

# The Influence of the Relative Molecular Weight of Natural Rubber on its Thermo-Oxidative Stability

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## Synopsis

The influence of relative molecular weight on rubber thermo-oxidation in air at  $130 \pm 1^\circ\text{C}$  has been studied by means of infrared spectroscopy. The carbonyl group formation in single fractions of natural rubber has been measured. It was found that the development of kinetic curves  $\Delta A_{\text{C=O}} = f(t)$  corresponds for both fractionated and unfractionated extracted samples. Kinetic curves of natural rubber formation are characterized by an induction period  $\tau$ . Its magnitude is a function of molecular weight up to the value  $[\eta] = 0.2 \text{ m}^3/\text{kg}$ , and then stays invariant to changes in  $[\eta]$ . In the range of low values of the internal viscosity up to  $0.2 \text{ m}^3/\text{kg}$ , the dependence  $\tau_{\text{C=O}} = f([\eta])$  has an exponential character as a consequence of the statistical character of chains breaking down during the degradation. It has been proved that the reciprocal value dependence of the mean viscosity molecular weight of unfractionated acetone-extracted natural rubber on the length of induction period is linear. The change in double-bond amount during the oxidation is not reflected in the induction period determined by infrared spectroscopy.

## INTRODUCTION

An important and always interesting problem in the field of macromolecular research is the relation between the polymer molecular weight and the physical, chemical, and rheological properties. Many studies in this area are devoted to the study of the influence of molecular weight and distribution function on the stability of polyethylene mechanical properties.<sup>1-3</sup> Karasev and co-workers<sup>4</sup> studied the molecular weight distribution of ten polyethylene samples with a high density and examined its influence on mechanical properties with a wide temperature range from  $-40$  to  $100^\circ\text{C}$ . The authors<sup>4</sup> have found that the improvement in the mechanical properties of polyethylene samples increases with high molecular weight fraction content, increasing from  $\bar{M}_w \sim 10^6$  and higher for the whole studied temperature interval. An absence of high molecular weight fractions in the sample tends to low mechanical properties stability in the case of polyethylene in a wide distribution curve, or a narrow one.

A similar study of natural rubber according to our experience has not yet been performed. It has been found that the differences in distribution of molecular weight in polyisobutylene<sup>5-7</sup> cause considerable changes in rheological properties of material, and this could not be devoid of any influence on production effectiveness in the final result. The thermal stability of poly(vinyl chloride) fractions was studied by Feldman and co-workers,<sup>8</sup> who found that the molecular weight of samples in the range of  $\bar{M}_n = (1.5-5.5) \times 10^4$  and  $\bar{M}_w = 3.9 \times 10^4-2.5 \times 10^5$  has no influence on the thermal stability of samples. With regard to the fact that  $\bar{M}_n$  values of single fractions do not change in series and the  $M_w$  change in one order only, the authors<sup>8</sup> could not find any correlation between molecular

weight distribution and the thermal stability of single fractions, not even when ingredients were removed by multiple extraction.

The aim of this work was to find an internal relation between molecular weight and the thermo-oxidative stability of natural rubber fractions during the aging process at an increased air temperature.

Literature data<sup>9-19</sup> concerning the thermo-oxidative stability of natural rubber are unhomogeneous and sometimes also controversial. The variety of views on the reaction mechanism in the oxidation degradation of natural rubber results above all from the lack of homogeneity on its substratum and also from the complexity of the simultaneous reactions proceeding in rubber. Natural rubber oxidation study has been complicated by a wide range of oxygen/polymer mutual reaction possibilities. In the original material wide changes in its physical properties can be induced by a small amount of bonded oxygen. The reaction of oxygen with the polyisoprene chain can take place in different positions. Especially tertiary carbon in the neighborhood of a double bond seems to be very reactive. Interpretation of experimental results is complicated by insufficient accuracy in the study of property changes in the initial stages of the oxidation process, although this first stage has a considerable influence on the whole reaction mechanism.

