

Silanes for Energy Efficient Elastomers

A. Blume, Evonik Industries AG, Wesseling (D): anke.blume@evonik.com

O. Klockmann, R. Moser, Evonik Industries AG, Wesseling (D);

E. Karasewitsch, W. Herrmann, S. Sostmann, ContiTech AG, Hannover (D)

Abstract

The most mechanical rubber goods are based on carbon black filled compounds. Rubber compounds which have to withstand dynamic-mechanical forces are investigated in detail. Different silica / silane systems were introduced. Epoxysilanes show an outstanding performance in different rubber compounds. A significant improvement in the dynamic behavior was observed surprisingly not only in a mixture with silica but also with carbon black without a considerable deterioration in all other in-rubber properties.

Introduction

Acrylic elastomers (ACM) were introduced in 1975 as high performance polymer designed to combine high heat ageing resistance (up to 200 °C) with physical strength and a high degree of oil, ozone and weather resistance and good low temperature properties (up to -40 °C) [1-3]. They show as well high damping characteristics. The disadvantages of this material are a poor water resistance and the difficult processability which can be managed by optimized processing procedures (e.g. flow simulation).

The main applications for this acrylate rubber are critical automotive seal applications like automatic-transmission, valve-stem, crankshaft, pinion and oil-pan seals (Fig. 1). Newer acrylate-rubber types are used in hoses e.g. for the outer layer in turbocharger hoses [4], in tubings, electrical-cable jacketings, rolls and beltings.



Fig. 1: Example for Seals [5]

Pure ACM compound shows low gum strength and lower abrasion resistance than e.g. NBR. Therefore, reinforcing agents like carbon blacks were added. They improve as well the conductivity of the compound. Addition of the e.g. N 330 or N 339 is most efficient to improve the abrasion resistance. There are as well compounds filled with lower surface area carbon blacks like N 550 or N 539, N 660 or N 774. Silica or aluminium silicates are commonly only added for improved electrical-resistance or color-coded applications. There are few applications where amino or vinyl silanes are added for improved vulcanizate properties.

It was investigated in the following study if it is possible to improve the energy efficiency of ACM compounds by introducing a new silica / silane system without deterioration of the other in-rubber properties. A special emphasis was placed on the influence of the newly introduced ingredients on the vulcanization mechanism.

Characteristics of Investigated ACM

HyTemp AR71 [6] was used as the reference ACM rubber in this study. It has a saturated backbone from acrylic esters content of 95-99% and contains a small percentage of chlorine cure sites (1-5%) (Fig. 2). It has a temperature resistance up to 175 °C, an excellent oil resistance, a Mooney-Viscosity ML (1+4), 100 °C of 42 to 54 and a glass transition temperature T_g of -18 °C.

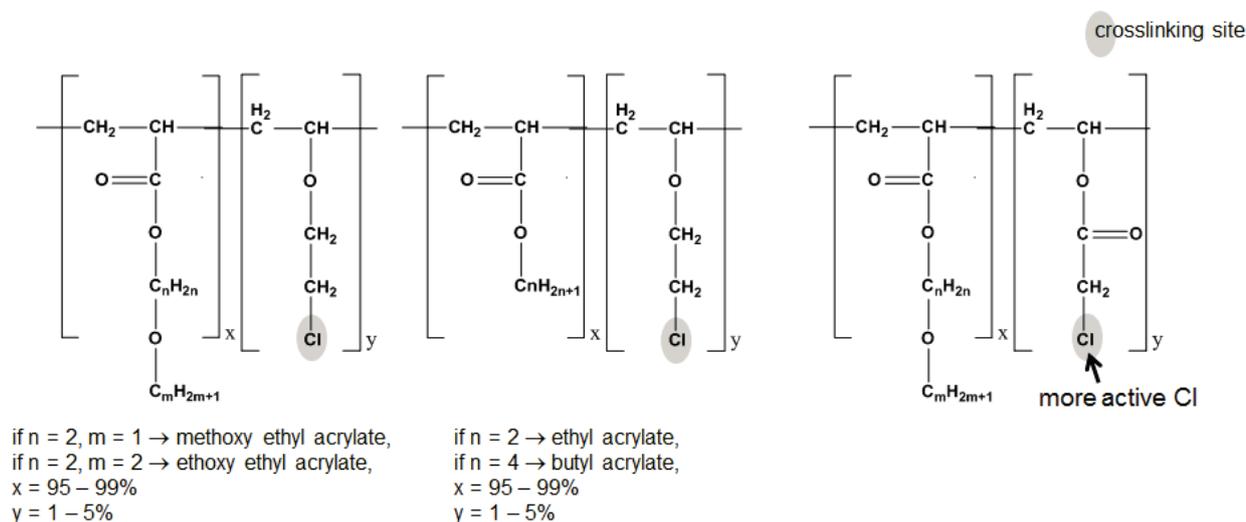


Fig. 2: Chemical Structure of ACM Rubber with Chlorine Cure Sites

ACM rubber can be vulcanized with diamines which have the risk of stickiness and poor scorch / cure balance. Another option is the use of a soap or a tertiary or quaternary amines e.g. ammonium benzoate or adipate, a combination of lead and thiourea, trithiocyanuric acid (TCY) or of an activated thiol [7, 8]. The most common vulcanization system is a combination of soap with sulfur or a sulfur donor. The soap (e.g. Na or K stearate) acts in this system as the primary curative, the sulfur as an accelerator, commonly used in a ratio of 10:1. Typical for ACM compounds is a long cure cycle or post-cured (tempered) in circulating hot-air environment to realize optimum compression-set resistance.

