Effect of Mastication Time on the Curing and Dynamic Properties of Natural Rubber Gum Compounds: Towards Sustainable Rubber Processing

R.D. Rathnayaka, E.M.D.H. Deegala, T.S. Warnasinghe, K.V.M. Chamara, E.K.A. Maduwantha, Siriwardena, S. and A. Weerakoan*

Division of Polymer and Chemical Engineering Technology, Institute of Technology, University of Moratuwa

Abstract

Because of the high molecular weight of NR, effective mastication of natural rubber is a fundamental prerequisite which consumes a considerable amount of energy. However, excessive mastication, can lead to degradation of the material's properties, potentially compromising final performance. Therefore, optimizing the mastication time is of great importance to ensure the energy efficiency and performance efficiency of the conversion process of natural rubber to rubber product. In this study, effect of mastication time on curing characteristics and dynamic properties of natural rubber compounds were investigated. The natural rubber compounds were masticated in an internal mixer with varying mastication time from 0 (control) to 7 minutes at six time intervals. Curing characteristics of the compounds and dynamic mechanical properties of the vulcanizates, were studied at 100 °C. It was found that curing characteristics were unaffected with the mastication time of 3 minutes, after which a delaying in both scorch time and cure time were observed. Similarly, dynamic properties of the rubber vulcanizates were also unaffected until the mastication is carried out within three minutes. It was evident from dynamic mechanical properties that possible natural rubber molecular changes are taking place as mastication time exceeds three minutes. Based on these observations, it is clear that sustainable rubber processing could be achieved through limitation of mastication for three minutes and prevention of excessive milling.

Introduction

In the case of natural rubber, being a polymer with very high average molecular weight, it is necessary to soften the rubber by the process known as "mastication". It is a fundamental and indispensable mechano-chemical process of almost all the dry natural rubber product manufacturing processes to break down high molecular weight Natural Rubber (NR) molecules into smaller fragments through mechanical means to facilitate subsequent manufacturing steps such as incorporation of other necessary ingredients and shaping (Phattarateera and Pattamaprom, 2019). It has been in practice since the invention of the masticator by Englishman Thomas Hancock in 1820 to apply a shearing force to the rubber on a two roll mill or an internal mixer. In a two roll-mill, the rolls rotate at different speeds, generating a shearing force on the rubber at the "nip" between the rolls. In an internal mixer, an eccentrically-shaped rotors apply shear force to rubber between the rotors and the walls of the mixing chamber under closed environment. While former is widely used in small scale factories, various types of internal mixers are used in large scale factories for mastication of natural rubber. Mastication using an internal mixer is energy-intensive and possible over mastication in the process adversely affects in achieving certain properties. In the context of rapid growing concerns of sustainable manufacturing approaches, lowering energy consumption and doing away with the usage of auxiliary chemicals are highly encouraged (Saidura and Mekhilef,2010). Despite limited work available in the literature focused on the effect of mastication time on some properties of NR vulcanizate, no much work has been reported on screening the effect of mastication time at short time intervals on cure characteristics and dynamic properties particularly when mastication is carried out in preparation of gum compounds where no fillers are incorporated.

Therefore, this study was aimed at investigating the effect of varying mastication time at short intervals in an internal mixer on the curing characteristics and dynamic properties of the vulcanizates namely, loss modulus, storage modulus and Tan delta with the objective of

estimation of the best minimum mastication time for NR gum compounds as shorter mastication cycles reduce the mastication energy consumption offering a sustainable approach for the mastication process.

Materials and methods

Ribbed smoked sheet rubber (RSS) no. 02 was purchased from the local rubber auction. They were cut into approximately 2" x 2" pieces and charged into an internal mixer which uses a Banbury-type rotor and masticated at a rotor speed of 40. Temperature was maintained at 45 °C. The mixer was loaded at a fill factor of 0.75. Mastication time was varied up to 7 minutes with 1-minute increments starting from 1 minute. A sample without mastication (0 min) was also prepared as the control. All the masticated samples were compounded using the same internal mixer following a standard recipe and following mixing sequence given in the Table 1. All the samples collected at the end of the first half of mixing cycle were cut into small strips and mixed again at room temperature (30°C) for 10 rounds for approximately 2 minutes on a two roll-mill keeping the nip at 3 mm. These rubber sheets were used for the second stage compounding for two minutes. Curing characteristics of the compounds and dynamic mechanical properties of the vulcanizates at 100 °C were tested using a Rubber Process Analyzer (D-RPA 3000-Mon Tech, Germany). Dynamic properties were studied at three frequencies at 0.1, 1 and 10 Hz.

Table 1: Rubber formulation used

Compound	Phr
Ribbed Smoked Sheet (RSS)	100
Zinc Oxide	4
Stearic acid	2
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine) (6PPD)	2
Sulphur	1.8
N-tert-butyl-2-benzothiazolesulfenamide (TBBS)	1.5
N-(cyclohexylthio)phthalimide (PVI)	0.2

Results and Discussion

Table 2: Cure characteristics of rubber gum vulcanizates prepared by rubber masticated at different mastication times

Mastication time (min)	ML	MH	MH-ML	TS2	T90	CRI
0 (Control)	1.46	8.46	7.4	3.51	7.65	13.56
1	1.09	9.24	8.15	4.48	9.01	12.26
2	1.27	9.03	7.76	4.28	8.18	12.87
3	1.10	9.05	7.98	4.48	8.97	12.57
5	1.29	8.79	7.5	3.63	7.32	13.32
7	0.92	9.02	8.1	6.03	11.62	12.33

Table 2 summarizes the curing characteristics of gum compounds that were subjected to varying mastication duration. The minimum torque (ML), indicative of the viscosity of un-cross-linked rubber and thus the processability, exhibited no significant variation across the mastication times investigated. Theoretically, ML is expected to decrease with prolonged mastication due to the breakdown of long-chain macromolecules and associated chain entanglements until it reaches a limited value. However, the results observed for compounds masticated within a short time range (1 to 7 minutes) suggest minimal effect of time duration on macromolecular breakdown during brief mastication cycles.