Rubber oxidation in comparison to that of substances of low molecular weight proceeds more slowly. The initial rate of oxygen absorption is insignificant. After a certain induction period the rate increases exponentially and the oxidation process proceeds in a short time interval in accordance with the known degenerate branching of the autocatalytic chain mechanism through unstable hydroperoxide production.

The presence of characteristic oxidation products of natural rubber can be conveniently examined by means of infrared spectroscopy.

A great advantage of this method is both the possibility of simultaneous examination of the independent origin of various atomic groups and elucidation of the quantitative changes which reflect the association of oxygen atomic groups.

## EXPERIMENTAL

The studied substrate was white, crepe natural rubber of *Hevea brasiliensis* with characteristic physical properties summarized in Table I.

### Chemicals

Benzene, analytical grade, Lachema n.p., Brno (ČSSR), thiophene free, was used. For kinetic measurement it was purified by rectification on a laboratory distillation column (30 TP) at atmospheric pressure and simultaneous drying by sodium metal. The boiling point was 80.4°C.

TABLE I  
Physical Properties of *Hevea brasiliensis* Natural Rubber

Property	Numerical value
Density, kg/m <sup>3</sup>	0.92 × 10 <sup>3</sup>
Limit viscosity no., m <sup>3</sup> /kg	0.64
$\bar{M}_w$ due to 20 kg/mole	8.94 × 10 <sup>7</sup>
S, svedbergs	0.32

Methyl alcohol was from p.a. Lachema Brno, a commercial product. The distillation range was 64.0–65.5°C.

### Rubber Sample Preparation

Samples with different molecular weights for oxidation tests were prepared by fractional precipitation of 1.5 wt % natural rubber benzene solution by gradual addition of methanol precipitant at laboratory temperature and nitrogen atmosphere and in darkness. Isolated fractions were dried to constant weight in a vacuum desiccator and characterized by intrinsic viscosity  $[\eta]$  at 25°C and further used for the preparation of film samples by casting on NaCl plates for oxidation testing. From the intrinsic viscosity, measured values of the mean viscosity molecular weight of the individual fractions were calculated by the Mark–Houwink–Sakurada equation.<sup>21</sup> The following values for  $K$  and  $\alpha$  constants have been used<sup>22</sup>:  $K = 5.0 \times 10^{-5} \text{ m}^3/\text{kg}$ ,  $\alpha = 0.665$ , temperature  $t = 25^\circ\text{C}$ . The values of  $K$  and  $\alpha$  are valid for the molecular weight range from 420 to 1,500,000. The integral weight distribution function of studied natural rubber is given in Figure 1.

### Preparation of Rubber Films for Oxidation Tests

For spectroscopy measurements of absorbance changes in carbonyl groups during the time of oxidation, natural rubber films of thickness from  $2.3 \times 10^{-5}$  to  $2.5 \times 10^{-5} \text{ m}$  were used on the NaCl plate. The samples were prepared by casting and successive solvent evaporation from 2 wt % polymer solution in

