Foaming of EPDM with water as blowing agent in injection molding

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ABSTRACT: Chemical foaming of elastomers is state of the art and preferred to the more complex systems engineering of physical foaming, yet, many commonly used chemical blowing agents often are hazardous. In current investigations, we introduced water bound to carrying substances (silica, carbon black) into elastomer compounds. A stable, reproducible foaming process can be implemented using water as physical blowing agent. In first tests, the average cell diameters in injection molded elastomer parts exceed the average cell diameters of chemically foamed parts. Yet, varied amounts of blowing agent can reduce the cell diameters. Furthermore, nucleating agents and water carriers are being examined to reduce cell diameters and reach cellular structures and mechanical properties of chemically foamed parts. In conclusion, foaming of elastomers with water is a promising. Yet, further examinations have to cover the effect mechanism of foaming and vulcanization as well as continuous processing and compounding. Rear end of an EPDM part foamed with water carried on silica in injection molding process (mold temperature 195 °C, breathing mold opening 2 mm) © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43613.

INTRODUCTION

Foamed elastomers have been increasingly used in many technical and industrial applications due to their insulation properties, their compressing properties, and their ability to modify the profile's physical properties.[1–3] Until now, foaming of elastomers is mainly implemented by using chemical blowing agents, which decompose at certain temperatures (parallel to the curing process) and generate a cellular structure. Despite the wide use, many chemical blowing agents are hazardous to health and, therefore, are subject to prohibition proceedings by the European Union. Therefore, available and safer blowing agents are required. Foaming induced by the phase transition of substances, using physical blowing agents may be an answer to this search. As a consequence of various studies on physical foaming, several substances such as inert gases or carbon dioxide have been examined.[4–8] The main limitations of physical foaming using gases as blowing agents lie in the additional machinery and thus more complex processes and in the separation of foaming and vulcanization processes, which can lead to uncontrolled foaming.

As a consequence, we have examined the use of water as a possible blowing agent for elastomers. Foaming with water has been subject to studies with several matrixes, excluding elastomers.[9] Thus, the processibility of water as a physical blowing agent in rubber mixtures presented in this article. Our investigations include the injection molding and extrusion process. In the following, the results from injection molding process are presented.

STATE OF THE ART

In the foaming process of elastomers, exothermic blowing agents are used in multiple applications. Most effective chemical blowing agent for foaming of cellular rubber are azodicarbonamides (ADC), p-p′oxybis(benzene sulfonyl hydrazide) (OBSH) and dinitroso pentamethylene tetramine (DPNT).[10] DPNT is usually used to produce closed cell structures. One disadvantage of DPNT is the fish type odor in the products. The odor can be reduced with the use of urea and borate. Azodicarbonamide (ADC) has the decomposition temperature of 210 °C, which is

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too high for sponge application. However, the composition temperature can be reduced by using glycols and glycerol as kicker-substances. As a result, the use of ADC in rubber and plastic industries has become state of the art. OBSH is mostly used in nitrile-vinyl insulation tubing. Mixtures of ADC and OBSH are also uses for foaming of rubber.[11] In these combinations, the decomposing OBSH is used as kicker for ADC. In spite of the easiness of handling and producing good foam structure, chemical blowing agents have some limitations, such as unwanted by-products and high cost and high ozone depletion potential. Therefore, the European Union is running on a trial to ban these chemical blowing agents.[12]

Until some years ago, chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) were the main physical blowing agents for insulation applications. One serious problem with these physical blowing agents is that they contain chlorine which breaks down the ozone layer protecting the Earth from UV radiation. Moreover, these blowing agents have very high global warming potentials, therefore, they are being phased out in the industrial use.

As a result to the ban of chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) according to Montreal Protocol,[13] hydrofluorocarbons (HFC) and hydrofluoroolefins (HFO) were invented. HFC do not damage the ozone layer because they do not contain chlorine in their structures. However, HFC are strong green-house gases, therefore, HFCs will no longer be used in some applications and the replacement is requested.[13,14] HFO have no ozone depletion potential combined with a low 100-year global warming potential, the amount of heat trapped by substances compared with heat trapped by carbon dioxide in 100 years, which could be a substitution. However, HFO are new and need more time for researches before any conclusion about long-term environmental effects can be made. Some reports about environmental effect of HFO are less negative.[15,16] In our recent research on the foaming EPDM and silicon elastomers in injection molding and extrusion we investigated the suitability of inert gases as blowing agents. Carbon dioxide has been introduced into EPDM in the solid state (as dry ice) or injected under high pressure before injection molding and extrusion. With silicone rubber, liquid carbon dioxide is introduced into the liquid silicone rubber after two components have been mixed. As the next step, the mixture is injected into cavity. Even though the concept is promising, the reproducibility is so far too low for applications.[17–19]

Water as blowing agent shows foaming capabilities in several matrixes, such as thermoplastics, thermoplastic elastomers or composites.[10,20–24] Water as single blowing agent can be mixed with a thermoplastic or TPE matrix in gaseous or liquid phase and extruded, formed and cooled afterward.[20,21] Furthermore, water has been reported as additional blowing agent in mixtures of different blowing agents.[22] Different surfactants, charged oppositely from the polymer, or carriers like NaCl can be used to create a more stable foam. Yet, too high amounts of surfactant may cause a precipitation.[23,24]

However, for elastomeric matrices there has been no significant research reported, yet. With the increasing use of foamed elastomers in multiple applications, a new physical blowing agent for elastomers would be highly advantageous. Thus, in this article, the evaluation of the foamability of EPDM with water is discussed. Being readily available, inexpensive, water can become an important blowing agent for elastomers in future.

EXPERIMENTAL

Materials

In the following, the compound recipe is presented and properties of water-carrying substances are discussed. Water is introduced into an elastomer compound bound on a water-carrying substance to avoid adding water to the internal mixer in liquid phase, which could result in water loss during mixing. In order to investigate foamability and processability of water in the foaming of elastomer, two different types of compounds are made: one using carbon black (Corax N550, Orion Engineered Carbons GmbH, Cologne, Germany) as the water carrier, the other one using precipitated silica (Ultrasil VN 3 GR, Evonik Industries AG, Wesseling, Germany) as the water carrier. The specific surface area of the silica used is 180 m^2 g^{-1} (nitrogen surface area), the surface area of the carbon black is 40 ± 5 m^2 g^{-1}. The silica contains 80% of particles bigger than 300 μm and 10% of particles smaller than 75 μm.[25,26] The smaller surface area of carbon black leads to lower solubility of water per gram carbon black compared with the same amount of silica. With respect to the high amounts of carbon black in many industrial rubber compounds, carbon black may still prove to be a suitable water carrier for the foaming process presented here.

