NA FREE SOLUTION FOR ETU REPLACEMENT IN POLYCHLOROPRENE

MLPC International has developed for more than fifty years its expertise in the Sulfur chemistry. As a wholly owned subsidiary of ARKEMA, MLPC International benefits from the group's R&D support and therefore is committed to research programs that produce ever more innovative, environmentally friendly and safe products.
In that spirit, MLPC International has developed a molecule named **"SD"** for **"Sulfur Donor"** which is **a Sulfur Donor NA Free alternative to the ETU**.

EKALAND™ ETU and MIXLAND®+ ETU 80 GA F140 are widely used in polychloroprene providing to the system unrivalled properties.

For the time being, ETU is classified as toxic and reprotoxic.
It was a great challenge for MLPC International to develop a technical and economical alternative to ETU while many have tried without any success.

We achieved our goal launching MIXLAND®+ SD 75 GA F250.
The new product performs just as or even greater than ETU molecule.

Experimental plan

The study is based on an experimental cubic, 3 variables, 3 levels, it means 9 recipes, as follows:

CR Base	
CR WRT	100
Carbon black N550	50
White Clay	20
DINP	20
Paraffin	1
Antioxidant	1
Stearic acid	0.5
MgO	4
ZnO 3C	5

Table 1

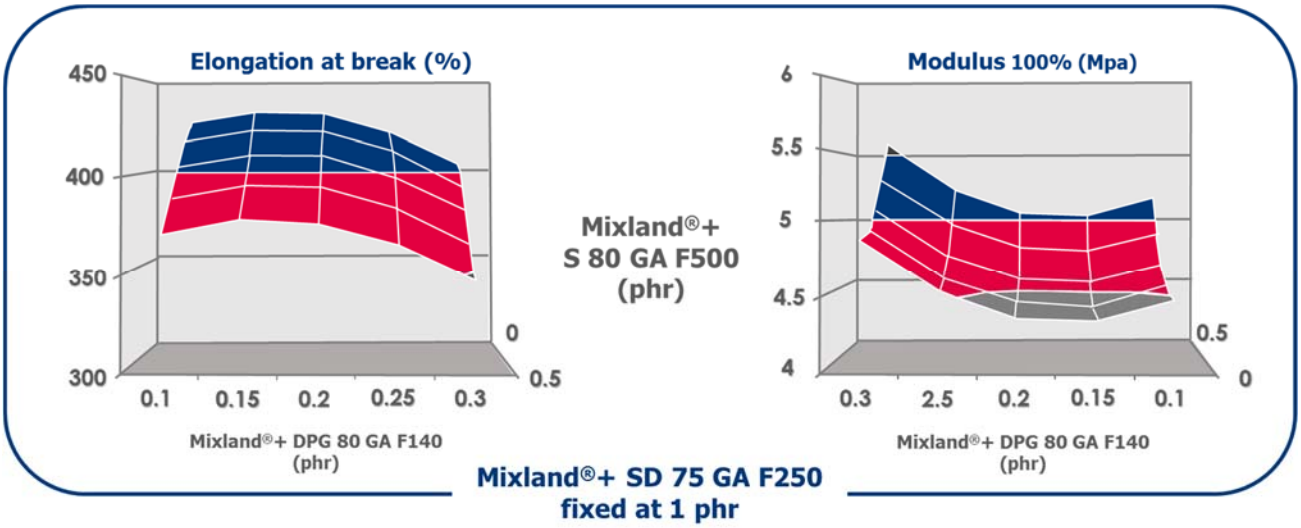
Compounds	1	2	3	4	5	6	7	8	9
CR Base	201.5	201.5	201.5	201.5	201.5	201.5	201.5	201.5	201.5
Mixland®+ SD 75 GA F250	**0.67**	**1**	**1.33**	**1.33**	**0.67**	**1**	**1**	**1.33**	**0.67**
Mixland®+ SM300 80 GA F140	0	0.25	0.5	0	0.25	0.5	0	0.25	0.5
Mixland®+ DPG 80 GA F140	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3

Table 2

This experimental plan allows us to conclude that this new molecule improves the cross-linking network: Results are better by using MIXLAND®+ SD 75 GA F250 in comparison with the conventional system using EKALAND™ ETU or MIXLAND®+ ETU 80 GA F140. Benchmarking was also made with alternative solutions like 3-methyl-2thiazolidinethione and showed that, clearly, the best solution remains MIXLAND®+ SD 75 GA F250.