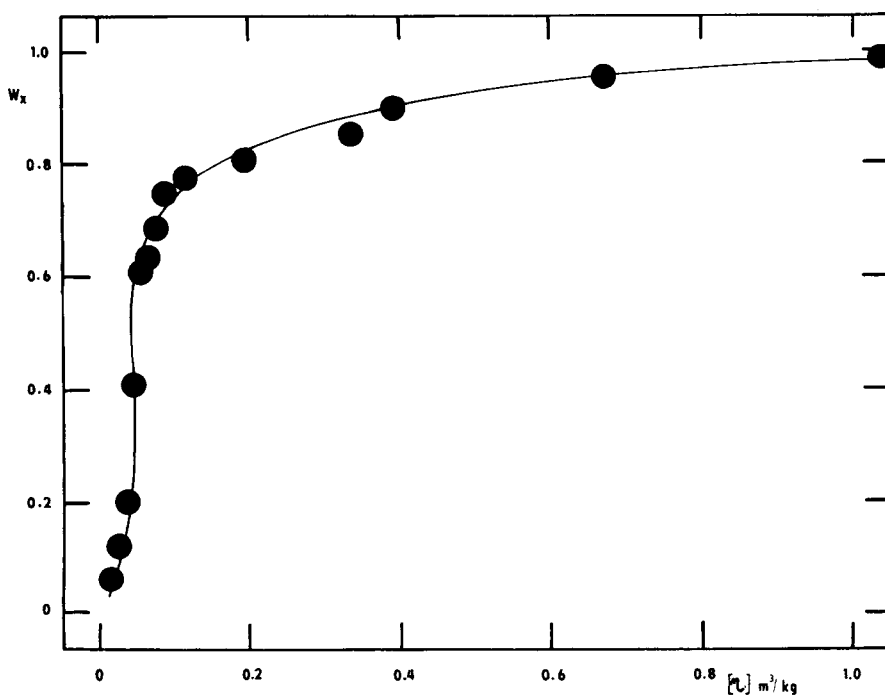


Fig. 1. Integral weight distribution function of natural rubber.

benzene. The benzene remains on rubber films were removed by drying the films in a vacuum (150 PA) desiccator in the dark. Film thickness was checked by spectroscopic measurement of band absorbance corresponding to C-H bond oscillations in  $\text{CH}_2$  and  $\text{CH}_3$  groups ( $\tilde{\nu} = 1458 \text{ cm}^{-1}$ ). The absorbance of this band follows the linear dependence on the film thickness checked by a mechanical dimension gauge, with accuracy of  $\pm 4 \times 10^{-6} \text{ m}$ . Deviation of the measured band absorbance determination was  $\pm 0.006 \text{ m}$  and the maximal deviation  $\pm 0.012 \text{ m}$ .<sup>23</sup>

The rubber samples on NaCl plates were stored in nitrogen atmosphere in darkness before thermal oxidation in order to prevent possible contamination by atmospheric oxygen in the samples examined before their oxidation.

For the measurements of absorption of individual samples the Perkin-Elmer IR spectrometer, Model 12-C, 234 Series, was used.

Thermo-oxidation of rubber fractions at  $130^\circ\text{C}$  in air was examined according to the increase in absorbance of  $-\text{CO}$  groups at  $\tilde{\nu} = 1720 \text{ cm}^{-1}$ . The oxidation was performed on a rubber film series for each fraction by an uninterrupted test.<sup>23</sup> The kinetic oxidation curves were evaluated according to the magnitude of induction periods which were determined as projections of the intersections of linear parts of real S curves projected on a time axis (see Fig. 2).

## RESULTS AND DISCUSSION

As was stated above, most of the authors dealing with the study of thermo-oxidation of polymers suppose that reactive places in chains are the groups which easily create peroxides with oxygen molecules. Davis and Golden<sup>24</sup> studying the poly(tetramethyleneoxide) degradation found that the decrease in molecular weight of destroyed products was accompanied by destruction of peroxide groups. On the basis of the measurements adduced, this cannot be acknowledged as a fact, because the presence of hydroperoxides and cyclic peroxides in the course of measurements has not been spectroscopically proved. It seems that the

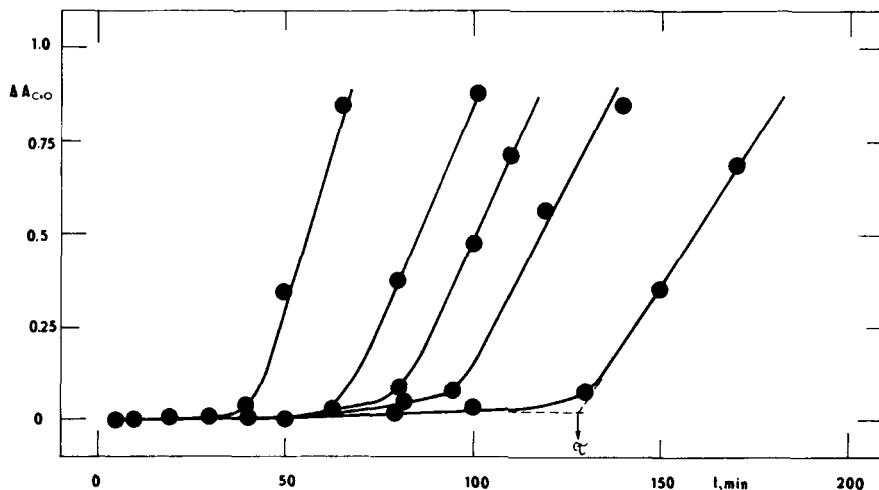


Fig. 2. Dependence of change in absorbance of carbonyl groups in fractions of natural rubber on the time of oxidation. Fraction numbers: (○) 1, (⊗) 2, (○) 3, (⊕) 4, (⊙) 5;  $\tau$  = induction period.

method of infrared spectroscopy in the above-mentioned system is not sensitive enough.

