

Mastication Behavior of *cis*-1,4-Polyisoprene as a Model for Natural Rubber

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ABSTRACT: The mastication behavior of synthetic *cis*-1,4-polyisoprene (IR), deproteinized natural rubber (DPNR), and natural rubber (NR) in an internal mixer has been investigated at mixing temperatures from 88 to 186°C and different levels of mechanical energy, using Mooney viscosity and size exclusion chromatography (SEC). An envelope-shaped mastication efficiency curve and high similarity in the mastication behavior can be observed for IR and NR but not for DPNR. The minimum of the envelope-shaped curve shifts to lower temperatures when the mechanical energy is increased. Based on these findings, a mathematical description for the contribution of mechanical and thermo-oxidative mastication mechanisms has been established. Distinct statistical distribution of thermo-oxidative scission can only be observed in SEC measurements of materials masticated at high temperatures over 170°C. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39989.

KEYWORDS: degradation; elastomers; viscosity and viscoelasticity; rubber; theory and modeling

Received 15 July 2013; accepted 20 September 2013

DOI: 10.1002/app.39989

INTRODUCTION

Very high viscosity and elasticity of raw natural rubber (NR) is one of the major challenges in the rubber industry. Therefore, the reduction of viscosity by chain scission, called mastication, is a crucial process element for NR based compounds, like widely used in the industry for tires and technical rubber goods. It is well known, that the efficiency of mastication depends on the temperature of the rubber during the mixing process, resulting in a minimum efficiency at a temperature around 100 to 130°C for mastication times of 20 to 30 min.^{1,2} This temperature dependency is a result of the presence of two mastication mechanisms. At low temperatures, the so called mechanical mastication arises from shear forces applied to the polymer chains during mixing, leading to a breaking of the chains and the formation of radicals. These radicals can either recombine or be stabilized by oxygen or other radical acceptors like peptizers.^{3–5} The mechanical induced nature of this process leads to a nonstatistical scission, predominantly very close to the middle of the polymer chain.⁶ The mechanical mastication becomes less efficient with rising temperatures due to the softening of the polymer.

The second mastication mechanism, the so called thermo-oxidative mastication, is based on an oxidation of the double bonds of the polymer backbone. There are various reactions taking place, leading to a variety of different oxidation prod-

ucts.⁷ Most of the previous works describe the thermo-oxidative mastication of NR as a statistical process, resulting in scission randomly distributed all over the polymer chains.^{8,9} Bueche proposes in his work that during mastication in the internal mixer and at moderate temperatures this mechanism does not take place randomly along the chain. He lines out that the mechanical deformation of the double bonds close to the center of the polymer chains leads to a reduction of the activation energy and therefore the scission of these bonds is thermodynamically preferred.⁶ The combination of these mechanisms leads to an envelope-shaped mastication efficiency curve giving a minimum at temperatures around 100 to 130°C (see Figure 1).^{1,4,10,11} Some articles report that no minimum was observed.⁸

Most of the mastication experiments have been performed on two roll mills or internal mixers with long mastication times of 20 or 30 min. Only little work has been done to quantify the contribution of both mastication mechanisms at varying mastication times and temperatures to predict and describe the impact of the mastication condition on the material properties.¹⁰

In this work, mechanical and thermo-oxidative mastication under systematic varied temperature and mixing energy conditions have been investigated by means of Mooney viscosity and size exclusion chromatography (SEC). Synthetic isoprene rubber

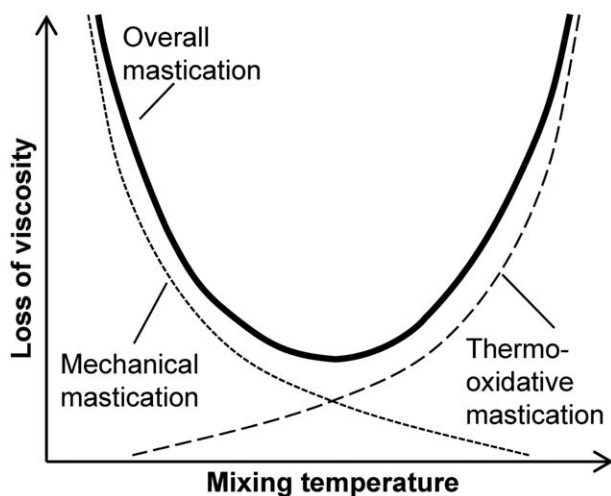


Figure 1. Schematic mastication efficiency curve based on Busse, Pike, and Watson.^{1,3}

has been used as a model for NR due to the complete accessibility in SEC. The main aim was to determine the influences of the mastication mechanisms on the material properties and to create a mathematical model to describe the contribution of both mechanisms to the overall mastication for different temperatures and mechanical mixing energies.