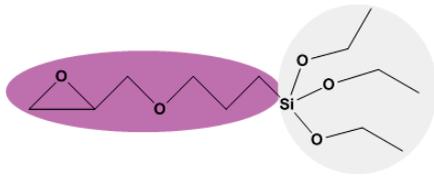
Investigated ACM Compound with New Filler System

The carbon black was replaced in a typical ACM formulation by using the low surface area silica ULTRASIL[®] 360 (Tab. 1) in combination with different epoxy- or amino-silanes (Fig. 3 and 4).

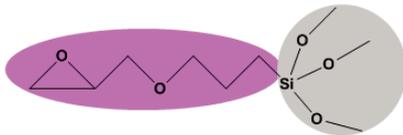
Tab. 1: Analytical Characteristics of ULTRASIL[®] 360

Test method	Value
BET (multipoint) in m^2/g , ISO 9277	55
Loss on drying (2h, 105 °C) in %, ISO 787-2	5.5
pH value (5% in water), ISO 787-9	9.0

Fig 3: Investigated Epoxysilanes

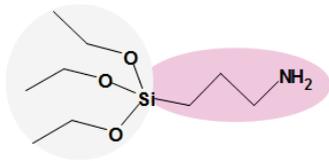


Dynasytan® GLYEO =
3-Glycidyloxy-propyl-triethoxy-silane

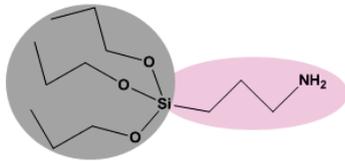


Dynasytan® GLYMO =
3-Glycidyloxy-propyl-trimethoxy-silane

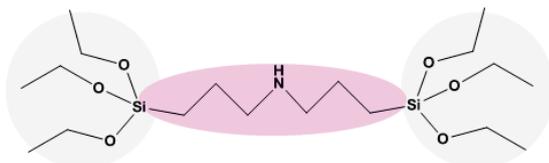
Fig. 4: Investigated Aminosilanes



Dynasytan® AMEO =
Amino-propyl-triethoxy-silane



AMPO = Propoxy-AMEO =
Amino-propyl-tripropoxy-silane



Dynasytan® 1122 =
Bis(triethoxysilylpropyl)amin

Tab. 2 shows the formulation, Tab. 3 the mixing procedure. The first test series were carried out with 50 phr silica. Compounds with N 339, N 550 and N 660 were used as references. The silane was added in an isomolar content. This means for example that 3 phr Dynasytan® GLYEO was added to 40 phr Silica, but 3.75 phr silane to 50 phr silica.

Tab.2: ACM Formulation

Stage 1		phr
ACM (HyTemp AR 71)	Acrylic polymer	100
Struktol WB 222	Anhydrous blend of high MW aliphatic fatty acid esters and condensates	2
Rhenofit OCD-SG	Octylated diphenylamine	2
Vulkanol 81	Mixture of thioester and carboxylic ester	5
Stearic acid		2
Silica		50 / 40 / 30 / 0
Carbon Black		0 / 0 / 0 / 50
Silane		isomolar
Stage 2		
Rhenofit Na-stearat 80		3.5
Sulfur		0.4

Tab. 3: Mixing Procedure

Stage 1

Internal Mixer	1,5l E- kneader
Batch temperature	140-150 °C
Mixing	0-1' polymer, silica, silane 1-5' other ingredients of stage 1 5' dump, mix directly on roll

Stage 2

Mixer	roll (150 * 350 mm)
Batch temperature	60 - 80 °C
Mixing	0 - 2' batch stage 1, dump, cool down 2 - 8' Na stearate, sulfur

The used vulcanization system was a combination of soap and sulfur, as described above. The vulcanisation was carried out at 160 °C for 30 min, followed by a post-cure treatment for 2 h at 180 °C.

Results

The aminosilanes show a very high Mooney-Viscosity (Fig. 5). The Mooney-Viscosity of the compounds with AMPO and Dynasylan® 1122 was even after the second mixing stage too high for detection. Aminosilanes are well-known for their high reactivity not only towards the silica but also towards the polymer. This can be seen by a high pre-scorch tendency of all these compounds. The mixing control of such a demanding polymer in combination with high-reactive aminosilanes is very challenging.

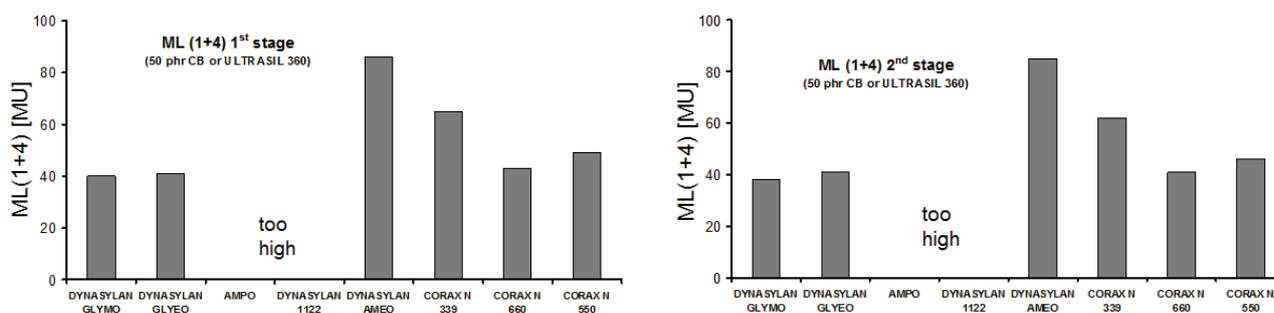


Fig. 5: Mooney-Viscosities of the Different ACM Compounds

In contrast to this, the viscosities of GLYMO und GLYEO are similar to the reference compounds with N 550 or N 660. A reason for this can be that the hydrophobation reaction of the silica has sufficiently taken place (Fig. 6).

