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Inherent Molar Mass Distribution of Clones and Properties of Crumb Natural Rubber

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Depending on the type of harvesting and processing adopted, the inherent molar mass distribution of natural rubber will govern the initial Wallace plasticity and the Mooney viscosity of the processed raw natural rubber. Two examples are described : constant viscosity processing from latex (5 CV 60 grade) and conventional processing from cup lumps (TSR 10 grade).

Natural rubber (NR), from *Hevea brasiliensis*, produced in crumb form is technically specified in accordance with an international standard (*ISO 2000*). The criteria adopted to characterise bulk viscosity are Wallace plasticity (P_0) and, for 5 CV 60 grade, the Mooney viscosity (M_L). Numerous studies[1–4] have shown that these two parameters provide a 'picture' of the NR microstructure. Nevertheless, they give insufficient information to manufacturers concerning NR processing ability. Other criteria that are more or less easy to use have been proposed to compensate for the inadequacy of P_0 and M_L, such as the Breakdown Index (BI)[5]. All these criteria require a substantial amount of NR (360 grams[6]) and are highly dependent upon numerous factors such as the clone[7], the tapping system, type of collection, *etc.* For breeders, it is very important to know whether a given new clone will tend to provide high viscosity NR, or whether it will be suitable for preparing 5 CV 60, for example. It is therefore necessary to proceed with at least two types of processed rubber (TSR 10, 5 CV 60), and numerous characterisations (P_0, M_L, BI, *etc.*), to acquire a clear idea of the properties of NR from a new clone.

The results given in this article show that a criterion exists, measured on fresh latex, that predicts a large number of properties offered by the resulting raw NR. It is the molar mass distribution (MMD) on leaving the tree (inherent MMD), obtained by Size Exclusion Chromatography (SEC). Knowledge of the inherent MMD enables a prediction to be made of the adequacy between clone and harvesting and / or processing.

MATERIALS AND METHODS

Samples

Two clones were studied namely PB 217 and PR 107, from trees tapped in ½ S d/3 d/4 stimulated 4 times per year.

Three types of samples were prepared from each clone : TSR 5 CV, TSR 10 and films from fresh latex.

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TSR 5 CV 60. Collected in latex form, they are coagulated with formic acid (pH 4.8). Subsequently, the crumbs are treated with a 5 % solution of hydroxylamine sulphate (HAS), [1 g HAS per latex litter] usually used to block aggregation phenomena and thereby obtain constant viscosity (CV) rubbers. Samples were granulated (rotary cutter) and dried for 2.5 h at 120°C (air speed : 1.5 m/s).

TSR 10. Collected in coagulated form, the samples were creped (12 passes with water), granulated (rotary cutter) and dried for 2.5 h at 120°C (air speed : 1.5 m/s).

Films. Around 40 drops of fresh field latex were deposited on a glass plate, spread out, then blown dry with compressed air for 30 min (room temperature). The films were washed by immersion in deionised water (50°C — 30 min), dried again with compressed air (30 min), then in a vacuum oven (40°C — 4 h), and placed overnight in a desiccator containing silica gel.

Characterisation

Wallace Plasticity (P_0) was determined in accordance with standard *ISO 2007*, and Mooney Viscosity (M_L) in accordance with standard ISO 289-1 ($M_{L(1+4)}$ 100°C).

Determination of gel rate. After centrifugation (17 000 r.p.m., *i.e.* 35 000 g — 1 h at 17°C) of the natural rubber solution, the solution was recovered for SEC analysis. The quantity of macrogel is determined by weighing the centrifugation residue after drying.

SEC analysis. The samples (120 mg) were dissolved in cyclohexane (30 mL) stabilised with 2,6-di-tert-butyl-4-methylphenol (BHT). After 14 days, the solutions were centrifuged, diluted (0.2 mg/mL), filtered (1 μm) and injected. The chromatograph used consisted of a Waters 510 pump, a Waters 486 UV detector (220 nm), and two PLGEL 30 cm mixed columns (porosity : 20 μm). The column temperature was 65°C. The flow rate of cyclohexane was 0.8 mL/min, the injected volume 100 μL. Calibration was carried out with synthetic poly(*cis*-isoprenes).

