Technical

# A comparative study looking at effects of curing kinetics and batch variation on SBR injection molding and numerical analytics

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## Executive summary

The effect of internal batch variations of industrially manufactured rubber compounds plays an important role in rubber processing because it has, among other things, considerable responsibility in quantitative usability of any injection molded product and, for this reason, affects the level of production costs.

Consequently, one of the main characteristics is the degree of crosslinking, which, depending on the polymer, curing system, activators and other additives on the one hand, and on physical properties such as internal forces or homogeneity on the other hand, defines the quality of the final part. Furthermore, reaction kinetics in terms of temperature represent an essential criteria for manufacturing.

In this study, the degree of cure is pointed out for multiple batches of industrially made, highly filled SBR by means of vulcanization temperature in the range of 150-170°C. To investigate the magnitude of the mentioned batch variations on the quality of the final part with respect to its curing behavior, the registered data were statistically evaluated to provide a time profile for part manufacturing that describes a considerable range of variability. The received rubber samples were then analyzed regarding their degree of cure with the aim of drawing conclusions between reaction temperature and reaction time with mechanical properties of cured rubber compounds.

In addition, a simulation program for rubber injection molding was used for a comparison of virtually manufactured parts with parts from real processing.

The manifoldness of rubbers is an issue that is well known by people working in this area, as the possibility to drive a compound's behavior according to specific requirements by changing only the relations between the ingredients seems almost infinite.

**TECHNICAL NOTEBOOK**
*Edited by John Dick*

A conventional illustration for this property is the famous "magic triangle" of tire performance, which indicates the cohesive effect of rolling resistance, wear resistance and wet grip when amounts of the base polymer, fillers, plasticizers or curing system are changed. From a more specific point of view, the ratio of the mentioned components also strongly affects the reactions and interactions on the molecular level of the compound. As a result, the curing kinetics, which are responsible for the final part properties such as dynamic and static modulus, compression set or tensile strength, differ.

Based on this viewpoint, it is of utmost importance for process engineers to have comprehensive knowledge on the distribution of the relative degree of cure in the final product.

At the present state, we know several different methods that allow us the exploration of the degree of cure in rubber parts. One example for a very fast responding possibility to analyze the conversion of rubber is Fourier-transform infrared spectroscopy (FT-IR), where changes of characteristic absorption peaks are concluded as an effect of crosslinking reaction that occurs upon heating.[1]

In recent times, an interesting and promising method to do qualitative and quantitative analysis on rubbers was found in ion mobility spectrometry (IMS), which tries to explore a specific fingerprint of these compounds and draws conclusions on the composition.[2] The swelling experiment is very popular in the analytical world of rubber in order to determine the degree of cure of parts. Its theory is based on an isotropic expansion and an opposed force, induced by the interaction of rubber and solvent.[3,4]

The compression set is a state-of-the art measurement method that determines the degree of cure, but also the mechanical behavior of rubber parts with respect to its relaxation after compressing the specimen for a defined time and temperature.[3,4]

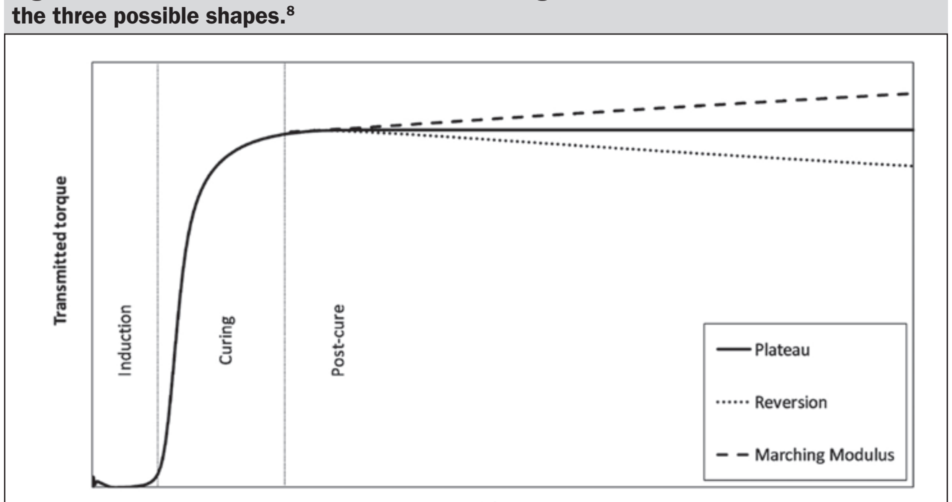
Another common way to obtain the degree of cure is to measure the formation of crosslinks at isothermal conditions with a rubber process analyzer (RPA). The principle behind this method is hidden in the change of the transmitted torque over time at a constant temperature between two plates, of which one is slightly oscillating and the other is recording the response.[3,5-7]

