MOONEY VISCOSITY, MOONEY ELASTICITY AND PROCESABILITY OF RAW NATURAL RUBBER

JIŘÍ MALÁČ

Department of Polymer Engineering
Faculty of Technology
Tomas Bata University in Zlín
CZ-762 72 Zlín
Czech Republic
e-mail: jmalac@ft.utb.cz

Abstract

Recently measured Mooney viscosity and Mooney relaxation data of different raw natural rubber grades were used to discuss the meaning of obtained results. Viscosity was characterized as $ML(1 + 4)\,100°C$ and stress relaxation by constant k and exponent a in power law model $M = k(t)^a$. The constant k in equation $M = k(t)^a$ give similar information about natural rubber quality as Mooney viscosity $ML(1 + 4)\,100°C$, because both values are highly correlated. Exponent a in equation $M = k(t)^a$ characterizes elastic response of raw natural rubbers, but negative values of exponent a from Mooney relaxation measurements impede its common utilization for characterization of material elasticity in rubber technology. As it is shown in this paper, elastic energy retention exponent $(a + 1)$ is positive, its values are decreasing with decreasing material elasticity, and for common characterization in rubber technology is therefore more practical to use $(a + 1)$ than exponent a. Thus, by measurement on Mooney

viscometer can be natural rubber procesability characterized not only by Mooney viscosity $ML(1 + 4)\,100°C$, but also by Mooney elasticity $(a + 1)$.

1. Introduction

Natural rubber is a biopolymer originating in trees. Properties of this biopolymer are influenced by genetics of tree as well as by other factors. Characterization of natural rubber has great meaning for both rubber processing technology and for resulting properties of rubber goods.

More natural rubber is consumed annually than any single synthetic elastomer; yet the quality of this natural product is influenced by many special factors not associated with synthetic rubber production [5]. Natural rubber and synthetic polyisoprene share the same monomer chemistry (isoprene is the building block of these polymers). Synthetic polyisoprene consists of up to 99% rubber hydrocarbon, while natural rubber is usually around 93% rubber hydrocarbon and molecular weight distribution of natural rubber is widely variable [6].

Molecular weight distribution of *Hevea brasiliensis* natural rubber shows considerable variation from clone to clone, ranging from 100,000 to over 1,000,000. Natural rubber has a broad, bimodal, molecular weight distribution. The polydispersity or Mw/Mn can be as high as 9.0 for some clones of natural rubber [11].

Mooney viscosity test is extensively used to measure the viscosity of raw rubbers. The Mooney test is so widely used that most rubber compounders tend to think in terms of Mooney units when judging the quality of a raw rubber. The Mooney viscometer consists of rotating a serrated rotor imbedded in a rubber specimen, contained within a sealed, pressurized cavity. The temperature of the cavity can be adjusted, and there is usually a preheat time after the dies are closed to allow the rubber to approach the set temperature of the instrument. The rotor then turns at constant speed and experiences a given resistance to rotation. This torque is converted into Mooney units (MU) in accordance with ASTM D 1646 and ISO 289, Part 1. Because of the thixotropic nature of rubber (where the measured viscosity decreases with time), the actual Mooney viscosity is the value preceeding the specified time of reading

[6, 7]. The disk-shaped rotor of Mooney viscometer does not induce a viscometric flow field due to significant edge effects, yelding shear stresses significantly higher than expected [10]. It is why the Mooney viscosity is given in the Mooney units (MU).

It was recently shown that $ML(1 + 4)\,100°C$ at 2rpm rotor speed (i.e., at standard conditions) the Mooney viscosity is not sensitive enough to average molecular weight of natural rubber and characterization at lower speeds (not greater than 0.2rpm) was recommended. When the rotor speed is high, the elastic response of the material becomes predominant [4]. But, fortunately, the measurement of both Mooney viscosity and Mooney relaxation enables now independent characterization of the viscous and elastic response of natural rubber.

The information obtained from a Mooney viscometer can so include:

- Mooney peak, which is the initial peak viscosity at the start of the test; it is a function of the green strength of rubber.

- Mooney viscosity, which depends on molecular weight and molecular weight distribution, molecular structure such as stereochemistry and polymer branching, and non-rubber constituents.

- Stress relaxation, which is the response to a sudden cessation of deformation when the rotor of the Mooney viscometer stops. The rate of stress relaxation can correlate with molecular structure characteristics such as molecular weight distribution, chain branching, and gel content [12].

Stress relaxation run on the same specimen as viscosity measurements. The normal Mooney apparatus has, in addition, to be capable of being stopped within 0.1s, resetting zero torque for a static rotor and recording the torque every 0.2s [1].

At Mooney stress relaxation test, the Mooney viscometer after completion of the viscosity test stops the rotation of rotor very quickly and after stopping of rotor, the torque values are recorded. The stress relaxation of rubber can usually be described through power law model:

$$M = k(t)^a, \tag{1}$$

where: $M =$ the torque value in Mooney units;

k = the torque value 1 *second* after the rotor has stopped;

a = the rate of stress relaxation (the slope of the relaxation function).

