Rhenogran® XLA-60 (GE 2014): DOTG-free curing systems for AEM compounds

Cristina Rosca, Applications Technology, Rubber Division/Automotive
Rhein Chemie Rheinau GmbH, Mannheim
[Contact: cristina.rosca@rheinchemie.com]

Key words: hose, O-ring, sealing, membrane, acrylic rubber, HMDC, DOTG replacement, AEM, ACM, dithiophosphate, CMR substance, o-toluidine, Vamac®

Summary

Harmful emissions of o-toluidine occur during the cross-linking of acrylate rubbers with a system made from HMDC (hexamethylene diamine carbamate) and DOTG (di-o-tolylguanidine).
Recent studies have shown that o-toluidine can cause cancer. It was classified in the 2006 MAK and BAT Value List of the Deutsche Forschungsgemeinschaft (German Research Foundation) as a category 1 carcinogen (DFG, 2006 edition).

O-toluidine can also be released from rubbers made using di-o-tolylguanidine (DOTG). For this reason, it is increasingly seen as a health risk in the rubber industry especially in association with DOTG.

In this regard, Rhein Chemie is introducing a less harmful alternative to DOTG. Rhenogran® XLA-60 (GE 2014), in combination with HMDC, replaces DOTG and prevents the formation of o-toluidine.

The following influences on vulcanization behavior and physical properties have been observed when using Rhenogran® XLA-60 in AEM mixtures:

- Good processability
- Equivalent physical properties
- Comparable aging and oil resistance
- Low compression sets
- Good storage stability at room temperature
- Very low risk potential to humans and the environment

The results of Rhenogran® XLA-60 in ACM compounds are presented in Technical Report No. 75.

Tab. 1: Formulation guide		
Compounds / Product	**DOTG-system [phr]**	**DOTG-free system [phr]**
AEM-G compounds (75-80 Shore A)		
Rhenogran® ZDDT-50 (GE 1864)	–	2.0
Aflux® 18 (GE 1855)	0.5	0.5
Rhenogran® HMDC-70/AEMD	2.3	2.3
Rhenogran® DOTG-70	5.0	–
Rhenogran® XLA-60 (GE 2014)	–	4.0
AEM-G compounds (50-55 Shore A)		
Rhenogran® ZDDT-50 (GE 1864)	–	2.0
Aflux® 18 (GE 1855)	0.5	0.5
HMDC	1.5	1.5
DOTG	4.0	–
Rhenogran® XLA-60 (GE 2014) [1]	–	2 to 4

[1]) Product also available as powder liquid concentrate, Rhenocure® XLA/S

1. Introduction

Guanidines like DOTG (di-o-tolylguanidine) have been subject of public debate for their hazardous potential for many years. To replace DOTG as widespread accelerator for acrylic rubber compounds, Rhein Chemie has developed a new accelerator as a safer alternative: Rhenogran® XLA-60. The established curative system of AEM terpolymer is hexamethylene diamine carbamate (HMDC) as curing agent in combination with a guanidine as accelerator. The latter can either be diphenyl guanidine (DPG) when good flex resistance and elongation are required or di-o-tolylguanidine (DOTG) for best compression set.

The presence of the guanidine in the vulcanization process of AEM or ACM polymer as an accelerator raised questions concerning the medical and toxicological aspects in the workplace area. Several studies carried out on the reaction mechanisms of the vulcanization with guanidine accelerators have shown that at elevated temperatures during vulcanization, reaction products such as aromatic amines (e.g., o-toluidine) must be taken into consideration. Those products can cause problems due to their toxicological and their carcinogenic potential. For the same reason they have been classified as unequivocally carcinogenic and are therefore included in the first category of the hazardous materials list [1]. The International Agency for Research on Cancer classified o-toluidine as probably carcinogenic to humans [2]. Extended studies focused on the noxious effects of o-toluidine [3-7] on the human health have underlined the necessity of the development of less hazardous alternatives for this accelerator.

2. Results and discussions

This technical report is part of extended studies focused on the performance of Rhenogran® XLA-60 in various compounds of cross-linked acrylate rubber (AEM, ACM) of different hardness.