Due to dispersion of particles in the mixing process, there is no reliable data on the particle size within the compound. A measurement is not possible, as in optical measurements silica and other fillers cannot be distinguished. Studies on the unvulcanised, solid compound using a DisperTester 3000 by Montech Werkstoffprüfmaschinen GmbH, Buchen, Germany, show, that maximum particle size of fillers in the compound does not exceed 50 μm, regardless of the variation investigated.

Besides particle sizes of carrier substances, the specific surface of the substances can be another important characteristic value, as water is bound to the surface of different fillers (silica and carbon black). Previous thermogravimetric investigations show, that for constant water-filler-ratios, water bound to carbon black vaporizes at lower temperatures compared with water bound to silica. Another influence on the desorption and vaporization of water is the water–carrier-ratio: Increased loading of fillers with water causes higher desorption temperatures as the energy necessary for desorption increases.[18,19] The influence of varied water–filler-ratios will be explored in further studies. In the following, water–silica-ratios are kept constant.

To compare the properties, one more compound with a common chemical foaming agent, an azodicarbonamide (Unicell D 200 A; Tramaco GmbH, Pinneberg, Germany), is made as a reference compound. For all compounds, an EPDM is used as polymer (Keltan 6750; Lanxess Deutschland GmbH, Cologne, Germany) in constant amount. Table I shows the compound recipes and material variations. For WCB compounds, the water content is stated out directly, while the amount of water in WSil compounds has to be measured and calculated, as

Table I. Varied EPDM Compound Recipes with Different Amounts of Blowing Agents and Types of Water Carriers

Compound name	WCB1	WCB2	WCB3	WSil1	WSil2	WSil3	Azo
Ingredients	Content (phr)						
Mixing step 1[a]							
Keltan 6750	100	100	100	100	100	100	100
Corax® N550	80	80	80	80	80	80	80
Lipoxol® 6000	3	3	3	3	3	3	3
Stearin acid	2	2	2	2	2	2	2
Sunpar® 2280	70	70	70	70	70	70	70
Water	2.5	5	7.5	–	–	–	–
Water-absorbed Silica (WAS)	–	–	–	5	10	15	–
Unicell D200A	–	–	–	–	–	–	5
Mixing step 2[a]							
Rhenofit® F	10	10	10	10	10	10	10
Rhenocure® ZAT	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Sulfur 90/95	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Vulkacit® DM/C	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc Oxide	5	5	5	5	5	5	5

[a] For all compounds, the curing system has been added in a separate compounding step.

explained in the following in this article. For compounding and dosage, the amount of water-absorbed silica was dosed and varied.

Compounding

For the evaluation of the foamability of EPDM with water as single blowing agent, all compounds are mixed using an internal mixer IM 1,5E with PES 5 rotor geometry of Harburg-Freudenberger Maschinenbau GmbH, Freudenberg, Germany. Afterward, the compounds are rolled on a lab-scale roll mill MT 8″ × 20″ from Rubicon Gummitechnik und Maschinenbau GmbH, Halle (Saale), Germany.

Although carbon black is hydrophobic, it can be observed to absorb small amounts of water when stored under high humidity conditions. Therefore, to prevent any loss of water during the mixing process, water is added directly into carbon black before mixing. On the contrary, silica has good water absorption. Water can be absorbed on the silica surface and introduced into the compound together with silica as an absorbate. To prevent the overlapping effect of free water carrying by other substances, the silica is stored in water for more than 24 hours. This storage allows silica to reach its saturation of water absorption and ensure first a defined amount of water on silica and second constant amounts of water per silica particle. Especially the homogeneous water distribution to all silica particles is necessary for a homogeneous cell nucleation within the part's cross section.

The compounds labeled WCB for water carrier carbon black and WSil for water carrier silica are mixed in the internal mixer. The mixing process contains two steps:

- Four minutes of mixing non-chemical active ingredients at 25 rpm.
- one minute of mixing chemical active ingredients at 20 rpm.

The compound is cooled down on the lab-scale roller mill and rolled up 20 times on the rollers after mixing in the internal mixer. Further ingredients of the reference compound include a processing aid (Lipoxol 6000; Sasol Germany GmbH, Hamburg), a plasticizer (Sunpar 2280; Petronas Lubricants Belgium NV, Aartselaar, Belgium), and a sulfur-based vulcanization system (Rhenofit F, Rhenocure ZAT, Rhein Chemie Rheinau GmbH, Mannheim, Germany; Vulkacit DM/C, Lanxess Deutschland GmbH, Cologne, Germany).

Material and Compound Testing

All compounds are analyzed with focus on relevant characteristics on the foaming behavior. As most important tests, the
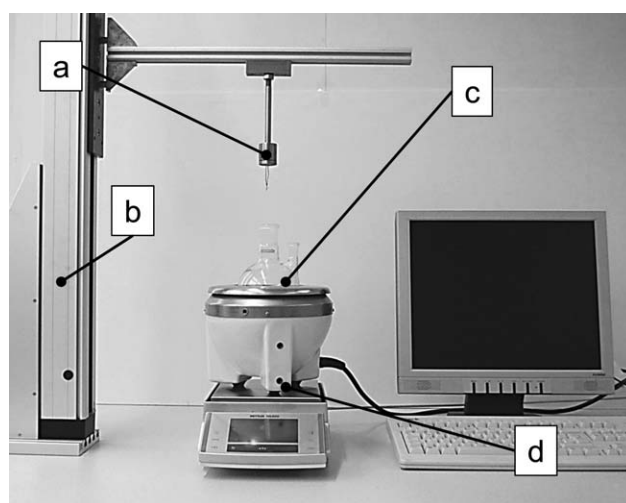

Figure 1. Measurement setup of the Sponge Rubber Analyzer (SRA). (a) Specimen holder for sponge rubber sample, (b) Traverse with control unit, (c) Vulcanization medium, (d) Heating unit and scale.