Thus, in log-log plot, we get

$$\log M = a(\log t) + \log k. \qquad (2)$$

If we place relaxation data in a log-log plot, and if the rubber is complying with the power law model in Equations (1) and (2), the stress relaxation becomes a straight line.

The slope a is then one method of quantifying uncured rubber elasticity. A steep slope indicates less uncured rubber elasticity and less elasticity can mean better processing. Mooney stress relaxation can therefore provide additional quality information, which Mooney viscosity cannot provide [6, 7].

A perfect elastic material would not give a stress decrease after stopping the rotor, whilst a perfect viscous material would give zero stress instantaneously. The deformation energy is stored in the material in the first case and dissipated in the second. On a log-log plot, elastomers being between these two extremes, they give a linear response of stress function of time. The slope of this linear function is a measure of the intrinsic elasticity of the material. A value close to zero would indicate a material more elastic. Most of the tested polymers give a strait regression line on a log-log scale, but some a curved regression line [2, 3].

When the relaxation data in a log-log plot is not a straight line, a model that give a better fit for the experimental decay of Mooney torque over time than the usual power law is needed. Recent results for natural rubber showed that there are other suitable models (e.g., a tri-exponential generalized Maxwell model) allowing in this cases better description of relaxation curve than the traditionally used power law model [8].

In this paper, recent Mooney viscometer measurements on different raw natural rubber grades are described and meaning of obtained results is discussed.

2. Experimental

Raw natural rubbers were tested as received (i.e., not milled). Samples for Mooney viscosity and Mooney relaxation measurements were cut from raw natural rubber strips with thickness about 1cm, and measured according to ASTM D 1646 at 100°C on Mooney viscometer MV2000 VS (Alpha Technologies) with large rotor. Preheat time 1 min with test time 4 min were applied and values of Mooney viscosity $ML(1 + 4)\,100°C$ were obtained. After stopping the rotor of Mooney viscometer, the Mooney relaxation was measured for next 3 min.

An example of Mooney viscosity and Mooney relaxation curve, i.e., an example of dependence of torque in Mooney units (MU) at 100°C on time, is apparent from Figure 1: After preheat time 1 min the measurement starts. At the start of measurement, the initial peak viscosity (i.e., the initial torque maximum) is reached. The Mooney viscosity $ML(1 + 4)\,100°C$ is in Figure 1 the value of torque (in MU) 5 min from the test beginning. After stopping of rotor (at this 5 min time), the Mooney relaxation of natural rubber sample (i.e., the decrease of torque in time) is visible.
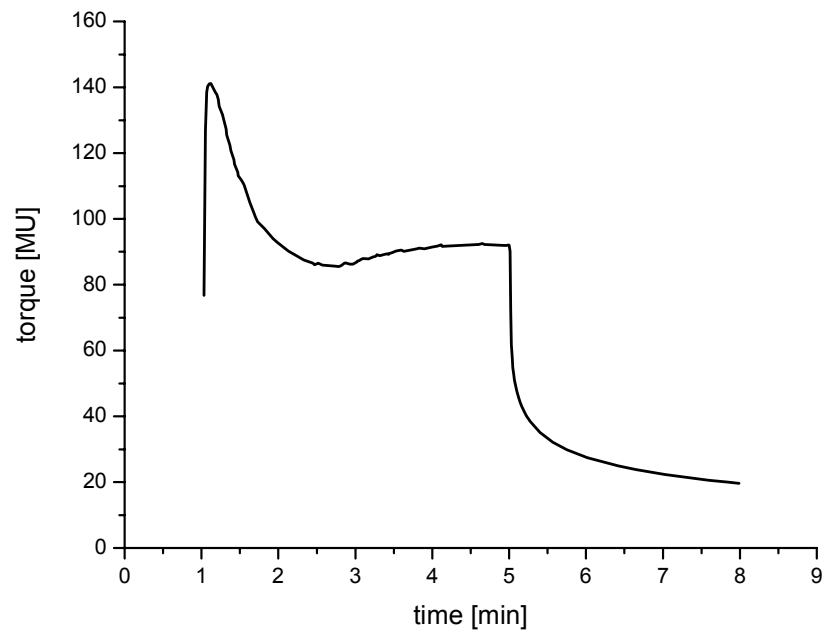
Figure 1. Typical Mooney viscosity and Mooney relaxation curve of natural rubber.

3. Results

Data for 18 raw natural rubber grades measured in [9] by Mooney viscometer and evaluated by its software are presented in Table 1.

