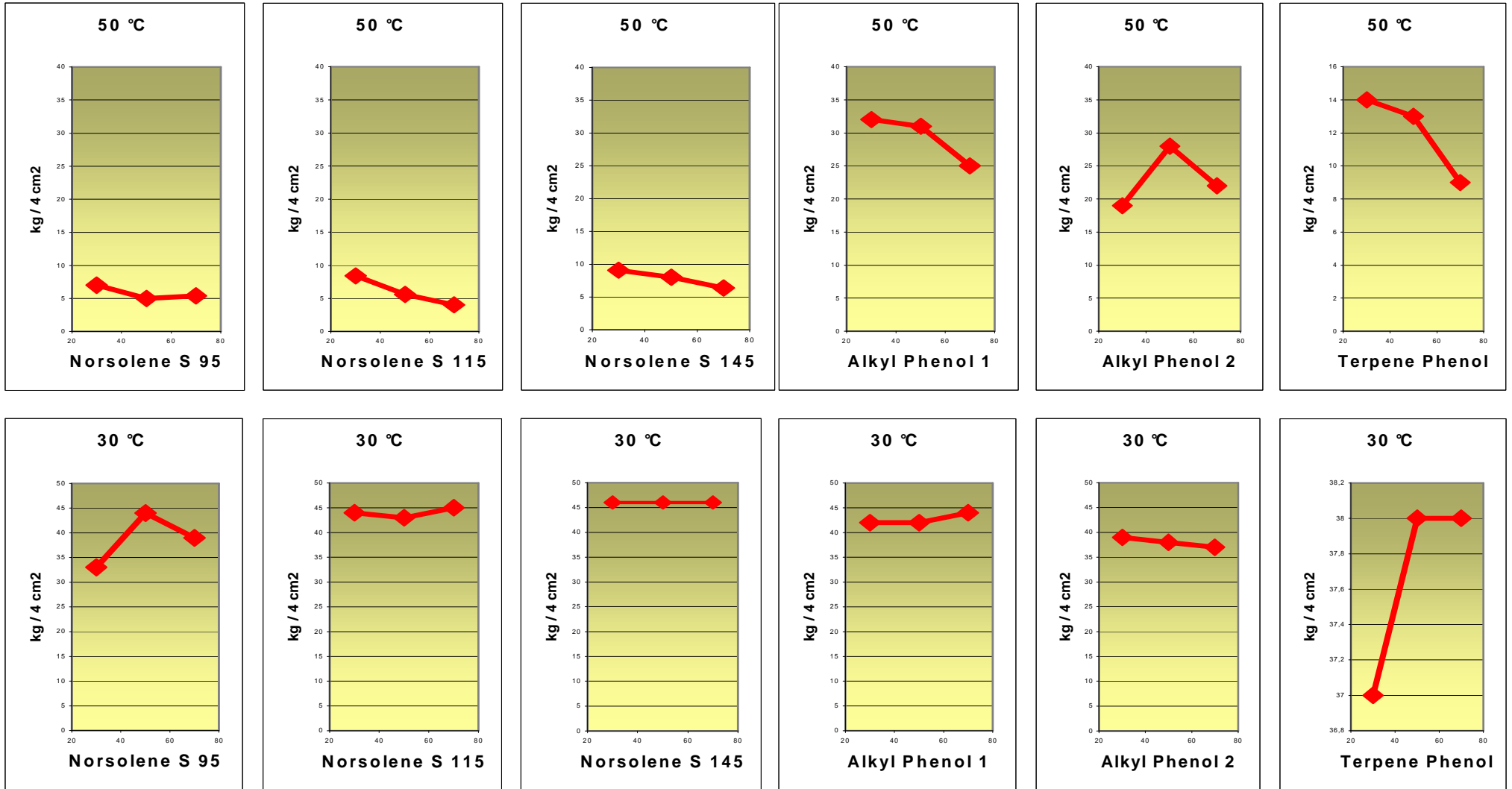
5.2 Viscosity at 20 °C



As far as the viscosities of terminated glues are concerned, the Norsolene resins act as alkyl phenol resins, and like them, lower the viscosity and facilitate the application of polychloroprene glues.