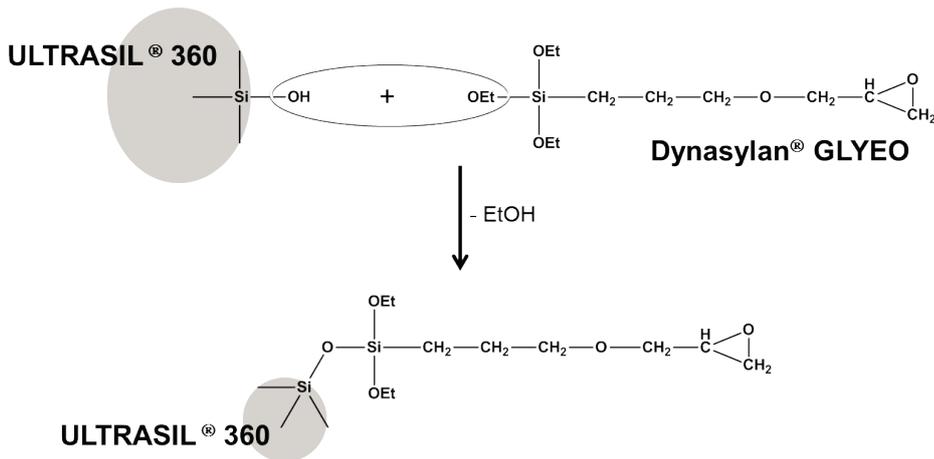


Fig. 6: Hydrophobation of the Silica by an Epoxysilane

The testing of the aminosilane containing compounds was not possible due to very bad sheet appearance. Therefore, the following discussion is focused on the epoxysilanes. The moduli of the epoxysilane containing compounds are higher compared to the references N 550 and N 660 and more similar to N 339, the tensile strength values are on the same level (Fig. 7), but the elongation at break occurs earlier. All in all, this is a clear hint that not only the hydrophobation of the silica has taken place but a filler-polymer coupling as well.

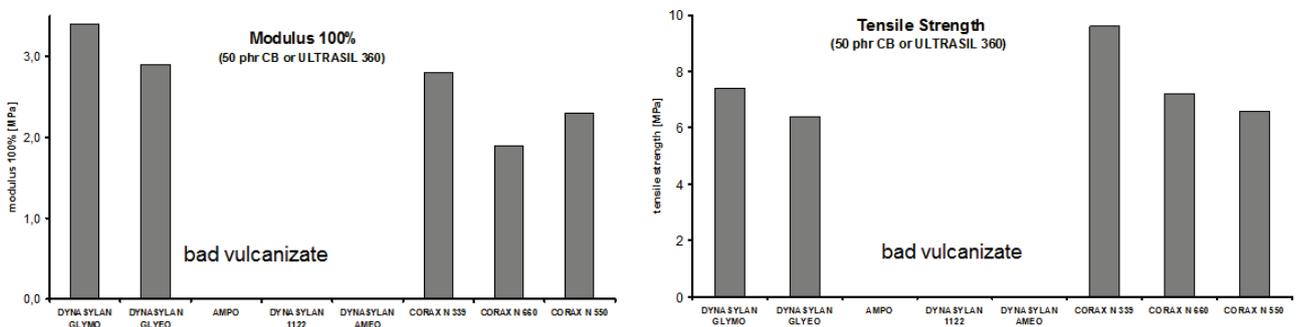


Fig. 7: Reinforcing Behavior of Different ACM Compounds

The Shore A hardness of both epoxysilane containing compounds is in between of that of the N 550 and N 660 compound (Fig. 8). Therefore, the dynamic data of all compounds are not perfectly comparable, but a general tendency can be discussed. The values of the Ball Rebound at 60 °C show clearly the big advantage of the compounds with GLYEO or GLYMO in comparison to carbon black: 50% improvement compared to N 339, 20% improvement to N 550 or N 660.

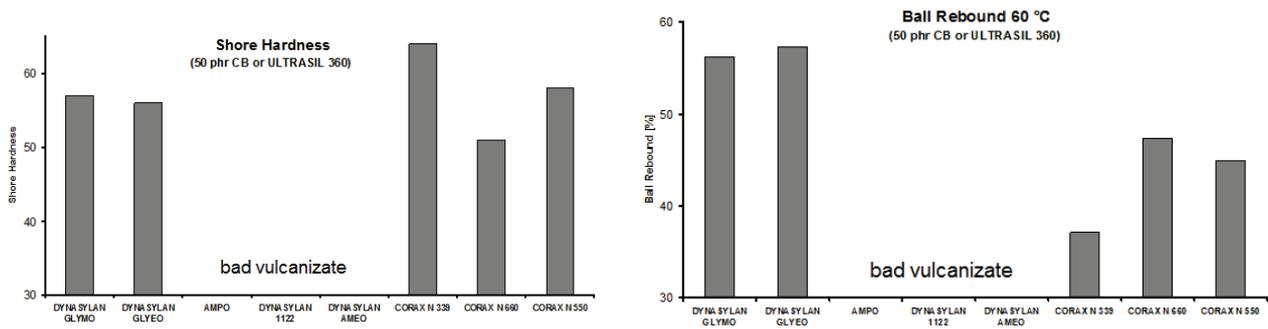


Fig. 8: Shore A Hardness and Ball Rebound of Different ACM Compounds

First Summary

Aminosilanes are too reactive in ACM compounds which make it difficult to control the reaction during the mixing process. Epoxysilanes lead to a good reinforcing behavior and significant improved dynamic data. Therefore, Dynasylan® GLYMO and Dynasylan® GLYEO show both a high potential to improve energy efficiency of ACM compounds.