In any case, the reliability of the obtained results is of fundamental importance, as it became a common trend that initial process simulations are increasingly required in order to predict mechanical issues of the final rubber part and to save time and resources. However, strong differences even within the same analytical method are no exception, as multiple batches of the same compound often indicate large internal variations.

Therefore, the remaining question is which results are trustworthy to be used as fundamental for simulative predictions in rubber processing. Based on this consideration, the aim of the present study is to examine the coherence between the degree of cure determined with an RPA and the mechanical properties of injection molded parts obtained from compression set.

Additionally, a simulation of the manufacturing process of a defined rubber part provides the bridge for the comparison of a real component with a virtually manufactured component.

**Fig. 1: Standard scheme of a cure curve indicating the three zones of vulcanization and the three possible shapes.[8]**




### Theory

Cure curves of rubbers are typically obtained from measurements on RPAs, which detect the change of a transmitted torque over time at constant temperature. The general equation to convert the measured torque into a relative degree of cure $\alpha$ is given in **Equation 1**:

$$\alpha = 100 \cdot \frac{S_t - S_0}{S_M - S_0}$$

where $S_t$, $S_M$ and $S_0$ are the current, maximum and minimum torques.

These cure curves are usually divided in three regions, as shown in **Fig. 1**, each indicating the current degree of cure. In the first section—known as the induction period, or scorch time—the analyzed compound is not yet forming crosslinks, and it shows a drop of torque at the beginning. This can be denoted as an effect of temperature difference between the sample and the heated rheometer plates.

In the second section of the curve, the torque starts to increase, indicating that activation energy of the vulcanization system was overcome and the crosslinking of the polymer chains was started. The last section of the curve (post-cure) can occur in three different ways, named constant plateau, marching modulus or reversion, describing the desired state, continuous increase of the measured torque or start of decreasing torque, respectively.[7-9]

In order to predict the progress of cure in a manufacturing process, empirical models are calculated from the experimentally measured data. Such models are basically implemented in a simulation software. In this study, the proposed model of Isayev and Deng[9] is used, which is given by **Equation 2**:

$$\alpha = \frac{K(T) \cdot t^n}{1 + K(T) \cdot t^n}$$

The coefficient $K$ represents the reaction speed that is dependent on the temperature T, $t$ equals the time and the dimensionless order of reaction is given by the coefficient $n$.

Traintinger

## The author

Martin Traintinger works at the Polymer Competence Center Leoben GmbH in Leoben, Austria, where he is entrusted with the task of managing the operative areas of a project collaboration between scientific and industrial partners in the field of rubber injection molding.

On behalf of the close relationship of the PCCL with the local university, he was able to pursue his doctorate as the chair for injection molding of polymers at Montanuniversitaet Leoben. Traintinger holds a master's degree in technical chemistry from the Technical University of Graz in Austria, and earned his bachelor's in chemistry from the same university.

The reaction speed is derived through an Arrhenius-type function, indicated by **Equation 3**:

$$K(T) = K_0 \cdot e^{\frac{-E_a}{R \cdot T}}$$

where $K_0$ is dedicated as parameter for the reaction speed, $E_a$ corresponds to the activation energy and R is the gas constant.

It should be pointed out that the values for $\alpha$ are in a range between 0 percent, representing an uncured rubber, and 100 percent, indicating a completely cured part. In other words, this means that the degree of cure representing torque curves are normalized according to **Equation 1**.

### Experimental

*Material and equipment*

An industrially manufactured, co-extruded SBR rubber compound from Semperit Technische Produkte GmbH (A-2632 Wimpassing, Austria) was used to carry out the experiments. Exact quantities of rubber, fillers and sulfur-based curing system of the compound are not known.

