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Distribution of Molar Mass and Branching Index of Natural Rubber from Hevea Brasiliensis Trees of Different Age by Size Exclusion Chromatography Coupled with Online Viscometry

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Summary: Natural rubber from hevea brasiliensis trees (Thailand, RRIM 600 clone) of different age (8, 20, and 35 years) were characterized by size exclusion chromatography (SEC) coupled with online viscometry with respect to their distribution of molar mass and branching index at a temperature of 70 °C using cyclohexane as solvent. The natural rubber samples were purified by washing with an aqueous solution of sodium dodecylsulfate and subsequent saponification. With this procedure physical branching points caused by phospholipids, proteins and hydrophobic terminal units, mainly fatty acids, of the natural rubber (cis-1,4-polyisoprene) molecule, could be removed leading to completely soluble polymer samples.

All samples investigated possess a very broad (10 to 50,000 kg/mol) and distinct bimodal molar mass distribution. With increasing age of the trees the peak area in the low molar mass region decreases favoring the peak area in the high molar mass region. By plotting the branching index as a function of the molar mass it could be shown that branching of the natural rubber increases with both, the molar mass and the age of the trees.

Introduction

The hevea brasiliensis tree is the most important commercial source of natural rubber for products like tires, gaskets, seals, or medical gloves. When natural rubber is received in the factory, its cure properties are usually tested in a rheometer using standard test methods. These test methods very often only deliver an average value e.g. of the molar mass which is insufficient, since the processing, elastic and mechanical properties[1,2] largely depend on the whole molar mass distribution, especially the high molar mass content, as well as the branching.[3] Therefore, for the rubber processing industry it is of great importance how the complete structure of the natural rubber effects the properties of the final product.

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A powerful method for an accurate determination of the distribution of molar mass and branching is size exclusion chromatography (SEC) coupled with viscometry. Recently, it has been shown that natural rubber contains molar mass fractions up to 10^7 g/mol.[3-7] Therefore, special care must be taken to avoid molecular degradation as it may occur in SEC even for molar masses not larger than 5,000,000 g/mol.[8-10]

In this paper we describe a reliable method to analyze natural rubber of very high molar mass as well as its branching distribution by comparing three different natural rubber samples from hevea brasiliensis trees of different age.

Experimental

Sample preparation.

Fresh field hevea rubber latex (clone RRIM 600) from Thailand provided by the Semperit Technische Produkte GmbH (Wimpassing, Austria) was purified according to the method of Tangpakdee and Tanaka[11] by saponification in the presence of 0.1 % (w/v) methanolic pyrogallol as an antioxidant. This method is known to remove proteins, phospholipids, and hydrophobic fatty acids from the latex[7,11] and completely soluble natural rubber samples with no remaining gel particles in cyclohexane at 70 °C were obtained.

Size exclusion chromatography (SEC) coupled with viscometry.

The distribution of the molar mass and branching index was determined at 70 °C with the "GPC 220" chromatograph (Polymer Laboratories, Church Stretton, UK) equipped with a differential refractive index (DRI) detector (Polymer Laboratories), and the differential viscometer 210 R (Viscotek, Houston, TX, USA). A set of two PLgel Mixed-A columns (particle size: 20 µm, length: 300 mm, inner diameter: 7.5 mm; Polymer Laboratories) was used. Cyclohexane (Merck, Darmstadt, Germany) containing 0.0125 % (w/v) 2,6-di-tert.-butyl-(4-methylphenol) (BHT) was used as solvent and degassed prior to entering the pump with the PL-DG2 (Erc Inc., Kawaguchi City, Japan) online degasser. The flow rate was set to 0.2 mL/min to avoid polymer degradation,[10,12] the sample loop had a volume of 103 µL.

The polymer solutions were prepared with a mass between 1 and 2 mg of the sample in 10 mL of the solvent and were flushed with nitrogen for 10 minutes.[10] The samples were then placed in an oven and were rolled with a self-assembled apparatus at about 3 revolutions/min for 3 h at 70 °C. This procedure homogenizes the samples with negligible thermal or mechanical stress.

For the determination of the branching index anionic polymerized, strictly linear cis-1,4-polyisoprene reference standards[13,14] obtained from Polymer Standards Service (Mainz, Germany) were used, with a molar mass at the peak maximum in the region from 10,000 to 4,000,000 g/mol and polydispersity factors smaller or equal 1.12.

Results and discussion

By coupling SEC with a viscometer, the intrinsic viscosity was determined from the tracings of the viscometer and the DRI detector as a function of the elution volume V_E. The refractometer signal is proportional to the concentration; this relation was determined by calibration to ensure proper mass balance.[10] The signal of the viscometer is proportional to the product of intrinsic viscosity and concentration. Dividing the viscometer signal by the normalized refractometer signal leads to the intrinsic viscosity at each elution volume increment, $[\eta](V)$.[15] The integration of this function leads to the intrinsic viscosity of the total eluted sample:

$$[\eta] = \int [\eta](V)\, dV \tag{1}$$

Since SEC separates molecules according to their hydrodynamic volume V_h
(with: $V_h \approx [\eta] \cdot M$), which means that at a certain elution volume V_E all polymers having the same hydrodynamic volume are being eluted, Benoit's method of universal calibration[16] can be applied (see Equation 2).

$$[\eta]_{lin} \cdot M_{lin} = [\eta]_{br} \cdot M_{br} \qquad | \; V_E = \text{constant} \tag{2}$$

with: $[\eta]_{lin}$, M_{lin}: intrinsic viscosity and molar mass of the linear cis-1,4-polyisoprene reference standards, $[\eta]_{br}$, M_{br} : intrinsic viscosity and molar mass of the branched natural rubber samples.