Table II. Water Content in WCB Compounds

Name	Amount of water (phr)	Amount of water (wt %)
WCB1	2.5	0.9
WCB2	5	1.8
WCB3	7.5	2.7

samples' density reduction is measured over time while foaming using a Sponge Rubber Analyzer (SRA), the overlapping vulcanization and decomposition reaction of the blowing agent are investigated using a RPA and a mooney viscosimeter. In addition, the shelf life of the compounds is examined by measuring water contents and free foaming behavior after different storage times.

Foaming Behavior. The foaming behavior of each compound is investigated using a Sponge Rubber Analyzer (SRA) (Figure 1). The SRA uses the Archimedes principle: A sample is dipped into a salt bath, filled with Sabalith, Rockwood Lithium GmbH, Frankfurt am Main, Germany, at 200 °C for 300 s. Due to the high temperature, foaming and vulcanizing reactions in the sample are initiated. With the initial weight of the sample and the density of the salt liquid, the sample's density can be measured for each time step. One central advantage of this principle of measurements is that the foaming reaction can occur mostly unhindered. This is an advantage for characterizing foaming behavior compared with RPA analysis, in which the foaming compound reacts within a closed chamber, which itself influences the foaming process.

Determination of Expected Water Content in WCB and WSil Compounds. The expected water content (wt %) of WCB can be calculated directly from the recipe (Table II).

To determine the expected water content of WSil2, the water content in water-absorbed silica (WAS) has to be determined first. Fixed amounts of WAS are dried in the oven for 5 hours at 180 °C in order to release absorbed water in WAS. After drying, the samples are weighed. The weight can be mainly attributed to the amount of water loaded in WAS. Due to the high amount of water the silica contains, other substances, which may decompose during the heating process, can be neglected. During the described tests an average water content in WAS samples was measured to be 67.88 ± 0.44 wt %. With the amount of WSil mixed into the compound, the water amounts in each compound are presented in Table III.

Measurement of Humidity Changes during Storing Time. Most elastomer compounds are stored for approximately 3–14 days

Table III. Water Content in WSil Compounds

Name	Amount of WSil (phr)	Amount of water (phr)	Amount of water (wt %)
WSil1	5	3.4	1.2
WSil2	10	6.8	2.4
WSil3	15	10.2	3.6

Table IV. Parameters for Humidity Measurements in KFT and Hydro Tracer

Parameter	Value
Measuring Temperature (KFT, °C)	100
Measuring time (KFT, min)	15
Measuring temperature (Hydro Tracer, °C)	210

between compounding and processing. Therefore, it is important that compounds maintain their properties during storage time. For this reason, the water content in two compounds is measured and analyzed over a storage time of 23 days. A changing amount of water may cause different processing behavior and varying foam qualities in the process.

For measurements of the compounds' humidity, two different methods are used.

Karl–Fischer-titration (KFT)[27] is the common method for measuring the amount of water in a sample. The basis of this titration is the oxidation of sulfur dioxide by iodine in a methanolic hydroxide solution. The titration is based on the following reaction[28,29]:

$$H_2O + I_2 + SO_2 + CH_3OH + 3RN$$
$$\rightarrow [RNH]SO_4CH_3 + 2 [RNH]I \qquad (1)$$
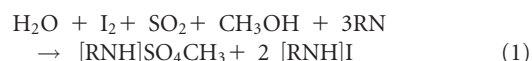
Karl–Fischer-titration is precise and accurate. The quantity of sample needed for one measurement is small, yet the measurement duration is quite long. Due to the accuracy, this method is used as a reference method for water amount determination.[26,27] Samples are heated up to 100 °C in an inert atmosphere of nitrogen to prevent thermal degradation and oxidation.

Apart from KFT, humidity measurements are done using the HydroTracer FMX by aboni GmbH, Schwielowsee, Germany. Hydro Tracer is a quick method to determine the water amount in samples based on the reaction of water and the reagent in the reactor under isothermal conditions (210 °C). Due to the quick and sufficiently precise measurements, Hydro Tracer seems suitable for measurements during production. The water within the sample evaporates and flows over the reagent. The following reaction produces hydrogen according to the following equation[30]:

$$CaH_2 + 2 H_2O \rightarrow Ca(OH)_2 + 2 H_2 \qquad (2)$$
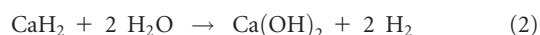
The concentration of hydrogen is measured by the thermal conductivity of the gas. From the amount of hydrogen measured the amount of water can be calculated. The measuring conditions are listed in Table IV. The measuring time in the hydro tracer varies over all measuring points as measurements stop at a constant measuring value.

Mooney-Viscosity. Mooney viscosity is one of the main key figures to classify elastomer compounds and compounding reproducibility. It gives first information on the processing behavior, for example, extrusion and injection molding properties. Moreover, the viscosity of an elastomer compound influences the foaming behavior. The necessary energy for cell growth is dependent on the melt stiffness at the time the blowing agent

Table V. Measuring Parameters for Vulkametric Investigations (RPA)

Parameter	Unit	Value
Temperature	(°C)	180
Preheating time	(min)	0.5
Measuring time	(min)	15
Frequency	(Hz)	1.667
Amplitude (Angle)	(%)	7

decomposes. That melt stiffness is contingent on the viscosity of the unvulcanized compound and the degree of vulcanization. To examine the compound's viscosity, the Mooney viscosity is measured by Mooney Rheometer MV2000 from Alpha Technologies, Akron, USA. The measurements were conducted using the measurement protocol ML(1 + 4), 100 °C.

Vulcanization and Pressure Build-up Measurements in the RPA. In addition to Mooney viscosity, vulcametric investigations in a RPA are another standard for classification of the properties of elastomer compounds. The RPA measurements with completely filled measuring chamber allow to measure the internal pressure development over vulcanizing time. Pressure measurements are especially helpful to characterize foaming compounds: It is crucial for later processing to get information on the degree of vulcanization, which influences the melt stiffness and its viscosity, at the time when maximum foaming pressure is reached. At maximum foaming pressure, the highest density drop rate and the highest cell growth rate are expected. Thus, the combination of foaming pressure and degree of vulcanization can be used to describe foaming. In the Vulkameter RPA 2000 of Alpha Technologies LLC, Akron, USA, the vulcanization behavior of all compounds is measured and overlapped with the pressure build up caused by the decomposing blowing agent. The samples are measured at 180 °C for 15 minutes. The measuring parameters are shown in Table V.