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5.3 Shear resistance

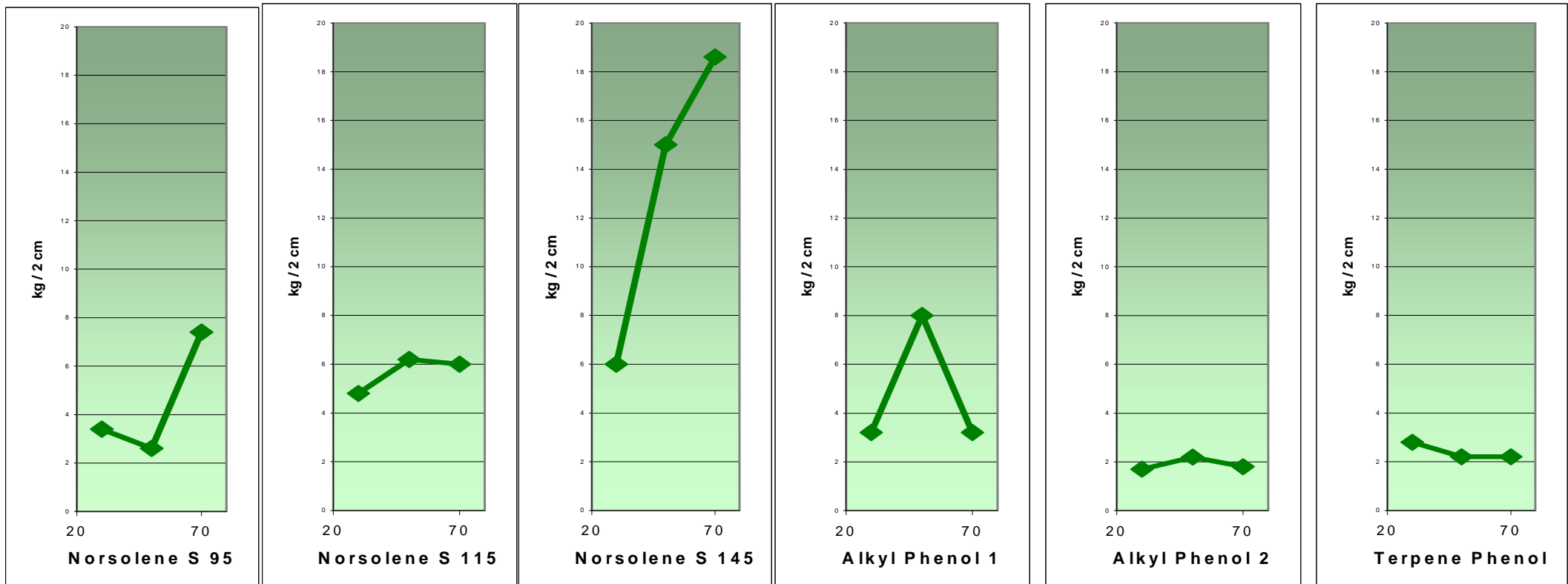


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At 30 °C, the reaction of Norsolene is similar to that of alkylphenol and terpene phenol resins, the Norsolene S 145 e further increasing the cohesion of the adhesive layer.

At 50°C, the thermofusible property of Norsolene resins is a disadvantage compared to traditional resins. However the use of Norsolene and alkyl phenol resins mixtures may be quite appropriate.

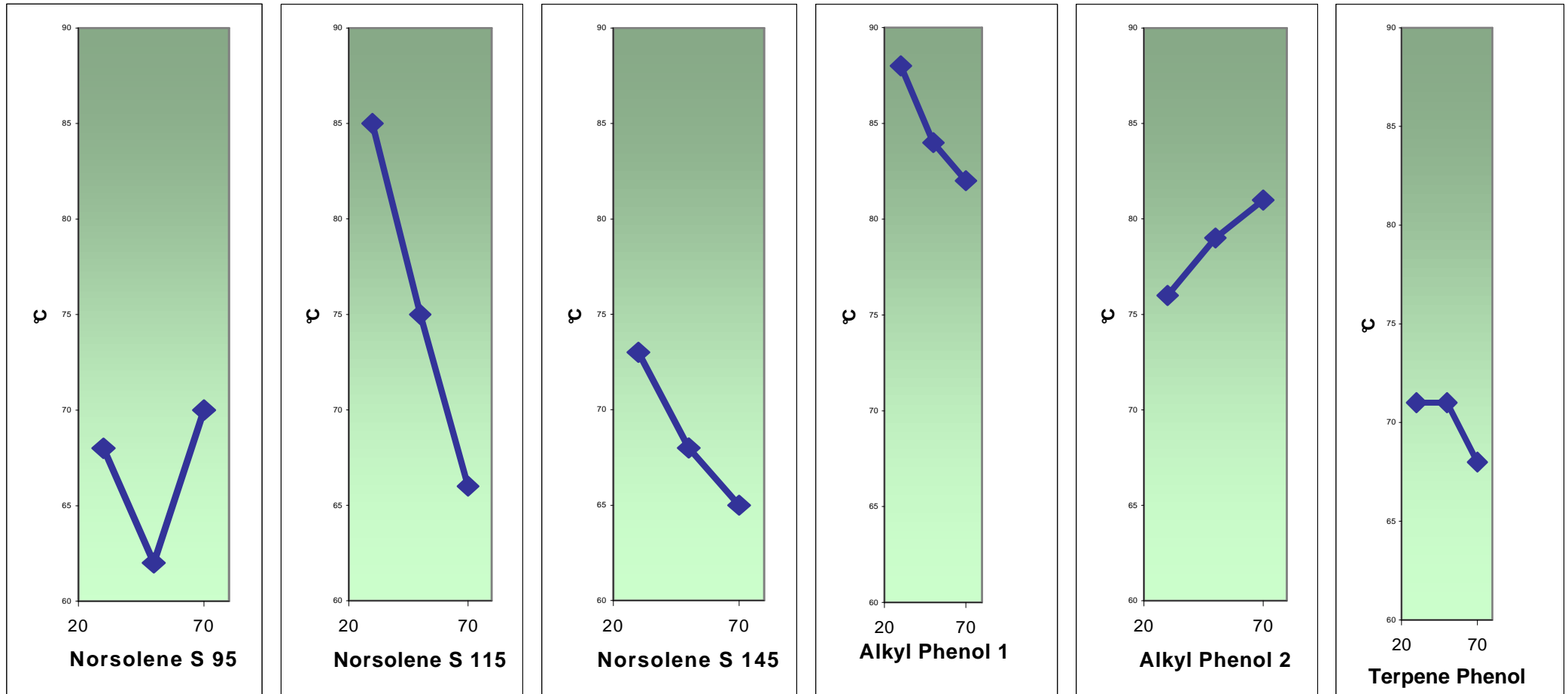
5.4 Peel resistance.



The behaviour of Norsolene resins is similar to that observed earlier, with respect to shear. The Norsolene resins with high softening point offer higher peel resistance.

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5.5 Thermal resistance.



The temperature resistance, determined in static shear, representative of the stress undergone by the systems assembled by pasting, shows that the Norsolene resins are closer to traditional resins, particularly terpene – phenol resins.