Kinetic curves of the oxidation of the first five natural rubber fractions, expressing absorption changes of CO groups as a function of reaction time, are to be found in Figure 2.

In agreement with the data stated in the literature,<sup>25-27</sup> the oxidation kinetic curves are characteristic by a typical sigmoidal shape with an expressive induction period  $\tau$  and part after its completion. Stationary parts of curves have not been evaluated.

The natural rubber films in the course of thermo-oxidative reaction undergo characteristic changes. At the beginning of the oxidation their appearance does not noticeably change. Near the completion of the induction period there are some observable changes in the rheological properties. Films become sticky and viscous. After these properties reach their maximum, the tackiness disappears and in the interval of the stationary part of the curve  $\Delta A_{C=O} = f(t)$  they become solid and lacquerlike, yellow to brown in color, according to the degree of oxidation. According to some authors<sup>28</sup> the tackiness is caused by successive degradation of the rubber chain. It is mainly in the final stages of oxidation that the spatial branching of macromolecules is taking place.<sup>29</sup>

Reich and Stivala with co-workers<sup>30,31</sup> have dealt in extensive studies with the molecular weight changes during the auto-oxidation of olefins and have tried to extend the general kinetic scheme of many of the above-mentioned workers for the change  $[\eta]$  as a function of time during atactic polybutylene-1 thermal oxidation. Earlier, Quackenbos<sup>32</sup> found that the changes in  $[\eta]$  during olefin oxidation involve carbonyl group formation. Starting from an assumption that the number of bond ruptures during oxidation is a function of carbonyl concentration, the authors<sup>30,31</sup> have derived an approximate kinetic oxidation equation. There was good agreement in the values of kinetic parameter  $A$  established by optical methods<sup>30</sup> and those obtained from the change of molecular weights dependent on oxidation time.<sup>31</sup> The above-mentioned authors when evolving the theoretical equation proceeded from the assumption that polymer samples during oxidation are monodisperse or follow the highly probable distribution  $\bar{M}_n/\bar{M}_v = \text{a constant}$ .

Most of the reports concerning the degradation of macromolecular substances point to random chain rupture. We have tried to establish this fact by measuring intrinsic viscosity of destroyed products in the case of unfractionated extracted natural rubber.

Let us consider the isotropic polymer chain formed by isoprene links only, which are regularly connected into a "head-tail-head" system. The rate of bond rupture in the given time  $t$  is equal to the number of broken bonds in the time unit, i.e.,<sup>33</sup>

$$(v)_t = \left[ \lim_{\Delta t \rightarrow 0} \Delta n / \Delta t \right]_t = -(dn/dt)_t \quad (1)$$

where the probability of the breaking of the assumed unstable and uniformly distributed bond is proportional to the total number of these bonds:

$$-dn/dt = kn \quad (2)$$

By integration of eq. (2) under limiting conditions  $t = 0; n = n_0, t = t; n = n$ , we obtain

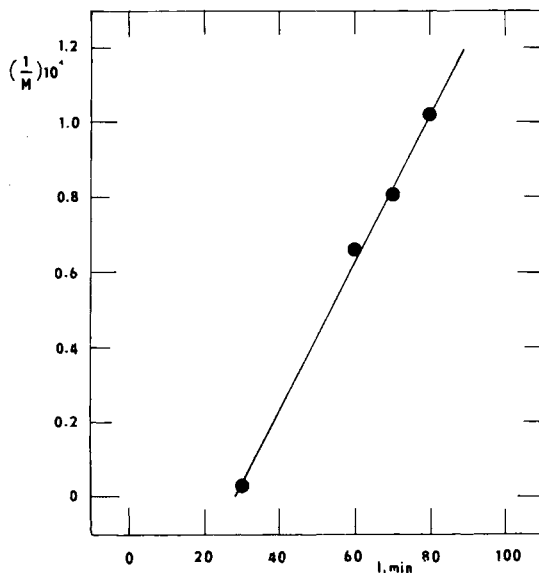


Fig. 3. Dependence of  $M_v$  reciprocal value of extracted natural rubber on time of oxidation.