Adjustment of the ACM Compound

The use of epoxysilanes in the ACM compound leads to higher moduli in comparison to the carbon black references and therefore to lower elongation at break data. For this reason, a further study was carried out with adjusted silica contents. The same formulation was used, not only with 50 phr silica, but as well with 40 phr and 30 phr silica respectively. Dynasylan® GLYEO was used as epoxysilane because of the release of ethanol in comparison to Dynasylan® GLYMO which releases the more critical methanol with regard to health issues. Three different carbon blacks with 50 phr were used again as references. The mixing and vulcanization conditions remained unchanged.

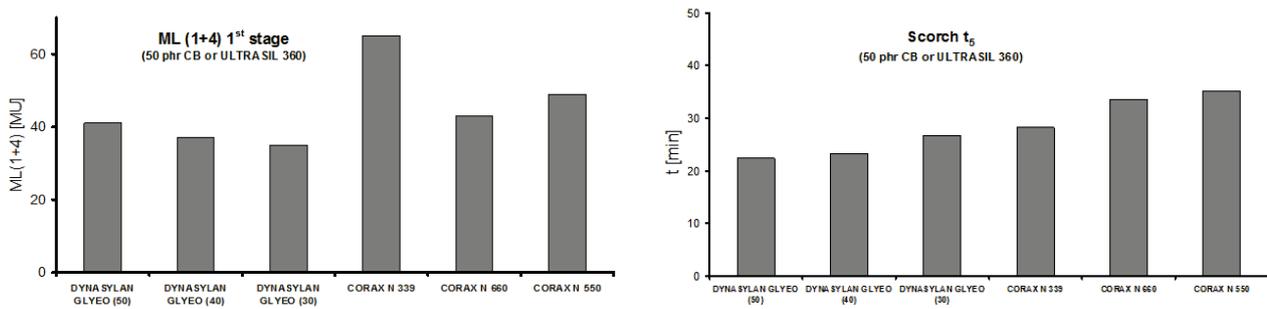


Fig. 9: Mooney-Viscosities and Scorch time t₅ for Adjusted ACM Compounds

Dynasylan® GLYEO shows low Mooney-Viscosities which depend on the silica content and therefore on the possible filler-filler network. The scorch time of all silica compounds is sufficient long to guarantee stable processing.

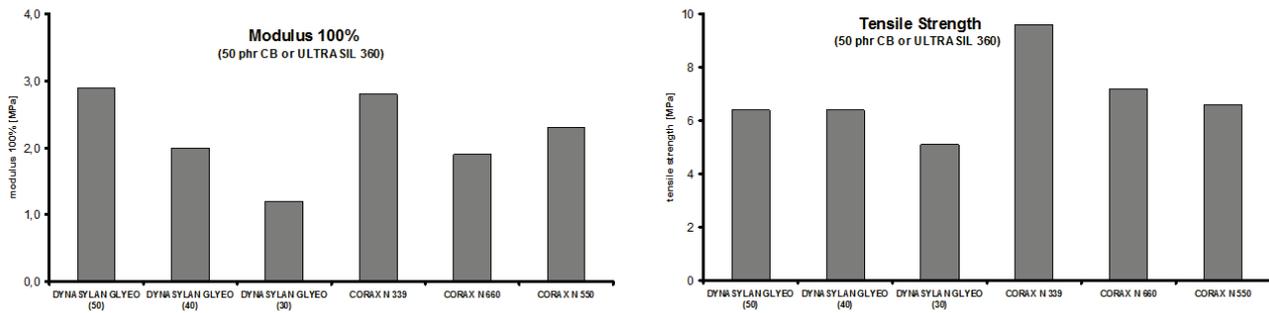


Fig. 10: Reinforcing Behavior of the Adjusted ACM Compounds

The results of the stress-strain measurements show the expected influence of the silica content (Fig. 10). A lower silica content leads to lower reinforcement. The modulus 100% of the 50 phr silica containing compound is on the same level as that of N 339. The reduction of 10 phr silica results in a modulus 100% on N 660 level. The tensile strength at 50 and 40 phr silica is comparable to that of N 550. The 30 phr silica containing compound leads to weaker reinforcement.