EXPERIMENTAL

Materials

The used *cis*-1,4-polyisoprene (IR) was SKI-3 produced by Nizhnekamskneftekhim (Nizhnekamsk, Russia). The NR used was a technically specified rubber SMR 10 BP1 produced by Lee (Kuala Krai, Malaysia). The deproteinized NR (DPNR) was manufactured by Plasticos Jurema (Jurema, Brazil).

Mastication of Rubber

For the mastication trials, an internal mixer was used based on the Haake PolyLab System from Thermo Scientific (Karlsruhe, Germany) equipped with a RheoMix 3010p chamber with a temperature sensor, banbury rotors, and a pneumatic ram. Before every mixing run, the measuring system was calibrated using the internal routine of the PolyLab System. In all trials, 230 g of the rubbers (~80% chamber fill factor) have been masticated with a fixed rotor speed of 60 rpm. To reach different temperature level of the rubber, the oil temperature control unit (TCU) Phoenix P1 (Thermo Scientific, Karlsruhe, Germany) was set between 50 and 170°C. In the literature typically, a fixed mastication time is used for this kind of trials. With rising temperatures and for a defined mastication time the amount of mechanical energy decreases due to the softening of the material. In this experiment, every mixing run was automatically stopped after a defined mechanical energy input between 100 and 600 kJ was reached. The idea behind this approach is to keep the contribution of mechanical mastication over the temperature range as constant as possible. It is worth to mention that due to the fixed rotor speed, the mixing time for every level of mechanical energy input is significantly different, starting from around 3 min for 100 kJ and resulting in around

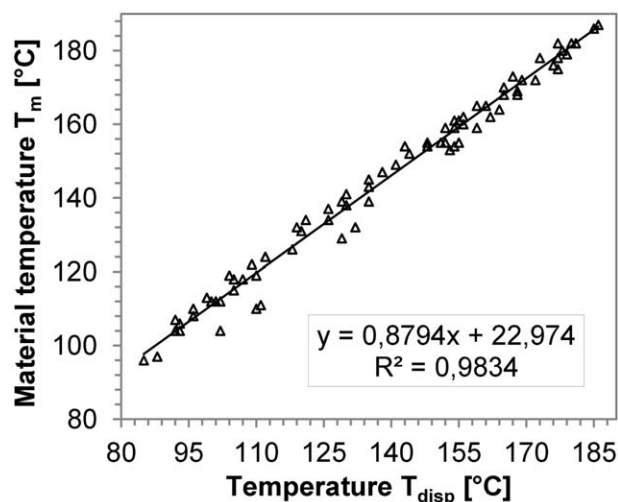


Figure 2. Correlation of T_{disp} and material temperature T_m for all level of mechanical energy input.

18 min for 600 kJ. At the end of each run, the material temperature has been measured with a needle pyrometer, so that a relation between the chamber sensor temperature (T_{disp}) and the material temperature (T_m) exists (see Figure 2).

To favor accuracy, all temperatures given in this work are from the sensor mounted in the chamber (T_{disp}).

Isolation of Mastication Mechanisms

The aim of these tests was to reach certain levels of viscosity having one of the mastication mechanisms eliminated as good as possible. To force the mechanical mastication, IR has been masticated several times in the cold internal mixer with a TCU temperature of 60°C and a mechanical energy input of 100 kJ, resulting in a rubber temperature T_{disp} less than 100°C. Between the single runs the rubber was cooled down to room temperature for 1 h.