To examine the effects of this new accel-erator, several compounds were prepared and tested.
They are presented in Table 1 and Table 2.
They include a commercial AEM polymer (Vamac®G), the vulcanization agent (HMDC as polymer bound material, Rhenogran® HMDC-70/AEMD), and the accelerator di-o-tolylguanidine (as polymer bound material, Rhenogran® DOTG-70, or as DOTG powder).
Rhenogran® XLA-60 has been developed and applied as alternative for DOTG. Each compound contains 30 to 80 parts by weight carbon black along with processing aids and antioxidants and was prepared and investigated as described[1].

Tab. 2: Formulations of AEM-G compounds (75-80 Shore A)

Material	Amount [phr]		
	5.0 phr DOTG-70	4.0 phr XLA-60	4.0 phr XLA-60 + ZDDT-50
AEM-G	100.0	100.0	100.0
Carbon black	80.0	80.0	80.0
Aflux® 18	0.5	0.5	0.5
Stearic acid	2.0	2.0	2.0
Phosphate ester	1.0	1.0	–
Cumylated diphenylamine	2.0	2.0	2.0
Rhenosin® W 759	8.0	8.0	8.0
Rhenogran® ZDDT-50	–	–	2.0
Rhenogran® HMDC-70/AEMD	2.3	2.3	2.3
Rhenogran® DOTG-70	5.0	–	–
Rhenogran® XLA-60	–	4.0	4.0

1) The respective compounds have been blended in an internal mixer (W&P GK 5E) with a 70% filling factor using an upside down procedure. The dump temperature was 100°C. In order to obtain a homogeneous mixture, the mixing process was continued on the mill (Rubicon MT 6”x13”) at 40°C for 6 min. The mixtures have been press-cured in slabs of 13.5 cm x 13.5 cm at 180°C and then post-cured at 175°C for four hours at ambient pressure.
The stress strain properties of the vulcanizates have been measured with a Zwick universal testing machine. The compression set test considering have been done considering both norms DIN 53517 [8] and PV 3307 [9].

Tab. 3: Formulations of AEM-G compounds (50-55 Shore A)

Material	Amount [phr]				
	4.0 phr DOTG-70	2.0 phr XLA-60	3.0 phr XLA-60	4.0 phr XLA-60	4.0 phr XLA-60 + ZDDT-50
AEM-G	100.0	100.0	100.0	100.0	100.0
Carbon black	30.0	30.0	30.0	30.0	30.0
Aflux® 18	0.5	0.5	0.5	0.5	0.5
Stearic acid	1.5	1.5	1.5	1.5	1.5
Phosphate ester	1.0	1.0	1.0	1.0	–
Cumylated diphenylamine	2.0	2.0	2.0	2.0	2.0
Rhenogran® ZDDT-50	–	–	–	–	2.0
HMDC	1.5	1.5	1.5	1.5	1.5
DOTG	4.0	–	–	–	–
Rhenogran® XLA-60	–	2.0	3.0	4.0	4.0

2.1 Analysis done in compounds based on AEM-G (75-80 Shore A)

The cure characteristics and scorch behavior for AEM compounds are shown in Fig. 1 and 2. As can be seen in Fig. 1, slightly higher cure rate and torque for compounds with Rhenogran® XLA-60 when compared with DOTG compound were observed.

The influence on scorch (Fig. 2) indicates that 4 phr Rhenogran® XLA-60 and 2 phr Rhenogran® ZDDT-50 (GE 1864) are sufficient to reach a comparable scorch resistance and mooney viscosity level as with DOTG.

Fig. 1: Cure characteristics of AEM-G compounds (75-80 Shore A)