Table 1. Data obtained by Mooney viscometer

Sample No.	Grade of NR	Init. [MU]	ML [MU]	Slope a [1M/1s]	Intercept k [MU]	RCoeff.
1	SVR 10, 1144	120.7	96.1	− 0.211	74.5	− 0.999
2	NAT 10, 1045	123.4	94.8	− 0.226	72.2	− 0.999
3	NAT 10, 1042	131.3	91.6	− 0.248	70.3	− 0.999
4	NAT 10, 1046	143.6	94.0	− 0.238	73.0	− 0.999
5	SMR L	108.4	64.8	− 0.247	40.9	− 0.999
6	PAKRUB 10, 1022	132.0	97.3	− 0.216	75.5	− 0.999
7	PAKRUB 10, 1025	122.7	94.6	− 0.232	71.7	− 0.999
8	PAKRUB 10, 1024	128.5	96.8	− 0.218	73.9	− 0.998
9	NR SVR 10	62.2	58.0	− 0.251	42.0	− 0.999
10	NR SVR 3L	179.0	97.5	− 0.201	76.5	− 0.998
11	NR PANRUB 5L	198.7	83.9	− 0.254	63.2	− 0.999
12	NR SVR CV 60	105.3	62.6	− 0.377	44.5	− 0.999
13	PANRUB 5 CV 60	130.3	72.2	− 0.291	52.5	− 0.999
14	SVR 10, 1383	113.2	97.4	− 0.250	75.1	− 0.998
15	NAT 10, 20	103.3	85.8	− 0.311	65.3	− 0.999
16	NAT 10, 22	88.2	78.2	− 0.316	56.4	− 0.999
17	SVR 3L, 1100	137.5	81.5	− 0.239	58.7	− 0.998
18	SVR CV 60, 31	118.5	71.6	− 0.214	48.4	− 0.998

Columns in Table 1:

Init. is initial maximum at the beginning of measurement (i.e., Mooney peak);

ML is Mooney viscosity $ML(1 + 4)$ 100°C;

Slope a and Intercept k are parameters of power law model $M = k(t)^a$; and

RCoeff. is correlation coefficient R for power law model.

4. Discussion

4.1. Initial torque maximum

Values of initial torque maximum (i.e., values of Mooney peak) for measured grades of raw natural rubber in Figure 2 differ appreciably. This could be caused by differences in composition, molecular weight distribution, and degree of crystallization for tested grades of natural rubber. Unknown influence can have also material and thermal inhomogenity of the measured NR samples at the beginning of experiment.
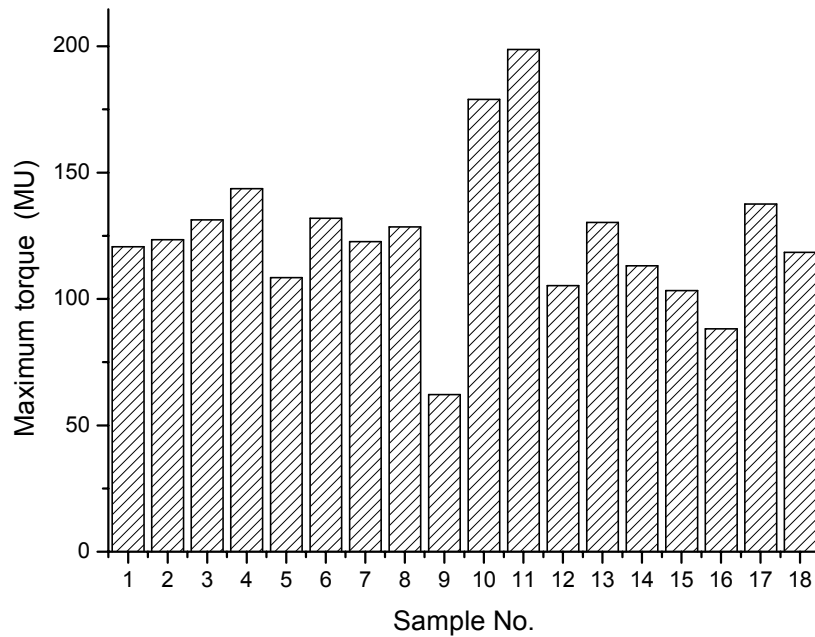
Figure 2. Initial torque maximum of measured raw natural rubbers.
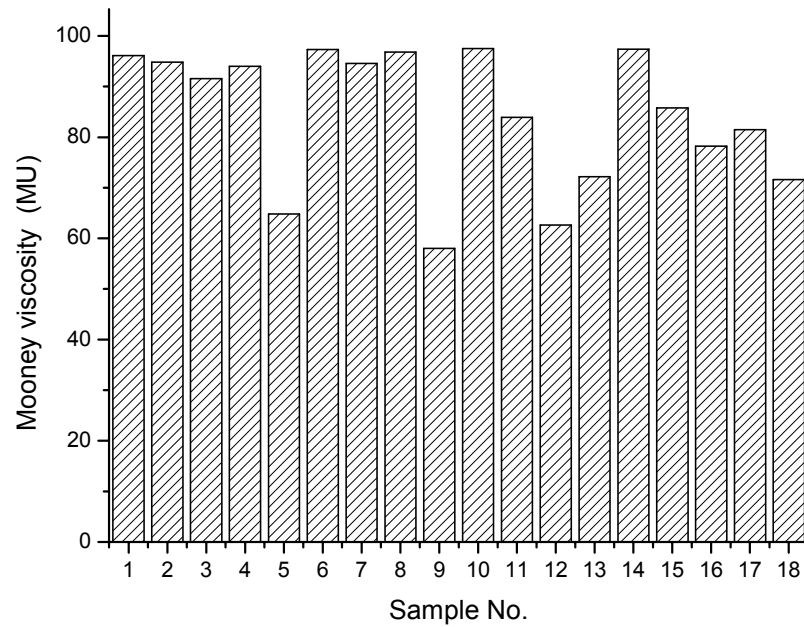
Figure 3. Mooney viscosity $ML(1 + 4)\,100°C$ of measured raw natural rubbers.