To force the thermo-oxidative mastication, the IR was prewarmed to 100°C for 30 min in an oven and then masticated in one single run for different times with the chamber being heated to 160°C. The prewarming was intended to reduce the contribution of the mechanical mastication to a minimum. The rubber temperature T_{disp} under these conditions was between 170 and 180°C. Afterwards, Mooney viscosity has been measured and the materials with a similar viscosity (± 0.5 mu) have been compared regarding molar weight distribution (SEC).

Mooney Viscosity

The Mooney viscosity measurements were performed according to ASTM D1646, using the small rotor to make sure that all samples can be measured with the same setup. Additionally, with every trial one unmasticated raw material reference has been measured, giving for IR a Mooney viscosity of 39.1 ± 1.0 mu as reference value based on 13 measurements. The evaluation is done in relation to the unmasticated raw material so that all values are given as the percental loss of viscosity based on MS (1+4) 100°C measurements. For example, a

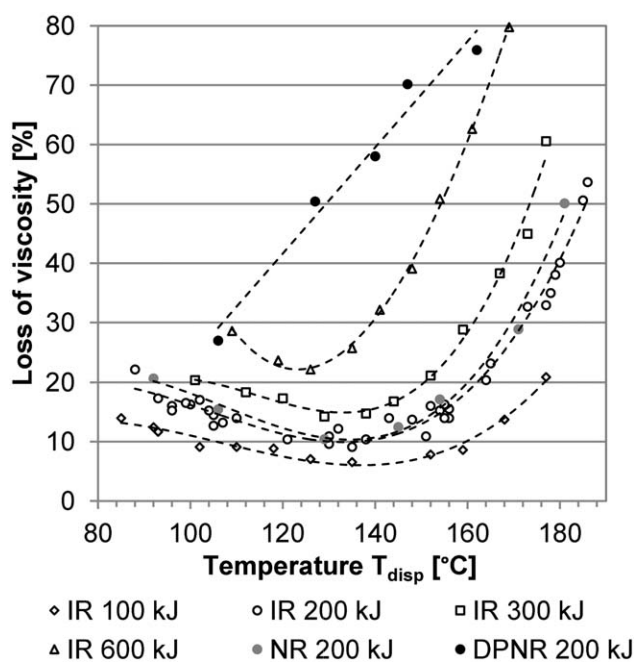


Figure 3. Mastication efficiency curves for different rubbers and energies.

value of 50% means a 50 percent lower viscosity compared to the unmasticated raw material.

Size Exclusion Chromatography

The SEC measurements were performed on a system consisting of a Series 1200 pump from Agilent Technologies Deutschland GmbH (Böblingen, Germany), Autosampler Midas from Spark (Emmen, The Netherlands), and a refractive index detector Shodex RI-71 from Showa Denko (Tokio, Japan). For the size exclusion, a set of SDV 10,⁶ SDV Mix, and SDV 10³ columns from polymer standards service (Mainz, Germany) was used. To prepare the samples, 50 mg of the rubber were solved in 15 mL freshly distilled toluene, containing 250 mg L⁻¹ of Jonol as internal standard. Toluene has also been used as eluent containing 100 mg L⁻¹ Jonol.

RESULTS AND DISCUSSION

Mastication Efficiency Curves

In Figure 3, the viscosity loss of IR, NR, and DPNR has been plotted versus the temperature T_{disp} for 4 levels of mechanical energy input (IR: 100, 200, 300, and 600 kJ; NR: 200 kJ; DPNR: 200 kJ). The principle shape of the IR and NR curves represents the findings of the former works regarding the envelope shape and the presence of a minimum in the mastication efficiency curve.

For IR and NR starting at the lowest temperatures, the loss in efficiency with rising temperatures indicates that even with constant mechanical energy input, the mechanical mastication becomes less efficient. This effect can be addressed to the increasing mobility of the polymer chains. With rising temperatures, the chains relaxate more often instead of being ruptured. The comparability of the percental loss of viscosity of IR and NR is unexpectedly good, especially, considering the very differ-

ent viscosity level of the unmasticated raw materials (IR: 39.1 mu; NR: 53.7 mu). This similarity is not expected to be transferable to the complete range of NRs.

Conversely, the mastication behavior of DPNR is completely different. The efficiency increases very fast even at moderate temperatures and does not show minimum efficiency. The reason for this very different behavior needs to be clarified. A possible explanation could be the absence of the antioxidants in the DPNR that naturally occur in the NR and are artificially added to the IR during production process.¹² It also has to be considered that this behavior may be based on the production process of this specific type of DPNR.