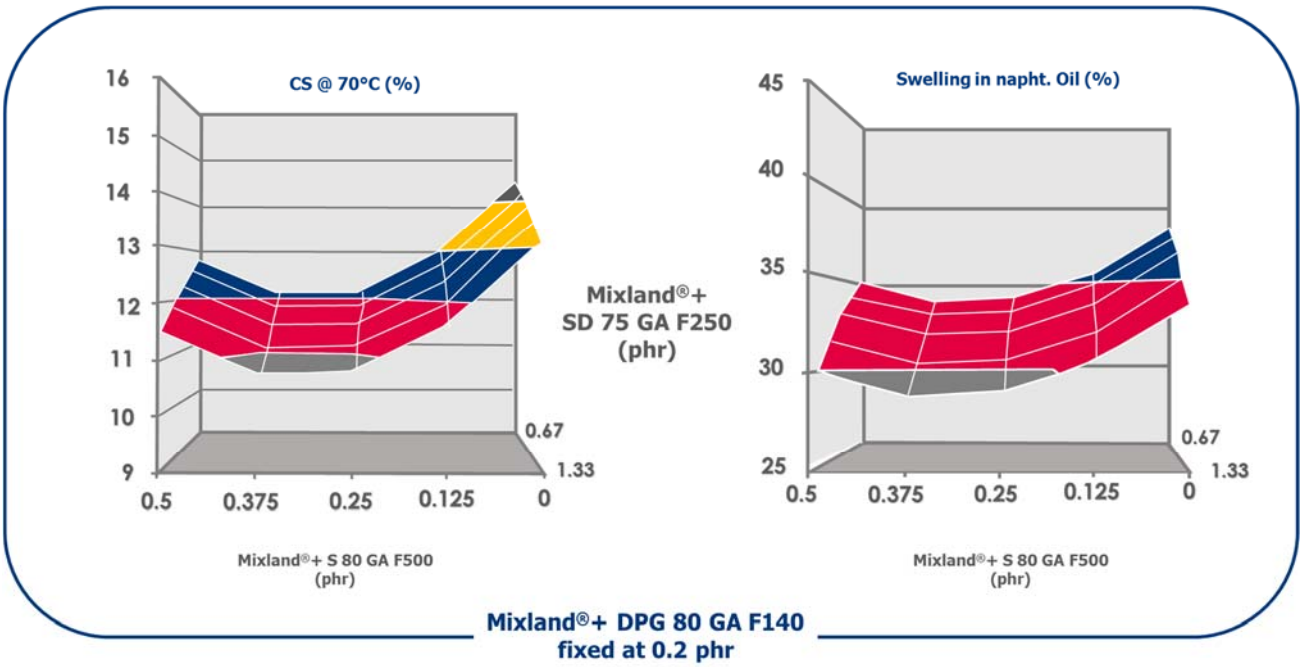
Mechanical properties, results before and after ageing requirements

According to this experimental plan, we obtain a significant synergy effect when combining MIXLAND®+ SD 75 GA F250 to EKALAND™ DPG and MIXLAND®+ DPG 80 GA F140.



Compression set and swelling at 70°C

We improve the compression set and swelling at 70°C with adding a small quantity of MIXLAND®+ S80 GA F500; Sulfur helps the reaction catalyse as well as increases the cross-linking density.



MLPC best solution

The best solution was defined through the experimental plan hereunder:

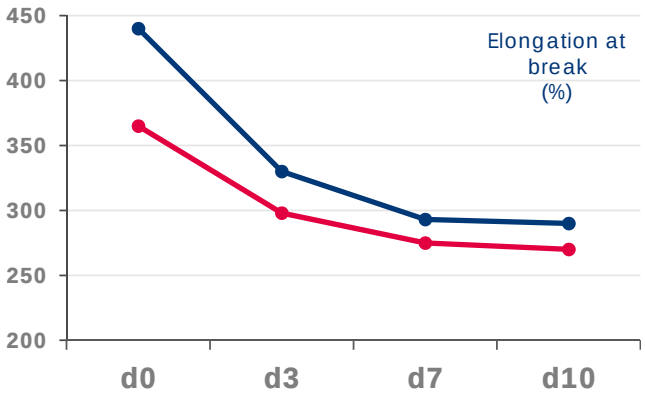
	Blank	Compound 7: the best for mechanical and ageing properties	Compound optimized for CS and oil swelling
CR Base		**194.5**	
ZnO		**5**	
Paraffin		**1**	
antioxidant		**1**	
Mixland® + ETU 80 GA F140	**0.75**		
New curing agent Mixland® + SD75 GA F250		**1**	**1.33**
Mixland® + DPG 80 GA F140		**0.3**	**0.25**
Mixland® + SM300 80 GA F140			**0.2**