4.2. Mooney viscosity

Mooney viscosity $ML(1 + 4)\,100°C$ is usually used as the main quality parameter of raw natural rubbers. As we can see, the individual values of measured grades of raw natural rubber in Figure 3 are different. Nevertheless, it is possible to suppose that the values of initial torque maximum in Figure 2 could increase with increasing values of Mooney viscosity $ML(1 + 4)\,100°C$ in Figure 3. The obtained dependence of initial torque maximum on the Mooney viscosity is in Figure 4.
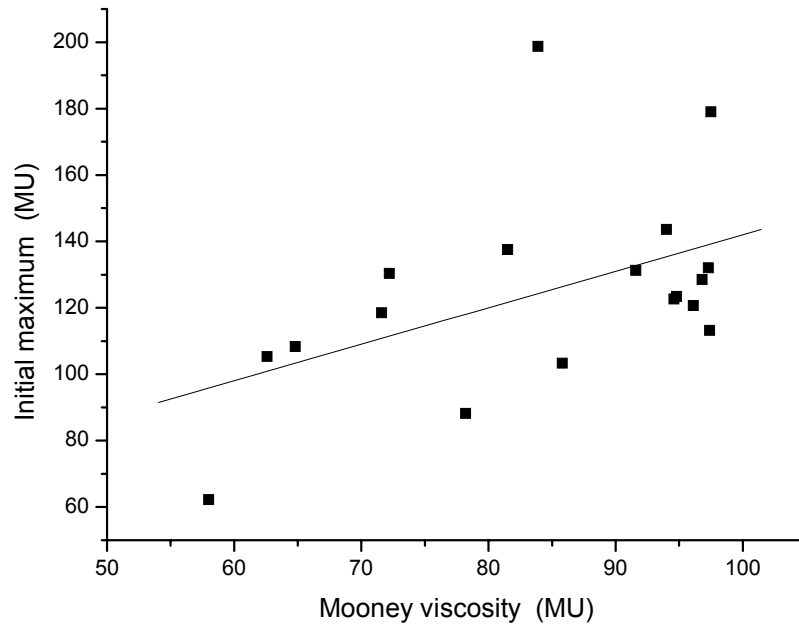
Figure 4. Dependence of initial torque maximum on Mooney viscosity $ML(1 + 4)\,100°C$ of measured raw natural rubbers ($R^2 = 0.2377$).

Linear fit in Figure 4 shows that initial torque maximum actually slightly increases with Mooney viscosity, but the scatter of values is considerable.

4.3. Mooney relaxation

In Table 1 is presented also an intercept k and slope a for Mooney relaxation log-log plot line of measured raw natural rubber grades. As the values of correlation coefficient R in Table l are all near to −1, the Equation (2) describes the obtained results reasonably well.

Intercept k of measured grades of raw natural rubber in Figure 5 and their Mooney viscosities in Figure 3 are at the first glance similar.
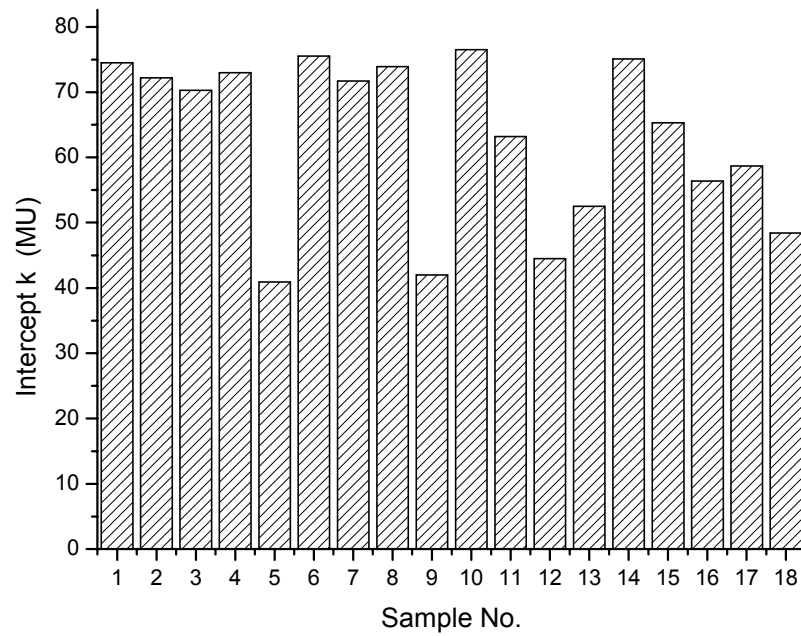
Figure 5. Intercept k in Equation (2) for measured raw natural rubbers.