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6/ Neoprene AD 20 base formulations

Formulation :- 100 parts of raw polychloroprene

- 30-50-70 parts of resin
- 5 parts of calcinated magnesia
- 4 parts of active zinc oxide
- X parts of solvent mixture

Solids content : 20%

6.1 Table of Results

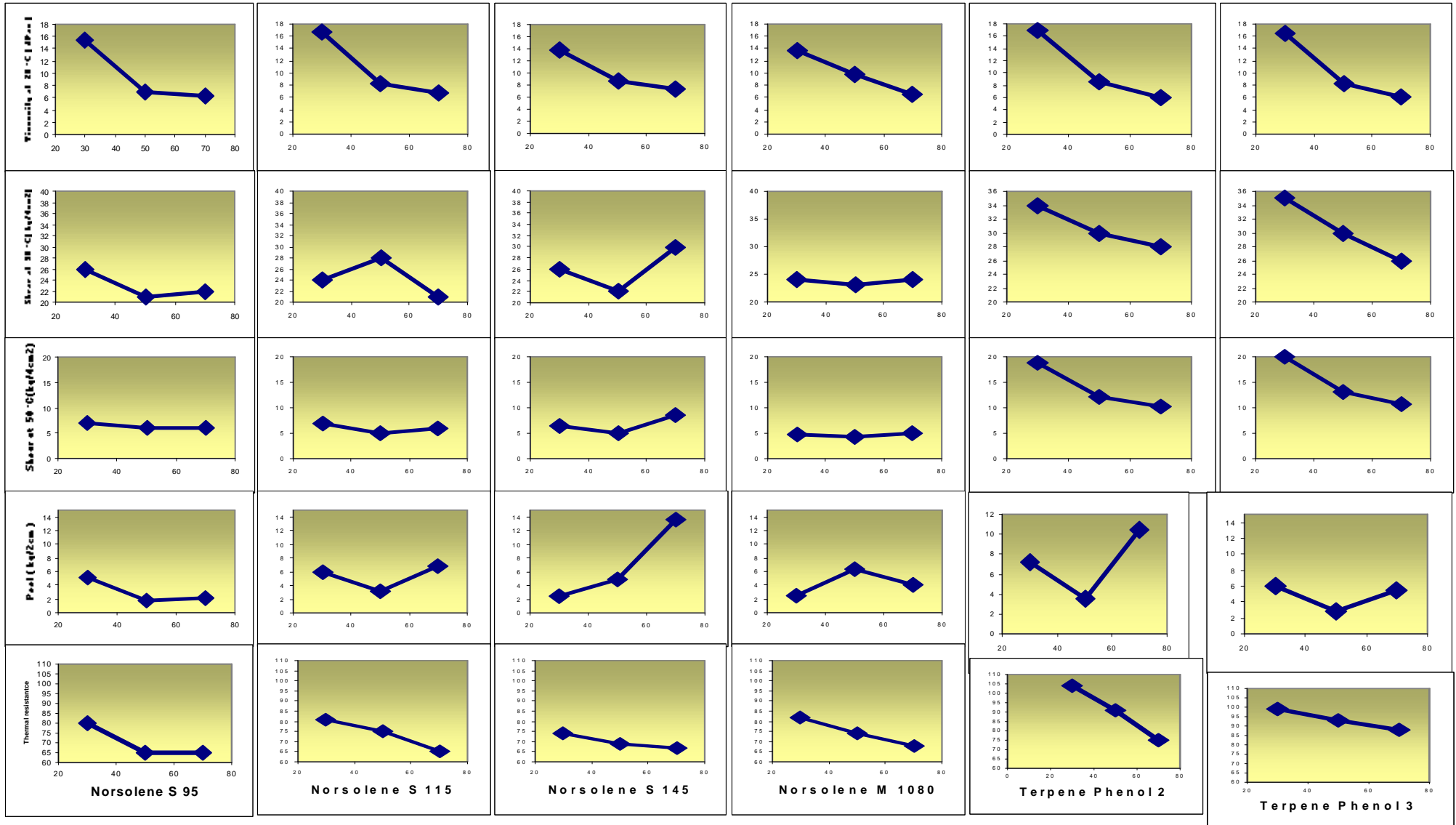
Number parts of resin for 100 parts of polychloroprene	PHR	Viscosity at 20°C dPas	Shear resistance kg/4cm ²		Peel resistanc e	Thermal resistanc e
			30°C	50°C	kg/2cm	°C
Terpene phenol 2	30	1.7	34	18.7	7.2	104
	50	8.5	30	12.1	3.5	91
	70	5.9	28	10.2	10.5	75
Terpene phenol 3	30	16.4	35	20.0	6.0	99.0
	50	8.2	30	13.0	2.9	93.0
	70	6	26	10.7	5.5	88.0
Norsolene S 95 e	30	15.3	26	7.0	5.2	80.0
	50	6.9	21	6.0	1.7	65.0
	70	6.2	22	6.0	2.2	65.0
Norsolene S 115 e	30	16.8	24	7.0	6	81.0
	50	8.3	28	5.0	3.1	75.0
	70	6.8	21	6.0	6.8	65.0
Norsoslene S 145 e	30	13.8	26	6.5	2.5	74.0
	50	8.6	22	4.9	4.9	69.0
	70	7.3	30	8.6	13.6	67.0
Norsolene M 1080	30	13.6	24	4.7	2.4	82.0
	50	9.7	23	4.2	6.4	74.0
	70	6.4	24	5.1	4.1	68.0

During the application of polychloroprene with low crystallisation tendency and low viscosity, the differences in the behaviour between the Norsolene resins and the alkyl phenol resins and the terpene phenol resins are slightly accentuated.

For gluing subjected to temperatures close to room temperature, the Norsolene resins will give satisfaction, the Norsolene resins with higher softening points provide better cohesion.

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6.2. Results graph.