Table 3

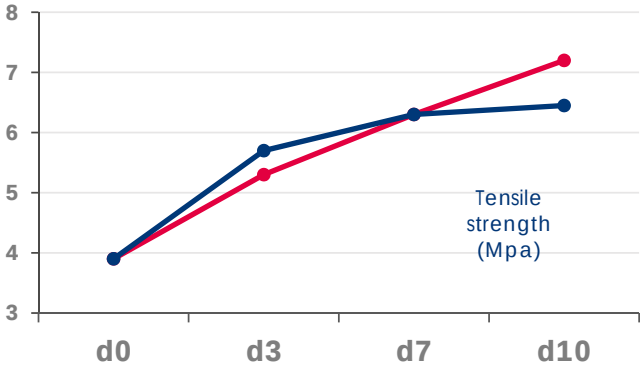
- So, we have defined that the best recipe to replace ETU is the compound n°7 due to a real improvement of our mechanical and ageing properties.

Cf. recipes Table 3

Evolution of the elongation at break

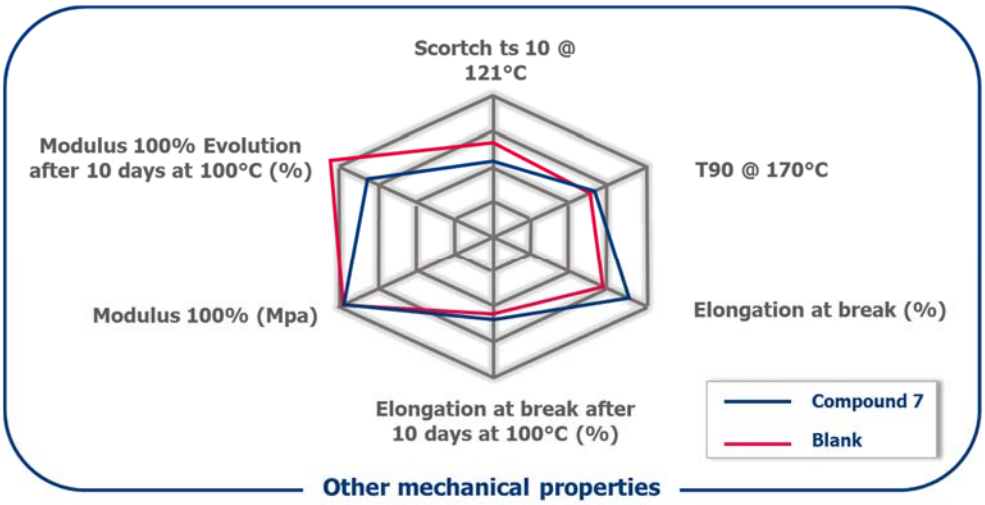


Evolution of the tensile at strength



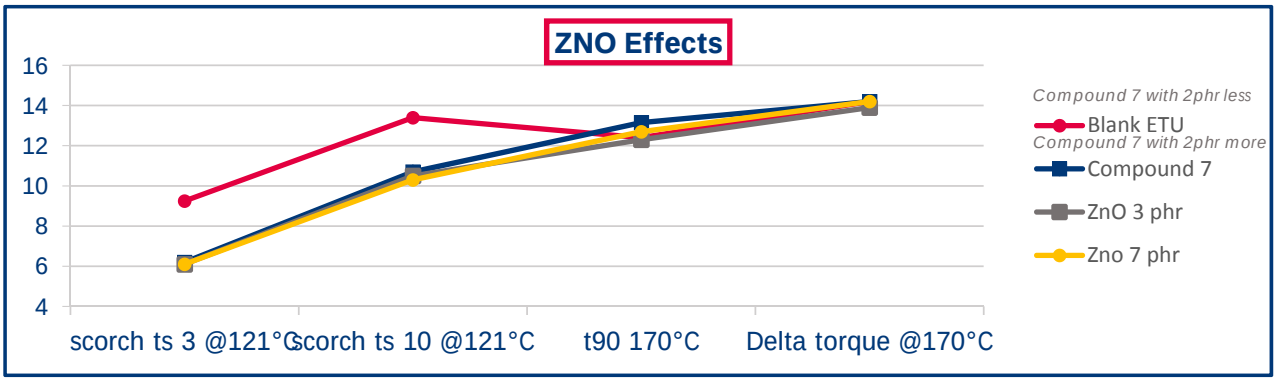
- Indeed, we improve tensile strength and elongation at break because our solution has a better cross-linking density, so we obtain a more stable curing system.