The intercept k from Figure 5 could therefore increase with increasing values of Mooney viscosity in Figure 3.
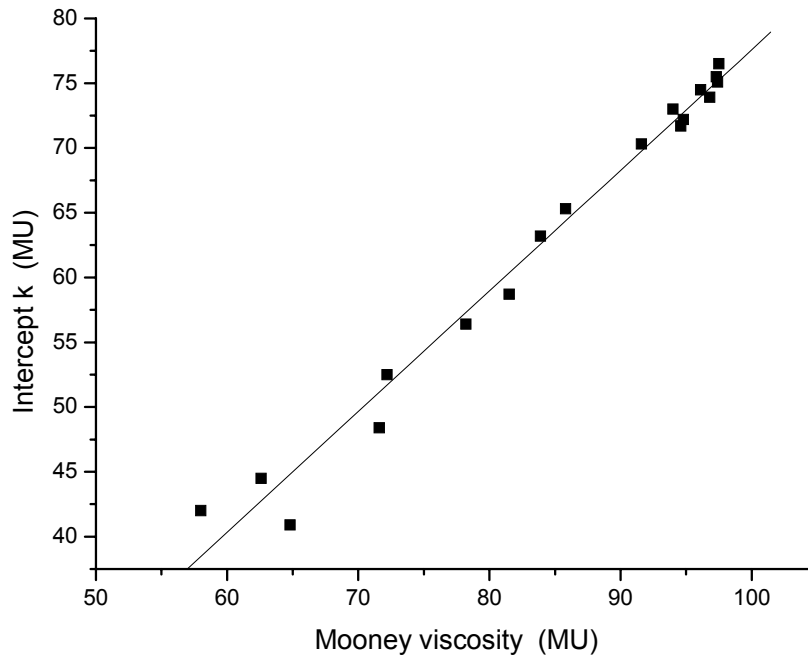
Figure 6. Dependence of intercept k in Equation (2) on Mooney viscosity $ML(1 + 4)\,100°C$ of measured raw natural rubbers ($R^2 = 0.9821$).

The dependence of intercept k on Mooney viscosity in Figure 6 seems to be linear with high correlation coefficient. This experimentally obtained dependence is described by:

$$\text{Intercept } k = 0.9312 * (\text{Mooney viscosity}) - 15.53. \qquad (3)$$

The Equation (3) is so approximately equal to

$$\text{Intercept } k \sim (\text{Mooney viscosity}) - \Delta\,[\text{MU}]. \qquad (4)$$

The intercept k in Equation (3) characterizes decrease of torque during first 1s after the rotor of Mooney viscometer has been stopped. The intercept k consists from two parts: The first part is nearly equal to Mooney viscosity and the second part (the constant Δ [MU]) is nearly the same for all grades of tested natural rubber.

As the intercept k from Equation (3) is in Figure 6 directly proportional to Mooney viscosity, values of intercept k in Figure 5 give practically the same information about natural rubber procesability as Mooney viscosity in Figure 3.

Slope a for measured grades of raw natural rubber is in Figure 7.
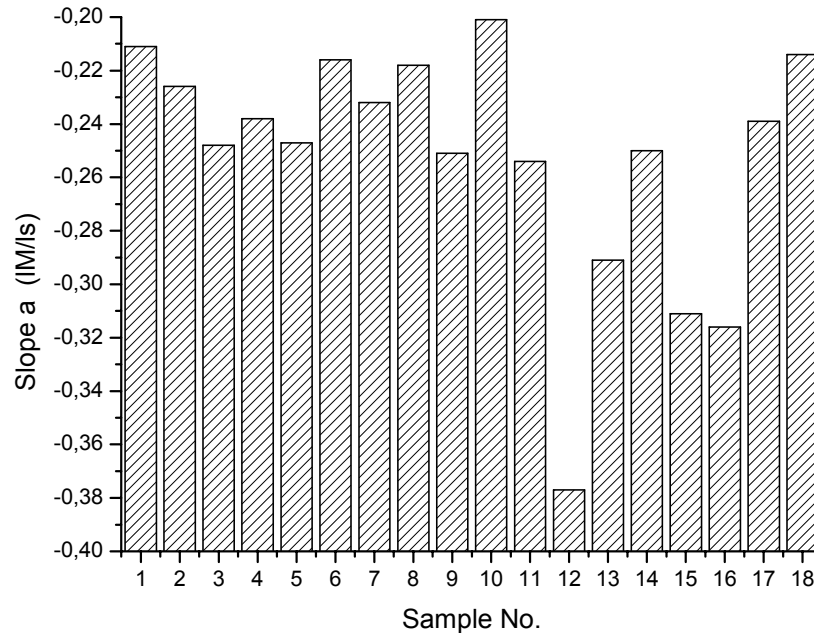
Figure 7. Slope a in Equation (2) for measured raw natural rubbers.