Injection Molding

Foamed elastomer molded parts are used in many applications due to their low weight, variable foam structures and densities and specifically adaptable mechanical properties. One exemplary application is dynamic sealings, which require good elastic recovery on the one hand, not too high pressure stiffnesses and a smooth, closed surface on the other hand. To validate whether water-foaming is suitable to meet these requirements and whether the compounds produced can be processed, injection molding tests were conducted using the injection molding machine Maplan MTF 750/160 from Maplan, Ternitz, Austria. The samples are made by breathing mold technique (Figure 2). This technique requires a compression mold: After injection of the melt, which completely fills the cavity and a residual time of 100 s, the mold is opened by 2 mm. The mold opening initiates the foaming process. After foaming and the heating time, the mold is opened and the sample demolded. Main advantage in the breathing mold concept is the controlled foaming process after a defined residual time and melt temperature. During the residual time, the injected melt is under pressure within the completely filled cavity, which prevents preliminary foaming. The pressure increases due to thermal expansion until the foaming process itself is initiated with the partial opening of the mold. Further investigations will include varied residual times as well as different melt pressures during the holding time in order to analyze the influence of the pressure drop rate and the degree of vulcanization at the initialization of the foaming process.

The mold is a circular disc with a diameter of 100 mm with capability to adjust sample thickness from 5.3 to 15 mm. Constant and varied process parameters for the injection molding trials are listed in Table VI.

RESULTS AND DISCUSSION

Foaming Behavior in SRA

The results of WCB compounds are shown in Figure 3, and of WSil in Figure 4.[31] The Azo sample is the reference. The
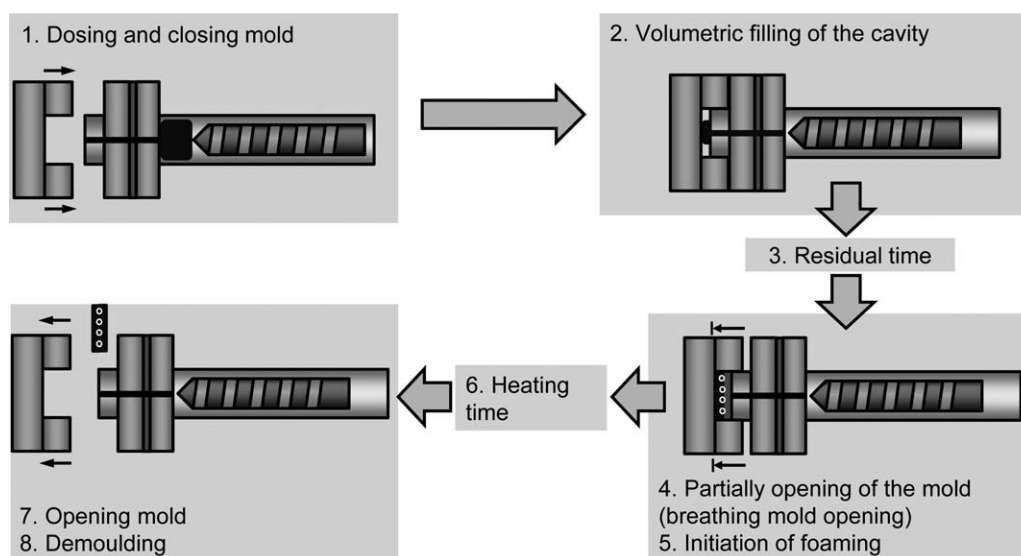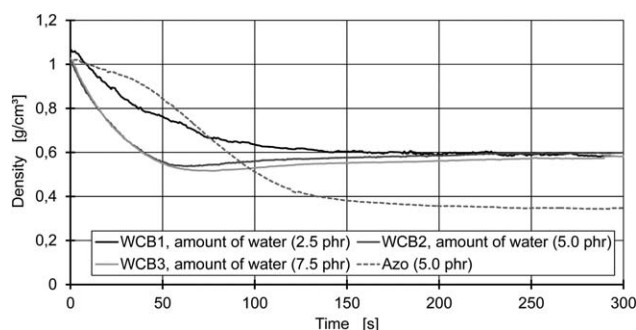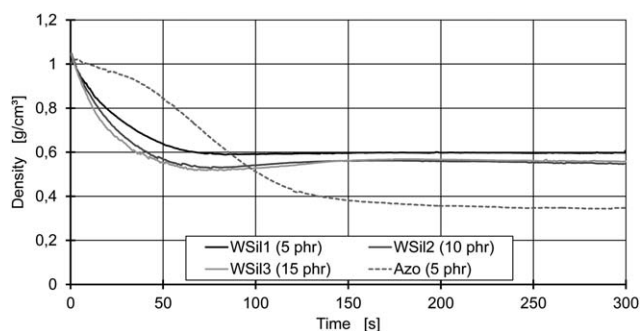

Figure 2. Process sequence of the breathing mold technique in injection molding.

Table VI. Process Parameters in Injection Molding

Constant parameters	
Process parameter	Values
Dosing volume (cm^3)	37
Injection speed (mm/s)	25
Strips intake temperature (°C)	80
Cooling channel temperature (°C)	50
Total cycle time (s)	200
Height of completely closed cavity (mm)	5.3
Breathing mold opening (mm)	2
Residual time (s)	100
Maximum injection pressure (bar)	75
Varied parameters	
Mold Temperature (°C) 180 185 190 195 200 205 210	

Figure 4. Density reduction curves of WSil in the SRA salt bath at 200 °C (Reproduced from [31]).

compounds used for this test have been stored 7–10 days before analysis, which represents a common storage time in elastomer processing. The density of the bulk material was measured to be 1.10 g cm^{-3}. The reference Azo reaches lowest density of all measurements (0.35 g cm^{-3}). During the first 40 s of the measurement, the density of Azo samples is reduced slowly, which can be explained by thermal expansion and a slow beginning of the decomposition of the blowing agent. Low thermal conductivities of the elastomer compound hinder the energy transport to the blowing agent. As more energy is delivered to the blowing agent, it decomposes and produces foaming gas. Thus, the density gradient increases. The final decrease of the gradient is explained by the increasing vulcanization, which ultimately ends the foaming process at about 200 s. All density reduction curves deliver information about the material behavior while heating up, foaming and vulcanizing at the same time. As a result, the density reduction itself describes an overlap of thermal expansion and foaming, which are both more and more slowed down by increasing degree of vulcanization. One limit of this measurement is the restricted possibility to isolate one single effect.