It has to be mentioned that it is not feasible to perform trials at TCU temperatures lower than 50°C. Unfortunately, the used mixer would break down due to the maximum torque that appears at the beginning of the mixing. Due to this, for high mechanical energies lower material temperatures cannot be observed. The dissipation of the mechanical energy leads to higher material temperatures when more mechanical energy is put into the material.

Compared to the results from Busse, the efficiency curve of IR and NR is more asymmetric, having a less steep decrease at low temperatures and a steeper increase at higher temperatures. This may result from the different experimental setups. Due to the fixed mastication time, Busse has used the amount of mechanical energy decreases with rising temperatures. In combination with the softening of the material, this results in a faster loss of efficiency. At higher temperatures, the fixed mechanical energy input used in this work results in a prolonged mixing time. This enables more thermo-oxidative mastication and therefore allows an increasing efficiency.¹

Only for the highest amount of mechanical energy, the temperature of the minimum efficiency can be found in the temperature region described in the literature. For the lower energies (100 to 300 kJ representing about 3 to 10 min of mastication), the minimum efficiency is shifted to higher temperatures. A potential explanation is that for low mechanical energies (reflecting short times), high temperatures, which are needed for the thermo-oxidative mastication, are only reached for a short period of time. With high energies (and long times) this phase becomes much longer. Therefore, the influence of the thermo-oxidative mastication becomes disproportionately intense with longer process times and the ratio of the mechanisms changes (see Figure 4).

Mathematical Model

To quantify the contribution of both mastication mechanisms to the overall loss of viscosity $\Delta\eta$, a mathematical model has been generated. The model is based on the assumption that both the mechanical mastication $\Delta\eta_{\text{mech}}$ and the thermo-oxidative mastication $\Delta\eta_{\text{thermo-ox}}$ do not interact and do not influence each other.

$$\Delta\eta = \Delta\eta_{\text{mech}} + \Delta\eta_{\text{thermo-oxidative}} \quad (1)$$

Because the mechanical mastication is based on the rupture of the chains, a linear dependence on the amount of mechanical

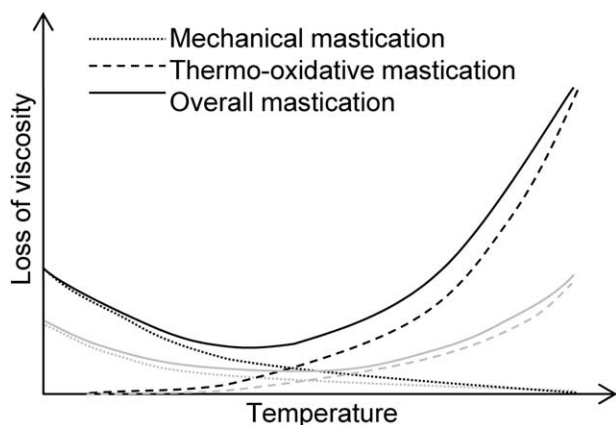


Figure 4. Principle of the shifting minimum efficiency. Grey lines indicate low mechanical energy (and time) and black lines indicate high mechanical energy.

energy put into the material is expected. To represent the temperature depending loss of efficiency of the mechanical mastication due to the softening of the material the mechanical energy input is multiplied with the Andrade equation. This equation is an empirical expression for the temperature dependency of the viscosity.^{13,14}

$$\Delta\eta_{\text{mech}} = E_{\text{spec}} \cdot a \cdot e^{\left(\frac{b}{T}\right)} \quad (2)$$

Here, the specific energy E_{spec} is the amount of mechanical energy per gram of rubber, a and b are material specific fit parameter.

To calculate the contribution of the thermo-oxidative mastication, an approach based on the calculation of chemical conversion has been chosen. The amount of thermo-oxidative mastication is assumed to be proportional to the chemical conversion indicated by the oxidation of the carbon-carbon-bonds. Only a fit factor α has been introduced. Following the Arrhenius law and the integrated rate law for a reaction of first order, the conversion X of a chemical reaction can be described with eq. (3).

$$X = 1 - e^{-\sum_0^t \Delta t k(T)} \quad (3)$$

Wherein Δt is the measuring interval, t is the overall mastication time, and $k(T)$ is the reaction rate for a defined temperature.

