JULY 2018

# RubberWorld

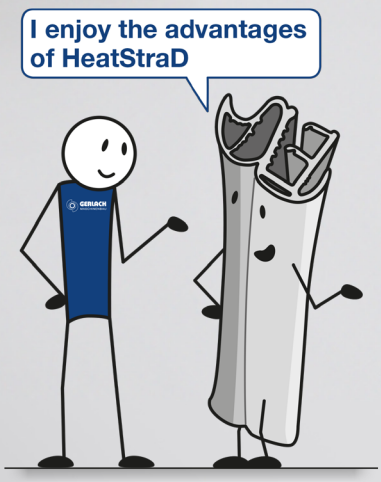
120 years

THE TECHNICAL SERVICE MAGAZINE FOR THE RUBBER INDUSTRY VOLUME 258, NO. 4


We Listen To Your Product

## Development of a novel vulcanization test and measuring system to support process optimization in continuous vulcanization

*by Christian Hopmann, Florian Lemke, Jan Philip Peter and Patrick Gahlen, Institute of Plastics Processing (IKV), and Jens Möckel, Gerlach Maschinenbau GmbH*




www.rubberworld.com

# Development of a novel vulcanization test and measuring system to support process optimization in continuous vulcanization

*by Christian Hopmann, Florian Lemke, Jan Philip Peter and Patrick Gahlen, Institute of Plastics Processing (IKV), and Jens Möckel, Gerlach Maschinenbau GmbH*

In the field of continuous vulcanization, combinations of infrared emitters (IR), hot air systems (HL) and microwave systems (UHF) are mainly used for heating sulfur crosslinked profiles (refs.1 and 2). Used individually, all energy transfer methods (radiation [IR], convection [HL] and dissipation [UHF]) result in inhomogeneous heating: Infrared radiation and convective hot air heating initially heat the profile surface and convey the energy inside the cross-section with a delay. According to literature, although microwave radiation heats the entire profile cross-section of the polar or electrically or ionic conductive materials, the resulting process is subject to high levels of fluctuation (refs.1-7). These fluctuations are often caused by a complex interaction between the distribution of the electromagnetic field in the UHF system and the temperature-dependent absorption capability of rubber materials. Overall, the implication is, therefore, that a reasonably homogeneous heating, and therefore vulcanization, can be achieved only through a combination, sequence and balancing of various vulcanization methods that are tailored to the specific material.

Although the heating behavior of rubber profiles for various vulcanization methods can be described in principle (refs. 5, and 8-12), a means of controlling the vulcanization process, for example based on process-integrated modeling of temperatures or crosslinking behavior, is not known to date. In industry, therefore, vulcanization processes are configured and optimized based on general recommendations, as well as knowledge and experience (ref. 13). A key problem that has not been solved to date, and which has largely prevented a closed-loop control of the continuous vulcanization process, is that it is not possible to measure local temperature within the cross-section of a profile or to determine the level of crosslinking. Although various, and in some cases patented, methods of measuring the level of crosslinking inline have been developed (refs. 14-16), none of these has achieved widespread use. This may be due to the fact that the instrumentation is prone to malfunction (in particular due to temperature), and that the measuring accuracy varies greatly between materials. Furthermore, an offline measurement of the level of crosslinking is not possible by any simple means to date, which is why many processing companies continue to work with compressive deformation set measurements for a final assessment of the crosslinking process.

Because no inline measurement during continuous vulcanization has established itself to date, it has also not been possible until now to perform an assessment of various vulcanization methods and approaches. Consequently, many, sometimes wildly differing approaches to continuous heating and vulcanization of profiles are being used (figure 1). One possibility is to use microwaves for primary energy input (Concept A), combined with a short shock crosslinking, for example using hot gas. The hot air channel merely has the function of maintaining an elevated temperature on the profile surface and is not used for further heating in Concept A. Concept B, by contrast, applies an intensive energy input by infrared radiation in the pre-shock before following the approach of heating the profile with very high hot air temperatures combined with microwaves (figure 1). Both of these concepts can achieve the desired results, but an assessment of their efficiency and process stability has not been possible to date due to a missing (temperature) measurement apparatus.

