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Cross-linking and foaming behavior of elastomers with water based blowing agents

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Abstract

Physiologically hazardous chemical blowing agents are state of the art for the foaming of extruded rubber profiles. Water is a potential alternative to these blowing agents and is incorporated into rubber compounds in the form of water-loaded hygroscopic substances such silica or hydrates. To achieve an optimum foaming result, the water desorption and cross-linking reaction has to be coordinated. Studies of the foaming behavior in the salt bath of the Sponge Rubber Analyzer show, that the density of an ethylene propylene diene monomer (EPDM) rubber compound is reduced to about 60% and a nitrile butadiene rubber (NBR) compound to approximately 70%. The low reference densities of chemically foamed EPDM of 30% and NBR of 45% are not achieved. This is attributed to the premature foaming when using water-loaded silica as blowing agent. Due to the low resistance of the rubber matrix, large cells are formed by coalescence, which collapse at low cross-linking densities. Investigations of the cross-linking behavior of EPDM and NBR with water-loaded silica as blowing agent state, that the cross-linking density is reduced to about 65% for EPDM and 50% for NBR when water is present. Furthermore, the incubation time is shortened by inhibition of the CBS retarder in the cross-linking system of the NBR. However, this is not sufficient to fix the foamed cells.

KEYWORDS

applications, extrusion, hydrophilic polymers, rubber

1 | INTRODUCTION

The insulating and sealing properties of foamed elastomers are outstanding, so that these materials are used in highly mechanical and environmental stressed components in the automotive and construction industries as well as for a wide range of industrial applications.[1–3] Up to now, mainly chemical blowing agents have been used for the foaming of elastomers. Chemical blowing agents decompose at a definite temperature during vulcanization and thereby produce a foam structure in the elastomer.[4,5] Chemical blowing agent systems such as azodicarbonamide (ADCA) in combination with hydrazine derivatives such as p,p' oxibis(benzenesulfonylhydrazide) (OBSH) have the greatest economic impact in rubber processing.[6] Regardless of their toxicity, chemical blowing agents are still widely used in

rubber processing. ADCA has been classified by the European Commission as a substance of very high concern (SVHC) and it is to be expected, that it will be subject to authorization in the European Union in accordance with the EU Regulation on the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH).[7,8] Thus, alternatives to chemical blowing agent systems, such as ADCA, have great potential to be applied in the future.

Physical foaming, in which the phase transition from fluid to gas is used, represents an alternative approach for foaming. In the past, numerous investigations were carried out with inert gases and CO_2 as physical blowing agents.[9–12] However, gases as physical blowing agents for the extrusion of foamed elastomers are not well established in industrial applications due to the temporally separated blowing and cross-linking reaction and the associated foaming at the die outlet (formation of surface defects) as well as the additionally necessary plant technology (gas injection and mixing elements). Despite the lower volatility and the lower solubility compared to most other physical blowing agents, water is attractive as a physical blowing agent from an ecological and economic point of view.[12] The foaming of extruded rubber profiles takes place at atmospheric pressure, so that the volume of 1 ml water can theoretically expand to up to 1700 ml during evaporation at 100 °C and 1 bar. In comparison the gas yield of ADCA is 280–320 $ml \cdot g^{-1}$.[13] In rubbers, water can be very well incorporated during compounding by binding it to hygroscopic powdery carrier substances or as water of crystallization. In the subsequent extrusion process, shaping of the profile takes place in the extrusion die without foaming. The blowing reaction starts when the water evaporates in the downstream vulcanization unit parallel to the cross-linking of the rubber. In preliminary studies, the foaming of EPDM rubber with water as a physical blowing agent showed great potential both in injection molding and extrusion.[12,14]

The foam structure and the mechanical properties of foamed elastomers depend largely on the coordination of the blowing and cross-linking reactions, which can be influenced both on the material and the process side.[15] In previous work the foaming behavior was investigated with the Sponge Rubber Analyzer (SRA).[16] The transient density reduction of a test specimen in a heated salt bath was measured according to the Archimedean principle.[16,17] Generally, the transient density curve for foaming with water differs from that with the chemical blowing agent ADCA. Due to the early foaming of the rubber with water, uncross-linked, near-surface areas show a coarse cell structure. The foam density of about 0.37 $g \cdot cm^{-3}$ achieved with ADCA has not been achieved by foaming with water. It was shown that both the type of carrier substance (carbon black N550 or silica Vulkasil S) and the water content in the rubber compound had an influence on the density over time during foaming.[16]

In previously published work, water-based blowing agents were presented and discussed with regard to their suitability for the foam extrusion of rubber.[16,18,19] It has been shown, that hydrates such as calcium sulfate dihydrate and water-loaded silica are well suited for foaming rubbers, since the release of water vapor occurs above 100 °C and thus in a range relevant for continuous vulcanization.[18] Furthermore, thermogravimetric measurements have shown, that the evaporation rate of water increases with the pH value of the silica carrier substance.[18]