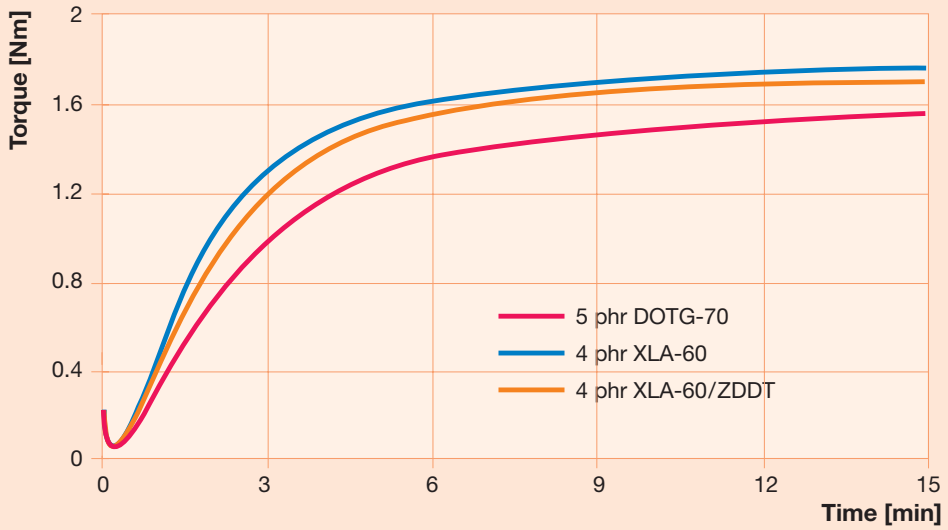
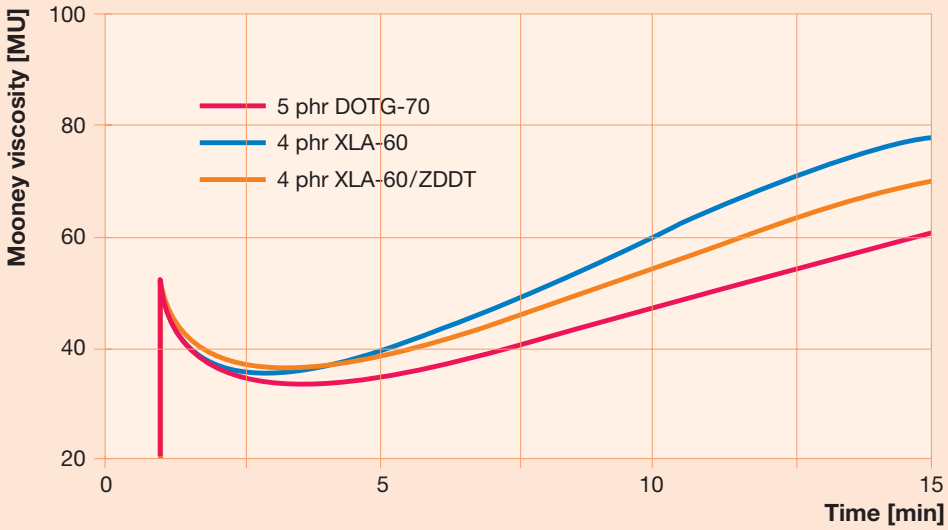


Fig. 2: Scorch behaviour of AEM-G compounds (75-80 Shore A)



Supplementary information about the cure and flow properties is given in Table 4.

Tab. 4: Cure characteristics and flow properties of AEM-G compounds (75-80 Shore A)

	5.0 phr DOTG	4.0 phr XLA-60	4.0 phr XLA-60 + ZDDT-50
ML (1+4) 100°C [MU]	52	55	56
Mooney scorch 120°C			
T5 [min]	6.3	5.3	5.6
T35 [min]	18.9	13.1	15.1
MDR 180°C / 15 min			
Smin [dNm]	0.6	0.7	0.7
Smax [dNm]	15.6	17.5	17
TC 10 [min]	0.7	0.6	0.7
TC 50 [min]	2.3	1.8	2.1
TC 90 [min]	7.0	5.6	5.6
Rheovulkameter at 180°C			
Flow max [cm3/s]	0.60	0.56	0.54

A shorter cure time (T90-T10) has been noticed at the vulcanization of AEM when Rhenogran® XLA-60 has been used, thus offering the opportunity of cost reductions in the production of the rubber article.

Fig. 3: Physical properties of AEM-G compounds (75-80 Shore A) before and after ageing in hot air (150°C): Elongation at break