By the way, all the other mechanical results are better, as it shows in the following figure:



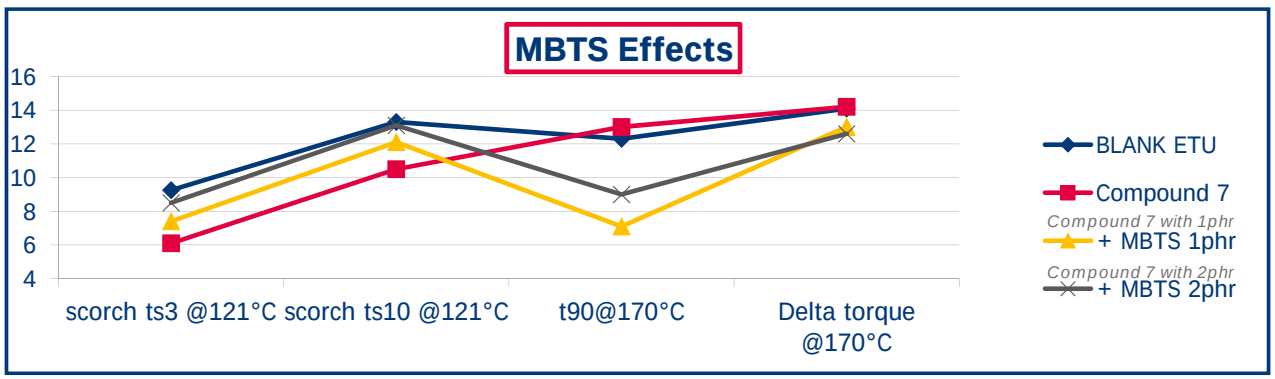
ZnO reduction

ZnO is not environmentally friendly, particularly concerning chronic aquatic toxicity (H410). But ZnO is primordial for ETU reaction in polychloroprene. However, with our MIXLAND®+ SD 75 GA F250, we can reduce ZnO level without decreasing the cross-linking density and, of course, the different properties:



Retarder

The best retarder for our new MIXLAND®+ SD 75 GA F250 is our MIXLAND®+ MBTS 75 GA F140. Effectively, with 2phr or even 1phr, we increase scorch time with a cure time decrease (improvement of the productivity) while keeping the same cross-linking density.



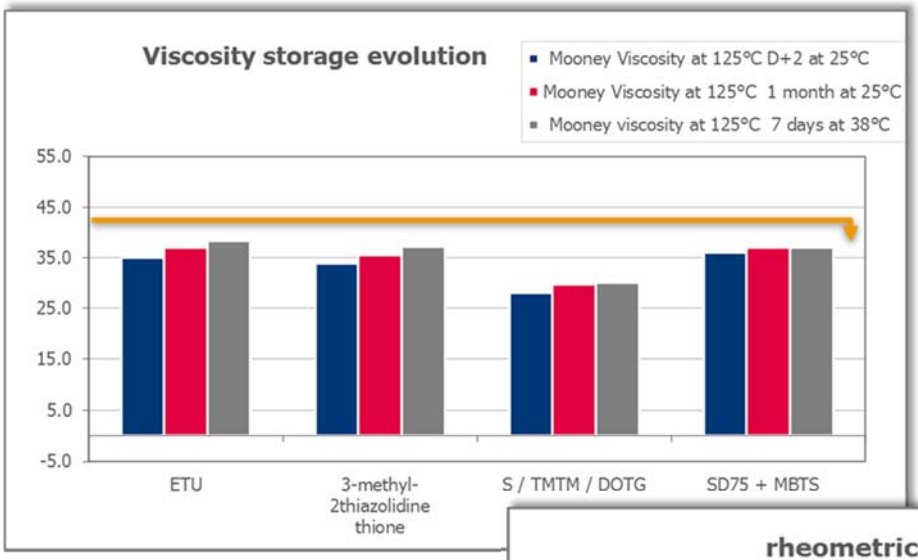
Comparison with alternative products

We benchmarked MLPC innovative product to other alternative solutions offered by the competition.