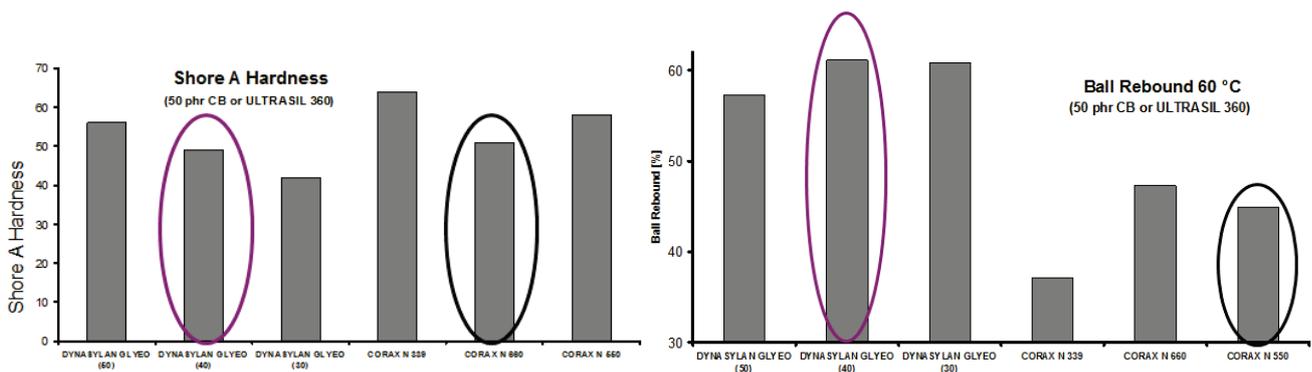


Fig. 11: Shore Hardness and Ball Rebound of the Adjusted ACM Compounds

The Shore hardness for the 40 phr silica containing compound is similar to that with N 550 (Fig. 11). Therefore, the comparison of these two data for the dynamic discussion is most valid. The measurement of the Ball Rebound at 60 °C shows again a significant improvement in comparison to the carbon black references (Tab. 4).

Tab. 4: Improvement in % of the Ball Rebound at 60 °C versus Carbon Black

	Dynasylan® GLYEO (50 phr)	Dynasylan® GLYEO (40 phr)	Dynasylan® GLYEO (30 phr)
N 339	54	64	64
N 550	21	29	29
N 660	28	36	35

Second Summary

The use of 40 phr silica leads to good processing and scorch times and a reinforcement which is similar to the N 660 reference. The dynamic behavior is significantly improved.

Therefore, the use of 40 phr ULTRASIL® 360 / 3 phr Dynasylan® GLYEO shows high potential to significantly improve energy efficiency in ACM compounds without deterioration of other in-rubber properties.

Investigation of the Coupling Mechanism

The above shown results can be explained by different theories. Is the improvement of the dynamic data only due to the known effect by replacing carbon black by silica ? Or is there a special role of the epoxysilanes ? And which role in the coupling plays the ACM polymer ?

In order to find an answer to this interesting topic the role of the epoxysilane was investigated in more detail. The reference carbon black containing compounds were mixed (as described in Tab. 2 and 3) by adding additionally the epoxysilane Dynasylan® GLYEO. There is no possibility of a coupling of the silane to the filler. Acts the liquid silane now just as a softener? Or is there any other effect ?

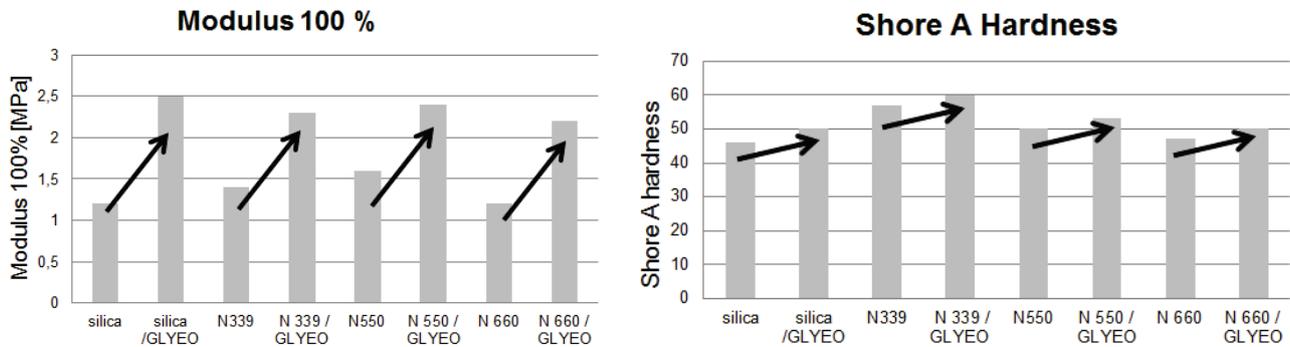


Fig. 12: Moduli and Shore A Hardness of Carbon Black / Epoxysilane Compounds

The moduli 100% as well as the Shore A hardness data (Fig. 12) show clearly that the presence of Dynasylan® GLYEO leads to increased reinforcement, not only in the silica containing compound, but as well as in the carbon black containing compounds. The Ball Rebound at 23 °C (Fig. 13) is improved as well, for carbon black / epoxysilane containing compounds less pronounced than for silica / epoxysilane containing compound.