In contrast, both the maximum torque (MH)—reflecting the stiffness of the cured compounds—and the torque difference (MH − ML) which indicates the total crosslink density of the vulcanizate, showed only a slight upward trend. This may be attributed to the limited formation of macromolecular radicals that promote crosslinking reactions. Given the low extent of radical formation, the corresponding increase in crosslink density remains modest.

Furthermore, the crosslinking rate indices of the rubber compounds were largely unaffected by short mastication durations. Although enhanced reactivity of shorter macromolecules with increased reactive ends associated with improved dispersion of curing ingredients results in reduction of both scorch time (TS2) and optimum cure time (T90), experimental data revealed no significant changes in either of the parameters up to five minutes' mastication cycle. This observation is in agreement with the results reported by Nabil et al, who studied the effect of mastication time in a wide range of tensile properties of rubber vulcanizates. The results reported by them indicate that there is no significant influence of mastication time on scorch time and cure time (Nabil *et. al 2020).* This stability may stem from insignificant effect of limited macromolecular free radicals formed and associated heat buildup during short mastication periods.

However, it is interesting to note that, as the mastication time exceeds five minutes, scorch time and cure time have been extended at a notable extent contrary to the typical expectations. The work reported by Hayeemasae et. al also have observed a *slight increase* of above parameters when mastication is increased beyond 5 minutes (Hayeemasae et al., 2021) Excessive chain **scission** reducing the **number of available double bonds and possible interference of** inactive or side reaction products formed such as epoxides, peroxides and hydroxyl containing products during excessive mastication time with curatives or crosslink intermediates may results in delay in the crosslinking process. This would be an added disadvantage of excessive mastication in addition to the high energy consumption and poor performance of the final product.

Table 3: Dynamic mechanical properties of the rubber vulcanizates prepared using different mastication times

Mastication time (min)	Frequency (Hz)								
	0.1			1			10		
	Storage modulus (kPa)	Loss modulus (kPa)	Tan δ	Storage modulus (kPa)	Loss modulus (kPa)	Tan δ	Storage modulus (kPa)	Loss modulus (kPa)	Tan δ
0	39.68	35.64	0.90	111.14	53.44	0.48	198.68	61.10	0.31
1	39.05	35.53	0.91	109.34	53.12	0.49	196.29	60.67	0.31
3	39.03	35.64	0.91	109.57	52.97	0.48	196.35	59.98	0.31
5	48.85	39.12	0.80	123.04	53.62	0.43	210.12	59.70	0.28

The dynamic property results presented in Table 3 indicate that mastication time has slightly reduced the storage modulus compared to that of the control measured at all three frequencies used in this study. This observation reflects the slight chain scission, which is not sufficient to significantly affect elasticity at a sizable level. Storage modulus which represents the **elastic (energy-storing)** portion of a material's response to dynamic deformation expected to decrease with increasing mastication time due to the breakdown of rubber molecules and molecular entanglements. Further, it is shown that beyond one-minute mastication, no significant impact observed on the storage modulus unless mastication time exceeds three minutes, after which there is an increase in the storage modulus. Formation of crystallites using oriented or aligned molecular chains during excessive mastication may be responsible for this behaviour (Choi,2000). With regard to the loss modulus which measures the **viscous (energy-dissipating)** behavior of the rubber, **non-responsive behavior of the loss modulus (E″)** to **mastication time** of the rubber compounds could be seen from the results presented in the Table 3. Loss modules depends more on **segmental motion** and **free volume**, which may not change drastically unless mastication is extreme. Tan delta values, which reflects heat energy dissipation, remains constant during the first three minutes of mastication, decreases thereafter contrary to the general trend, suggesting decreasing loss modulus, i.e. lowering viscosity with mastication (more than 3 minutes). Huang et al. has reported that, for *unfilled natural rubber (NR),* both **storage modulus (G′)** and **loss modulus (G″)** decreased dramatically that with increased mastication time (Huang, 2019). Therefore, when the rate of reduction of storage modulus surpasses the reduction of loss modulus, lowering of Tan δ could be expected. Variation of Internal molecular structure such as loss of entanglements and formation of crystalline structures may lead to the reduction of Tan δ values with excessive mastication time

Conclusions

Effect of mastication time of natural rubber at relatively small time intervals on curing properties and dynamic properties were studied. The results showed that responses of natural rubber to the excessive mastication deviate from the standard trends showing the importance of determination of optimum mastication time, even within the short mastication cycles. It could be concluded from this study that gum compounds masticated for short durations, a mastication time of just 1 to 3 minutes yields comparable curing properties along with prevention of destruction of internal natural rubber molecular structure. Therefore, this finding suggests that limiting of the mastication time of natural rubber compounds to 1–3 minutes particularly when mastication is carried out in an internal mixer leads to conserving energy and retention of properties at desired levels contributing to sustainable manufacturing practices.

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