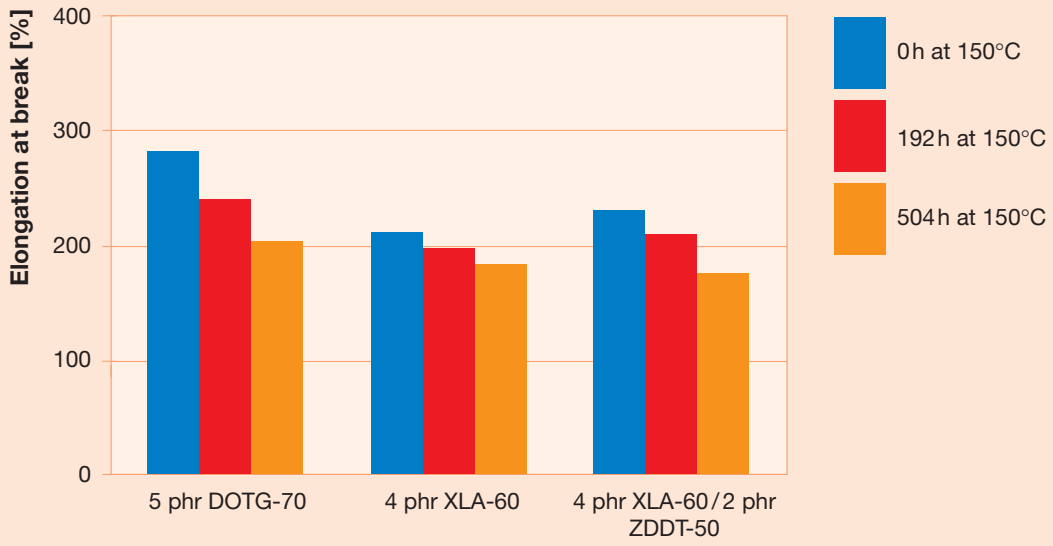
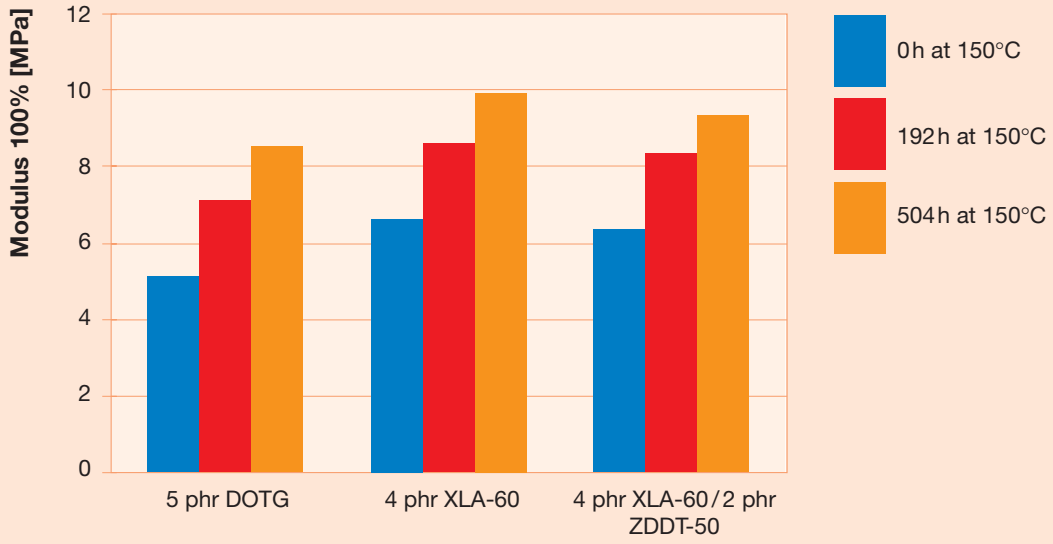


Figure 3 to 4 are showing the physical properties of AEM-G compounds before and after heat ageing (150°C) in comparison with the control compound. In accordance with the observed cure level, the experimental results demonstrated a similar trend of the evolution of the elongation at break.
When DOTG was replaced by Rhenogran® XLA-60, the elongation at break before ageing was decreased by 25%.