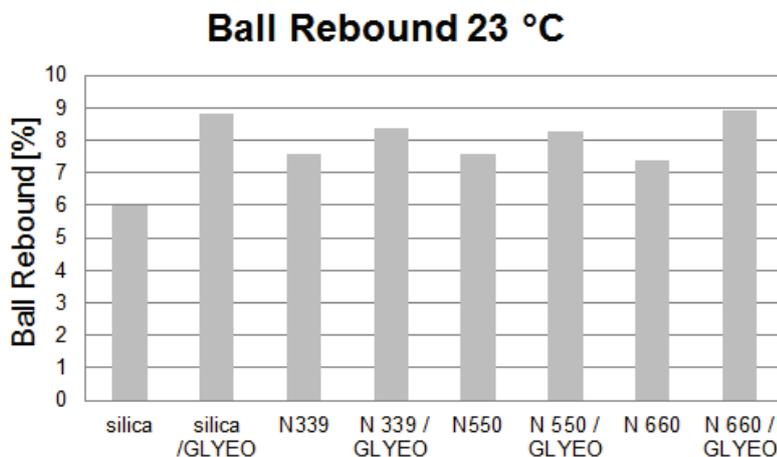


Fig. 13: Ball Rebound at 23 °C of Carbon Black / Epoxysilane Compounds

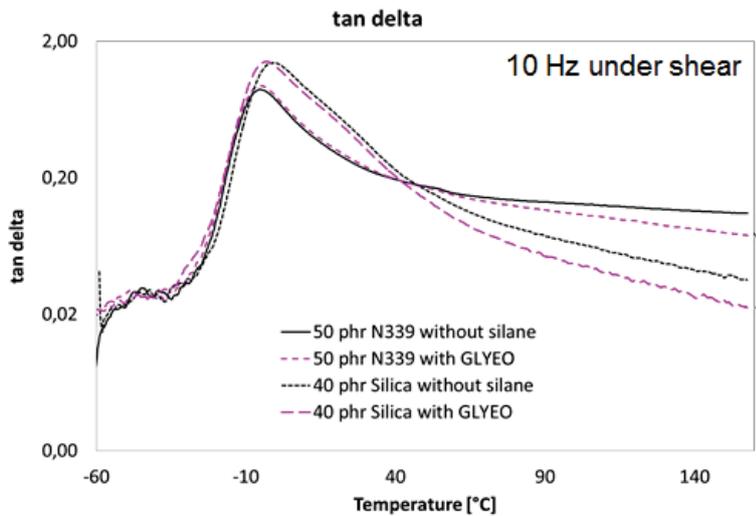


Fig. 14: $\tan \delta$ Curve of Carbon Black / Epoxysilane Compounds

The $\tan \delta$ curve (Fig. 14) shows explicitly the effect of the presence of an epoxysilane in a carbon black compound. The dynamic behavior is improved by using epoxysilane together with carbon black.

As mentioned before, the combination of carbon black and epoxysilanes cannot lead to any silane–filler coupling. It is expected that there is in all cases the same polymer–polymer coupling. Therefore, an explanation for the positive effect of adding epoxysilane to a carbon black filled ACM compound can be an additional silane–polymer coupling. The change of the Mooney-Viscosities (Fig. 15) by adding epoxysilane does not give a clear picture. The addition of epoxysilane increases the Mooney-Viscosities in the case of silica and N 339. This can be a hint for a pre-sorch, an early coupling of the silane to the polymer. But on the other hand, the Mooney-Viscosities of the compounds with N 550 and N 660 do not increase by adding the epoxysilane. Therefore, if a silane–polymer coupling occurs it happens mainly during the vulcanization. There seems to be only for silica and N 339 a certain amount of silane–polymer coupling as well during the mixing process.

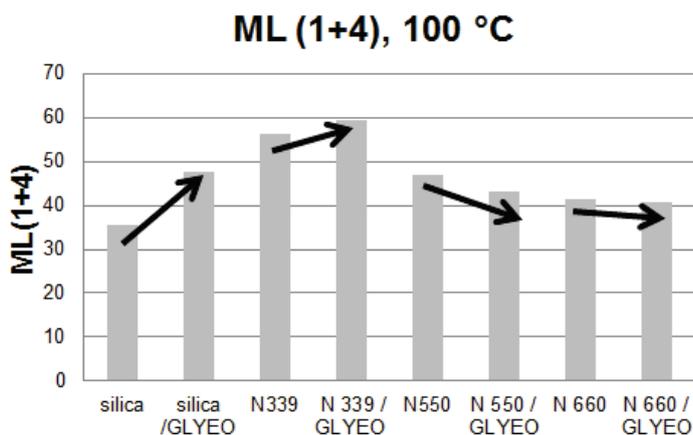


Fig. 15: Mooney-Viscosities of Carbon Black / Epoxysilane Compounds

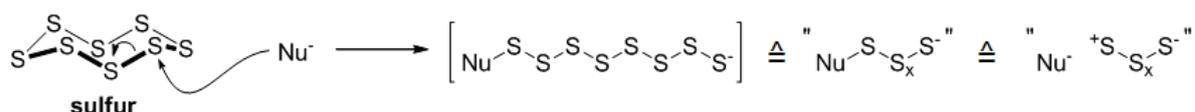
Although a detailed understanding of the vulcanization mechanism of ACM compounds was not part of this study, the following pathways based on non-radical processes can be

proposed¹. In the presence of e.g. sodium stearate and sulfur a cured polymer is obtained through polymer-polymer coupling (Scheme 1). The presence of various nucleophiles (e.g. stearate, chlorides, etc.) leads to the activation of elemental sulfur for subsequent nucleophilic attack and replacement of chloride on the ACM polymer. In a similar fashion the sulfur chain can now be activated on the opposite end for coupling with another ACM polymer leading to a sulfur bridged polymer-polymer crosslink.