The part manufacturing was done on a "First-In, First-Out" rubber injection molding machine MTF750/160editionS provided by Maplan GmbH (A-2542 Kottingbrunn, Austria), mounted with a 4-cavity test mold, including a cold runner manufactured by Peta Formenbau GmbH (D-63628 Bad Soden-Salmuenster, Germany).

The simulation of the injection mold-

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**Table 1: Settings for the determination of degree of cure curves of SBR on an RPA.**

| | Temperature | Time | Frequency | Amplitude |
|---|---|---|---|---|
| Setting 1 | 150 °C | | | |
| Setting 2 | 160 °C | 120 min | 1.66 Hz | 0.5° |
| Setting 3 | 170 °C | | | |

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Fig. 2: (a) Experimental curve of the transmitted torque over time at isothermal conditions, measured on an RPA, (b) normalized curve for degree of cure calculated from the torque following the mathematical relation stated in equation 1 and approximated curves following the model of Isayev and Deng (DI).

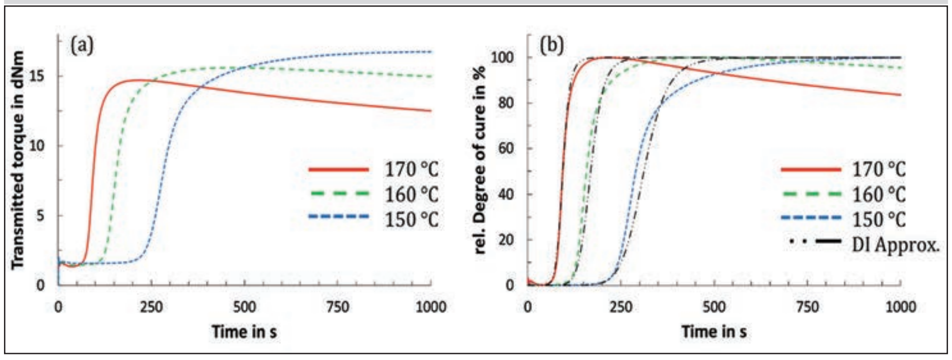



Table 2: Vulcanization temperature and time settings for part manufacturing on the IMM.

| | Temperature | $t'_{90}$ | $t^{+}_{90}$ | $t^{-}_{90}$ |
|---|---|---|---|---|
| Setting 1 | 150 °C | 455 s | 475 s | 435 s |
| Setting 2 | 160 °C | 227 s | 247 s | 207 s |
| Setting 3 | 170 °C | 125 s | 145 s | 105 s |

Fig. 3: Compression set of injection molded SBR parts considering a Δt90 and a deviation of ±20s.

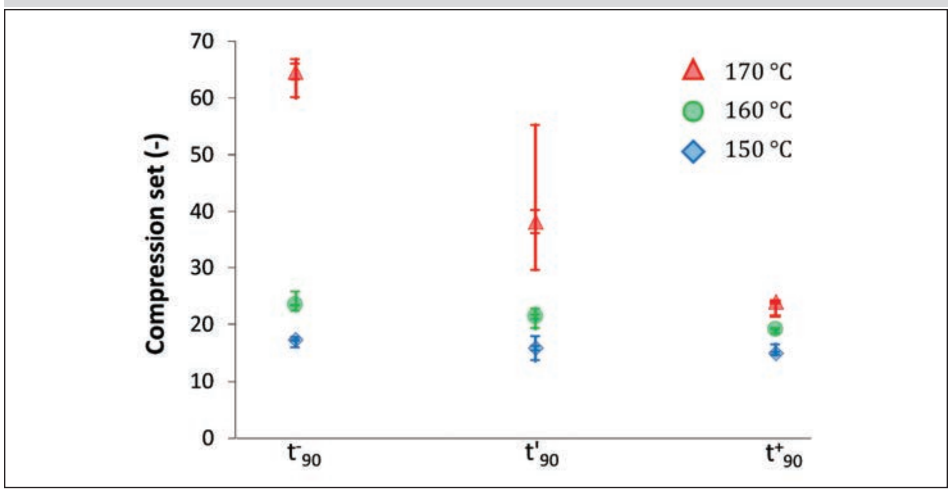



Fig. 4: Degree of cure (in %) of SBR parts simulated according to machine settings.