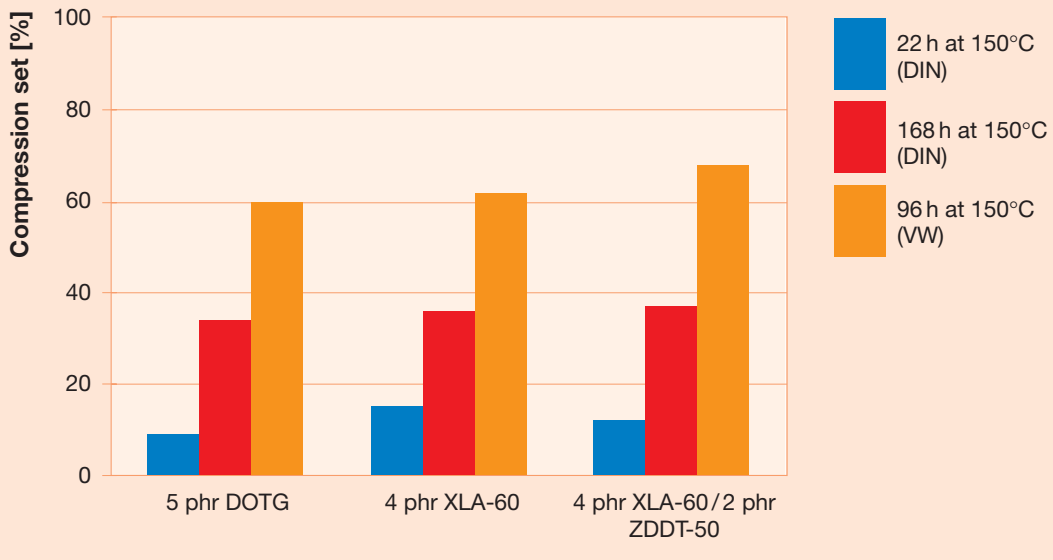
By addition of 2 phr Rhenogran® ZDDT-50, the drop of elongation is only 18% (Fig. 3). This result was confirmed by the values of modulus at 100%, which has comparable values for Rhenogran® XLA-60 without or in combination with Rhenogran® ZDDT-50 (Fig. 4). After 21 days ageing, the elongation, tensile strength as well as tear strength values are comparable with the corresponding property of the control compound.

Fig. 4: Physical properties of AEM-G compounds (75-80 Shore A) before and after ageing in hot air (150°C): Modulus 100%



The compression tests were performed for different periods and the results are presented in Figure 5. Examination of the data reveals that the Rhenogran® XLA-60 with and without Rhenogran® ZDDT-50 displays the same results as DOTG.

Fig. 5: Compression set of AEM-G compounds (75-80 Shore A) at 150°C



2.2 Compounds based on AEM-G (50-55 Shore A)

In Figure 6 and Figure 7, the results of the cure characteristics comparison are displayed. A parallel between the cure characteristics and the scorch behaviour for AEM-G compounds with hardness in the range of 50-55 Shore A was found. Moreover, a comparable cure rate for Rhenogran® XLA-60 with the standard DOTG was found.

By addition of Rhenogran® ZDDT-50, the maximum rheometer torque and the scorch resistance remain unchanged.

Fig. 6: Cure characteristics of AEM-G compounds (50-55 Shore A)