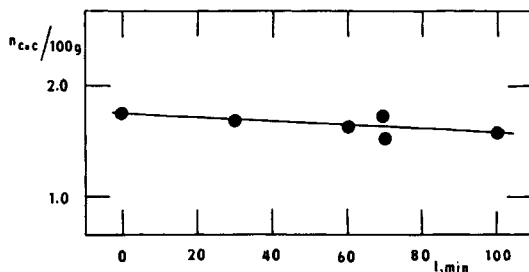


Fig. 4. Dependence of number of C=C bonds in extracted natural rubber on time of oxidation.

$$\ln(n/n_0) = -kt \quad (3)$$

and assuming that the chain breaking will happen predominantly in their center and neglecting the higher powers of the series of the logarithmic function, eq. (3) can be rewritten

$$\begin{aligned} n_0/n - 1 &= kt \\ 0 &\leq n_0/n \leq 2 \\ M &\approx \bar{M}_v \\ 1/\bar{M}_v &= k t / \bar{M}_{v,0} + 1/\bar{M}_{v,0} \end{aligned} \quad (4)$$

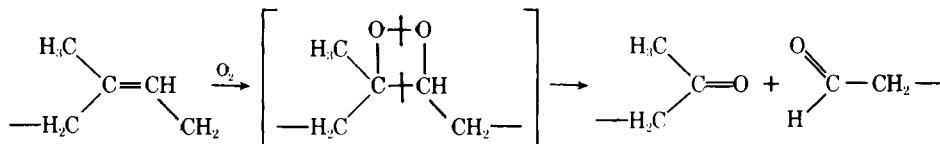
where  $\bar{M}_{v,0}$  is the mean viscosity molecular weight of a sample before the oxidation,  $\bar{M}_v$  is the mean viscosity molecular weight in time  $t$ , and  $k$  is the rate constant of the chain breaking process.

Experimentally established values of the mean viscosity molecular weight  $\bar{M}_v$  of the natural unfractionated extracted rubber in individual time intervals  $t$  of thermo-oxidative destruction are shown in Figure 3. Values of C=C bonds determined are in Figure 4. It is necessary to mention that the extrapolated value  $1/\bar{M}_v$  for zero destruction time does not agree with the value experimentally

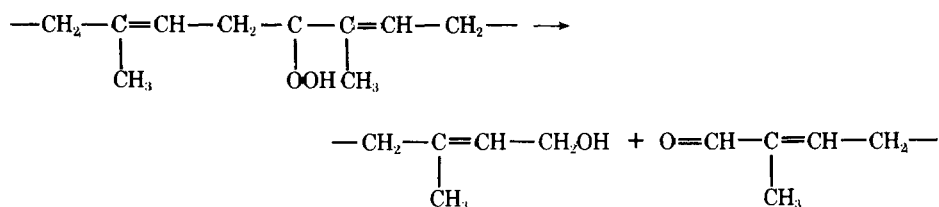
obtained by direct measurement before oxidation. This might be explained by partial preoxidation of the sample studied, and that cannot be prevented.

As evident from the comparison of thermo-oxidative tests of single fractions, the length of the induction period for carbonyl group formation is a function of molecular weight, as shown in Figure 5.

Exponential dependence of oxidation induction period on molecular weight may be explained by the statistical character of the degradation, this being accompanied by a random C-C bond breaking<sup>34</sup> in the main chain through: (1) cyclic peroxide, as the degradation intermediate<sup>14-16</sup>



(2) hydroperoxide in the  $\alpha$ -position in relation to a double bond<sup>17-19</sup>:



Similarly, Farmer<sup>35</sup> and Bevilacqua,<sup>36</sup> on the basis of model oxygen compound degradation study, accepted as the possible degradation mechanism the process taking place in the breaking of peroxides and hydroperoxides and in a certain case through interstaged epoxides.