Compared with Azo samples, both, WCB and WSil compounds show different foaming behaviors: Due to changed foaming mechanisms and lower decomposition temperatures,[18,19] foaming occurs immediately after a sample is dipped into the salt bath. Other than the Azo compound, for both WCB and WSil, the highest density gradient is between 0 and 40 s. As the maximum content of water-based blowing agent is 8.5 wt % (WSil3), a significant change in the thermal expansion behavior of the varied material combinations can be ruled out as main reason for the high density reductions at the measurement's beginning. Apart from the lower decomposition temperatures of water, one further effect can be, that vaporizing water draws energy from the vulcanizing system. An argument against this thesis is the earlier end of the foaming process, which is usually stopped by too high degrees of vulcanization. The different measuring curves indicate different cause–effect relationships when using water as blowing agent. These mechanisms cannot be completely explained yet.

The minimum density of 0.5 g cm^{-3} is reached after 60 s, 140 s earlier compared with the reference. This equals an expansion ratio between 1.8 (WCB samples and WSil 1) and 2.2 (WSil2 and WSil3). The low gradient and late end of the foaming process after 150 s for WCB1 and the slightly reduced gradient for WSil1 can be explained by the lower amount of blowing agent within the compound, which leads to lower blowing pressures. Altogether, an influence of the amount of water on density reductions can be found: Increasing amounts of water increase the density gradient, because they cause higher blowing pressures. For the same reason, a slight decrease in the final density can be found for increasing amounts of water. Yet, the final

Figure 3. Density reduction curves of WCB in the SRA salt bath at 200 °C [Reproduced from (31)].
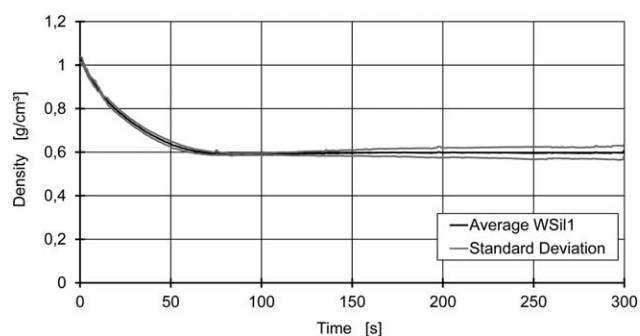
Figure 5. Standard deviations of SRA measurements of WSil1.

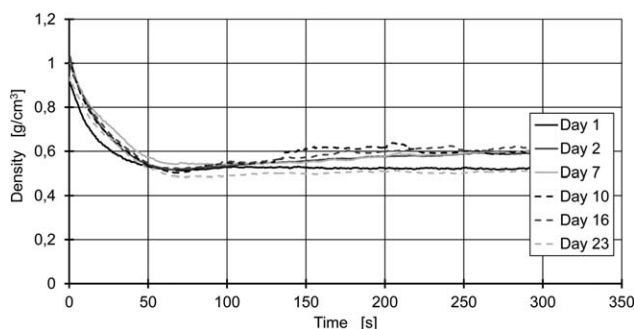**Figure 6.** Density curves of WCB2 over time after storage.

Figure 8. Water content of WCB2 over storage time.

density is only slightly affected by the amount of blowing agent, which leads to the conclusion, that also the vulcanization reaction is influenced by the amount of water.

Representing all measurements in the SRA, Figure 5 shows the high reproducibility of the SRA principle. Especially during the foaming phase, the standard deviations are very low. Variations after long time may be caused by diffusion of the blowing agent through more or less thick wall areas of the samples.

Humidity Changes in the Compound over Storage Time

It is expected, that, due to the hydrophobic matrix (EPDM), water contents within the compounds may cluster over a long storage time. Moreover, a water concentration gradient between the compound and the surrounding air can influence both global water content within the loaded compounds and the local water content beneath the surface. Consequently, it is assumed, that the water content within water loaded elastomer compounds does not remain constant over a long storage. The diffusion-caused change of water contents is dependent on the bond energy between water and carrier substance.

In the following, the representative results for WCB2 and WSil2 are presented. The density reduction over time from SRA for different storage times of the compounds WCB2 and WSil2 are shown on Figures 6 and 7. As can be seen from the graphs, the density reduction of both compounds does not change much after long time of storage. The density reduction achieved for both compounds during 23 days of storage is in the range of 0.5 g–0.6 g cm^{-3}. Variations of the measurement are within the accuracy of the experimental setup. These results lead to the conclusion, that the physical bond between both examined water carriers, carbon black and silica, and the added water is high enough to bind water even during storage.
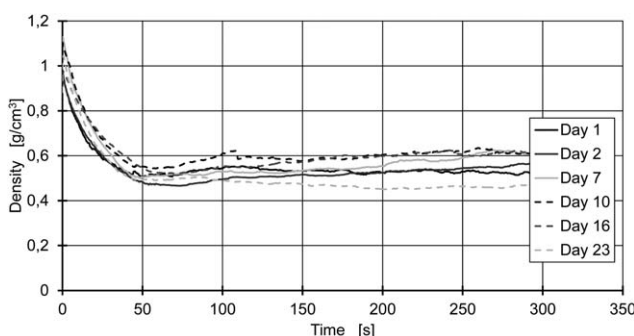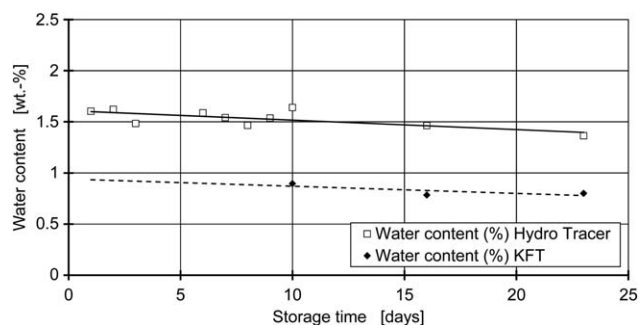
Figures 8 and 9 show the humidity measurements made with Hydro Tracer and KFT for WCB2 and WSil2. For both materials, the measurements with Hydro Tracer differ from the results from KFT. Main reason for this difference may be found in the different measuring temperatures. As a result, KFT measurements may differ from the real water content in samples: Silica with bound water emits water over a temperature range, which may exceed 100 °C, dependent on the amount of water loaded to the silica and the specific surface energy, which has to be provided. In future, KFT measurements will be done at higher temperatures as the measurement itself is assumed to be more accurate. The Hydro Tracer results are close to the calculated water amounts (1.8 wt % for WCB2 and 2.4 wt % for WSil2). The tendency of both measurements remains the same: A small decrease of water amounts can be seen over storage time for both compounds. Solved water diffuses out of the compound. This decrease is slightly higher for WCB compounds, because the carbon black used has a smaller specific surface and a weaker physical bond to water. Yet, due to the mentioned variations within both measurements, the amount of water remains nearly constant over a long storage time. These results also confirm the foaming measurements in the SRA. In order to explain the diffusion effects more detailed, further measurements including a wider variation of water carriers, amounts of water and water fractions attached to carriers, will be necessary.