M_{lin} was given by the supplier of the cis-1,4-polyisoprene standards, $[\eta]_{lin}$ and $[\eta]_{br}$ were calculated according to Equation 1 from the experimental data as described above.

Figure 1 shows the universal calibration curve log(M·[η]) as a function of V_E derived from the cis-1,4-polyisoprene standards. By rearranging Equation 2, M_{br} can be calculated with the aid of the universal calibration curve (cf. Figure 1) from the elution chromatograms leading to the molar mass distribution curves of the purified natural rubber samples of different age as shown in Figure 2.

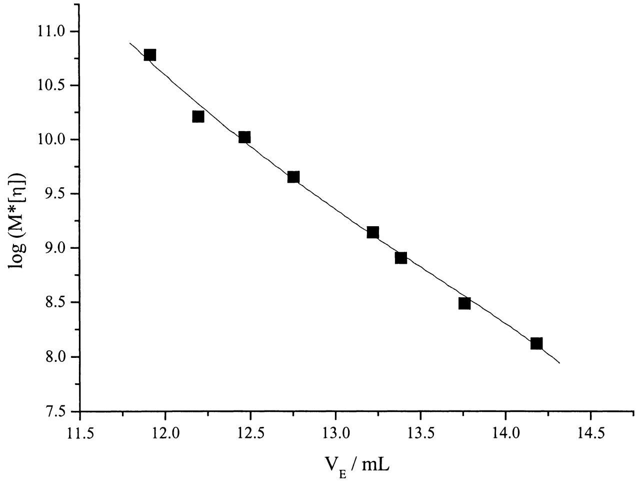

Figure 1. Universal calibration curve derived from the cis-1,4-polyisoprene standards with known molar mass by SEC coupled with online viscometry at 70 °C with cyclohexane.

As can be seen from Figure 2 the purified natural rubber samples possess a very broad and bimodal molar mass distribution with distinct peaks in the low and high molar mass region. With increasing age of the trees the area representing the low molar mass content decreases and the peak area in the high molar mass region increases. It is remarkable that with increasing age of the trees no distinct shift of the molar mass distribution curves towards higher molar masses occurs. Even the tree with an age of 8 years possesses molecules of natural rubber of very high molar masses up to 50,000,000 g/mol. This suggests that during the ageing of the trees only a change in the composition with respect to the low and high molar mass content occurs, as can be seen in Figure 3, where the composition is plotted as a function of the age of the tree. The relation of the high and low molar mass peaks in percentage was determined by fitting the bimodal molar mass distribution with two separate Gaussian functions leading to two separate peaks with the same total peak areas as the original distribution curve.

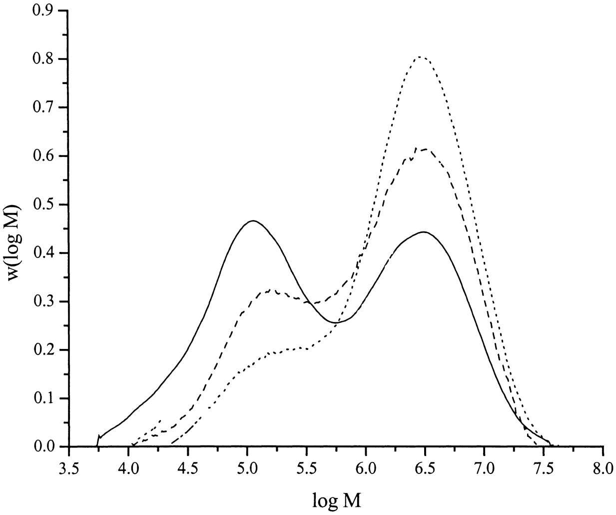

Figure 2. Molar mass distribution curves of the natural rubber samples from hevea trees of different age. Solid line: 8, dashed line: 20, dotted line: 35 years.

This behaviour is also reflected in the values of the weight average molar mass, M_w, and the polydispersity parameter, PD (with PD = M_w / M_n, M_n: number average molar mass) of the total eluted sample, and M_w and PD of the peaks of the low and high molar mass region which are collected in Table 1.