The energy needed for C-C bond rupture is about 338.5 kJ/mole. The inner

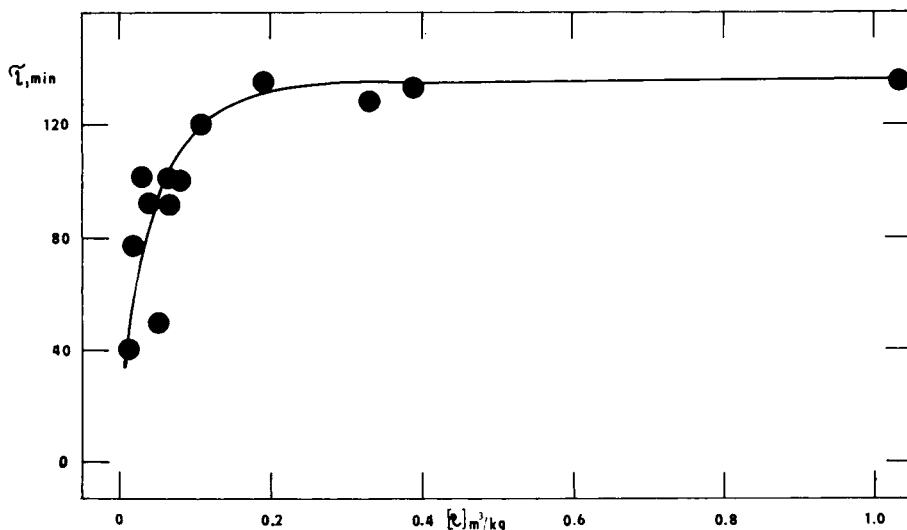


Fig. 5. Dependence of carbonyl group induction period value on intrinsic viscosity  $[\eta]$  for fractionated natural rubber.

bond in polyisoprene splits much more easily in forming the isoprene and dependent units, because in this way of breaking there are two allyl radicals formed, each with resonance energy of 79.5 kJ/mole. In this way the energy needed for C-C bond breaking can be lowered to 179.7 kJ/mole. Sarfare and co-workers<sup>37</sup> have determined that the activation energy of C-C bond rupture of natural rubber in two inert solvents at a temperature interval from 60 to 100°C equals 179.7 kJ/mole. The authors<sup>37</sup> incline to the opinion that normal C-C bonds stay undisturbed and only some of the weak lines break. Other workers<sup>38,39</sup> in their papers dealing with degradation postulate the existence of the weak links from the evidence of the low activation energy observed. Watson<sup>40</sup> reports that the activation energy for a thermal degradation of purified natural rubber equals 66.5 kJ/mole and sets this value down to rupture of some sort of weak links. Therefore, it is possible to assume that there are present certain kinds of weakly rupturing bonds in polymers the character of which has not yet been explained. Sekhar<sup>41</sup> had pointed out the possibility of a structural defect in carbonyl-type formation during biosynthesis of rubber in nature that is not without influence on the thermal degradation process.

By degradation, chain fractions are formed, fragments that have approximately the same molecular weight and that are terminated by a polar group. It seems to be reasonable not to exclude the possibility of a gradual destruction of a chain, because both processes sometimes take place simultaneously, and this is evidenced by the presence of CO<sub>2</sub>, CH<sub>2</sub>O, and lower hydrocarbons among the products of oxidation. With regard to a complexity and wide stereovariability of the possible conformations of the polyisoprene chain, it is also possible to suppose that the oxidation process has not a strictly defined character, but it is realized by a system of simultaneous reactions accompanied mainly by statistical breakage (oxidative, heat "cracking"), gradual degradation (depolymerization, oxidative degradation), chain crosslinking (the formation of C-C bridges during radical recombination, oxygen bridges), and by mutual reactions of oxidative products.

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