Regarding the achievable quality parameters (foam structure and mechanical properties) of the foamed rubbers, it was found that temperature control plays a decisive role in the vulcanization process. The degree of cross-linking achieved (measured as tensile deformation set) of the ethylene propylene diene monomer rubber (EPDM) and nitrile butadiene rubber (NBR) compounds increased as the vulcanization temperature was raised from 180 °C to 220 °C. The higher degree of cross-linking was more pronounced in the NBR compound than in the EPDM compound. With regard to foam structure, a varying cell size distribution over the radius of the vulcanized round strands was observed. In NBR and especially in EPDM, the surface layer was fine porous and the cell size increased up to half the radius from the surface and then decreased again towards the center of the sample. This variance of the cell size distribution over the radius was more pronounced than in the sample foamed with azodicarbonamide.[19]

2 | OBJECTIVE

The objective of the following investigations is to reduce the density of the rubber by foaming with water as blowing agent to achieve the reference density of rubber foamed with ADCA. The findings of previous investigations[16,19] lead to the question of how temperature and water content affect the foaming and cross-linking behavior of EPDM and NBR. The working hypothesis is that with increasing water content more gas volume is available for foaming and thus the density decreases proportionally to the water content. Additionally, it is assumed that the bubble growth (minimum density) is limited by the merging of bubbles (coalescence) and the associated destabilization of the matrix (collapsing cells). Furthermore, it is to be expected that the water could affect the cross-linking system and thus alter the balancing of the blowing and cross-linking reactions. For this purpose, it is necessary to determine the ideal amount of water for

foaming and to propose specific recipe adjustments. It is in this work shown, that water significantly reduces the incubation time and the degree of cross-linking of the NBR mixture, although this effect decreases with increasing temperature. With regard to foaming behavior, it will be presented that, in contrast to the EPDM mixture, a variation in the amount of water in the NBR mixture has only a minor effect on the minimum density that can be achieved. Furthermore, when foaming rubber with water as blowing agent in a salt bath, the density increases again after passing through a minimum density. This increase in density depends on the water content and is in principle higher for NBR than for EPDM.

3 | EXPERIMENTAL

3.1 | Preparation of rubber compounds

The rubber compounds used (Table 1 and Table 2) are industrially produced by Hexpol Compunding s.p.r.l, Eupen, Belgium. Two rubber compounds are selected which differ in the polarity of the polymer. The nitrile butadiene rubber (NBR) polymer contains 28% of the polar (but not hydrophilic) functional acrylonitrile group. Compared to NBR, ethylene propylene diene rubber (EPDM) is nonpolar. These are rubber compounds, that have already been used in earlier works for foaming with chemical blowing agents and water as blowing agent.[15,16] As an indicator for the viscosity of the rubber compounds, the Mooney viscosity is determined with shearing-disc viscometer according ISO 289-1:2015. The torque of the shaft is measured after 1 min heating to 100°C and 4 min rotation at a constant shear rate of 1.56 s^{-1} (ML [1 + 4], 100°C). The Mooney viscosity is an instrument-specific measured parameter (torque) and is given in Mooney units (MU). The higher the MU value the higher the viscosity of the measured compound. The Mooney viscosity of the EPDM master batch is 35 MU and the NBR has a viscosity of 52 MU.

3.2 | Blowing agents

For the investigation of foaming and vulcanization behavior of the rubber compounds, water-loaded silica (Ultrasil 360) is incorporated into the EPDM and NBR rubber compounds (Table 5 and Table 6) on a roller mill of type MT 8″ × 20″ of Rubicon Gummitechnik und Maschinenbau GmbH, Halle/Saale, Germany. As Silica the precipitated Ultrasil 360 with a BET specific surface area (DIN 66132) of 55 $m^2 \cdot g^{-1}$ and a pH-Value of 9 by Evonik AG, Essen, Germany, was used.[20,21] In previous investigations Ultrasil 360 showed the highest evaporation rate, so this carrier substance seems to be most suitable for foaming [HKF20]. The mixture of silica and water (1:3 ratio) was prepared 3 days in advance. Four different mixtures of each compound with a water content of 0 wt% to 3 wt% were produced (Table 3). Based on previous studies[16] in which a water content of 2 wt% was used, the water content is varied by ±1 wt% in order to identify an optimum amount of water. In addition, mixtures without water are included in the studies as a reference. The surface of the roller mill is tempered to 40°C to minimize evaporation of the water during incorporation.