Joint research and development, therefore, has the aim of systematically assessing various process sequences and combinations of hot air and infrared and microwave radiation for heating and vulcanizing profiles using a newly developed vulcanization test and measuring system, as well as a laboratory vulcanization line.

### Crosslinking behavior of the EPDM blend used

For the experimental investigations, representative data for a sulfur crosslinking EPDM blend with carbon black filler will be presented. In addition to calorific material data, which are used for heating simulations, crosslinking isotherms were measured and used for calibrating a crosslinking model (refs. 18 and 19). The crosslinking model can in future be used for calculating a degree of crosslinking from a measured or simulated (local) temperature profile for a rubber profile (figure 2).

### Experiment planning and implementation

To conduct the experimental investigations, a novel vulcaniza-

**Figure 1 - schematic representation of various vulcanization concepts (ref. 17)**

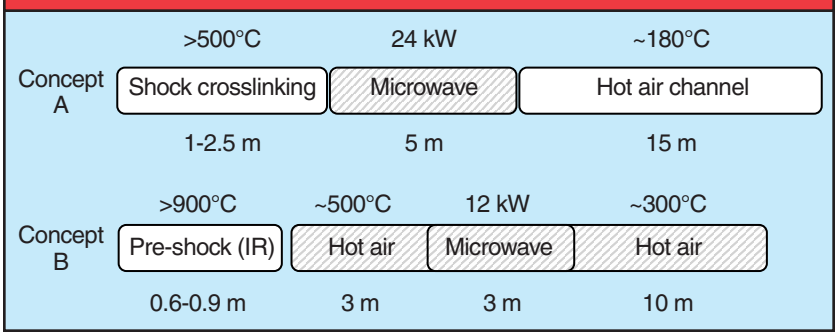
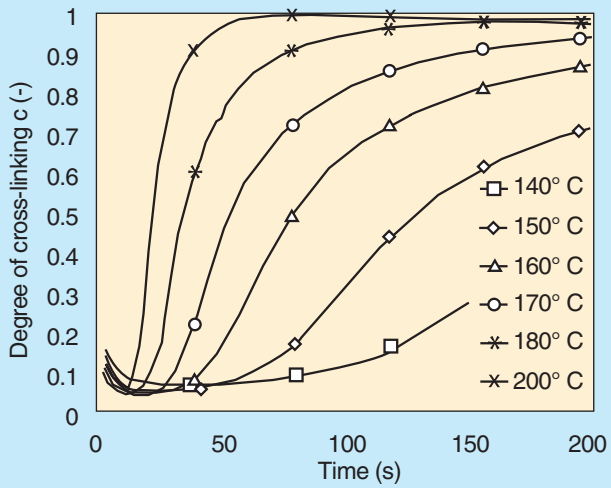


**Figure 2 - measured crosslinking isotherms of the EPDM blend**




tion test and measuring system has been developed, produced and employed for process optimization. This method allows a simultaneous or consecutive heating of a section of rubber profile using hot air, infrared radiation and microwave radiation, while at the same time continually measuring temperature in the profile cross-section (figure 3). The piercing thermocouples used are inserted into the profile to various depths to be able to measure the temperature at various points within the profile cross-section. Furthermore, continuous measurement and recording of the energy consumed by the system allows an energy assessment of the vulcanization process. In the investigation using the vulcanization test and measuring system, rectangular profiles with a cross-section of 20 × 30 mm² were vulcanized using hot air and infrared radiation in each case. The hot air temperature was 320°C, and the infrared emitter had a rating of 2 kW. The chosen vulcanization times were 180 seconds for hot air vulcanization and 48 seconds for infrared vulcanization. These times correspond to the dwell time of a profile in the laboratory vulcanization systems at the IKV at a