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7/ Baypren 233 base formulations with or without pre-reaction

Formulation : 50 parts of masticated Baypren 233

50 parts of premasticated Baypren 233

70 parts of resin

X parts of solvent mixture

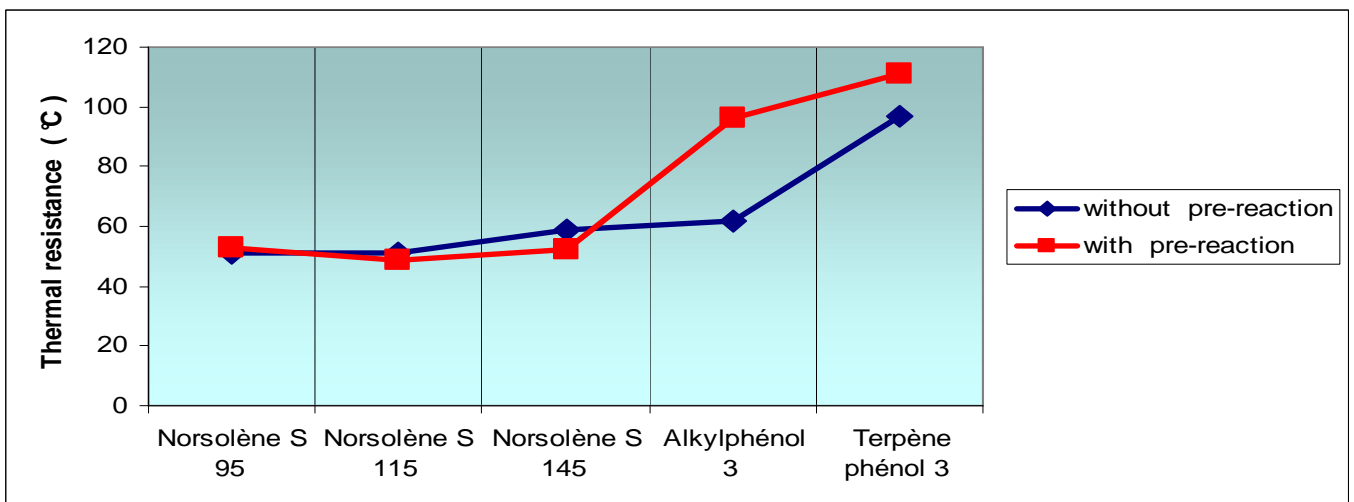
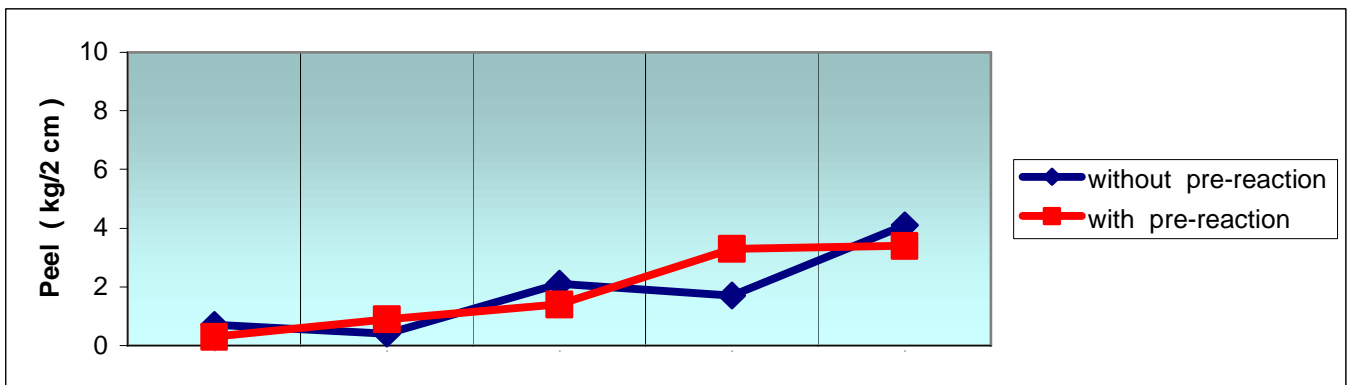
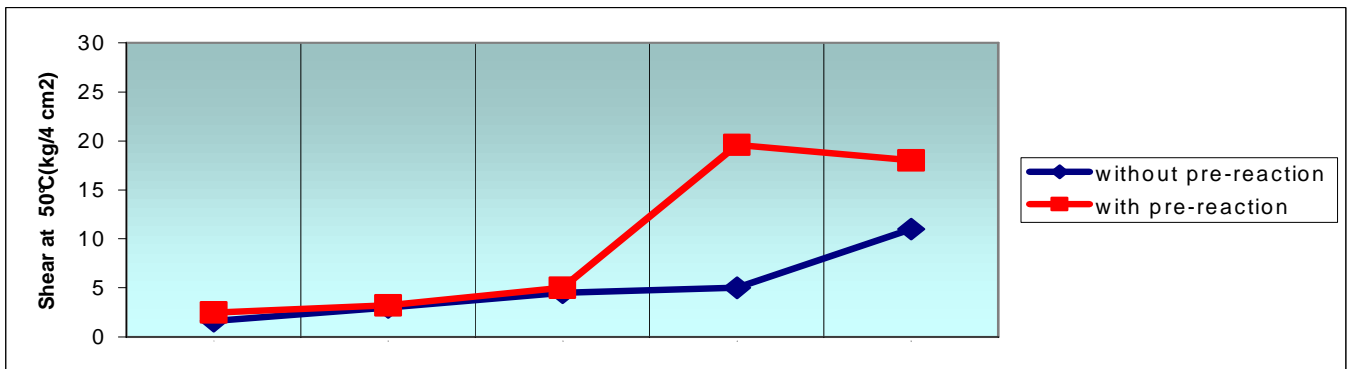
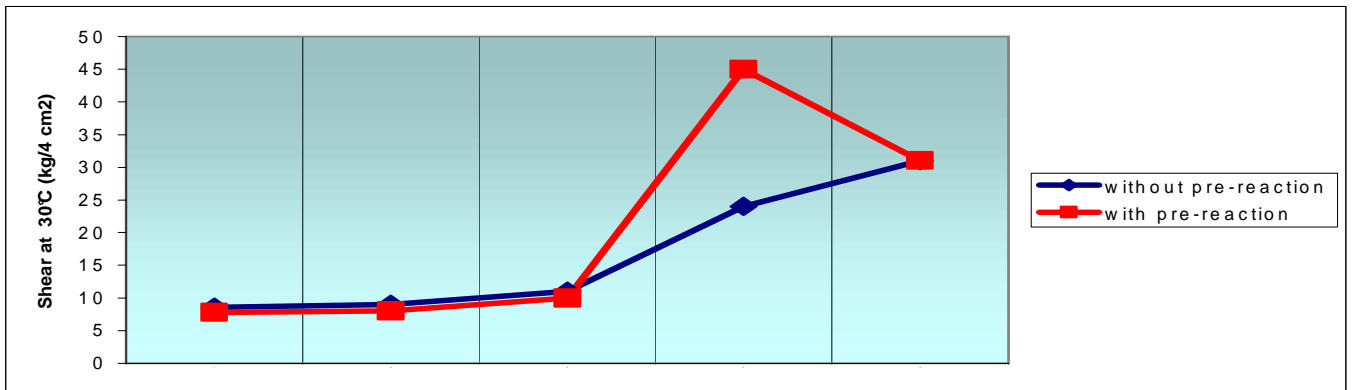
Solids content 25%