We are able to conclude that due to the specificity of MIXLAND®+ SD 75 GA F250 combined to MIXLAND®+ DPG 80 GA F140 and MIXLAND®+ MBTS 75 GA F140, it offers the best and optimum solution in order to match the properties needed for polychloroprene compound as demonstrated in our results summarized hereafter.

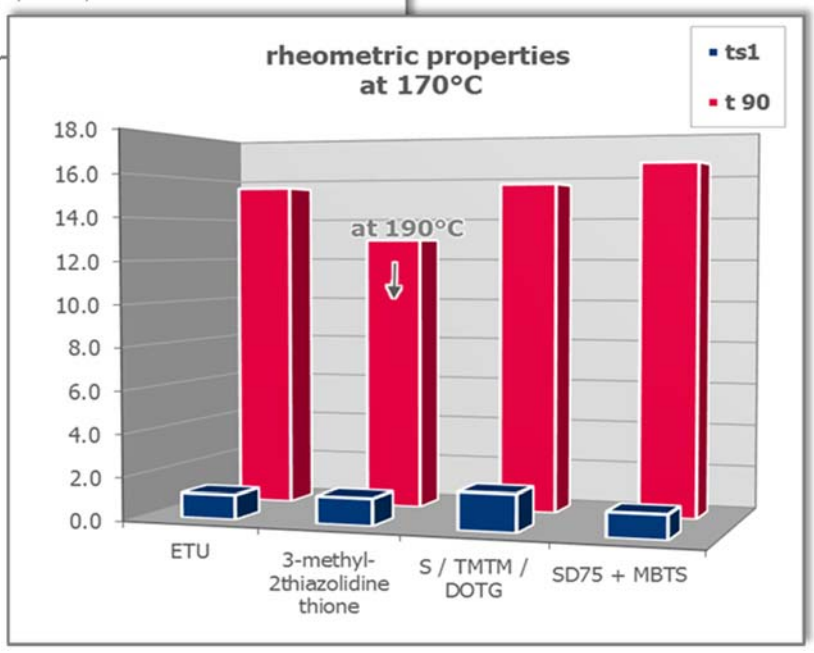
	Compound reference	Compound 1	Compound 2	Compound 3
CR Compound *Cf Table 1*	198	198	198	198
Mixland®+ZnO 80 GA F140	5.6	5.6	5.6	3.4
Mixland®+ ETU 80 GA F 140	0.75			
3-methyl-2thiazolidinethione		0.75		
Mixland®+ SD 75 GA F250				1
Mixland®+ DPG 80 GA F140				0.3
Mixland®+ MBTS 75 GA F140				2
Mixland®+ S 80 GA F500			1.56	
Mixland®+ TMTM 80 GA F500			0.94	
Mixland®+ DOTG 75 GA F140			1	