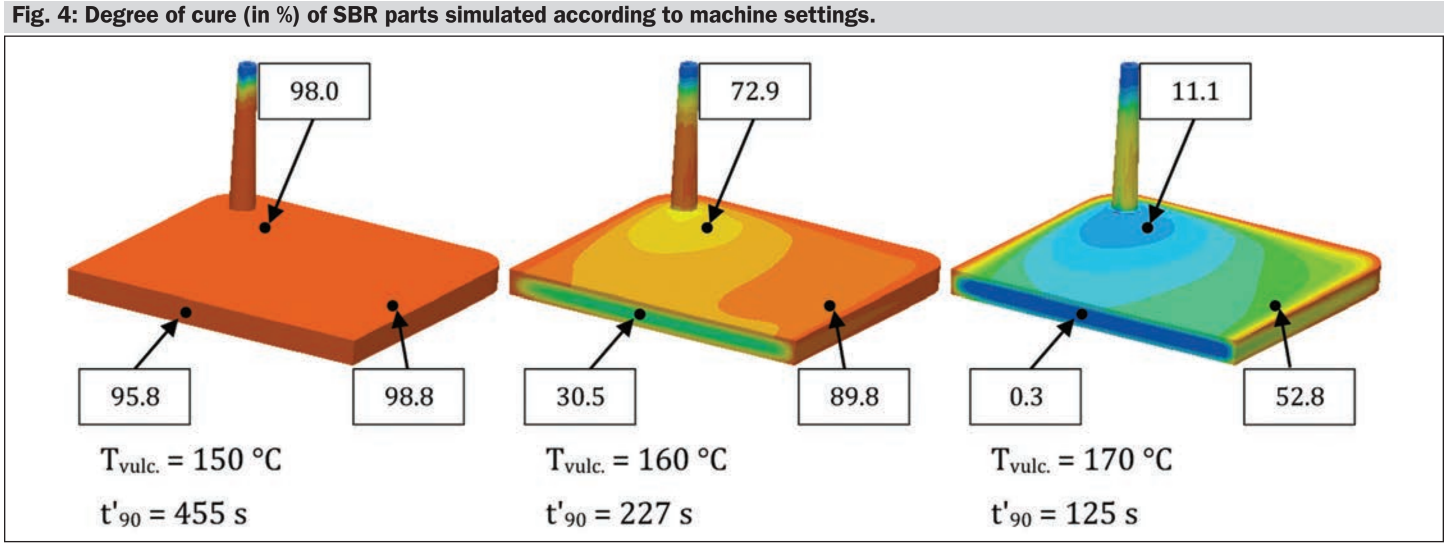
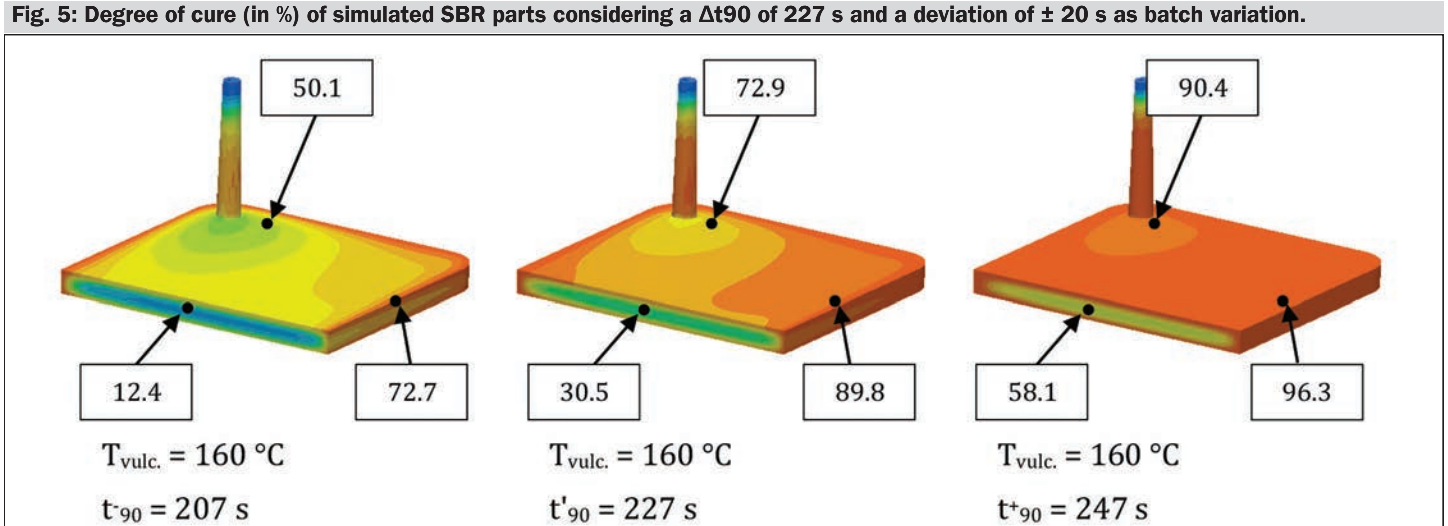