The vaporization of the water extends over a temperature range from 100°C to 150°C.[18] The theoretical gas yield of water is between 1673 $ml \cdot g^{-1}$ (100°C, 1 bar) and 2121 $ml \cdot g^{-1}$ (200°C, 1 bar) assuming complete vaporization of the water.[13] As a reference EPDM and NBR mixtures with 1.8 wt%, 2.15 wt%, and 2.5 wt% of the powdery chemical blowing agent Azodicarbonamide of the type Unicell D 200A from TRAMACO GmbH, Pinneberg, Germany, is prepared. The variation of the amount of ADCA is based on material supplier's recommendation. The decomposition temperature of the ADCA is given as 210°C and the gas yield is 280–320 $ml \cdot g^{-1}$.[14] Although the gas yield of water-loaded silica compounds is many times higher than that of compounds with ADCA as blowing agent, previous work has shown, that with these quantities of water and silica as carrier substance, the foams with the lowest densities can be produced.

3.3 | Characterization of the vulcanization behavior

The temperature-dependent course of the cross-linking reaction of the rubber compounds is determined by means of the rubber process analyzer (RPA). In principle, the volcameter test is based on the dynamic measurement of shear stress under isothermal conditions. The test chamber consists of two heated plates. The lower plate is subjected to an oscillating motion with constant frequency and amplitude of a sinusoidal movement. This periodic mechanical alternating stress generates an oscillating shear stress in the sample and is transmitted through the sample material to the upper plate where the torque is measured. The cross-linking isotherm, describes the time course of the periodic shear stress at constant temperature or the torque, which is proportional to the shear stress. Important characteristic values of a cross-linking isotherm are the incubation time (start of the cross-linking reaction) and the maximum elastic fraction of the torque. In addition to the minimum torque S'_{min}, which is proportional to the deformation resistance of

TABLE 1 NBR compound recipe

Trade name	Chemical composition	Amount (phr)
Perbunan NT 2845	Nitrile butadiene rubber (ACN content: 28 wt%)	100
Corax N550	Carbon black	60
Vulkanol 81	Mixture of thioesters and carboxylic acid esters	20
Zinc Oxide	Zinc Oxide	5
Sulfur 95C	Sulfur	2
Vulkacit CZ/C	N-cyclohexyl-2-benzothiazolesulfenamide (CBS)	1.5

TABLE 2 EPDM compound recipe

Ingredients	Chemical composition	Amount (phr)
Keltan 6950C	Ethylene propylene diene monomer rubber (Ethylene content: 44 wt%)	100
Corax N550	Carbon black	80
Sunpar 2280	Paraffinic oil	70
Zinc Oxide	Zinc Oxide	5
Stearic Acid	Stearic Acid	2
Lipoxol 6000	Polyethylene glycol	3
Vulkacit DM/C	Di(benzothiazol-2-yl) disulfide (MBTS)	1.5
Sulfur 90/95	Sulfur	1.5
Rhenocure ZAT	Zinc amine dithiophosphate	3.5

TABLE 3 EPDM and NBR compound recipe

Compound type	Water content (wt%)	Weight ratio of Ultrasil 360 to H_2O
EPDM	0; 1; 2; 3	1:3
NBR	0; 1; 2; 3	1:3

the uncross-linked sample, the maximum torque S'_{max} can be used for evaluation. This is a measure for the deformation resistance of the vulcanized sample at the respective temperature. The final value of the elastic fraction of the torque of the vulcanization curve corresponds to the cross-linking density.[2] The degree of cross-linking is a quantitative measure for the characterization of polymeric networks. It describes the percentage of cross-linked points actually linked in relation to the number of all maximum possible cross-linking bridges. Based on the incubation time, the time until 10% of the maximum measured elastic fraction of the torque (t_{10}) is reached is used in the following, since this t_{10} value is a default output by the RPA. The measurement is carried out in accordance with DIN 53529–2 using a rotorless torsional shear volcameter of type RPA2000 from Alpha Technologies, Akron, Ohio, USA.[22] Here, the torque transmitted through the sample is measured at a constant angular amplitude of 7% and a frequency of 5/3 Hz. The weight per sample is 3 g ± 0.005 g. The tests are performed at temperatures of 160°C, 180°C and 200°C. Three samples are measured for each experiment. The measuring time is set to a limit of 6 min. The samples were not conditioned and the measurements were not carried out in a standard climate.

3.4 | Characterization of foaming behavior

The aim of this measurement is to gain insights into the temperature dependent time course of the foam density. The influence of temperature on the foaming of the different compounds as well as the effects of polarity will be analyzed by studying polar NBR compounds and non-polar EPDM compounds. In addition, the foaming behavior as a function of the amount of water used as well as the achievable density reduction will be characterized.