**Figure 3 - illustration of the vulcanization test and measuring system for process optimization**

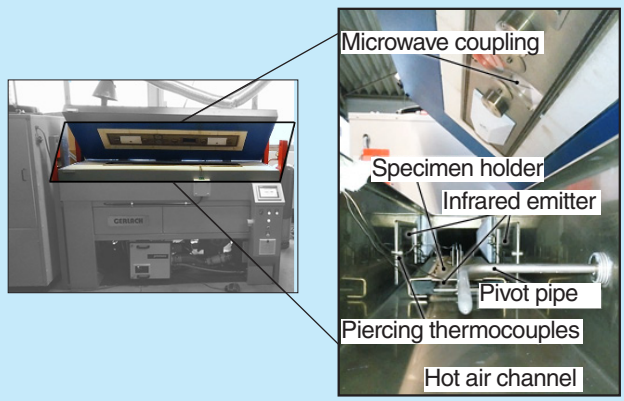



**Table 1 - set and varying parameters in continuous vulcanization**

| *Setting parameter* | *Unit* | *Value range* |
|---|---|---|
| Set air temperature | (°C) | 280-380 (9 stages) |
| Conveyor belt speed | (m/min.) | 0.3 1 1.5 2 3 |

throughput of 1 m/minute. A comprehensive parameter variation will be the subject of future investigations.

In addition to the new measuring device, experimental investigations are also being carried out on a laboratory extrusion line at the IKV, which consists of an infrared pre-shock and a hot air UHF combination plant. The data presented in this article are based exclusively on hot air vulcanization at various conveyor belt speeds and hot air temperatures (table 1). For the presented results, profiles with a rectangular cross-section (3 × 15 mm²) were vulcanized. To ensure consistent starting conditions for vulcanization, the profiles were initially stored after extrusion and fed into the vulcanization plant at room temperature.

At the same time, the energy consumed by the respective vulcanization plant was measured with energy meters at each process point. In addition, the material throughput for every conveyor belt speed was measured. From the energy consumed for vulcanization and the material throughput, the specific vulcanization energy was calculated:

$$e = P/\dot{m} \quad (1)$$

where:

e: Specific vulcanization energy

P: Energy consumed by the plant for vulcanization

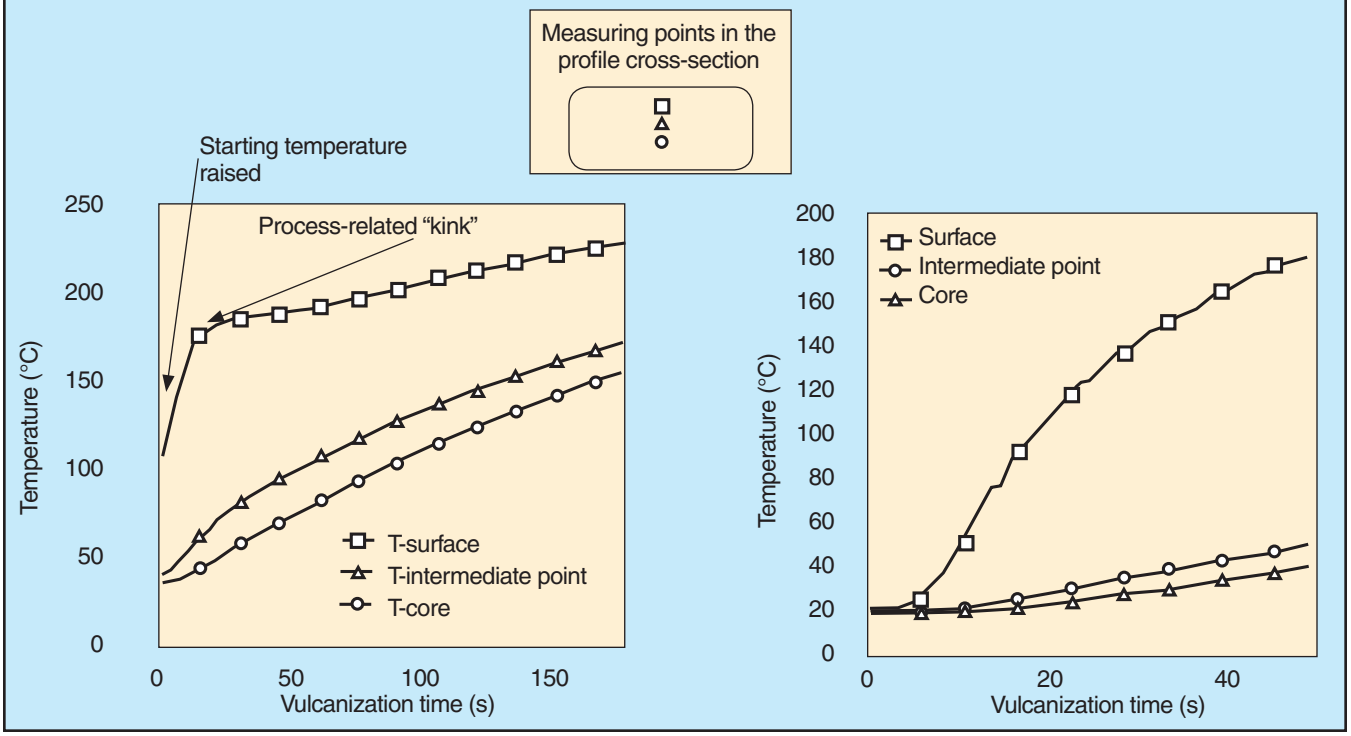
$\dot{m}$: Material throughput

By evaluating the specific vulcanization energy, the results of the parameter variation can be transferred to other throughputs, materials and, to some extent, also profile geometries, facilitating a generalization of the results. It will also be possible in the future to assess the energy efficiency of various process points, vulcanization processes or vulcanization methods by including in the equation the minimum energy required for heating and vulcanizing the material.

To be able to assess the state of crosslinking of the vulcanized profile not only globally, but also locally, in the cross-section, the durometer A hardness was measured at two points in the profile cross-section (in the center and near the surface) at room temperature. A decisive argument for using the durometer A hardness to determine the crosslinking state in the context of the presented investigations is the ease of preparing samples and the extremely short measurement duration, which also makes the method suitable for use in production, and its low susceptibility (with multiple measurements) to ambient conditions. The downside is a relatively high scatter compared with chemical or physical methods (e.g., DSC), which does, however, require significantly longer measurement durations and can be applied to only very small sections of a profile.

As a reference for a fully cured product, a pressed plate (press duration 10 minutes, temperature 160°C) was used. The reference of a fully unvulcanized product was measured on an

**Figure 4 - heating of rectangular rubber profiles in cross-section using hot air (left) and infrared radiation (right)**




unvulcanized profile cross-section at room temperature (ref. 18). The degree of crosslinking was calculated using the following formula (ref. 18):

$$c = (Sh_A - Sh_{Amin})/(Sh_{Amax} - Sh_{Amin}) \quad (2)$$

where:

c: (Local) degree of crosslinking

$Sh_A$: Durometer A hardness at measuring point

$Sh_{Amin}$: Minimum durometer A hardness (unvulcanized profile)

$Sh_{Amax}$: Maximum durometer A hardness (pressed plate)

**Heating mechanisms in the profile cross-section**

Figure 4 shows the heating trends over time of rectangular EPDM profiles heated using hot air (left) and infrared radiation (right). The temperature was measured in the center (core) of the sample cross-section, near the surface inside the profile (surface) and at a point between core and surface (intermediate point). The temperature profile near the surface on heating with hot air shows a starting value of 100°C, which is explained by the fact that the measurements were started only after the profile was fully inserted in the vulcanization test and measuring system, at which time it had already been exposed to the hot plant environment. The delayed temperature rise inside the profile is due to the material's low thermal conductivity.

A special characteristic of hot air vulcanization is highlighted by the kink in the temperature profile, which can be reproduced in all hot air measurements, irrespective of the material. The kink in the temperature profile can be explained by the fact that the rate of heating on the profile surface using convective heating is initially very high because of the high temperature difference between the hot air and the comparatively cold profile surface. The profile surface nearly reaches the temperature of the air after only a few seconds ("applied temperature"), after which the surface no longer heats up further. On further heating of the profile, the surface only absorbs the amount of energy that is transported into the inner part of the profile through thermal conduction. Because the measurement curve is recorded near, but not directly on, the surface, the further temperature rise, resulting only from thermal conduction, is less steep.