RESULTS AND DISCUSSION

We know that MMD of natural rubber, on leaving the tree differs from one clone to another, primarily through the quantity of short chains[8,9]. For the two clones studied, the inherent MMD of PB 217 is unimodal and that for PR 107 is bimodal (*Figure 1*). The main difference between the two clones therefore lay in the relative quantity of short chains. There were more short chain rubbers for clone PR 107.

If TSR 10 samples are prepared from the same two clones, the inherent MMD is no longer maintained (*Figure 2*). There are very few significant differences in MMD between the two clones (*Figure 2*). For the PR 107 clone, the short chains, responsible for aggregation[10], have disappeared, leading to an increase in P_0 and M_L, and of course a greater gel rate than in its counterpart PB 217 (*Table 1*). For TSR 10 samples, industrialists, who wish to use as little energy as possible during the mixing stage, usually demand for rubbers with a low P_0. Therefore, clones like PB 217, with few short chains, are more suitable than PR 107 for cup-lump production.

If 5 CV 60 (Constant Viscosity) samples are prepared from the same two clones, the inherent MMD is maintained (*Figure 3*). Nevertheless, when the M_L of the sample obtained from PR 107 corresponded to specifications (ML = 60 ± 2), that of the sample from PB 217 was

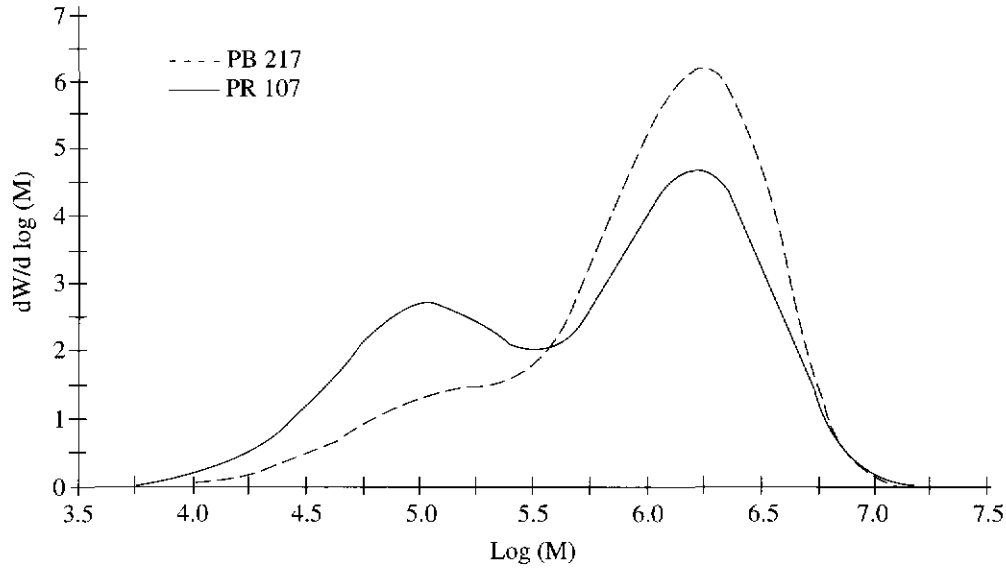

Figure 1. MMD curve obtained for raw films prepared from fresh latex.