The Sponge Rubber Analyzer (SRA) is used to characterize the free foaming behavior of elastomer compounds without counter pressure and shape constraints. The measuring instrument works according to the Archimedean

principle and allows the interaction of the cross-linking reaction and the blowing agent decomposition to be investigated in the form of the temporal expansion course of the material. In this method, a rubber sample determined with respect to its mass is attached to a needle on a vertically movable cross beam (Figure 1) and automatically immersed in a tempered salt mixture of known density. The liquid salt mixture serves simultaneously as measuring fluid and heat transfer medium for the vulcanization of the sample. During the measurement, the balance continuously records the mass of the displaced liquid. According to Archimedes, the buoyancy force experienced by a body completely immersed in a liquid is directly proportional to its volume and thus to the weight of the liquid that the body displaces. By measuring the weight force caused by the immersion of the specimen or its progressive expansion, the buoyancy force can be determined, which enables the calculation of the specimen density.[23] The tests are carried out at temperatures of 160°C, 180°C and 200°C. The measurement time for each experiment is 360 s. The sample size of each experiment is $n = 3$. The samples were not conditioned and the measurements were not carried out in a standard climate.

Due to the different initial densities of the compounds, the normalized density ρ_{norm} is used to evaluate the foaming behavior (Equation 1). The normalized density is the ratio of the density at a given time, relative to the maximum density ρ_{max}.

$$\rho_{norm}(t) = \frac{\rho(t)}{\rho_{max}} \quad (1)$$

The maximum density ρ_{max} is the density of the unfoamed compounds and is 1.05 $g \cdot m^{-3}$ for EPDM and 1.20 $g \cdot m^{-3}$ for NBR. The value for the minimum density is the absolute minimum density. Since an increase in density was observed in water-foamed rubbers after passing through a density minimum (reversion of density), the percental increase in density after reaching the density minimum is considered. This increase is calculated as follows:

$$\rho_{rev} = \frac{\rho_{end} - \rho_{min}}{\rho_{min}} \cdot 100\% \quad (2)$$

4 | RESULTS AND DISCUSSION

4.1 | Influence of the water on the cross-linking

Figure 2 shows selected cross-linking isotherms of EPDM and NBR without and with water-loaded silica as blowing agent (3 wt% H_2O) at a temperature of 180°C. In the case

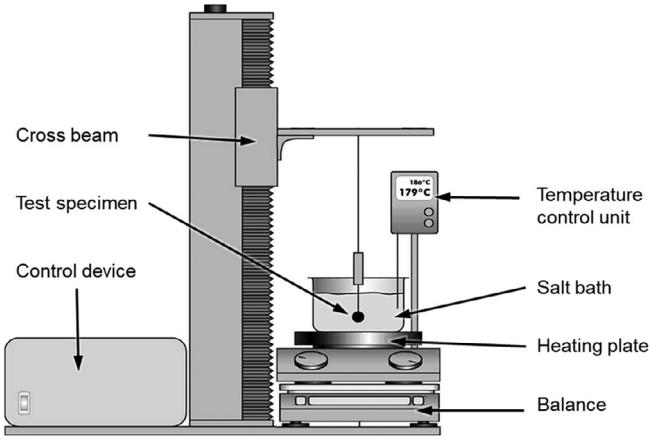

FIGURE 1 Schematic illustration of the sponge rubber analyzer (SRA) for the analysis of the foaming behavior of rubber compounds

of EPDM, it can be seen, that the addition of water does not change the start of the cross-linking reaction (incubation time). With NBR, the incubation time is reduced if water is present and is delayed when the chemical blowing agent ADCA is added. For both NBR and EPDM, the elastic fraction of the torque, which is a measure of the cross-linking density, is reduced by adding 3% water to the compound. When adding ADCA to NBR the cross-linking density is reduced and has the same level as with added water. The cross-linking reaction consists of a sequence of simultaneous or consecutive reactions. For this reason, many cross-linking systems do not achieve a stable state. There can be a continuous increase in cross-linking density (marching modulus) as well as the formation of a maximum.[2] The EPDM without water and with ADCA shows a marching modulus.

As shown in Figure 3, the relationship between the t_{10} time and water content of the mixture can be well approximated by a linear model given in Equation 3, where w is the water content in wt% and a the slope of curve. All measured values are plotted as data points in the diagram. Linear regression was performed using the least squares method. The coefficient of determination R^2 indicates how well the model is fitted to the measured data. It can be derived that especially the NBR mixture reacts very strongly with a reduction of the t_{10} time at a vulcanization temperature of 160°C from about 105 s to 40 s by adding water. The coefficients of the models and the coefficient of determination are summarized in Table 4. It becomes clear that for both EPDM and NBR, the shortening of the incubation time decreases with increasing temperature as the water content is raised (coefficient a). The influence of temperature on the coefficient a is less for EPDM than for NBR.