Where only infrared emitters were used for heating (figure 4, right), this kink does not occur. Because the temperature difference between emitter temperature and profile surface temperature enters the transferred heat flow in the fourth power in each case (Stefan-Boltzmann law), and the emitter temperature is significantly higher than the hot air temperature, a thermal equilibrium is not reached on the profile surface during the observed process times: The kink does not occur in the measuring range and the temperature rise on the profile surface remains steeper.

Applied to continuous vulcanization processes, this means that heating using infrared radiation at constant radiation intensity must not take place over a longer period because the surface, which continues to heat up, can quickly reach its decomposition temperature. A process-oriented approach could be, for example, a successive reduction of the emitter output along the production route, so that immediately after shock heating of the surface, an equilibrium of the surface temperature between applied radiation energy and energy dissipated to the environment through convection is reached. Heating or vulcanization using

hot air at hot air temperatures below the decomposition temperature, on the other hand, is possible over a longer period.

**Continuous vulcanization**

To ensure that the findings obtained with the vulcanization test and measuring system can be applied to continuous processes, experimental investigations were performed on a hot air plant using various air temperatures and conveyor belt speeds. Figure 5 shows that a high specific energy input is required for hot air vulcanization to vulcanize a profile to 80% (at least 10 kWh/kg). Because, as discussed above, a pressed plate was used as reference for measuring the degree of crosslinking, which, for process-related reasons, has a higher hardness than can be achieved with extruded products, the actual degree of crosslinking can be assumed to be significantly above 80% at this process point.

At a constant degree of crosslinking, process points with a higher throughput at a higher temperature generally make sense in terms of energy usage: The influence of the shorter dwell time clearly more than compensates the additional energy required for higher air temperatures (figure 5).

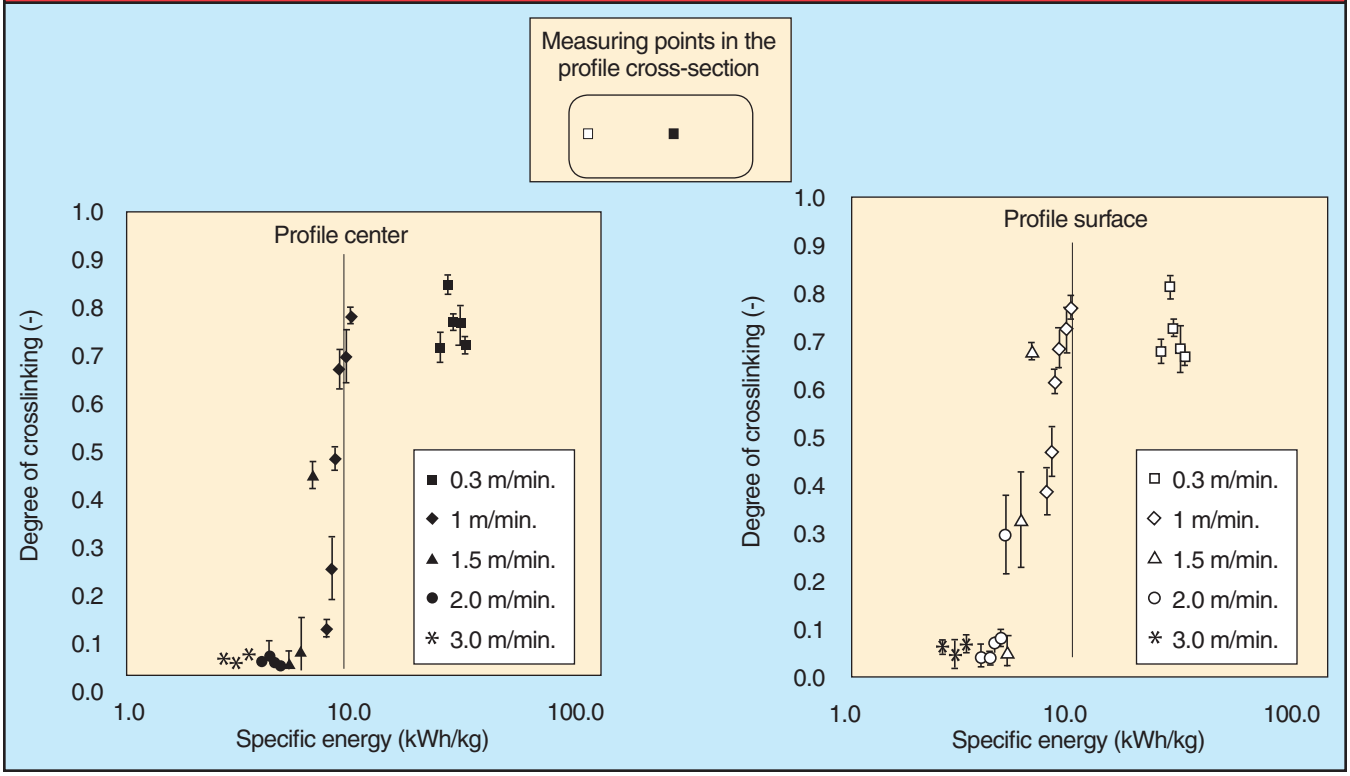
Figure 5 also shows that the difference between the degrees of crosslinking near the surface and those inside the profile is comparatively small in the case of hot air vulcanization, provided that the degree of crosslinking is already high. Especially at a low specific energy, inhomogeneous crosslinking can occur in the cross-section; i.e., a high degree of crosslinking at the profile surface and a low degree of crosslinking inside the profile. A significant reversion can generally be observed at low throughput and high vulcanization energy, although the high scatter requires further investigation. Overall, hot air vulcanization is a comparatively robust process, in which, as already demonstrated through measurement, very high energy levels and air temperatures are generally required for crosslinking.