7-1 Table of Results

		Shear resistance kg/4cm ²		Peel resistance kg/2cm	Thermal resistance °C
		30°C	50°C		
Without pre- reaction	Norsolene S 95 e	8.6	1.6	0.7	51
	Norsolene S 115 e	9	3	0.4	51
	Norsolene S 145 e	11	4.5	2.1	59
	Alkyl Phenol 3	24	5	1.7	62
	Terpene Phenol 3	31	11	4.1	97
With pre-reaction	Norsolene S 95 e	7.8	2.5	0.3	53
	Norsolene S 115 e	8	3.2	0.9	49
	Norsolene S 145 e	10	5	1.4	52
	Alkyl Phenol 3	45	19.6	3.3	96
	Terpene Phenol	31	18	3.4	116

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7.2 results



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8/ Application of resin mixtures

If in some applications, the performances obtained with Norsolene resins used alone do not give the desired values, it is quite possible to use mixtures of resins.

This solution is often suitable for obtaining an attractive performance to cost ratio.

Formulation : 100 parts of Neoprene AD 20
 50 parts of resin
 5 parts of calcinated magnesium oxide
 4 parts of active zinc oxide
 X parts of solvent mixture

Solids content : 20%

8-1 Results

Resins	PH R	Viscosity 20° dPas	Open time	Shear kg/4cm ²		Peel resistance kg/2cm	Thermal resistance	
				30°C	50°C		Peel °C	Shear °C
Terpene phenol	50	12.1	3 h	> 40	6	6.4	55	86
Alkyl phenol	50	14.6	20 min	39.2	8.2	5	68	91
Norsolene S 115 e	50	13.3	>24 h	42.5	6	6.5	58	82
Norsolene S 145 e	50	13.1	> 8 h	> 40	6.2	5	49	81
Alkyl Phenol	35	13.1	15 min	> 40	11.8	8.5	67	130
Terpene Phenol	15							
Alkyl Phenol	25	9.6	30 min	> 40	6.5	6.6	68	90
Terpene phenol	25							
Alkyl Phenol	15	10.3	4 h	> 40	8.1	6.8	64	83
Terpene phenol	35							
Alkyl Phenol	35	14.1	> 24 h	42	9.3	5.7	66	81
Norsolene S 115 e	15							
Alkyl Phenol	25	13.6	> 24 h	> 40	13.5	4	55	85
Norsolene S 115 e	25							
Alkyl Phenol	15	14.1	> 24 h	> 40	12.5	3.6	52	80
Norsolene S 115 e	35							
Alkyl Phenol	35	13.4	> 8 h	> 40	9	3.2	57	87
Norsolene S 145 e	15							
Alkyl Phenol	25	13.6	> 8 h	> 40	6.2	5.6	54	80
Norsolene S 145 e	25							
Alkyl Phenol	15	17.7	> 8 h	34.5	4.4	5.9	56	78
Norsolene S 145 e	35							