Fig. 5: Degree of cure (in %) of simulated SBR parts considering a Δt90 of 227 s and a deviation of ± 20 s as batch variation.

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ing process was performed with Sigmasoft 5.2, a simulation software distributed by Sigma Engineering GmbH (D-52072 Aachen, Germany). Measurements of the degree of cure were done on a D-RPA 3000 from MonTech Werkstoffpruefmaschinen GmbH (D-74722 Buchen, Germany).

*Experimental conditions*

The determination of the degree of cure for the coextruded SBR used in this experiment was done according to the settings given in **Table 1**. From the resulting curves, the value of t90 was calculated and applied on the injection molding machine (IMM) and the simulation software.

In the next step, rectangular shaped SBR rubber parts (100 x 80 x 6.3 mm) were manufactured with the 4-cavity test mold on the IMM. The vulcanization temperature and time were chosen with respect to RPA t90 measurements. In order to preserve the desired degree of cure, the parts were cooled instantly after de-molding.

Furthermore, each measured t90 was varied by ±20 seconds, which should indicate potential differences of the mechanical properties when the proposed batch variation is taken into account. The mentioned delta time (Δt) was found to be representative for effects of batch variations on the kinetics. It was the result of a previously conducted experiment.

Testing of the mechanical properties of the manufactured rubber parts was obtained by compression set analysis, according to the regulations given in standard ISO 815.[10]

## Results and discussion

The results of the measured torque of the SBR shown in **Fig. 2a** reveal an obvious increase of the transmitted torque, when temperature decreases and simultaneously the time to obtain maximal transmission increases. Physical laws describe the torque as an arithmetic product of a rotational force acting on a compound and a path required for this movement.

In rubber science, the increasing torque goes hand in hand with a higher resistance, indicating the force of the analyzed material to the applied amplitude, representing the path. Under the assumption of the polymer chains being randomly mixed to a bundle in an uncured state, the resistance is denoted as an effect of entanglement and disentanglement of the polymer chains, of which both are considered equally strong.

However, when the sample starts to cure, the effects of disentanglement start to be increasingly suppressed, which indicates a rising number of crosslinks within the system. Thus, as the crosslink density increases, the resistant force in the bundle has to behave similarly and for this reason, the transmitted torque gets higher.

For simulations of an injection molding process, it is necessary to normalize the RPA data to a relative degree of cure according to **Equation 1**. From these results, the software calculates a mathematical approximation, depending on the chosen model.

In the present study, the model of Isayev and Deng was applied, following the **Equations 2 and 3.**[9] The resulting curves for both, the relative degree of cure and the calculated fit are depicted in **Fig. 2b**. The graph shows that reality and calculation fit together quite well up to approximately 80 percent conversion.

However, the upper region of the curves shows an increasing deviation, which becomes even worse the lower the vulcanization temperature and the longer the time is. This problematic issue can be ascribed to the mathematics, as available models are not able to describe an S-shaped curve yet. They can focus on either the initial or the final sweep, but not on both at the same time.