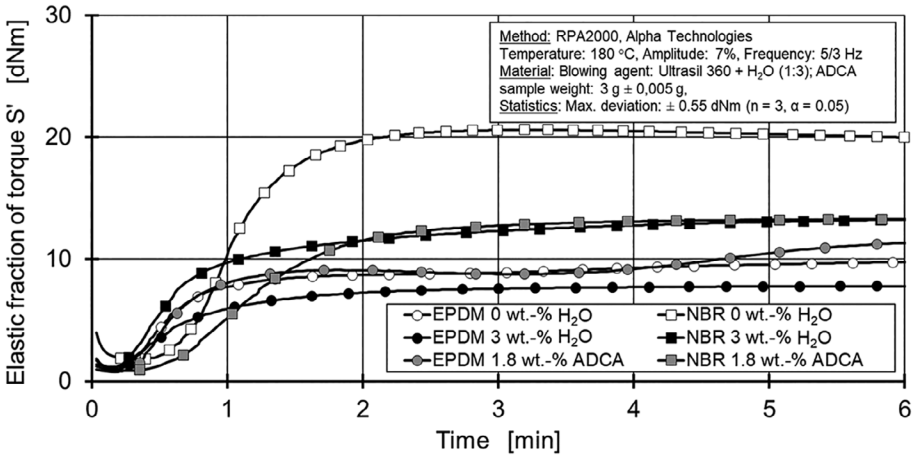

FIGURE 2 Cross-linking isotherms at 180°C of EPDM and NBR compounds with 3 wt% water as blowing agent and without water

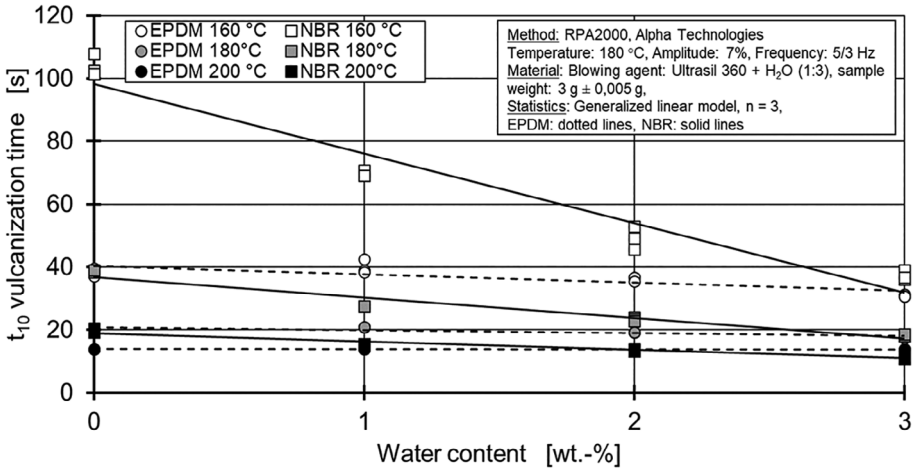

FIGURE 3 Influence of water content on t_{10} vulcanization (incubation) time of EPDM and NBR with silica as water carrying substance

$$t_{10}(w) = a \cdot w + t_{10}(w = 0) \quad (3)$$

$$S'_{max}(T) = b \cdot T + S'_{max}(T = 0°C) \quad (4)$$

The influence of temperature without the use of water is reflected in coefficient b. Based on the values in Table 4, it is clear that the incubation time is regressively shortened with an increase in temperature from 160°C to 200°C. This reduces the incubation time of NBR to about 20% and of EPDM to about 35%.The maximum value of the elastic fraction of the torque is plotted over temperature for the EPDM and NBR compounds with different water content in Figure 4. With higher temperature, the cross-linking density decreases for all compounds. The relationship is approximated with a linear model given in Equation 4. The coefficients of the models and their determination coefficients are summarized in Table 5.

The elastic component of the torque S'_{max} which correlates with the cross-link density depends on the coefficient b, the cross-linking temperature T and the extrapolated torque at 0°C.

The temperature-related change in the cross-linking density of EPDM and NBR decreases with increasing water content. In the case of EPDM, the coefficient b is reduced from −0.11 to −0.06 by adding 3 wt% water, while in the case of NBR the coefficient b is −0.18 without and − 0.05 with 3 wt% water.

The theoretical cross-linking density at 0°C is reduced by about half from 32.6 dNm to 17.7 dNm for EPDM and by about one third for NBR as the water content increases from 0 wt% to 3 wt%.

4.2 | Influence of the water content on foaming behavior

The initial density of the EPDM compounds is 1.05 g·cm^{-3} and the NBR compound is 1.2 g·cm^{-3}. Figure 5 shows the time course of the normalized density at a temperature of 180 °C for the water-foamed rubber

TABLE 4 Coefficients of the fitted linear model to calculate the relationship between water content and incubation time of the EPDM and NBR

Rubber compound	Temperature (°C)	a	$t_{10}(w=0)$	R^2
EPDM	160	−2.66	40.34	0.67
EPDM	180	−0.90	20.90	0.69
EPDM	200	−0.02	13.88	0.01[a]
NBR	160	−22.10	98.20	0.94
NBR	180	−6.48	36.72	0.94
NBR	200	−2.69	19.03	0.96

[a]the poor model quality of $R^2 = 0.01$ is mathematically due to the fact that the incubation time at 200°C is constant, that is, invariant of the water content. Furthermore, all values except one were identical, so that the variance in this model is not explained by a change of the water content.