As viscosity and elasticity of polymer melts both frequently increase with increasing molecular weight, it is in Figure 8 shown the dependence of slope a from Figure 7 on Mooney viscosity from Figure 3. As we can see from Figure 8, the slope a and Mooney viscosity are slightly depend on each other, but correlation coefficient of linear fit is here very low.

Slope a in Figure 7 therefore gives more or less independent value from that of Mooney viscosity in Figure 3 and can be used for characterization of raw natural rubber elasticity. The difference between Mooney viscosity and slope a could be result of different effect of molecular weight distribution on behaviour of both values.
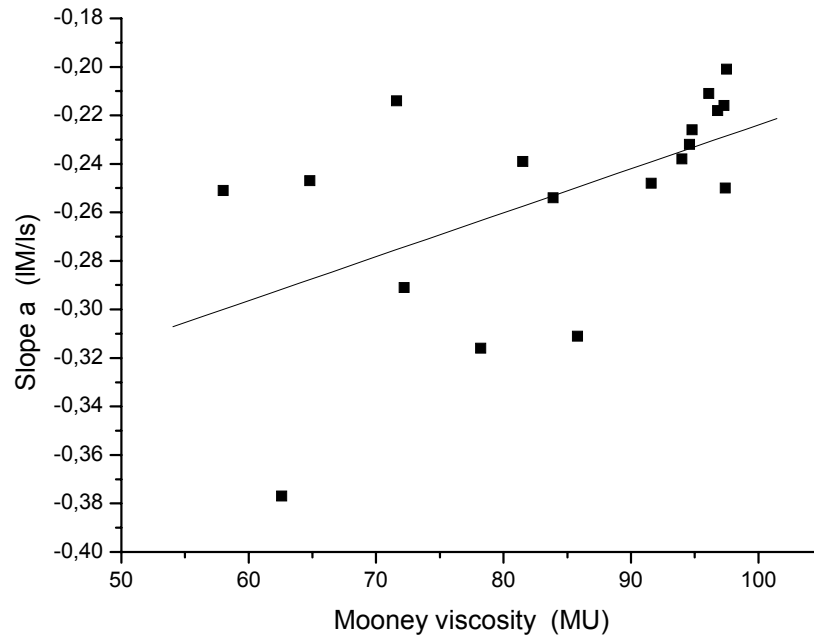
Figure 8. Dependence of slope a in Equation (2) on Mooney viscosity $ML(1+4)\,100°C$ of measured raw natural rubbers ($R^2 = 0.2931$).

As we can see in Figures 7 and 8, all measured values of slope a are negative. Slope a equal to zero would indicate a perfect elastic material and materials with decreasing elasticity have more and more negative slope a values. This complicated behaviour of slope a from Mooney relaxation measurements impedes its common utilization for characterization of material elasticity in rubber technology.

4.4. Deformation energy

When a rotor of Mooney viscometer turns in material at constant speed, necessary deformation energy is partly dissipated and partly stored in rubber sample. At the same time, the rotor experiences resistance to rotation given by torque M, which is so partly caused by viscosity and partly by elasticity of the material.

Relation between the measured rotor torque M and power needed for rotor rotation P is equal to

$$P = \omega M, \tag{5}$$

where P is power, ω is angular velocity, and M is torque. Energy consumed by rotor rotating in the material in time dt is then

$$dE = Pdt. \tag{6}$$

After stopping of Mooney viscometer rotor part of rotor torque M caused by viscosity of material ceases immediately. Part of rotor torque M caused by material elasticity manifests itself as time-dependent rotor torque M. Decrease of the rotor torque M in time is measured in Mooney relaxation test and depends on energy stored in material due to rubber elasticity at previous rotor rotation. After stopping of Mooney viscometer rotor, the part of elastically stored deformation energy decreases in time because of stress relaxation.

When the power law in Equation (1) holds for Mooney relaxation, the decrease of torque in time is $M = k(t)^a$, and we can suppose that decrease of elastically stored part of deformation energy E_s in time dt is proportional to the torque M

$$dE_s \sim Mdt = k(t)^a dt. \tag{7}$$

Integration of Equation (7) gives then relation between elastically stored part of deformation energy and time as

$$E_s \sim \frac{k}{a+1}(t)^{(a+1)}. \tag{8}$$

From point of view of material properties is meaning of parameter $k/(a+1)$ in Equation (8) not quite clear. But intercept k characterizes energy dissipated in material (as we can see from dependence of k on Mooney viscosity in Figure 6) and exponent $(a+1)$ characterizes rate of decrease of elastically stored part of deformation energy (i.e., stress relaxation).