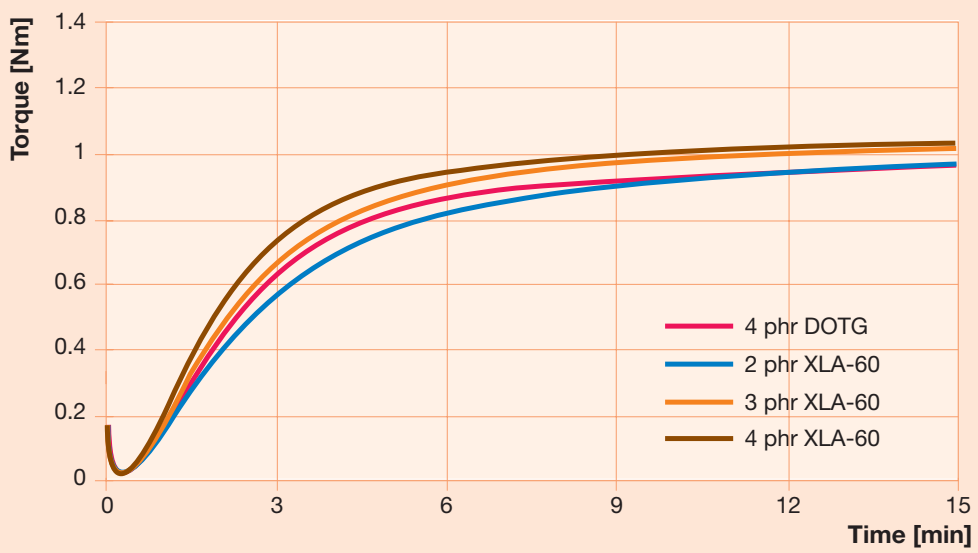
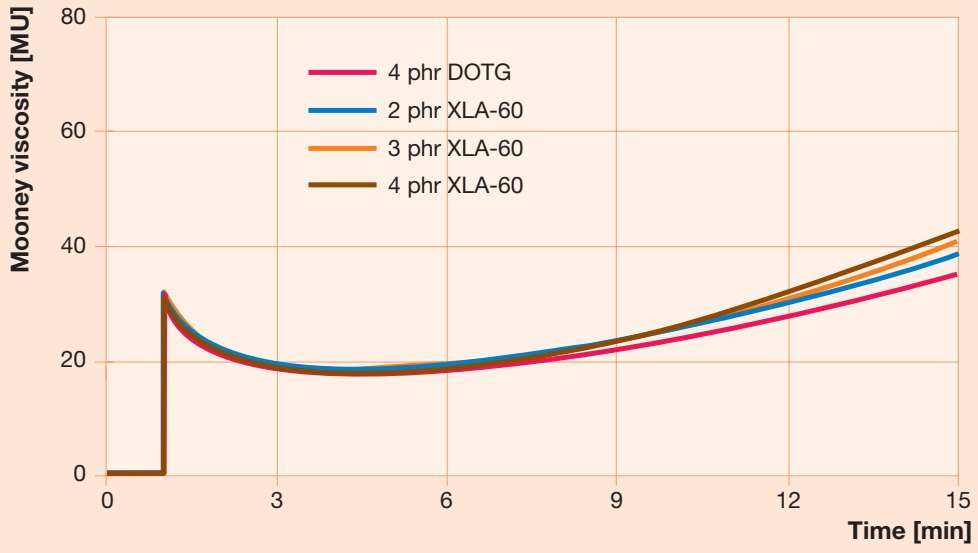


Fig. 7: Scorch behaviour of AEM-G compounds (50-55 Shore A)



The physical properties of the compounds are grossly comparable with the standard DOTG and are shown in Figures 8 to 9. It can be seen that a higher amount of Rhenogran® XLA-60 lowers the elongation, this being an indication for a higher cross-linking density in the system. This statement is confirmed by the high values of the modulus 100%, which can also be observed in the compression set results (Figure 10). Similar levels of the elongation at break and tear strength before and after ageing as the conventional DOTG can be obtained if 2 phr Rhenogran® ZDDT-50 are added to the formulation.

Fig. 8: Physical properties of AEM-G compounds (50-55 Shore A) before and after ageing in hot air (150°C): Elongation at break