**Conclusion and outlook**

In terms of thermal energy, continuous vulcanization is a highly complex process. Conveyed rubber profiles must be heated up in as short a time as possible and as homogeneously as possible across their entire cross-section with as low an energy input as possible. To this end, hot air, microwave and infrared radiation methods, which are usually used in combination, have established themselves in industrial environments. The combination, material-specific vulcanization strategy and required energy for vulcanization has, to date, been chosen and set based on knowledge and experience. An in-depth energy analysis, let alone process-integrated measurement, was not possible to date, because no measuring device capable of measuring the profile temperatures inside the profile during vulcanization was available.

As part of the cooperation between Gerlach Maschinenbau and the IKV, a vulcanization test and measuring system for process optimization has been developed, which allows temperature measurements during vulcanization of sections of rubber profiles. For vulcanization, hot air, microwave and infrared radiation are available, which can be used either successively or simultaneously. At the same time, a continuous measurement of the profile temperature is possible, for the first time allowing the heating-up behavior of rubber profiles to be measured.

**Figure 5 - influence of the specific vulcanization energy and the conveyor belt speed on the degree of crosslinking of rubber profiles vulcanized with hot air**



It was demonstrated that infrared vulcanization results in successive heating of the surface. An intensive use of infrared emitters over a longer period results in reversion and decomposition of the rubber profile's surface. Although the energy input also takes place via the surface when using hot air, it is possible here to expose a profile to the hot air over a longer period of time because a different energy transfer mechanism comes into play here: The profile surface reaches the temperature of the air after only a few seconds, after which it no longer heats up further. Subsequently, only the amount of energy that is transported into the inner profile through thermal conduction is applied to the profile. This implies, however, that the additional energy input in hot air vulcanization is theoretically not required or does not contribute to the crosslinking of the profile.

Experimental investigations confirm the findings from the measurements, and furthermore show that hot air vulcanization is a very robust, albeit extremely energy intensive process.

To be able to assess the energy efficiency of the various energy transfer mechanisms in the future, the energy required for a material for heating and vulcanization is currently being measured using dynamic scanning calorimetry (DSC). The efficiency of each process results from the ratio between the required energy for a material and the actually applied (specific) energy. To minimize the need for experiments, for example for engineering a process for new products, and to provide comprehensive explanatory approaches, heating simulations are currently being carried out for various materials and profile geometries.