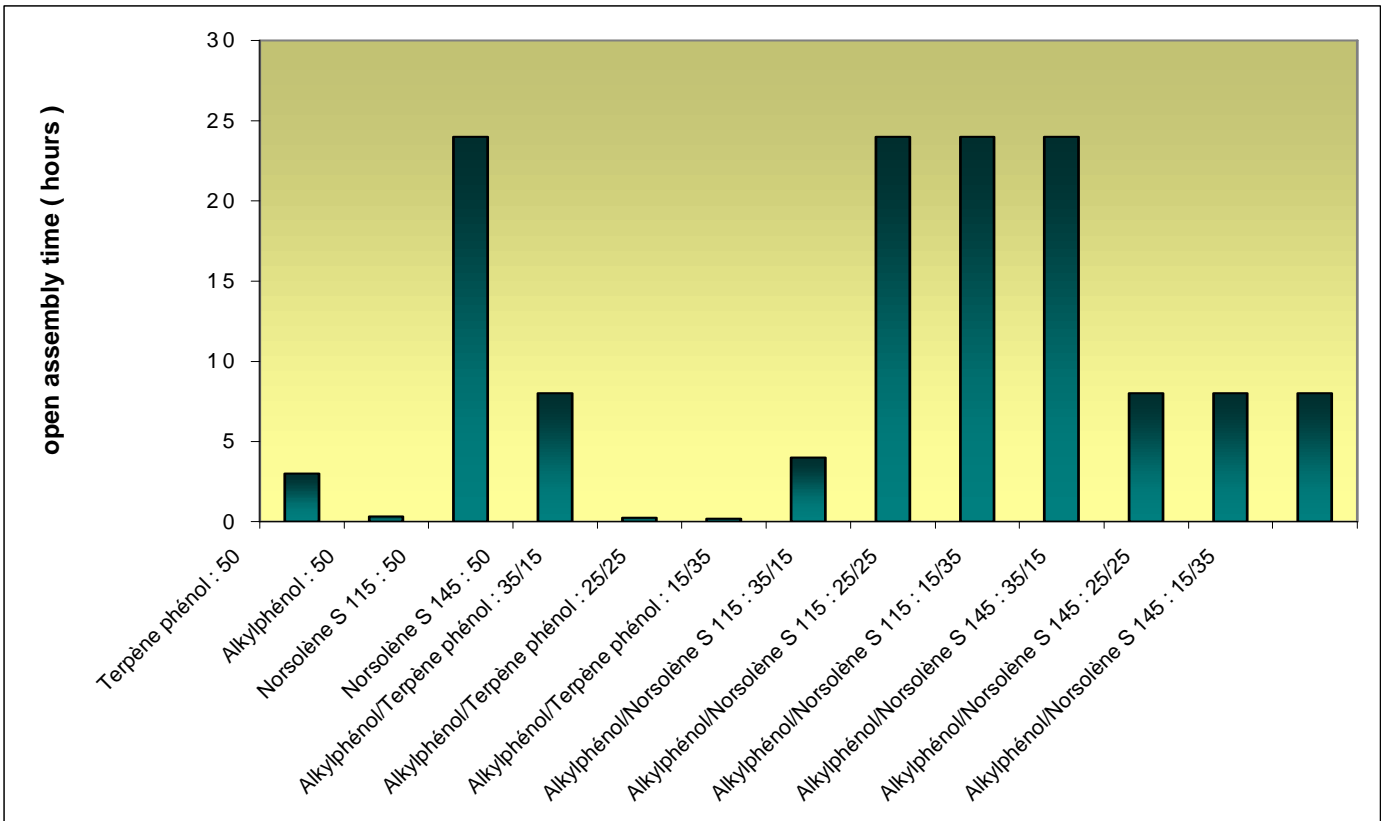
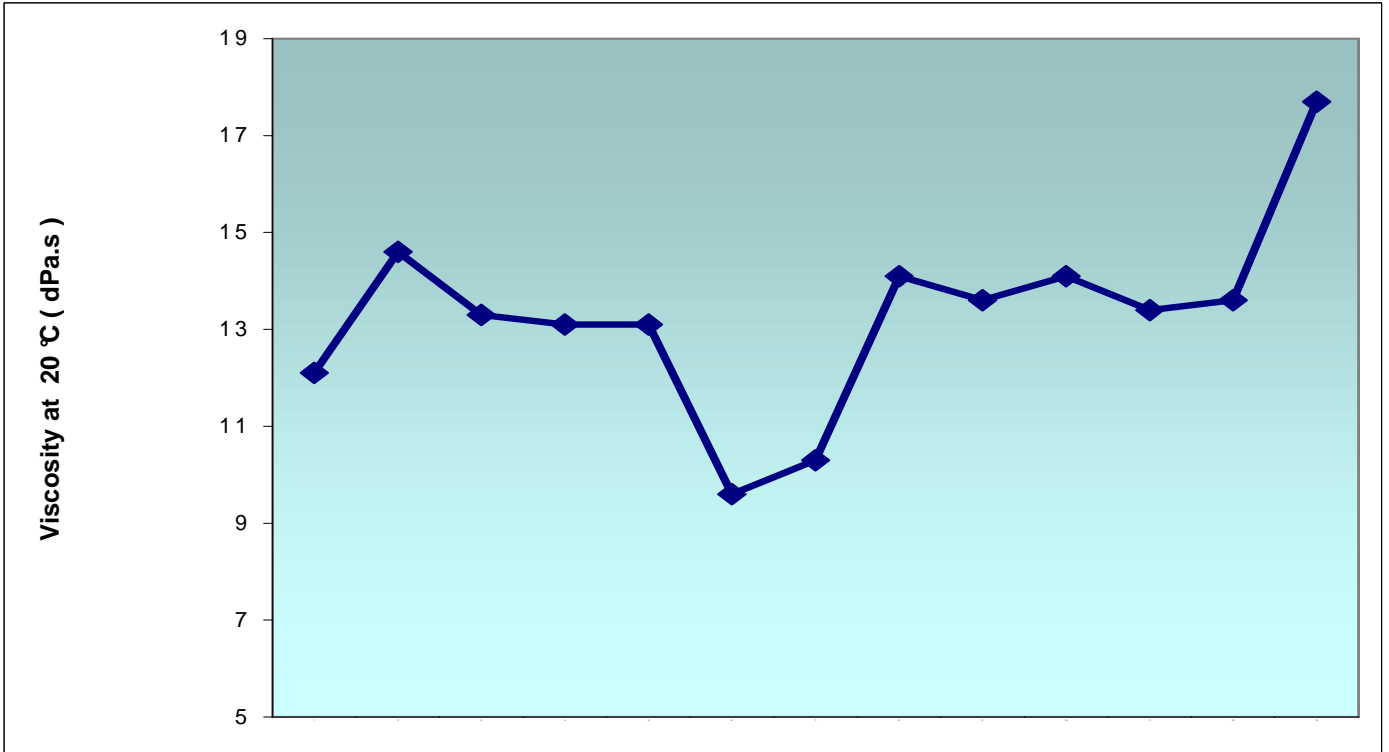
The NORSOLENE resins, like the traditional alkyl and terpene phenols contribute to facilitating preparation of polychloroprenes and application of glues.

The use of NORSOLENE resins helps to obtain medium and long open periods.

By blending Norsolene resins and alkyl phenol resins, it is possible to adjust the properties of viscosity and open assembly times.