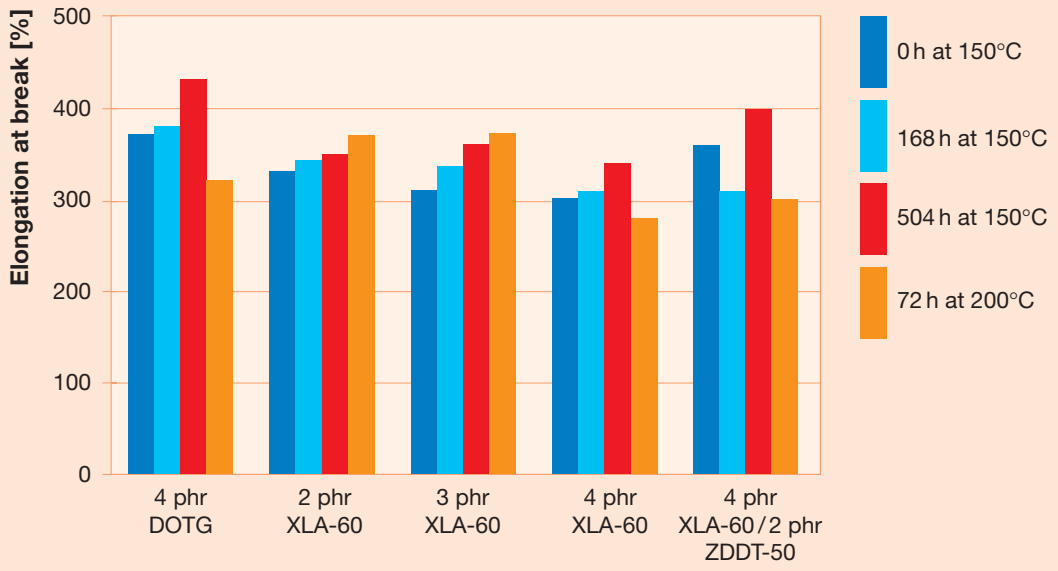
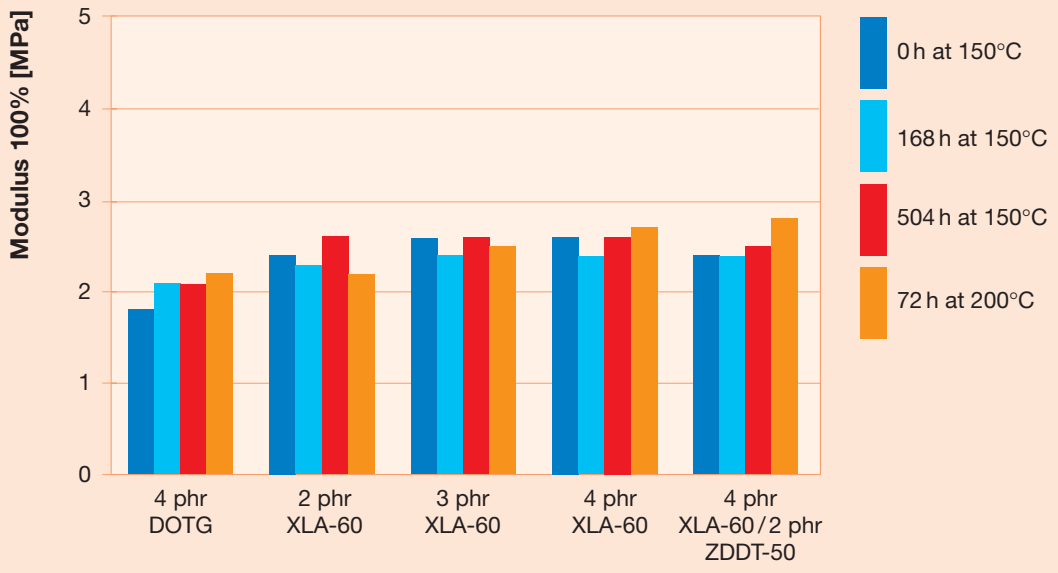
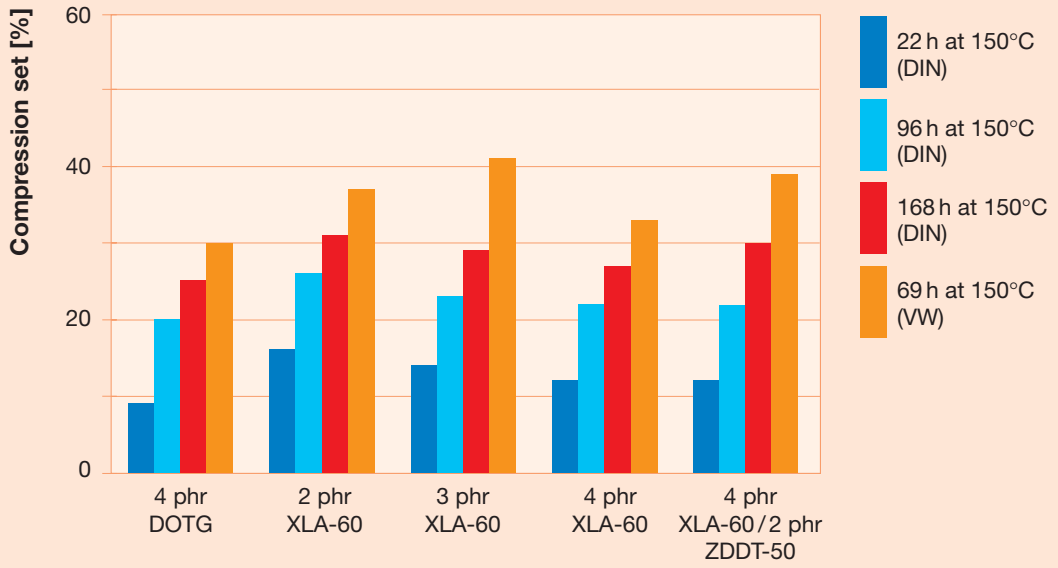


Fig. 9: Physical properties of AEM-G compounds (50-55 Shore A) before and after ageing in hot air (150°C): Modulus 100%



The compression set results of DOTG versus Rhenogran® XLA-60 are presented in Figure 10. It has been found that a dosage of 4 phr Rhenogran® XLA-60 is leading to similar values as with DOTG. The addition of 4 phr Rhenogran® ZDDT-50 is resulting in slightly higher compression set values.