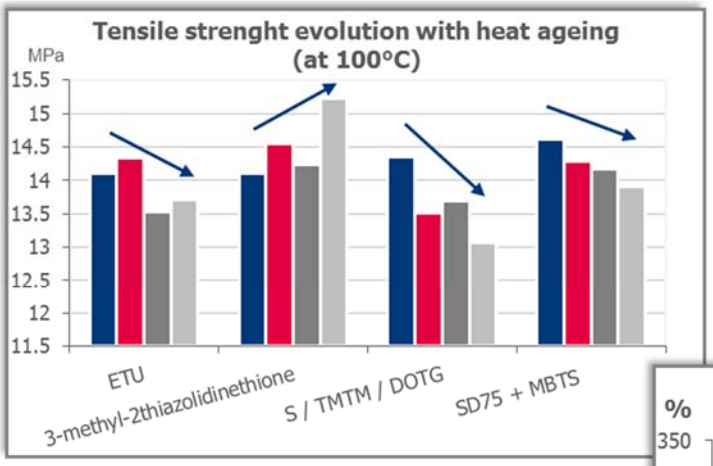
Table 4



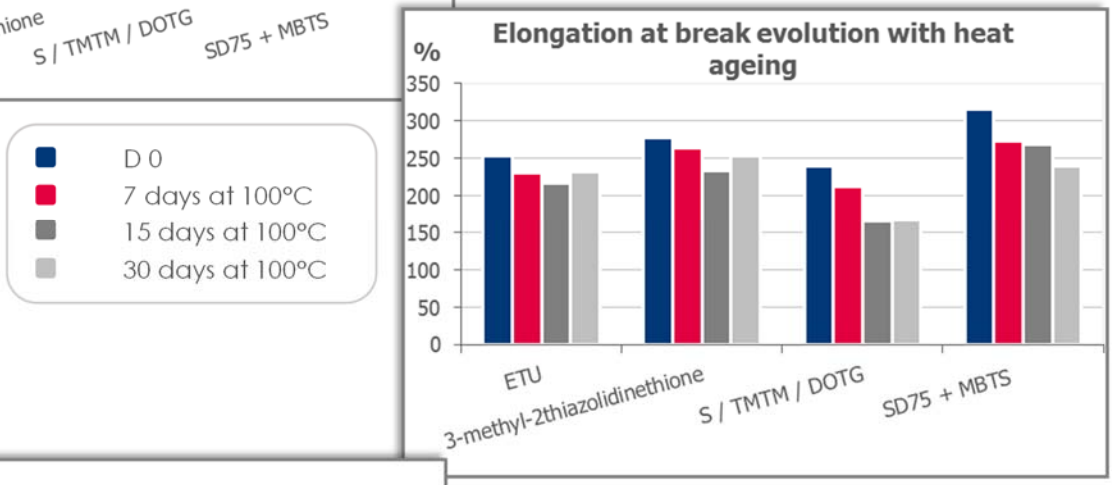
- In terms of curing and process control, with our MIXLAND®+ SD 75 GA F250 solution, we got similar behaviour to "ETU blank" without any viscosity evolution further to 7 days of storage.

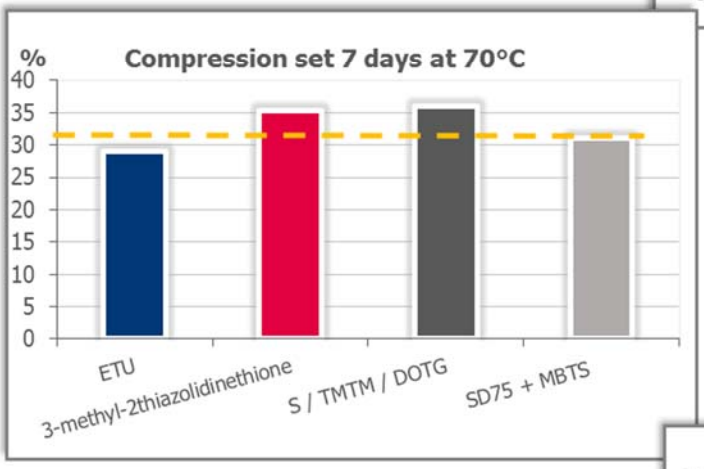
- Some of competition products need 20°C more to be cured (= more energy = consumption and additional time). Case of 3-methyl-2thiazolidine thione.



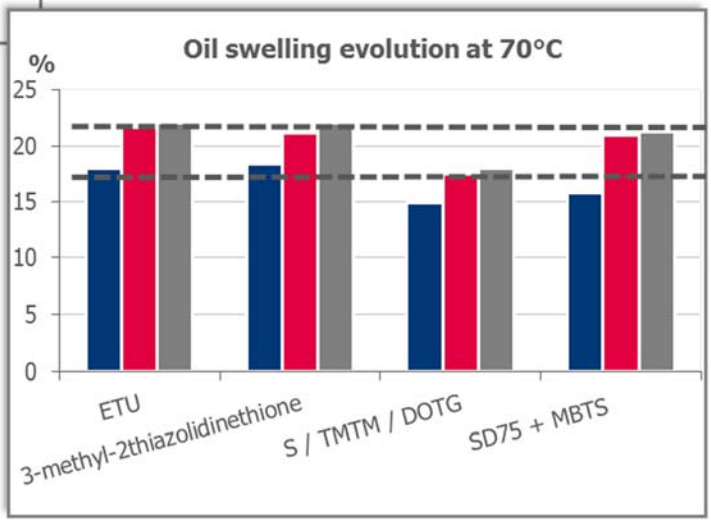


- 1 month later, Tensile Strength and Elongation at Break are equivalent to the "ETU blank" before ageing.





- Our solution provides better results than "ETU blank" even 1 month after ageing.



Mixland®+ SD 75 GA F250 in combination with Mixland®+ DPG 80 GA F140 for CR curing is a great solution :

Friendly product for HSE issues:

- **Suitable for REACH regulation**
- **NA Free solution**
- **Zinc level reduction**

Better properties:

- **Cross-linking network is improved**
- **Better compression set and oil swelling**
- **Ageing properties improved**
- **Less crystallization**