Parameter $k/(a + 1)$ therefore represents the ratio of values standing for viscous and for elastic part of deformation and could eventually depend on mechanical loss factor tan δ from dynamic mechanical testing (where tan δ is ratio of viscous to elastic part of modulus).
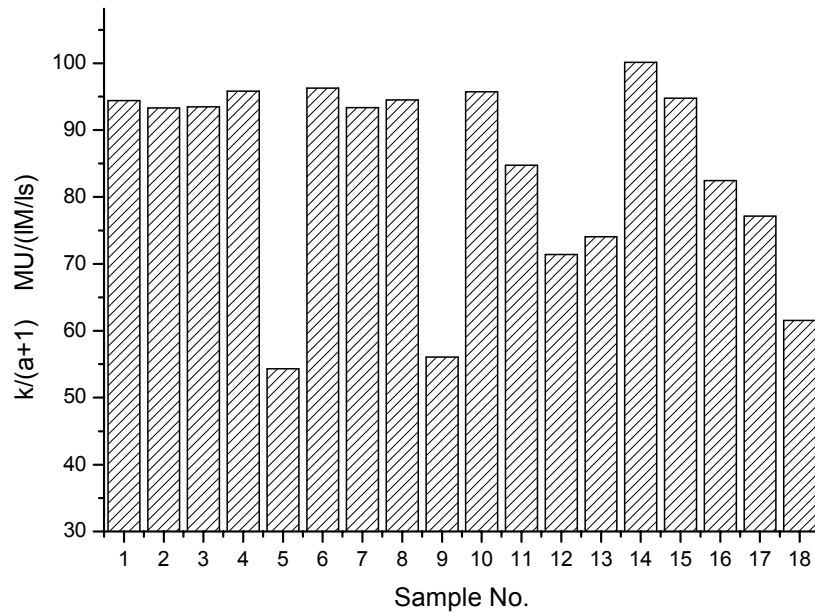
**Figure 9.** Parameter $k/(a + 1)$ for our measured grades of raw natural rubber.
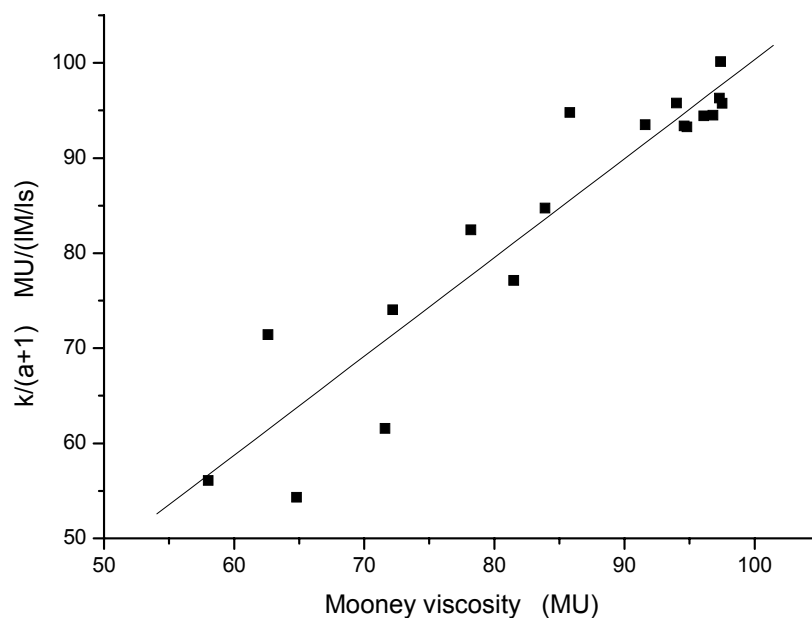
Figure 10. Dependence of parameter $k/(a+1)$ from Figure 9 on Mooney viscosity $ML(1+4)\,100°C$ from Figure 3 for measured raw natural rubbers ($R^2 = 0.8835$).

Dependence of parameter $k/(a+1)$ from Figure 9 on the Mooney viscosity from Figure 3 shown in Figure 10 seems to be linear, but as we can see, the correlation coefficient of parameter $k/(a+1)$ in Figure 10 is lower than that of intercept k in Figure 6 and this difference is caused by values of exponent $(a+1)$. Parameter $k/(a+1)$ so seems not to be the same material characteristic as Mooney viscosity.

It is obvious that the values of slope a from Equation (1) in Figure 7 and the values of exponent $(a+1)$ from Equation (8) in Figure 11 give in principle the same information about elasticity of measured material (both exponents characterize stress relaxation of natural rubber).
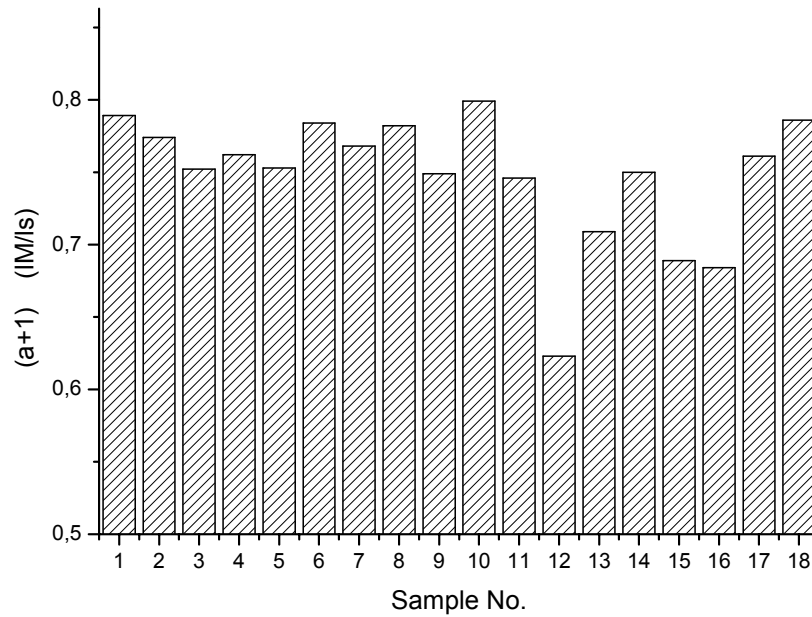
Figure 11. Values of exponent $(a + 1)$ from Equation (8) for our measured grades of raw natural rubber.