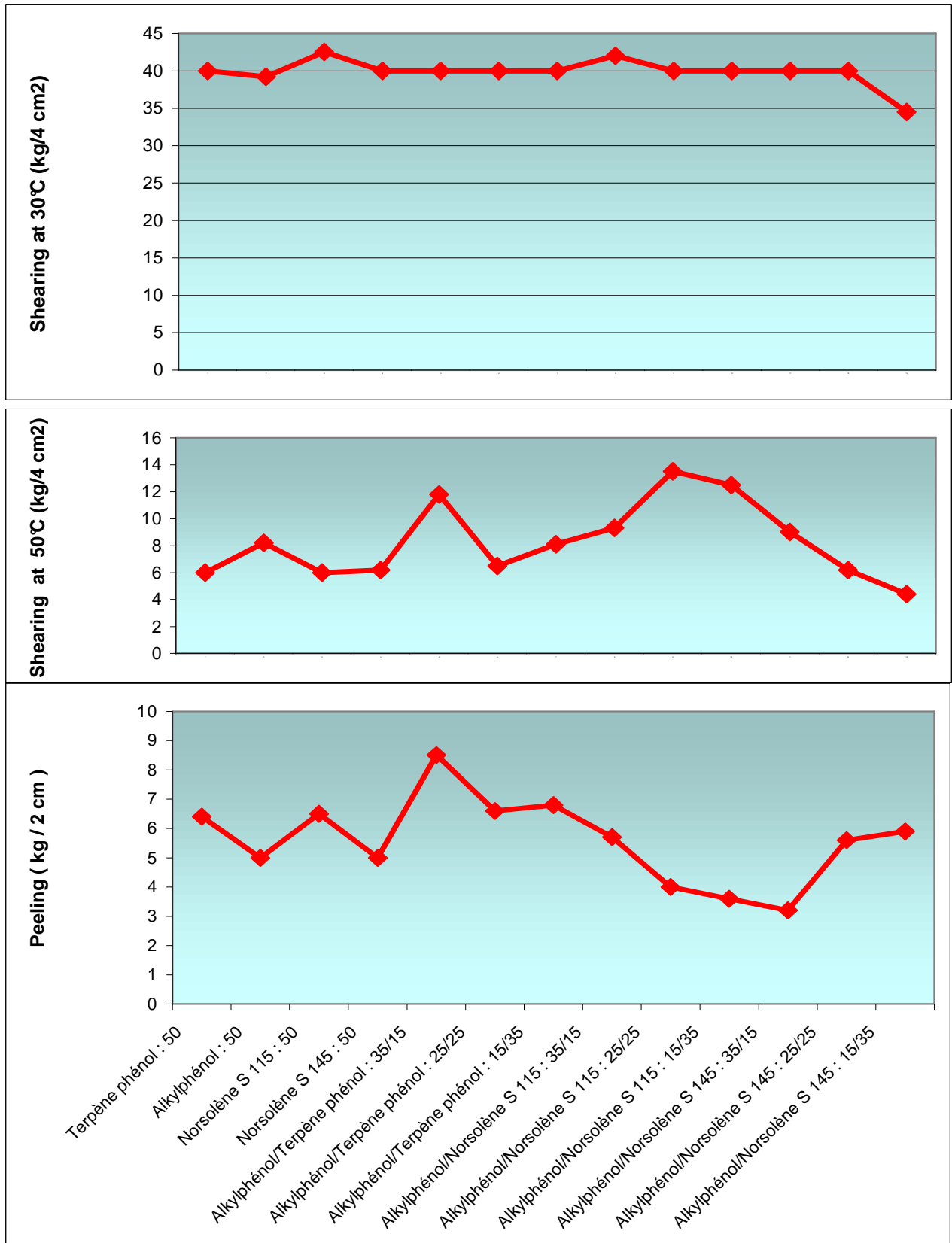
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8.2. Viscosity (20°C) and open assembly time.



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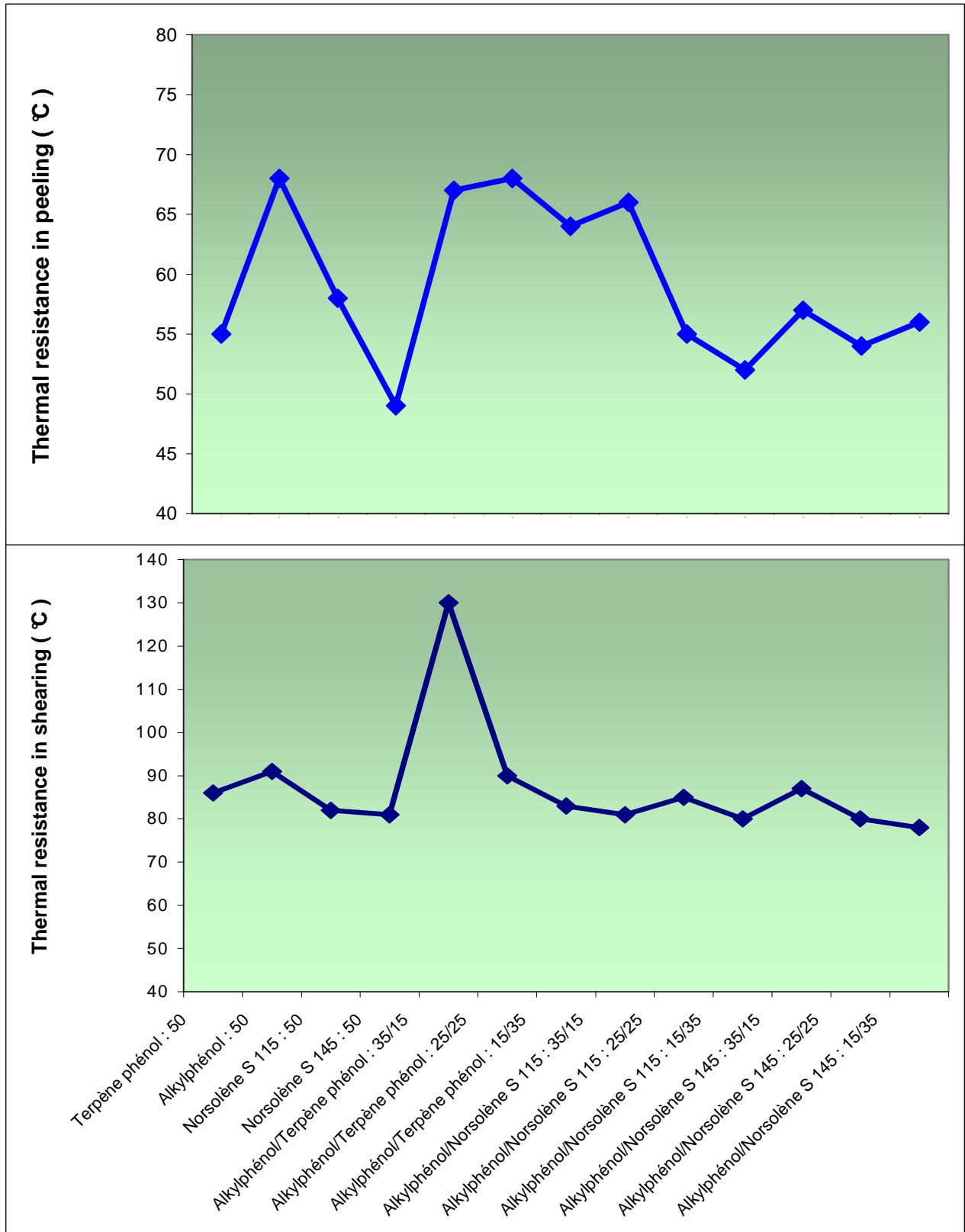
8.3. Shear and peel