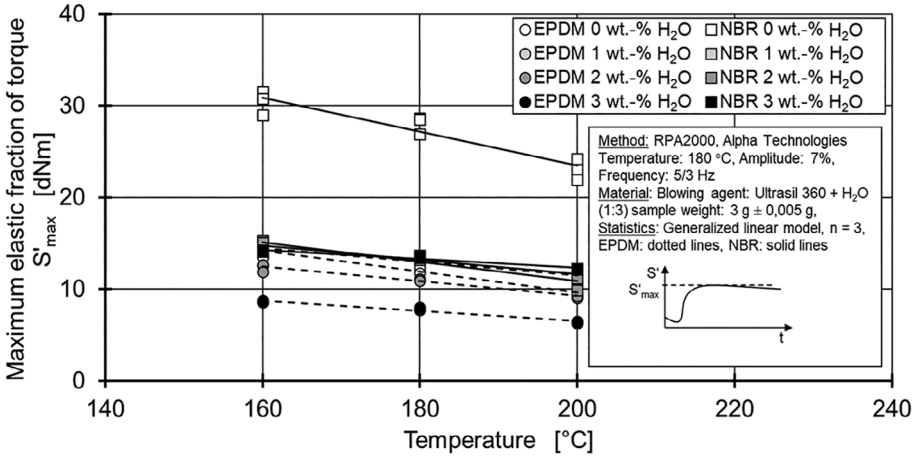

FIGURE 4 Influence of temperature and water content of EPDM and NBR on the maximum cross-linking degree

TABLE 5 Coefficients of the fitted model for the relationship between temperature T and S'_{max} (as a measure of the cross-linking density) of the EPDM and NBR

Rubber compound	Water content (wt%)	b (dNm·K^{-1})	$S'_{max}(T=0°C)$(dNm)	R^2
EPDM	0	−0.11	32.6	0.97
EPDM	1	−0.08	26.5	0.93
EPDM	2	−0.08	25.1	0.97
EPDM	3	−0.06	17.7	0.97
NBR	0	−0.18	60.5	0.88
NBR	1	−0.08	27.0	0.97
NBR	2	−0.11	32.0	0.91
NBR	3	−0.05	22.2	0.95

compounds and at 220 °C for the compounds foamed with ADCA. In each case, the mean value of three measurements is shown. The 95% confidence interval of the mean values ($n = 3$) was calculated to be maximally ±8%. The density of the reference compounds with ADCA as blowing agent was reduced to about 28% for EPDM and 33% for NBR. The density of the water foamed EPDM and NBR compounds was reduced to about 65% at 3 wt% H_2O. The water naturally contained in the rubber compounds results in a reduction in density of about 20% for EPDM and 30% for the more hygroscopic NBR compound. This is in accordance to previous measurements of the different water content in EPDM and NBR compounds (HKF20). In the case of water-foamed rubber compounds, after reaching a minimum density of about 55%, an increase in density occurs at 120 s. The minimum density of ADCA is reached after 150 s for NBR and after 180 s for EPDM.

In Figure 6, the minimum density is plotted over the mixed in blowing agent content at 180°C for the water-

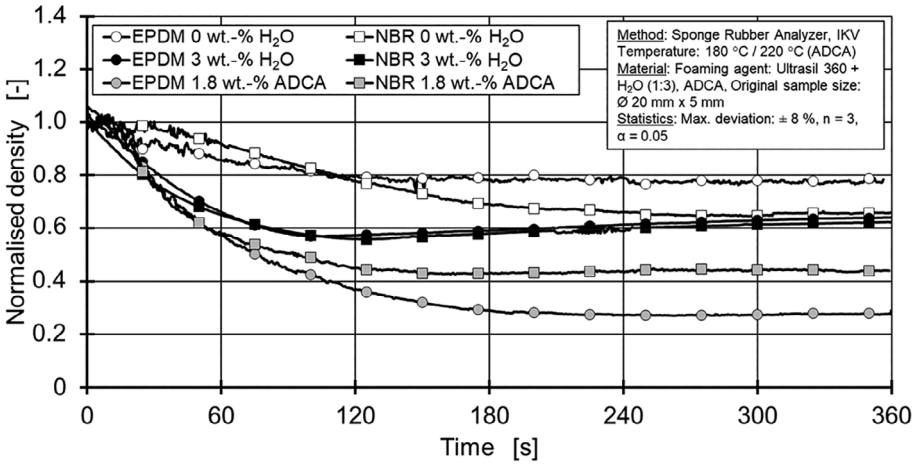

FIGURE 5 Foaming behavior of EPDM and NBR rubber compounds at 180°C (220°C for ADCA) without blowing agent, with water-loaded silica as blowing agent and with ADCA as blowing agent