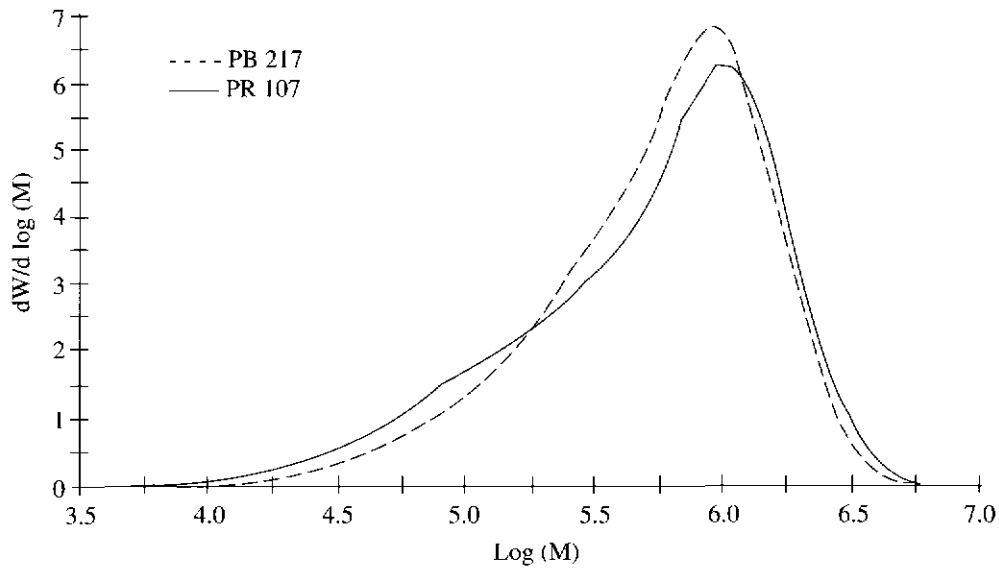

Figure 2. MMD curve obtained for TSR 10 natural rubber.

much higher than the specifications set down for 5 CV 60 (*Table 1*). Treatment with SHA inactivates the sites responsible for the aggregations that result in gel formation. Thus, the short

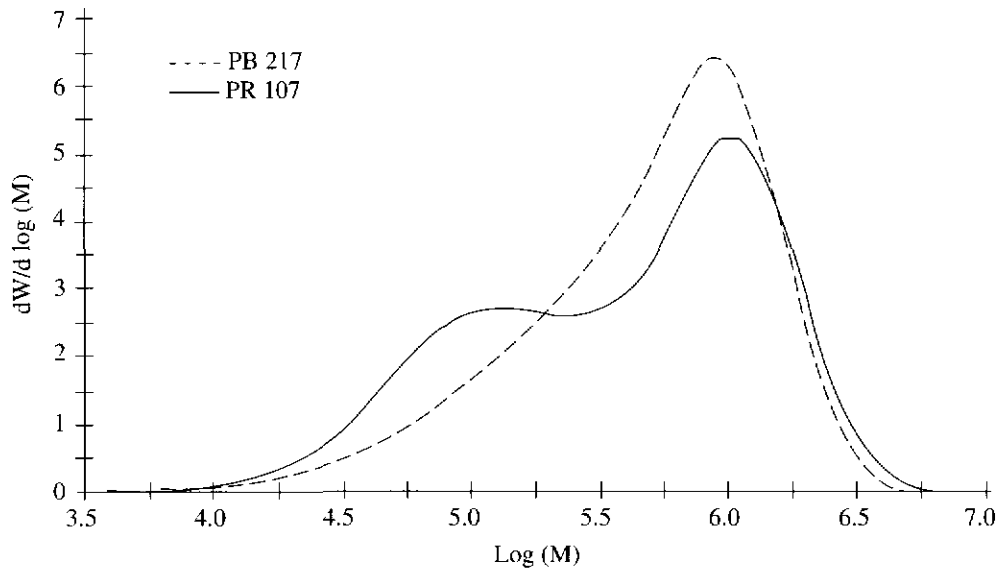

Figure 3. MMD curve obtained for 5 CV 60 natural rubber.

TABLE 1. P_0, M_L, GEL RATE, M_n AND M_w OBTAINED FOR THE SAMPLES ANAYLSED

Sample	Clone	Type of processing	P_0	M_L	M_w (Kg/mole)	M_n (Kg/mole)	Gel (%)
PR 107 E5	PR 107	5 CV 60	32	57	746	147	8.5
PB 217 E4	PB 217	5 CV 60	41	78	739	209	5.5
PR 1 T9	PR 107	TSR 10	62	104	834	203	26
PB 1 T9	PB 217	TSR 10	54	92	799	258	11

chains will serve as an internal plasticiser and lower the P_0, M_L and the number-average molar mass (M_n) (*Table 1*). Therefore, PR 107, with its inherent bimodal MMD, is a very suitable clone for 5 CV 60 processing, it is possible to achieve the desired specifications. On the other hand, PB 217 raises problems for 5 CV 60, probably because it does not contain enough short chains to plasticise raw NR.

CONCLUSION

The two examples described show that depending on the type of harvesting and processing adopted, one type of clone rather than another needs to be chosen to meet customer requirements. That choice can be made by characterising the inherent MMD of each clone by SEC. Indeed, clones with an

unimodal inherent MMD are not suitable for 5 CV 60, unlike those with a bimodal MMD. On the other hand, clones with an unimodal inherent MMD seem preferable for coagulum collection or cuplump form.

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