Scheme 1: Proposal for a Mechanism of the Polymer-Polymer Coupling of ACM

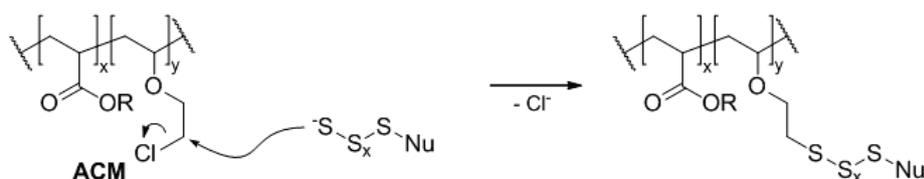
Polymer-Polymer-Coupling

(a) Primary sulfur activation step

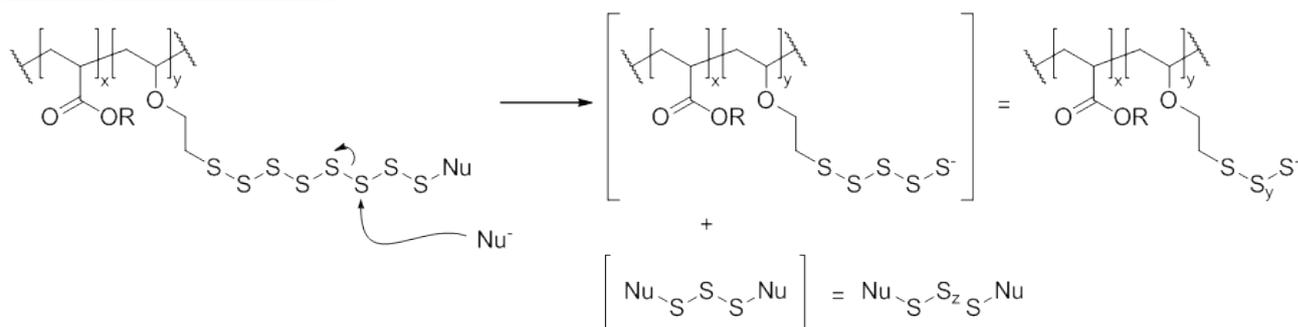


examples for Nu⁻ = chlorides (Cl⁻)
 carboxylates (RCOO⁻, e.g. stearate)
 alcoholates (RO⁻)
 amines (R₃N)

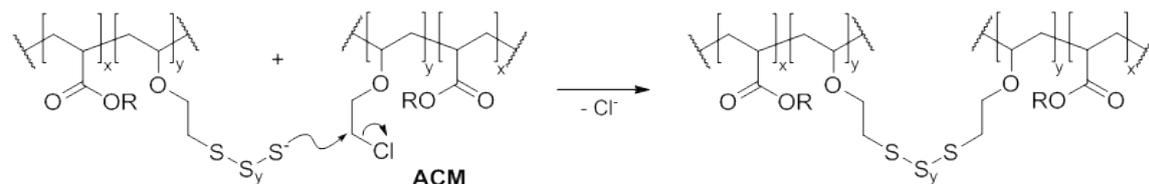
(b) Primary sulfur polymer coupling



(c) Secondary sulfur activation step



(d) Secondary sulfur polymer coupling



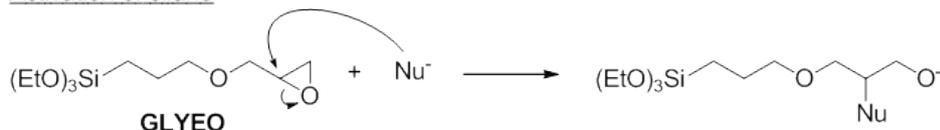
¹ Other mechanisms can also be postulated including radical pathways.

In the presence of epoxysilanes another route towards silane-crosslinked polymers can be envisioned (Scheme 2). Nucleophiles can open the ring of the epoxy group which then in turn replaces the chloride in the ACM polymer in a similar fashion described above. The resulting silane-modified ACM polymer chains can undergo hydrolysis and condensation reactions to either crosslink two polymer chains or if silica is present to yield strong filler-polymer bonds.

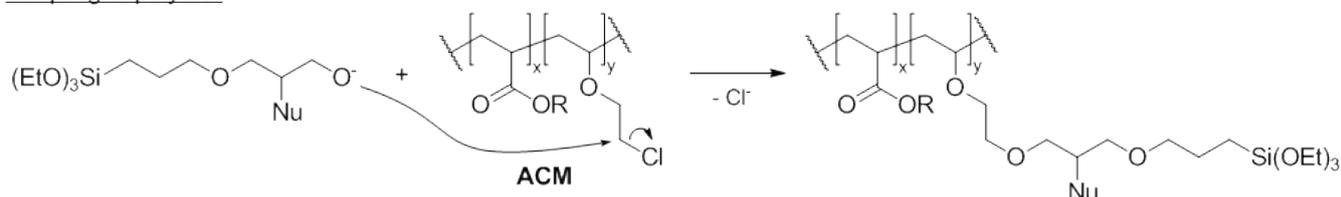
Scheme 2: Proposal for a Mechanism of the Polymer-Silane Coupling of ACM

Polymer-Silane-Coupling

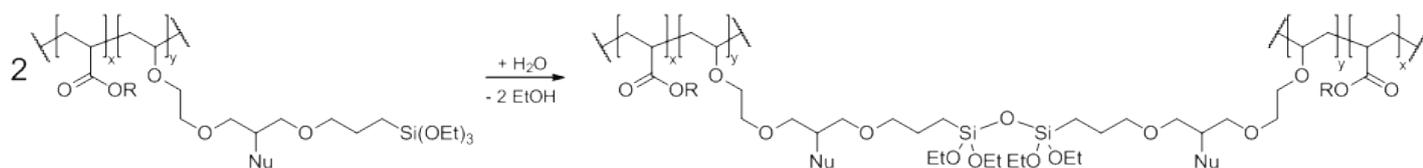
(a) Activation of silane



(b) Coupling to polymer



(c) Silane-mediated cross-coupling of polymer



In order to have a first proof for this theory, the vulcameter curve of a pure ACM, an ACM polymer where 3 phr of Dynasylan[®] GLYEO were added, an ACM compound with 3 phr Dynasylan[®] GLYEO where additionally 3.5 phr Na-stearate was added and an ACM compound with 3 phr Dynasylan[®] GLYEO and 3.5 phr of Na-stearate where additionally 0.4 phr sulfur was added (Fig. 16). The addition of Dynasylan[®] GLYEO alone to the ACM polymer leads to a softening of the compound. The further addition of Na-stearate results in a slightly increased crosslinking network. Only the addition of further sulfur increases the crosslinking density significantly. Therefore, it seems to be that the presence of stearate leads indeed to a small amount of polymer-silane coupling.