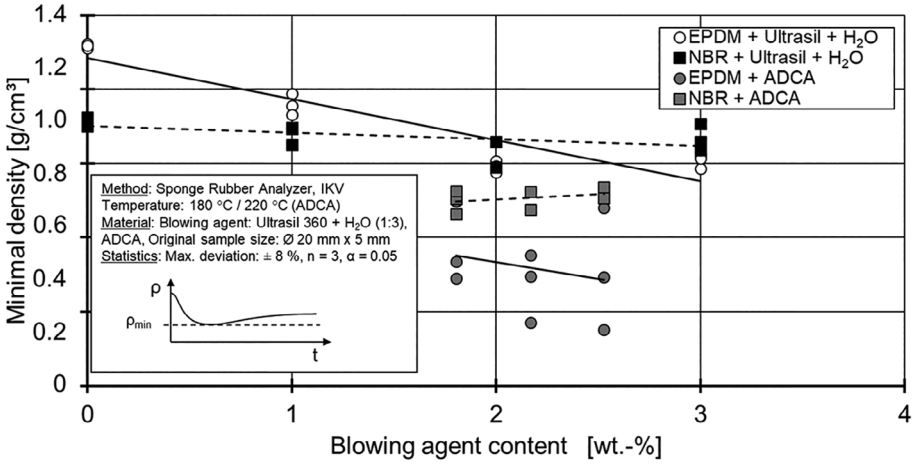

FIGURE 6 Influence of the blowing agent content of EPDM and NBR at 180°C (220°C for ADCA)

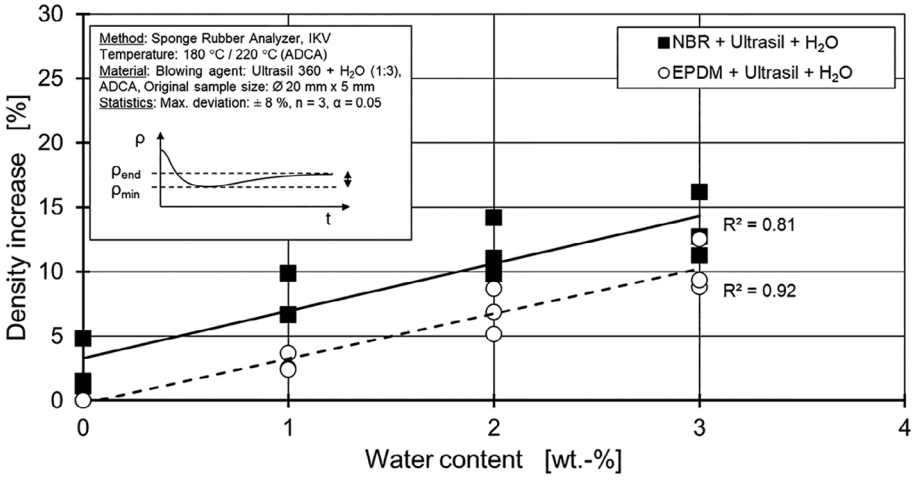

FIGURE 7 Influence of the water content on the increase in density after passing through a density minimum

foamed and at 220°C for the ADCA foamed compounds. All measured values are plotted as data points in the diagram. Linear regression was performed using the least squares method. With increasing water content, the minimum density decreases, although in the case of EPDM this does not decrease further above 2 wt% H_2O. For the water-foamed NBR, the minimum density does not decrease significantly as the water content changes. Similarly, the minimum density is not significantly different for EPDM and NBR when the amount of the chemical

blowing agent ADCA is changed. The minimum density of NBR with ADCA is 0.5 $g \cdot cm^{-3}$ and 0.3 $g \cdot cm^{-3}$ for EPDM.

As it can be seen in Figure 5, water-foamed mixtures show an increase in density after passing through a density minimum. This increase in density increases in proportion to the water content, it can be derived from Figure 7. All measured values are plotted as data points in the diagram. Linear regression was performed using the least squares method. The increase in density for EPDM is up to 10% for 3 wt% H_2O and for NBR it is always up to 5% higher.

The reason for this reversion of density are collapsing cells. This is caused by a too low degree of cross-linking during foaming, so that the resistance of the rubber matrix to the cell pressure is insufficient with the result that cells become too large, connect with each other and collapse due to the open-pored cell structure and the associated decreasing cell pressure.

The theory of collapsing cells is supported by the observations from further investigations where the foaming behavior in a vulcanization channel was studied.[18] At low temperatures in the vulcanization channel and the associated lower cross-linking rate of the rubber, a coarser mixed-cell foam structure was observed. In this context, a shriveled profile surface was also noticed, which was the result of a collapsing sponge profile that was observed during cooling of the profile.