With the chemically exact expression of eq. (3), it would not be possible to predict the mastication behavior for a certain combination of time and temperature without having an experiment, because the mastication is a nonisothermal process and therefore the reaction rate constant k would have to be calculated for every interval of measurement. Additionally, the exact mastication time for a certain energy temperature combination is not known and cannot be predicted easily so that the time needs to be replaced by a known value. To make both predictions possible, it has been assumed that the process is isothermal using k_{end} ; the reaction rate for the temperature at the end of the trial and the mastication time has been replaced by the specific energy due to good correlation. The validation of these assumptions with the existing experimental data can be seen in Figure 5.

k_{end} can be calculated using the Arrhenius law (4):

$$k_{\text{end}} = A \cdot e^{-\frac{E_A}{RT}} = 183.33 \cdot e^{-\frac{55,000}{8.341 \cdot T}} \quad (4)$$

Wherein A is the pre-exponential factor, E_A is the activation energy of the oxidation of the rubber, T is the temperature of the rubber measured at the end of the mastication time, and R is the universal gas constant. This leads to eq. (5).

$$X = 1 - e^{-\sum_0^t \Delta t k(T)} \approx 1 - e^{-E_{\text{spec}} \cdot k_{\text{end}}} \quad (5)$$

For the calculations, the values for A and E_A have been taken from a work of Santoso, Giese, and Schuster who experimentally determined the kinetics of the oxidation reaction of NR using the oxidation induction time method.¹⁵

This leads to eq. (6) for the overall mastication efficiency:

$$\Delta\eta = E_{\text{spec}} \cdot a \cdot e^{\left(\frac{b}{T}\right)} + \alpha(1 - e^{-E_{\text{spec}} \cdot k_{\text{end}}}) \quad (6)$$

The outcome of these estimations is a fit with following values for the parameters:

$$a = 1.8802 \cdot 10^{-8} \text{ g/J}$$

$$b = 7638.9 \text{ K}$$

$$\alpha = 5.2941 \cdot 10^6$$

The estimated fit matches very well to the fit using the exact calculation (see Figure 5).

In principle, this model describes the mastication efficiency curve for different amounts of mechanical energy very well. The deviation of measured and calculated data exceeds the accuracy of the Mooney viscosity measurement only for few points. Unfortunately, the model does not represent the shifting of the minimum efficiency. As the difference in the loss of viscosity that leads to the temperature of the minimum are very small, it seems not to be suggestive to modify the equation.

Based on the plotted functions, the mastication efficiency curve can be extrapolated for combinations of temperature and mechanical energy that are not accessible with the used mixer.

This prediction for 100, 200, 300, and 600 kJ can be seen in Figure 6. This diagram also unveils the boundaries of the model. For extreme conditions (very high or very low temperatures in combination with high energies) the mastication would exceed 100%, which is impossible. The calculated mastication efficiency curves for 100 to 300 kJ represent the expected behavior very well (see Figure 7).

Only for the 600 kJ curve, the predicted very high mastication efficiency at low temperatures seems to be overestimated. For this temperature area, no additional experimental data are accessible but at least this behavior is physically expected. Additionally, the experiments on which the model is based did not cover points, where the mastication becomes so extreme that the resulting softening becomes the dominant factor. When the viscosity of the rubber becomes very low, the mastication will become very inefficient. This kind of "limiting viscosity" cannot be covered by the model.

An approach that may describe the mastication efficiency for high energies and low temperatures more precisely has