The storage properties of the water-loaded elastomer samples provide an important basis for production: A flexible production needs storage time of elastomer compounds, as the lot sizes become smaller while the compounding aggregates remain the same. As storing is basically possible for the examined compounds, one important requirement for the material was met.
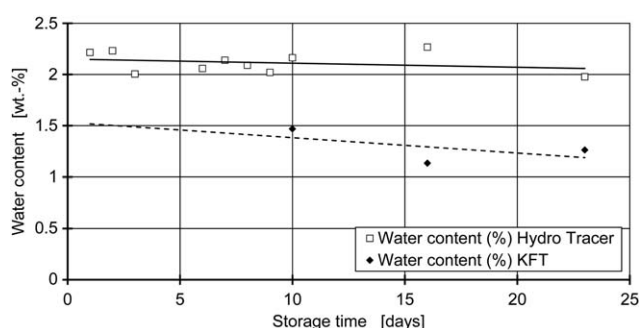

Figure 7. Density curves of WSil2 over time after storage.

Figure 9. Water content of WSil2 over storage time.

Table VII. Mooney Viscosity of all Compounds

Mixture	Mooney viscosity [ML(1 + 4) 100 °C]
Azo	34.20 ± 0.16^a
WCB1	41.67 ± 0.12
WCB2	40.60 ± 0.14
WCB3	42.37 ± 0.19
WSil1	41.17 ± 1.54
WSil2	39.77 ± 1.84
WSil3	40.40 ± 0.22

[a] Previous measurements with the same compound result in 38.83 ± 0.4 MU.[32]

Mooney-Viscosity

The Mooney-Viscosity for all samples, averaged over three samples, is shown in Table VII.

The viscosity of all water-containing compounds is around 40 ml (1 + 4) 100 °C within measuring accuracy of the viscosimeter. Consequently, the amount of water added to the compounds does not significantly influence the viscosity, which leads to the assumption, that the processing properties in extrusion are constant for all the water-filled compounds.

The Azo compound shows a significantly lower Mooney viscosity (34.2 MU). A lower viscosity not only improves the ease of processing, but may also increase the risk of cell walls to rip open while foaming. This can be an explanation for lower densities measured for the compound as well as varying cell structures: Cell walls can rip open while foaming, if the viscosity and with that the melt stiffness are too low when the blowing agent decomposes. Yet, previous investigations with the same Azo compound resulted in significantly higher Mooney viscosities (38.83 ± 0.4 MU).[32] Thus, an error in the measurement of this compound cannot be ruled out.

Still, the Mooney viscosity of Azo compounds remains lower than the viscosity of water-loaded compounds. A possible explanation for the higher viscosity of water-loaded compounds may be a worse filler dispersion: During the mixing process the compound suffers high shear energy and temperature increase, which can partially vaporize the bound water within the compound. Then, water acts as plasticizer, less shear tension can be transferred to the compound and the dispersion rate decreases. The influence of mixing process, mixing sequence, and compound recipe on material properties have to be cleared before transferring water-foaming to industrial application.

Vulcametric Investigations: Curing Behavior and Foaming Pressure

Another influential factor on the melt stiffness is the vulcanization degree of the sample in the moment of the blowing agent's decomposition.

The results of the vulcametric measurements are shown in Figure 10 (WCB compounds compared with Azo) and 11 (WSil compounds compared with Azo). In vulcanizing reactions, the
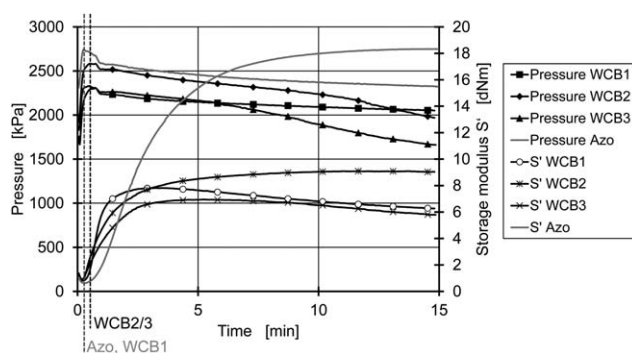

Figure 10. Pressure and storage modulus of WCB and Azo compounds from RPA.

maximum storage modulus for all water-loaded compounds is reduced by at least 50% compared with Azo compounds. Moreover, the vulcanization reaction is initiated earlier for all WCB and WSil compounds. In previous literature it has been stated out that the vulcanizing system, especially activators or accelerators like zinc oxide can influence the vulcanization process and contribute to forming a catalyst.[33,34] This may be one explanation for earlier initiation of the curing process. Further possible explanations, which have to be examined in future, may be found the influence of different viscosities (all water-containing compounds have nearly the same viscosity and start of vulcanization reaction, while the viscosity of Azo compounds has a lower viscosity and thus a lower shear heating), varying thermal conductivities or plasticizing effects due to the water.