It was shown in Figures 2 and 3, that the incubation time barely decreases with the water content in the case of EPDM and strongly decreases with the water content in the case of NBR. This earlier starting cross-linking reaction actually counteracts fast cell growth, but does not seem to be sufficient. It can also be seen in Figure 4 that the cross-linking density is reduced by the presence of water. This can promote coalescence effects during foaming. Finally, it can also be attributed to poor nucleation, which favors coalescence. A direct comparison with the ADCA foamed compounds is difficult due to the higher temperature. The temperature of 220 °C was necessary to start the decomposition reaction of the ADCA. But higher temperatures are also accompanied by a higher reaction speed, which leads to different degrees of cross-linking in comparison to the water-foamed samples, based on the time of measurement.

The investigations on the foaming behavior demonstrate that the foaming's full potential has not yet been fully exploited and that a recipe adjustment is appropriate. To prevent premature foaming, the extensional viscosity of the compounds should be increased. This can be achieved by using a branched polymer or by adding stiffness-increasing fillers such as chalk or more carbon black. In addition, there are interactions with the curing system as the water inhibits the zinc complex of the curing system, leading to much lower degree of vulcanization.[2] CBS in NBR and MBTS in EPDM act as retarders of the cross-linking reaction. It is conceivable that the water may hydroxilise the activator zinc oxide, which impairs the formation of active sulfur accelerator complexes of sulphenamide, zinc oxide and sulfur in the NBR compound, so that the induction period is shortened. [2]

In summary, the compound recipe used for EPDM and NBR is not ideal for foaming and has potential for optimization. The aim of a recipe optimization should be to get the density reversion under control so that low densities are achieved. NBR has a higher Mooney viscosity than EPDM and a faster cross-linking when water is used as blowing agent. Nevertheless, the cells collapse earlier, which leads to a renewed increase in density. Possibly the resistance of the matrix is not high enough to keep the cells fine pored. Therefore, a cross-linking system should be selected that is not so sensitive to water, so that higher cross-linking densities are produced and growing cells got fixed. Additionally, reinforcing material (e.g., active carbon black) and nucleating agent (chalk) could be added. It has also been demonstrated, that the water evaporates very early. Compared to the density curve of the ADCA and the hydrate, it is observed that the minimum density of the ADCA is reached much later. This means that bubble fixation takes place at higher cross-linking levels, so that no collapse is observed. Therefore, it might be useful to further accelerate the cross-linking reaction when foaming with water-loaded silica. Alternatively, a water-containing blowing agent should be used, where the blowing reaction is initiated at higher temperatures. For calcium sulfate dihydrate, this temperature is between 125°C and 200°C.[19]

5 | CONCLUSIONS

The cross-linking and foaming behavior of EPDM and NBR rubber compounds with water-loaded silica as blowing agent was investigated. The goal of using water as blowing agent to achieve a low density such as with the chemical blowing agent ADCA was not attained with the rubber recipes used in this study. The presumption that water influences the cross-linking behavior was confirmed by RPA measurements. It was shown, that water reduces the cross-linking density and, in the case of NBR, water reduces the incubation time. When using ADCA, the cross-linking density is higher and the incubation time is not affected. The hypothesis that with increasing water content the resulting density decreases was confirmed for the EPDM compound. However, when water

is used as a blowing agent during the foaming process, the minimum density was not maintained (reversion of density). This is attributed to collapsing cells due to destabilization of the not fully cross-linked rubber matrix and coalescence of the cells. In terms of foaming behavior, it is observed with the SRA method that the minimum density is reached earlier with rubber compounds foamed with water-loaded silica than with ADCA. Furthermore, increasing water content leads to a reversion of the density after passing through the minimum density. The comparison with the chemical blowing agent illustrates that the delay of the blowing reaction leads to lower foam densities without reversion effects. Therefore, when using EPDM and NBR, foaming with water requires a change in the compound formulation. The cross-linking system should be faster and less sensitive to water. In addition, an increase in extensional viscosity due to branched polymers or more active carbon black can be useful. The use of calcium sulfate dihydrate has already shown promising results with regard to the attainable density at a much lower water content, since the release temperature is between 125°C and 200°C.[18,19]

Furthermore, a weakness in the applied methods became apparent. The thermal conditions in the test samples of SRA and RPA are not comparable. The RPA has a preheating time and assumes isothermal measurements. In the case of SRA, there is a transient temperature field in the test specimens cross section, which makes it impossible to compare the characteristic times (incubation of vulcanization and foaming behavior. Therefore, it is highly recommended to measure the temperature in the cross section by using the SRA in the future. As a control experiment for the detection of collapsing cells, samples should be taken from the SRA at different times in further investigations. Based on the cell size, structure and degree of cross-linking, the theory of collapsing cells could then be verified. Alternatively, the foaming in the vulcanization oven should be considered. However, this cannot be done in a continuous oven, but in a discontinuous vulcanization oven. Here, the conditions occurring in a production process for the development of foam recipes or process adjustments for existing recipes can also be investigated.

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