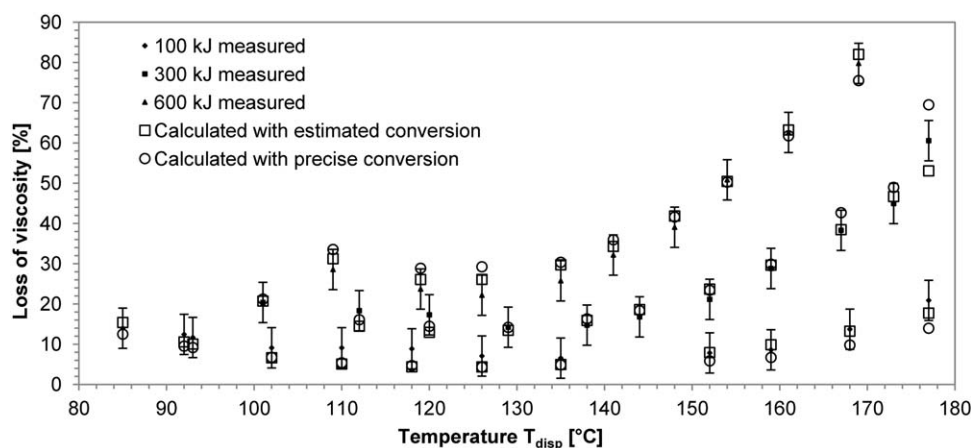


Figure 5. Comparison of the quality of fit for precise and estimated conversion.

additionally been evaluated. In their work, Dimier et al. described that the relation between a property changing with mastication (in their case an energy shift factor for master curves) and the specific energy E_{spec} should be exponential.¹⁶ In this case, additional parameters c and d need to be introduced leading to the following term for the mechanical mastication:

$$\Delta\eta = a \cdot e^{E_{\text{spec}} + \left(\frac{c}{T}\right)} + \alpha(1 - e^{-E_{\text{spec}} \cdot k_{\text{end}}}) \quad (7)$$

This modification of the equation leads to a slightly lower error of the fit which might be addressed to the additional parameters. As no major benefit has been found for the prediction of the mastication efficiency curves, the simple linear dependency has been favored.

Isolation of Mechanisms

The comparison of the molecular weight distributions of the IR after mastication with isolated mechanisms is presented in Figures 8 and 9.

The isolated mechanical mastication leads to increasing peak height, but the position of the peak only slightly shifts to a lower molecular weight. Almost all molecules with a molecular

weight over $5 \cdot 10^6 \text{ g mol}^{-1}$ have been broken down and no molecules with a molecular weight under $2 \cdot 10^5 \text{ g mol}^{-1}$ have been formed. This kind of change in the molar weight distribution is a clear indicator for nonstatistical scission of the molecules and correlates very well to the findings from Bueche.⁶

In contrast, the isolated thermo-oxidative mastication exhibits a completely different picture. The height of the peak only changes insignificantly while the complete curve is shifted to lower molecular weights. This results in the formation of molecules even below a molecular weight of $5 \cdot 10^4 \text{ g mol}^{-1}$. On the other side, not all molecules over $5 \cdot 10^6 \text{ g mol}^{-1}$ have been broken down. This random creation and destruction of molecules clearly indicates a statistical scission so it can be stated that under these special conditions both mechanisms display the theoretically expected results according to the former literature.^{1,6,8,9,11}

The comparison of molecular weight distributions of samples that have been masticated to a Mooney viscosity of 33 mu using different combinations of temperatures and mechanical energy shows a different picture. The according distributions can be seen in Figure 10 including two distributions of unmasticated raw IR samples from the polymer bale used for these trials. It