Another conclusion, which can be drawn from the vulcametric investigations, is an influence of water on the vulcanization accelerator: Increasing amounts of water lead to lower reaction rates for both WCB and WSil. Yet, the effect described is stronger with water bound to silica particles. One possible explanation is the high surface of silica particles and thus high surface of water within rubber compounds when bound to silica particles. Water, which is added to the compound in combination with carbon black, can cluster together and thus have less surface to interfere with the vulcanization system, while water bound to small silica particles has a higher degree of dispersion within the compound. This theory can be supported by the fact, that increasing amounts of water in WCB compounds also delay the point of maximum pressure: Bigger the water clusters
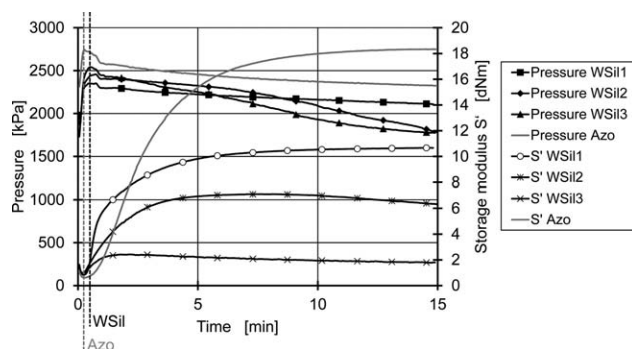

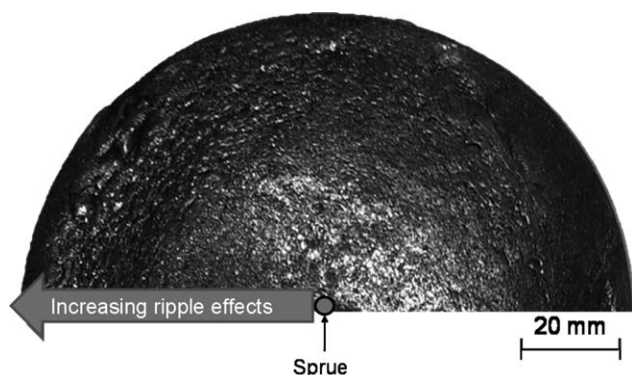**Figure 11.** Pressure and storage modulus of WSil and Azo compounds from RPA.

Figure 12. Rippled surface due to condensation of water within foam cells.

within a compound require more energy to vaporize.[35] Moreover, due to the enthalpy of evaporation of water, the foaming process draws energy out of the compound. This reduces the energy provided to the vulcanizing system. To prove this assumption, the material and reciprocal interactions between different substances will have to be measured by DSC analysis, as it was found, that RPA analysis is not sufficient to describe all working effects. As the density reduction observed is the same for all amounts of water, the reduced storage modulus for increasing amounts of water cannot be explained by foam specific reduction of hardness.

As can be seen from Figures 10 and 11, the reference compound, which is foamed with Azo, the foaming reaction occurs at minimum vulcanization degree (i.e., viscosity). This supports nucleation. For WCB as well as WSil, foaming starts while vulcanization process has been initialized. The storage modulus in WCB and WSil compounds in the moment of maximum pressure is twice as high as in Azo compounds. So far, no explanation for this effect could be found. Due to a higher reaction temperature of ADC compared with a vaporization temperature of water and the exothermic reaction of ADC, an inverted effect would have been assumed.

Due to the early state of investigations on foaming elastomers with water, none of the theories mentioned could be proven so far. The cause–effect relationships between water vaporization and vulcanization reaction are a central aspect of further investigations.

Influence of Varied Mold Temperatures on the Processability in Injection Molding

During processing it can be seen that produced parts are deformed due to the expansion within the restricted volume of the mold: While foaming in the rear end of a part is limited by the vulcanized edge, foaming in the parts' center causes a bulge of the whole part. After demolding and cooling, water within the cells condensates and creates a vacuum. As a result, the parts' surface becomes rippled. This effect increases from center (sprue) to the parts' rear end (Figure 12).

The rippled surface of the samples remains for months of storage, which may be an indicator, that diffusion of condensed water is low. Furthermore, the static spring constant of parts, which is not discussed in this article in detail, remains constant over time. However, when cutting samples, no water leaks out of cut cells, which contradicts the assumption of water remaining within cells due to low diffusion rates. Stored as well as freshly produced samples do not show significant change in spring constants. Until now, this question could not be answered finally. Currently, we are conducting precise gravimetric measurements of samples during a long storing time as well as at increased temperatures in order to measure the amount of condensed water on the one hand and, on the other hand, if water diffuses out of cells during processing and storage.

For the evaluation of injection molding trials, the cell structure is analyzed with focus on cell diameters. To measure average cell diameters, cross sections of the circular parts are analyzed using the digital image processing software OZELLA, which we have developed. The average cell diameters for WCB and WSil at different mold temperatures and compared with the Azo compound as reference are shown in Figure 13 and 14.
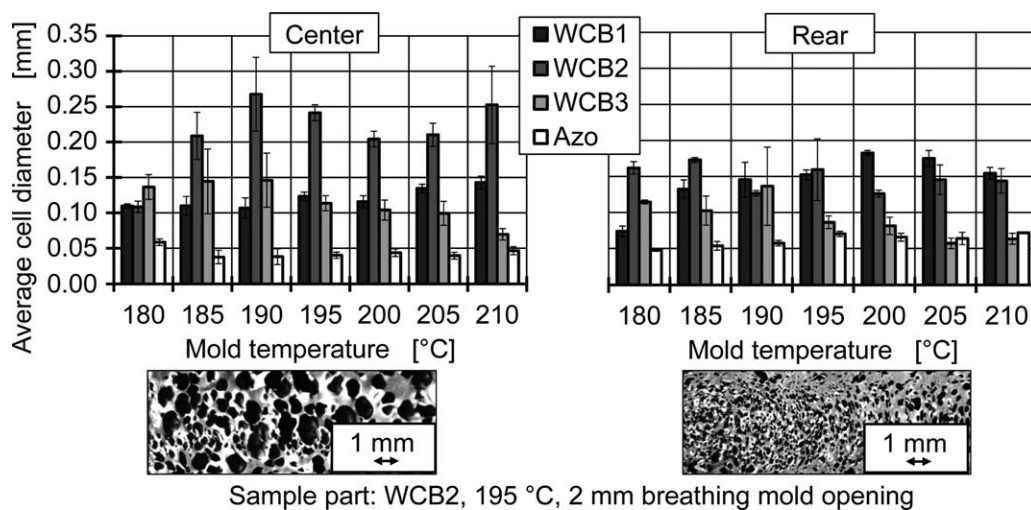