Beyond that, this problem was neglected herein as the eyes were set on the step of normalization. Within this step, each curve is related to its individual maximum, but the simultaneously occurring change of the mechanical behavior is not considered. Moreover, the normalized curve suggests that the properties at the same level of the relative degree of cure for parts manufactured at different temperatures are the same.

This theory was refuted with compression set testing. The vulcanization time to obtain 90 percent cure at a given temperature was filtered from RPA measurements. **Table 2** summarizes the specific time values and indicates the delta time Δt of t90.

With respect to preliminary findings, the crosslink density for rubber parts manufactured on the IMM at 150°C has to be higher than in those parts obtained with the IMM settings at 170°C.

For the theoretically expected compression set, the higher amount of crosslinks indicate that the remaining deformation after the test is lower, which is indeed observable from the results presented in **Fig. 3**. Interestingly, it can be seen that the compression set for the parts cured at 170°C is significantly higher, except for the maximum limit of time variation t+90. This leads to the suggestion that a considerable degree of cure is not only depending on the vulcanization temperature, but also on a minimum requirement of heating time due to

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# Outdoor interests boost Carlstar brands

**By David Manley**
Tire Business

FRANKLIN, Tenn.—If there's a silver lining in the COVID-19 pandemic, it's that many people have embraced outdoor activities for the first time.

For specialty tire and wheel maker Carlstar Group L.L.C., this is reason to be optimistic for the future.

The company is a global supplier of specialty tires and wheels serving the agricultural, industrial, lawn and garden, and power sports markets. Most of Carlstar's products carry the Carlisle flagship brand, but the Franklin-based company also goes to market with the ITP and Marastar brands, covering ATV/UTV tires and wheels, and small specialty tires, respectively.

Carlstar is considered the 48th largest tire company in the world, according to *Rubber & Plastics News*' 2020 Global Tire Report rankings, with estimated tire-related sales of $495 million in 2019.

The company's balance between original equipment and aftermarket customers has kept it competitive during the pandemic, said Laren Harmon, Carlstar executive vice president of sales and marketing.


Harmon

"The strength we have experienced in 2020 in our aftermarket business has offset the OE weakness caused by the pandemic," he said. "In fact, certain segments in which we operate are having a record year for demand as our products are incorporated into many different social-distancing activities. These activities include such things as ATV trail riding, boating and RV, lawn and garden activities."

Harmon also noted ag tire sales—compact tractor, implement and semi-pneumatic tires—have done well this year. The construction segment has been sluggish, though, he said, as local and federal projects may have been put on hold during the pandemic, or funding was diverted because of it.

"We are the industry leaders in many of these product segments like lawn and garden, ST trailer and power sports, and, as a result, we have seen strong growth," Harmon said.

The firm has been busy in 2020, despite a two-week manufacturing shutdown in March.

"Carlstar has a flexible global manufacturing footprint; it is one of our strengths," Harmon said. "The fact that we produce most of our power sports, agriculture and construction products domestically has given us the ability to quickly respond to changing market demand and ensure our loyal customers have inventory."

As the pandemic spread in late winter, Harmon said the company's first priority was to ensure the safety of its employees—a task that continues to be very important, he said.

"Manufacturing locations were closed temporarily out of an abundance of caution for the pandemic and to ensure we had the proper safety protocols implemented in the facilities," Harmon said.


**Carlstar is seeing growth in the power sports market and plans to expand ATV/UTV products.**

"Our factories remained closed for approximately two weeks as we further assessed the falling demand from our OEM customers in particular, who also shuttered their factories in the wake of the pandemic."

## Power sports booms

Carlstar—one of the few remaining U.S.-owned producers of pneumatic tires—manufactures tires at plants in Clinton and Jackson, Tenn., and Meizhou, China. It has more than 3,400 employees at facilities in the U.S., Canada, China and Europe. It also produces custom wheels under the Cragar, Black Rock and Unique brands.

"In terms of the pandemic's effect on the market, power sports is seeing an increase in popularity due to it becoming a social-distancing recreational activity," Harmon said. "We believe that popularity will continue even after the pandemic as many more people have been introduced and enjoy this form of recreation."