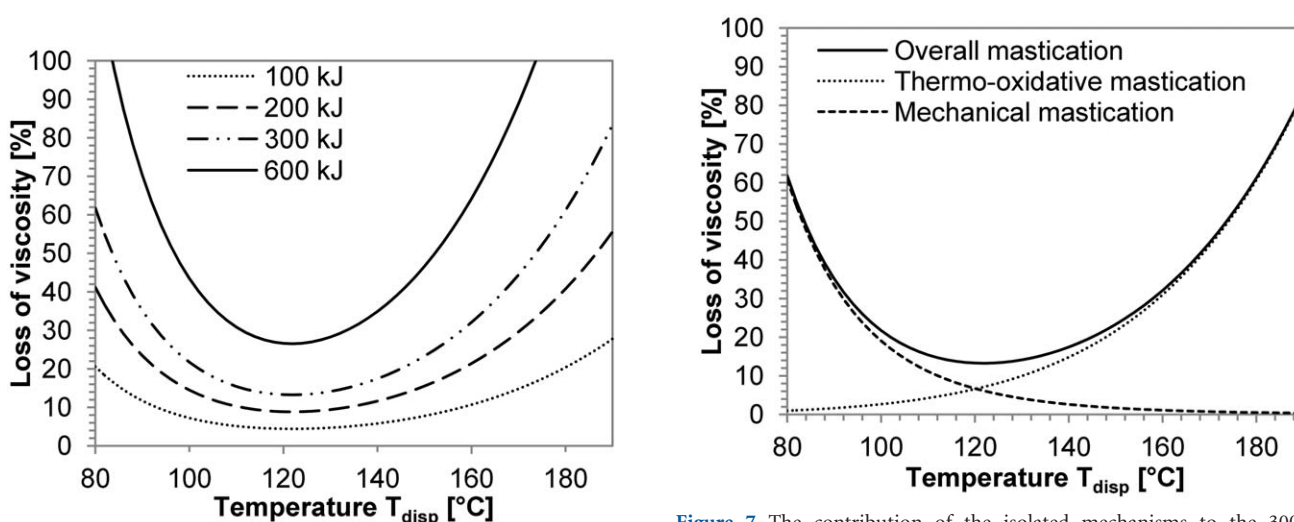


Figure 6. Extrapolated mastication efficiency curves.

Figure 7. The contribution of the isolated mechanisms to the 300 kJ curve.

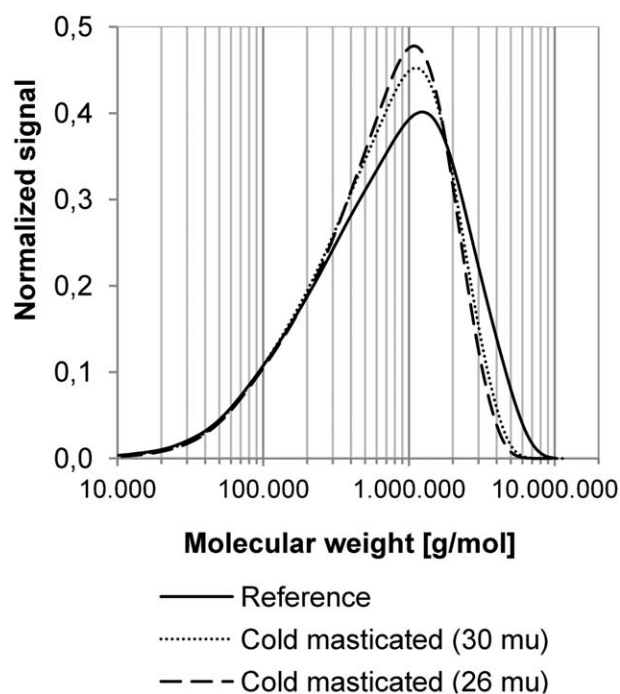


Figure 8. SEC diagrams of mechanically masticated IR (100°C).

can be observed that the changes in the molar weight distributions of the masticates are more comparable to the changes coming from pure mechanical mastication. This is indicated by the increasing peak height and almost unchanged molar weight of the peak. Only the sample that was masticated at 168°C shows a trend toward a lower molecular weight of the peak.

The deviations in the diagrams compared to that of the raw polymers exhibit that the changes are comparably small. Espe-

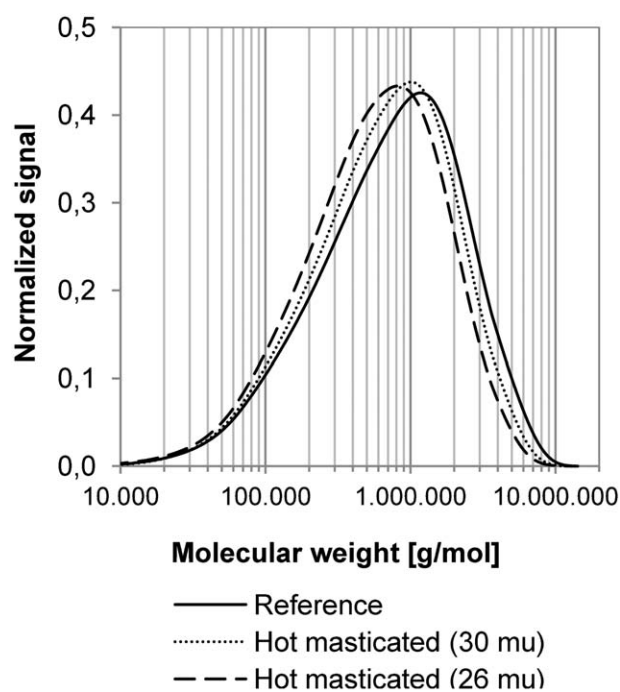


Figure 9. SEC diagrams of thermo-oxidatively masticated IR (170–180°C).