Main advantage of utilization of elastic energy retention exponent $(a + 1)$ instead of slope a for common characterization of material elasticity in rubber technology would be that the values of exponent $(a + 1)$ are positive, and interpretation of these values is therefore simple: Higher values of exponent $(a + 1)$ mean higher deformation energy retention in material in time and therefore higher elasticity of sample. The highest theoretical value of this exponent is $(a + 1) = 1$, when elastic part of deformation energy stored at rotation in sample would not decrease in time.

On the basis of Mooney relaxation is for practical applications therefore better use Mooney elasticity as a value of elastic energy retention exponent, i.e., as

$$\text{Mooney elasticity} \quad = (a + 1). \tag{9}$$

5. Conclusions

Mooney viscosity $ML(1 + 4)\,100°C$ was measured and after stopping of rotor, the decrease of rotor torque M was recorded for next 3 min. As usual, the rotor torque decrease in time was described by power law model $M = k(t)^a$ with slope a and intercept k as parameters of log-log plot.

On the basis of recent measurements on different raw natural rubber grades, the meaning of results obtained by Mooney viscometer was discussed.

It was shown that initial torque maximum probably slightly increases with Mooney viscosity $ML(1 + 4)\,100°C$, but the scatter of the values is significant.

As the intercept k in equation $M = k(t)^a$ is directly proportional to Mooney viscosity, the values of intercept k give practically the same information about natural rubber procesability as values of Mooney viscosity.

Values of slope a in equation $M = k(t)^a$ give independent information about natural rubber procesability from values of Mooney viscosity, and characterize elastic response of the material.

All measured values of slope a are negative and materials with decreasing elasticity have more and more negative slope values. This complicated behaviour of slope a impedes its common utilization for characterization of material elasticity in rubber technology.

Main advantage of using elastic energy retention exponent $(a + 1)$ for characterization of material elasticity in rubber technology would be that the values of exponent $(a + 1)$ are positive and higher values of exponent $(a + 1)$ mean higher elasticity of sample. For common characterization of elasticity in rubber technology is therefore more practical to use $(a + 1)$ than exponent a.

By measurement on Mooney viscometer can so procesability of natural rubber be characterized not only by Mooney viscosity $ML(1 + 4)\,100°C,$ but also by Mooney elasticity $(a + 1).$

Graphical Abstract
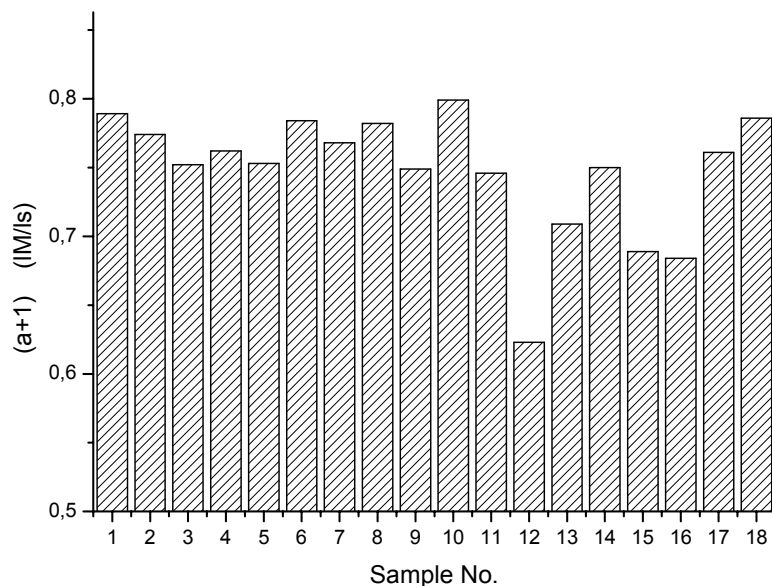
Procesability of raw natural rubber is now usually characterized by Mooney viscosity. Exponent a from Mooney relaxation measurements can be used for characterization of natural rubber elasticity, but its negative values impede this utilization. Elastic energy retention exponent $(a + 1),$ shown here for 18 raw natural rubbers, is positive (its values decrease with decreasing material elasticity). Mooney elasticity $= (a + 1)$ is therefore more practical for characterization of elasticity in rubber technology than exponent $a.$

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