Figure 13. Average cell diameters in parts'center (left) and at rear end (right) (WCB).
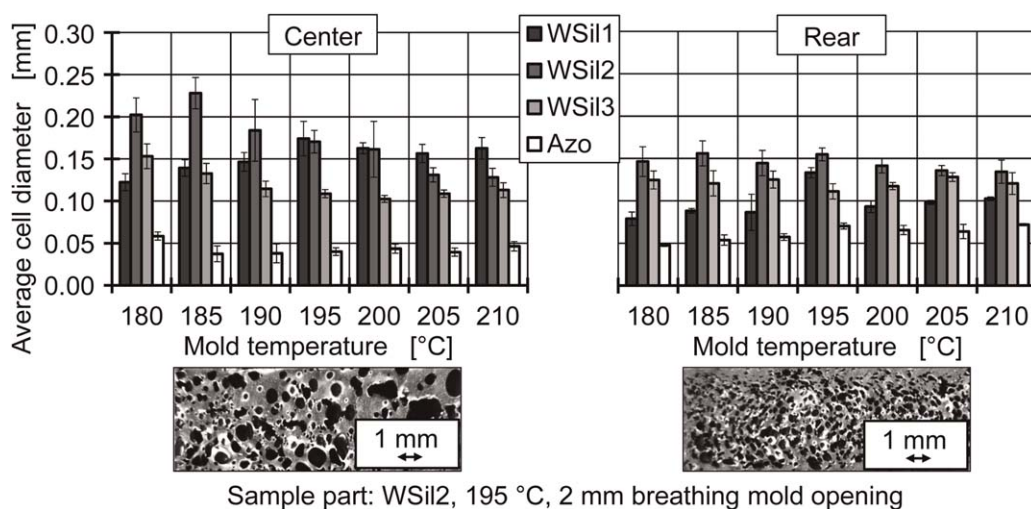
Figure 14. Average cell diameters in parts' center (left) and at rear end (right) (WSil).

The cell structures are evaluated separately in the center and the rear edge of each part. The cell structures differ due to the melt flow through the hot mold and thus the temperature increase in the melt. Furthermore, due to the bigger surface in the parts' rear end (including edge region), the vulcanized surface limits local volume increase, while the parts' center is subject to less limitations. Thus, the average cell diameters in the parts' center exceed the average cell diameters in the rear end. The average cell diameters in the parts' center range from 0.10 mm up to 0.25 mm for WCB and WSil compounds. For Azo compounds, average cell diameters are constant over the parts' cross sections with 0.05 mm.

For the reference compound (Azo), no significant influence of the mold temperature can be seen. This is a result of the breathing mold technique, which was initially built to maintain a counter pressure in physical foaming processes. In chemical foaming the blowing reaction occurs after melt temperature exceeds a certain temperature. A further increase of temperature does not influence the blowing reaction anymore, especially as long as the volume increase is limited by the closed mold.

As the main mechanisms of water foaming and chemical foaming are comparable during processing, it can be explained that varying mold temperatures do not significantly and strongly influence the average cell diameters for both WCB and WSil samples. Variations in WCB samples may be caused by dispersed water in the compound, which can migrate during plasticizing. This migration does not occur for WSil, because of the physical bonding between water and silica.

For high amounts of blowing agent, especially in WCB compounds, the average cell diameter decreases slightly with increasing mold temperature. This effect can be caused first, by the pressure drop over time, which can also be seen in RPA investigations: Due to high temperatures, the diffusion barrier in the elastomer is decreased and water can diffuse out of the rubber. Second, higher temperatures increase the vulcanization rate and thus, considering the constant residual time, the vulcanization degree, when the breathing mold is opened for foaming.

CONCLUSIONS

In the context of this research, water as a physical foaming agent, its foamability, and processability are characterized. Water containing substances (carbon black and silica) have significant effects on the properties of the samples in compounding, storage conditions and processes.

The results of material characterization show great potential of water as a physical foaming agent. All compounds examined reach a final density of 0.5–0.6 g cm^{-3}. These values are stable over time as shown in the time standing test. In the RPA results, compared with reference compounds, the storage modulus of all water-containing compounds is much lower. Water-loaded compounds show time-dependent properties and water content reduces the maximum reached vulcanization degree measured in the RPA.

The behavior of water-loaded compounds in injection molding process shows low procedural influences on cell properties: The average cell diameters remain mostly constant, which can be explained by the process technique used (breathing mold). Furthermore, the average cell diameters still exceed those of chemical blowing agents (ADC) and the variance between average cell structures close to the sprue and at the far end of a part is higher for water foaming.

In further investigations, variations of the curing system will be made in order to increase the degree of vulcanization. The effect mechanisms of foaming with water overlapped with the effect of vulcanization has not been explained sufficiently yet, and have to be a central aspect of further investigations. Apart from the curing the water carrying substances strongly influence the whole process chain from compounding to further processing. These water carriers, as well as their influence on nucleation and evaporation temperatures, will be another focus of further investigations. Moreover, separate nucleating agents (e.g., glass fibers, flax fibers, talc) can be used, to homogenize cellular structures and stabilize the foaming process.

After foaming water will condense and consequently create a vacuum within foam cells. Further investigations will be

necessary to measure the influence of the vacuum on foam structures, surface quality of injection molded parts and extruded profiles. Especially the dependence of vacuum and material-dependent diffusion of water out of the foamed part or profile will be focused in these investigations.

Concerning process investigations, extensive tests will be done on the influence of process parameters in compounding as well as injection molding and extrusion process. As it is known from production, the presence of water can strongly influence a continuous extrusion process and cause pressure fluctuations, the process stability is an important factor for further studies. Moreover, the continuous vulcanization process, especially the type of energy input into the compound shows a high impact on the foaming behavior, which has to be examined in follow-up studies.

ACKNOWLEDGMENTS

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