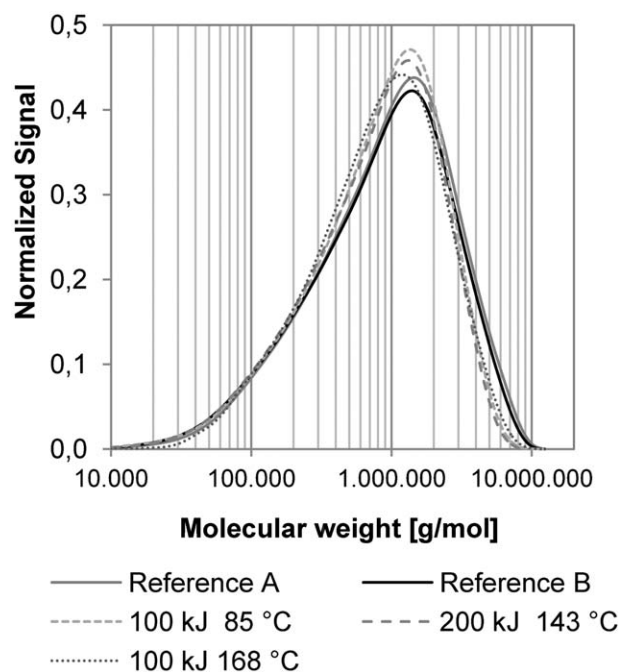


Figure 10. SEC diagrams of masticates with 33 mu.

cially when the material masticated at the highest temperature is compared with the reference with the lower peak height, the intensity of the thermo-oxidative mastication cannot be determined exactly. Regardless this uncertainty, under a molecular weight of $2 \cdot 10^5 \text{ g mol}^{-1}$ no chains are appearing. Furthermore, the differences of the distributions above $5 \cdot 10^6 \text{ g mol}^{-1}$ are comparably small. Both findings indicate that under the investigated conditions even at very high temperatures the thermo-oxidative mastication does not take place in a completely statistical way. This supports the proposals from Bueche.⁶

CONCLUSIONS

The efficiency of isoprene mastication has been investigated for defined combinations of mechanical energy input and material temperature. The envelope-shaped mastication efficiency curve and the contribution of the mechanical and thermo-oxidative mastication have been quantified. Additionally, a mathematical model has been developed by which it is possible to predict the mastication efficiency for various combinations of energy input and temperature.

Using SEC, it has been shown that the mechanical mastication mechanism gives predominant breakage of the chains close to their center while the thermo-oxidative mastication breaks the polymer chains statistically, but only when extreme conditions are applied. Under common conditions, the thermo-oxidative mastication is not truly statistical, even at high temperatures up to 170°C. This fits very well to the proposal of Bueche that the chain breakage by thermo-oxidative mastication is not statistically distributed because the shear stress applied to the bonds during the mixing reduces their activation energy especially at the center of the chains. It seems that the “moderate temperature” stated by Bueche over which the chain breakage becomes

statistical is higher than the temperatures investigated in this work.⁶

ACKNOWLEDGMENTS

The authors would like to thank the Continental Reifen Deutschland GmbH, Hannover, Germany for the financial support and Lukas Weger (Niederrhein University of Applied Sciences) for the very fruitful discussions regarding the mathematical model.

AUTHOR CONTRIBUTIONS

Mr. Dettmer, Mr. Steiner, and Mr. Wortmann designed the experimental layout and testing concepts and performed the experiments. Additionally they have evaluated and reviewed all experimental data. The focus of Mr. Scheper and Mr. Lindner was the experimental design for the isolation of the mechanisms and they have essentially contributed to the development and validation of the mathematical model, including the calculations. All listed authors have contributed to the writing and revised the paper in all phases of the process.

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