Under experimental conditions, the Norsolene resins with medium softening points do not alter the cohesive properties of the glues.

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8.4. Thermal resistance



The blending of a phenol alkyl resin by a Norsolene resin alters very little the heat resistance of the pasting.

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9/ Butachlor MA 424 base formulation

9-1 Formulations applied :

Solid : Butachlor MA 424	100	
BHT	1	
Ecepox PB1	2	
Transparent ZnO	2	
Resin	40	
Solvent: Toluene	10	
MEK		18
Ethyl acetate	28	
Gasoline 60/95	10	
Cyclohexane		34

Resins

Resin	Norsolene S 95 e	Norsolene S 155 e	Terpene Phenolic	Penta erythrytol rosin ester	Hydro genated glycerol rosin ester	Pure aromatic monomers
Softening point (R&B, °C)	88-98	150-160	146-156	108	86	151-155
Gardner colour 50% Toluene	4-7	3-6	-	< 1	5	< 1

Basic characteristics of the glues tested :

Solids content = 19.7%
 Brookfield viscosity : 1600 mPas

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9.2 Table of Results

Resins		Norsolene S 95 e	Norsolene S 155 e	Terpene Phenolic	Penta rosin ester	Hydrogenated glycerol rosin ester	Pure aromatic monomers
ADHESIVE PROPERTIES							
Viscosity	mPas	1500	1550	1450	1490	1500	1640
Cotton – Cotton adhesion kg/cm	Initial	1.1	1.2	1.3	1.0	1.0	1.4
	48 h – 23°C	2.8	4.8	4.6	3.9	3.8	5.6
Cotton – Cotton heat resistance	0.5 kg/cm 2°C/min	40	41	47	46	43	50
Open time (hours)	Estimate	> 24	> 24	24	48	48	1
Change in colour under UV-B at 50°C (L*, a*, b* co-ordinates of MINOLTA colorimeter)							
L*	Initial	+89.4	+89.6	+88.3	+89.4	+88.9	+90.0
+ white	1 h	+87.7	+88.0	+86.6	+87.7	+86.9	+88.6
- black	2 h	+86.6	+86.8	+85.8	+86.5	+85.9	+87.4
	4 h	+81.7	+82.6	+82.2	+85.2	+85.3	+85.5
a*	Initial	-0.1	+0.3	+0.3	+0.1	+0.15	+0.3
	1 h	+0.9	+1.5	+1.3	+1.6	+0.9	+1.3
	+ red	2 h	+1.4	+1.9	+1.5	+1.9	+1.09
(-green)	4 h	+4.6	+4.3	+3.3	+2.3	+1.33	+2.7
b*	Initial	+2.7	+1.1	+5.3	+2.5	+5.27	+1.2
	1 h	+8.5	+7.3	+11.0	+8.6	+10.3	+5.8
	(+ yellow)	2 h	+11.9	+10.3	+13.3	+11.0	+12.9
(-blue)	4 h	+19.8	+17.0	+18.4	+14.5	+16.3	+12.3

9.3 Conclusions

Tested in a translucent formula where the colour and the colour stability are important, Norsolene S 95 e and S 155 e have been compared to normal resins (terpene phenolic resins, rosin esters, hydrogenated or otherwise) and also to aromatic resins of pure monomers with high softening point.

Norsolene S 155 e gives good adhesive properties, with a slightly lower thermal resistance, as is known for this type of resins (see above). The use of blending will improve this feature if required, by considerably lowering the cost price of the final formula, the price of other resins being rather high, especially the pure aromatic monomer resins with high softening point and hydrogenated rosin esters.

Norsolene S 155 e helps obtain low initial colouring formulas, close to those obtained with pure monomer resins.

Norsolene S 155 e also shows a good UV-B temperature resistance to yellowing, greater than that obtained with terpene phenolic resins and almost identical to that obtained with hydrogenated rosin ester.

Norsolene S 155 e has a good quality to price ratio for the translucent polychloroprene glues, by itself or blended with resins having better heat resistance, but more expensive, with which it is compatible.

10 Safety Data Sheets

The Safety Data Sheets are available on the CRAY VALLEY web site:
<http://www.crayvalley.com>

These results obtained in our laboratory are given in good faith according to the method used and the samples checked. The values cannot be used to set specifications. They are indicated without Cray Valley's guarantee or liability. All given formulations are starting formulations and they are indicated without Cray Valley's guarantee or liability. They are based on our present technical knowledge and experience. They do not relieve processors of the responsibility of carrying out their own tests and experiments, because many factors that could influence the result may arise during processing and application; neither do they imply and legally binding assurance of certain properties or of suitability for a specific purpose. Any proprietary should be respected.

Shelf life : Norsolene resins are inert and stable. Their shelf life mainly depends on the storage conditions and end use. Their average shelf life is about 2 years. This average shelf life is given without Cray Valley's guarantee because Cray Valley does not control end uses and the storage conditions at customers.

Storage : all resins with a low softening point present a risk of solidifying, which increases in hot weather. Therefore for softening points of less or equal to 100 °C, we recommend : storage in a cool (25 °C max), ventilated area, out of the sunlight; do not stack pallets; avoid storage for prolonged period