Fig. 10: Compression set of AEM-G compounds (50-55 Shore A) at 150°C



3. Conclusions

- Rhenogran® XLA-60 is a technically equivalent replacement of the hazardous DOTG.
- Rhenogran® XLA-60 has a significantly lower irritant and toxic potential.
- Rhenogran® XLA-60 is predispersed in an acrylic polymer binder system and is easy to incorporate in the compound.
- With Rhenogran® XLA-60 comparable physical properties to traditional DOTG can be achieved.
- For curing of acrylic rubber, Rhein Chemie is offering special curing additives, e.g. Rhenogran® HMDC-70/AEMD, Rhenogran® ZDDT-50/AEMD, and Aflux® 18.

4. Literature

[1] Liste aller Änderungen und Neuaufnahmen in der MAK- und BAT-Werte-Liste 2006.

[2] IARC. Monographs on the evaluation of carcinogenic risks to humans. Publ. no. 77, Lyon: IARC Scientific Press, 2000

[3] Toxikologische Bewertung. Heidelberg, Berufsgenossenschaft der chemischen Industrie, 221 (1997) 16.

[4] Progress in Clinical and Biological Research, 141 (1984) 407.

[5] Practical Toxicology of Plastics, Cleveland, CRC Press Inc., (1968), 177.

[6] Vo E, Berardinelli SP, Hall RC, et al. A quantitative study of aromatic amine, permeation trough protective gloves using amine adsorptive pads. AIHAJ, 2000, 61, 837-841

[7] G Korinth, T Weiss, S Penkert, K H Schaller, J Angerer, H Dexler, Occup. Environ. Med. 2007, 64, 366-372

[8] DIN 53517 / ISO 815.

[9] PV 3307, Elastomer-Bauteile, Plastische und Elastische Verformbarkeit, Volkswagen AG, Klass.-Nr. 55161, August 2004.

Our technical advice - whether verbal, in writing or by way of trials - is given in good faith but without warranty, and this also applies where proprietary rights of third parties are involved. It does not release you from the obligation to test the products supplied by us as to their suitability for the intended processes and uses. The application, use and processing of the products are beyond our control and, therefore, entirely your own responsibility. Should, in spite of this, liability be established for any damage, it will be limited to the value of the goods delivered by us and used by you. We will, of course, provide products of consistent quality within the scope of our General Conditions of Sale and Delivery.

Aflux®, Rhenogran®, Rhenocure® are registered trademarks of Rhein Chemie Rheinau GmbH, Deutschland.
Vamac® is a registered trademark of E.I. du Pont de Nemours and Company, USA.

Rhein Chemie Rheinau GmbH
Duesseldorfer Strasse 23-27
68219 Mannheim, Germany
Phone: +49 (0)621-8907-0
Fax: +49 (0)621-8907-269
rubber.rcr@rheinchemie.com

Rhein Chemie Corporation
145 Parker Court
Chardon, OH 44024, USA
Phone: +1-440-285-3547
Fax: +1-440-285-2464
rubber.rcc@rheinchemie.com

Rhein Chemie Japan Ltd.
Marunouchi Kitaguchi, Bldg. 23 F
1-6-5 Marunouchi, Chiyoda-ku
Tokyo 100-0005, Japan
Phone: +81 3-5293-8041
Fax: +81 3-5219-9779
Rubber.rcj@rheinchemie.com

Rhein Chemie (Qingdao) Ltd.
43 Siliubei Road
Li Cang District
Qingdao 266043, PR China
Phone: +86-532-8482-1670
Fax: +86-532-8482-5961
rc.asia@rheinchemie.com

www.rheinchemie.com

A company of the LANXESS Group

G324/pdf/KR/0108