There are probably three different networks in such silica filled ACM compound: a silica-silane-polymer network, a polymer-silane-polymer network and a polymer-polymer network. The possible combination of a polymer-silane-polymer and a polymer-polymer network in a carbon black filled compound can explain the astonishingly positive effects of epoxysilanes on the reinforcing and dynamic properties.

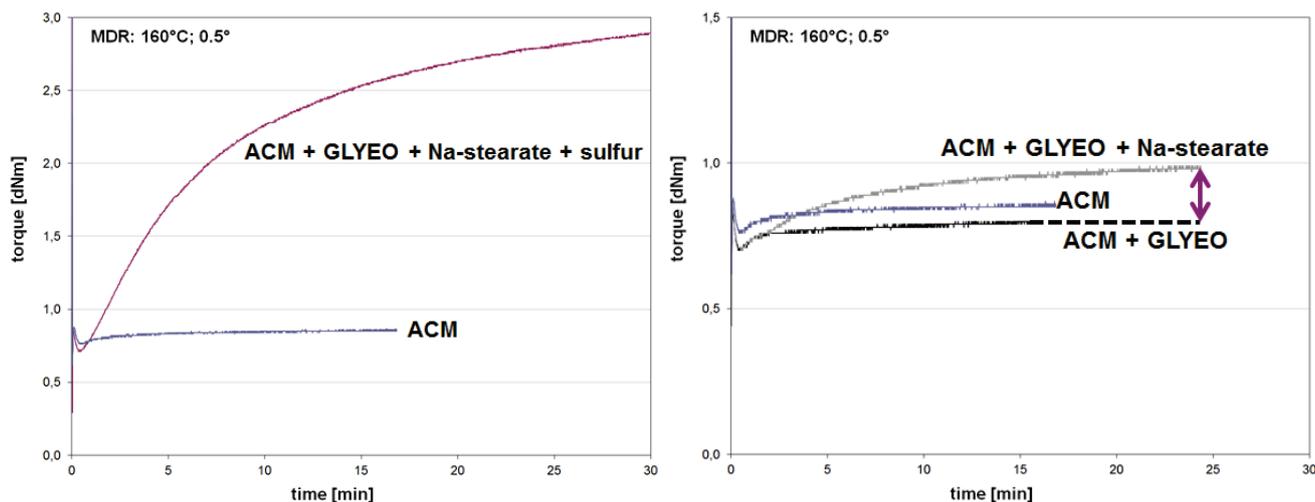


Fig 16: Vulcameter Curve of Special ACM Compounds

Overall Summary

The use of Dynasylan[®] GLYEO, an epoxysilane, results in ACM compounds (filled with carbon black as well as with silica) in a significant improvement in reinforcement and in the dynamic behavior. A theory was developed that this effect is caused by additional crosslinks which are formed by a polymer-silane-polymer network. This very flexible network seems to be mainly formed during the vulcanization. Additional to this network, a polymer-polymer network and for silica filled compounds a silica-silane-polymer network seems to exist. Dynasylan[®] GLYEO can be consumed as a crosslinker but react as well as a hydrophobation agent for the silica.

The use of the silica ULTRASIL[®] 360 together with Dynasylan[®] GLYEO in an ACM compounds improves finally the Ball Rebound of 30-60% compared to different reference carbon black compounds [9].

Literature

- [1] R.O. Babbit (ed.), the Vanderbilt Rubber handbook, R.T. Vanderbilt Company, Norwalk CT (1978) 262-271
- [2] M. Morton (ed.), Rubber Technology, 3rd edition, Chapman & Hall, 1995
- [3] B. Rodgers (ed.), Rubber Compounding, Marcel Dekker, New York, Basel (2004) 120-124
- [4] C. Grant et al, Rubber World (April, 2013) 27-31
- [5] www.contitech.de, accessed at April 24, 2015
- [6] http://www.zeonchemicals.com/hytempacm/product_grade_ar71.aspx, webside of Zeon Chemicals, accessed at April 30, 2015
- [7] T.M. Vial, Rubber Chem. Technol. 44 (1971) 344-362
- [8] R.D. Marco, Rubber Chem. Technol. 52 (1979) 173-186
- [9] A. Blume, E. Karasewitsch, EP 2612882 and US 2013/0178566

Acknowledgement

The whole work was carried out in the frame of the BMBF-project “ENEFEEL” (Development of new ENergy EFFicient ELastomeric compounds) (Förderkennzeichen 03X3533B, duration: 01.04.2009 - 31.03.2014). Further project partners were Orion Engineered Carbons, Deutsches Institut für Kautschuktechnologie (DIK) and Leibniz-Institut für Polymerforschung Dresden (IPF). We would like to say thank you to all project partners and a special thanks to the BMBF for the financial support especially to Dr. Andrea Geschewski (Projektträger Jülich, Neue Materialien und Chemie).