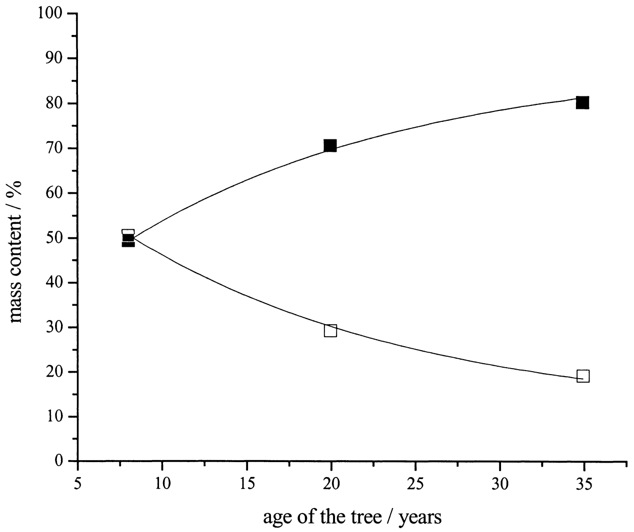

Figure 3. Mass content of the high (filled symbols) and low (open symbols) molar mass peaks of the natural rubber samples from hevea trees of different age.

Table 1. Weight average molar masses, M_w, and polydispersity parameter, PD, of the total eluted and the separated areas of the low and high molar mass peaks of the natural rubber samples of different age.

Age of the tree / years	total peak area		high molar mass peak		low molar mass peak	
	M_w / $kg \cdot mol^{-1}$	PD	M_w / $kg \cdot mol^{-1}$	PD	M_w / $kg \cdot mol^{-1}$	PD
8	2,120	20.0	4,190	2.2	1,450	2.2
20	2,850	10.0	4,100	2.1	1,880	1.8
35	3,750	6.0	4,360	2.2	1,670	1.8

As can be seen from Table 1, M_w and PD of the low and high molar mass peaks show no pronounced changes as the tree is ageing. However, M_w of the overall samples increases since more molecules of higher molar mass are built. Consequently the polydispersity factor decreases as the content of low molar mass fraction decreases.

According to Zimm and Stockmayer[17] the branching index g' of a molecule with a certain molar mass M can be expressed by Equation 3.

$$g' \equiv [\eta]_{br} / [\eta]_{lin} \qquad | \; M = \text{constant} \tag{3}$$

with $[\eta]_{br}$: intrinsic viscosity of the branched molecule, and $[\eta]_{lin}$: intrinsic viscosity of the linear molecule with the same molar mass.

Since a branched molecule has a smaller hydrodynamic volume than a linear molecule with the same total chain length, its density must be higher, and leads to a lower intrinsic viscosity. Thus, g' must be smaller than the value of 1 for branched molecules.

Using the cis-1,4-polyisoprene standards as linear reference samples, the branching index g' can be determined as a function of the molar mass according to Equation 3 for each of the natural rubber samples.

Figure 4 shows the distribution of the branching index g' as a function of the molar mas for the natural rubber samples from the hevea trees of different age. As can be seen the branching indecreases with both, the molar mass and the age of the tree. Included in Figure 4 is a plot of the branching index of the natural rubber sample from the tree of 35 years, which had not been saponificated.

As it was also observed by Tangpakdee et al.[6,7,11] by a decrease of the Huggins' constant k' the saponification process leads to a breakdown of physical branching points whereas untreated natural rubber samples show a significant higher content of long-chain branching. However, our findings show, that even after a complete removal of physical branchings points caused by e.g. hydrophobic fatty acids, phospholipids, or proteins, no strictly linear natural rubber molecules are present. This suggests the presence of chemical branches or other abnormal groups as reported by other authors, e.g. lactones,[18] or aldehydes and epoxides.[19]

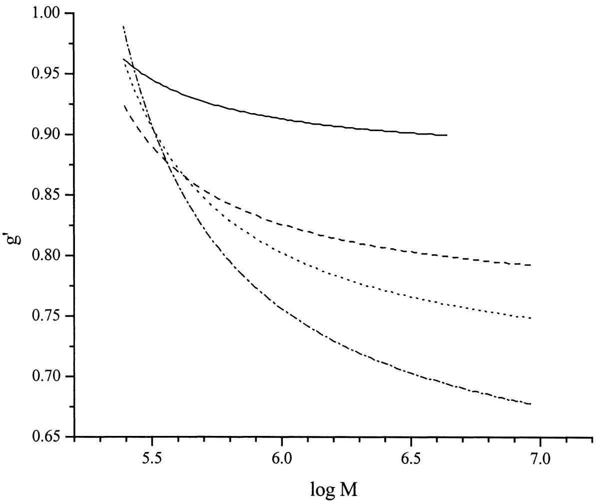

Figure 4. Branching index g' as a function of the molar mass M of the natural rubber samples from hevea trees of different age. Purified samples: 8 (solid line), 20 (dashed line), 35 (dotted line) years. Dash-dotted line: 35 years; not purified by saponification.

Conclusions

Size exclusion chromatography coupled with online viscometry is a powerful method to characterize natural rubber according to its distribution of molar mass and branching. The natural rubber samples from hevea brasiliensis trees of different age possess a very broad, bimodal molar mass distribution. No shift of the molar mass distribution curves towards higher molar masses with increasing age of the trees was observed. With increasing age, the size of the low molar mass peak of the natural rubber decreases favoring the size of the high molar mass peak. The branching index of the natural rubber molecules decreases with both, the molar mass and the age of the tree.

Acknowledgements

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