The company released a number of new products into the market this year, including:

- The Carlisle Versa Turf, a radial R3 tire designed for reduced turf impact in lawn and garden applications;
- The Carlisle PaveMaster, a tire designed for UTVs and side-by-side (SxS) vehicles, running often on hard-packed surfaces and paved roads;
- The ITP Terra Claw, an 8-ply high-performance, multi-terrain tire line for ATV/UTVs and SxS vehicles; and
- The 10-ply ITP Tenacity XSR Xtreme Steel Radial and Tenacity XNR Xtreme Nylon Radial tires for Super Sport SxS enthusiasts.

The Marastar brand of specialty tires and casters is having a "wonderful 2020 as well," Harmon said. He noted its popularity among farm and home-improvement retailers as more people have been doing home projects during the pandemic.

"Our Marastar brand is doing very well. They'll have a record year in 2020," he said.

While he said the OEM and construction tire markets may be down in 2021, the company believes ag, lawn and garden, and power sports sales will be up.

"Our challenge is to stay in front of the demand and make sure our loyal customers have the inventory to take advantage of this market," Harmon said. "We are leveraging our global footprint to ensure we are prioritizing production to meet the changing demand for our customers."

## New products

The company plans to roll out several products in 2021, Harmon said, including:

- A broadline power sports radial tire to expand the size coverage for Carlisle's UTV tires;
- Expanding the Carlisle agricultural and construction product portfolio with new Carlisle Radial Tractor treads and sizes as well as steel-belted skid steer and implement tires; and
- Eight tire and two wheels projects coming to the ITP brand portfolio.

The company also hinted at "a very special product launch" from its Jackson plant that is the result of a strategic partnership with an end-user to provide a unique "Made in the USA" product.

The project—which he said required a significant investment in the plant — will be announced in the fourth quarter.

Carlstar also is developing new sales channels with the recently launched national account and government sales department.

"We are targeting markets that are currently underserved for our product segments," Harmon said. "One example is the rental equipment channel, where our products offer the best fit for these customer's very diverse portfolios. As for the government, many agencies, municipalities and state governments favor a 'Made in the USA' product. We feel we are in a unique position to deliver that request for the specialty tire business."

The growth in the aftermarket has Carlstar optimistic about the future.

"At the end of the day, 2020 is going to be tough for a lot of tire manufacturers, and we're going to have a pretty nice year," Harmon said. "We should stand tall going forward, and we're pretty excited about all of that here."


**Dustin Jones competes in the UTV Pro Turbo class at the 2020 Mint 400 off-road desert race outside Las Vegas in March.**

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low thermal conductivity values.

Further, this is evidence that the degree of cure calculated from RPA measurements does not correspond to reality after the normalization step was conducted. Therefore, an adaption of available models or an introduction of new approaches is necessary.

The time-temperature relation is also confirmed from the view of IM simulation shown in **Figs. 4 and 5**. The results clearly show that part manufacturing with a curing temperature $T_{vulc.}$ of 170°C is far from any dimensionally stable product, as the cure value in the core has not even exceeded scorch time.

In contrast to that, the degree of cure from parts processed at 160°C possess a stable surface, even though the core of the part has reached only 30 percent relative degree of cure. Nevertheless, taking the effect of post-curing into account, which is due to residual heat, it can be concluded that this setting can be sufficient.

However, this is a question of batch variations, as those can additionally affect the results, as shown in **Fig. 5**, which indicates the different percentage of the degree of cure when Δt is considered.

## Conclusion

Successful simulative prediction of the degree of cure of injection molded rubber parts requires comprehensive mathematical models. It is a common method that measured data at the RPA has to be converted into a degree of cure in order to be applied in one of these models. This includes the step of normalization, which represents the degree of cure with respect to the measured maximum torque.

In this study, it was shown that the normalization step introduces an error to the simulation at least for the used SBR because the degree of cure calculated for the compound at temperature A does not coincide with the degree of cure for the same compound at a temperature B. Therefore, the mechanical properties are evidently different for both and do not coincide either.

The compression set analysis has revealed that different process temperatures end up with different crosslink densities. Besides, the reaction requires a minimum time to obtain a dimensionally stable product. In order to achieve more accuracy in process simulation, it is inevitable to improve available models or to find new approaches.


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