This article was first published in the *Dichtungstechnik Jahrbuch* (in German language) in October 2017.

**References**

*1. A. Hill, Die Kontinuierliche Vulkanisation von Elastomerdichtprofilen: Stand der Technik und Neuentwicklungen, In: Verein Deutscher Ingenieure (pub.): Spritzgießen und Extrudieren von Elastomeren, Düsseldorf: VDI-Verlag, 1996.*

*2. F. Röthemeyer and F. Sommer, Kautschuk Technologie, Munich, Vienna: Carl Hanser Verlag, 2013.*

*3. V. Bovtun, W. Stark, J. Kelm, V. Porokhonsky and Y. Yakimenko, "Microwave dielectric properties of rubber compounds undergoing vulcanization," Kautschuk Gummi Kunststoffe, 54 (2001), 12, pp. 673-678.*

*4. L. Köster, H. Perz and G. Tsiwikis, Praxis der Kautschukextrusion, Munich: Carl Hanser Verlag, 2007.*

*5. B. Krieger, "Microwave vulcanization: A lesson in business and technology," In: MRS Proceedings, Cambridge University Press, 1994.*

*6. A. Limper, P. Barth and F. Grajewski, Technologie der Kautschukverarbeitung, Munich, Vienna: Carl Hanser Verlag, 1989.*

*7. N. Makul and P. Rattanadecho, "Microwave pre-curing of natural rubber compounding using a rectangular wave guide," Communications in Heat and Mass Transfer, 37 (2010), pp. 914-932.*

*8. P. Le Bideau, J.P. Ploteau, P. Duturnie and P. Glouannec, "Experimental and modeling study of superficial elastomer vulcanization by shortwave infrared radiation," International Journal of Thermal Sciences, 48 (2009), 3, pp. 573-582.*

*9. G. Milani and F. Milani, "A numerical model for the optimal vulcanization of 2-D polar rubber compounds using microwaves," Macromolecular Theory and Simulations, 18 (2009), 6, pp. 336-354.*

*10. G. Milani and F. Milani, "Optimization of extrusion production lines for EPDM rubber vulcanized with sulfur: A two-phase model based on finite elements and kinetic second order differential equation," Computers & Chemical Engineering, 43 (2012), pp. 173-190.*

*11. G. Milani and F. Milani, "Kinetic finite element model to optimize sulfur vulcanization: Application to extruded EPDM weatherstrips," Polymer Engineering & Science, 53 (2013), 2, pp. 353-369.*

*12. F. Podzelny, "Mikrowellen- und heißluftenergie," Kautschuk Gummi Kunststoffe, 56 (2003), 7-8, pp. 372-373.*

*13. H. Klein, "Vulkanisationsverfahren richtig ausgewählt," GAK, 56 (2003), 4, pp. 232-235.*

*14. J. Kirchhoff, Die Messung des Vernetzungsgrades an Elastomeren Werk-stoffen mit einem Ultraschallverfahren, Düsseldorf: VDI Verlag, 2001.*

*15. N.N.: DE 10 2010 021 260 A1 2001.11.24: Verfahren und System zur Qualitätskontrolle, Offenlegungsschrift, Deutsches Patent- und Markenamt, November 24, 2011.*

*16. G. Zimmer, A. Guthhausen and B. Blümich, "Characterization of crosslink density in technical elastomers by the NMR-MOUSE," Solid State Nuclear Magnetic Resonance, 12 (1998), 2, pp. 183-190.*

*17. S. Sitz, Kontinuierlich Arbeitende Vulkanisationsstrecken - Stand der Technik und Potenziale, Promotionsvortrag, RWTH Aachen University, February 2, 2015.*

*18. C. Hopmann, F. Lemke and J. Möckel, "Simulation and energetic optimization of continuous vulcanization processes," 190th Technical Meeting, International Elastomer Conference (IEC), Rubber Division, ACS, Pittsburgh, PA, October 10-13, 2016.*

*19. C. Hopmann, F. Lemke and J. Möckel, "Analysis of the efficiency of continuous vulcanization processes," Kautschuk Gummi Kunststoffe, 70 (2017), 4, pp. 20-24.*