Relations Between Wallace Plasticity and M_w for Natural Rubber

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ABSTRACT: Wallace plasticity and the weight-average molar mass (M_w) were measured on natural rubber samples of different origins. A sigmoidal model describes the relations between Wallace plasticity and M_w ($0.872 > r^2 > 0.992$) for given families of samples. The families of samples analyzed differed through their clonal origin, collection method (cup lumps or latex), and type of processing (CV or non-CV). This study showed that two samples of natural rubber can be identical in terms of plasticity, but very different in terms of the average polyisoprene chain length or M_w. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3078–3087, 1999

Key words: natural rubber; Wallace plasticity; weight-average molar mass

INTRODUCTION

Natural rubber produced in crumb form is technically specified in accordance with an international standard (ISO2000). The rheological, or pseudorheological, criteria adopted are Wallace plasticity (P_0) and the Plasticity Retention Index (PRI). The PRI reflects the susceptibility of the product to thermo-oxidation, whereas P_0 provides a "picture" of the microstructure of the raw material. A Wallace plastimeter, a constant stress relaxometer, is used in the quality control laboratories of most natural-rubber-producing factories. It is simple in design, but does not provide access to fundamental rheological parameters.[1,2] The principle (Fig. 1) is based on rapid compression of a disk-shaped test piece between two heated (100°C) parallel platens and its thickness, measured after 15 s, is considered to be a measurement of the plasticity. Plasticity measured on this type of plastimeter can be likened to a flow measurement. This criterion is important insofar as it provides important, although insufficient, information to manufacturers concerning plasticization ability during blending in relation to the energy used.[3] Using batches of natural rubber with the same P_0 often avoids natural rubber mixing problems, but does not prevent certain incidents. Forecasting natural rubber mixing performance, therefore, requires an understanding of both the effect of its microstructure on rheological, or pseudorheological, measurements used for such forecasting, and of what becomes of that microstructure during mixing.

Natural rubber differs from its synthetic counterparts through its more complex microstructure due to the interaction of nonrubber compounds with the polyisoprene chains. This "associative" microstructure is gradually destroyed, and partly when the polyisoprene is dissolved in a conventional solvent. However, in very many cases, a proportion of the natural rubber remains insoluble in such solvents; this fraction is commonly called the gel or macrogel phase,[4–6] and is usually eliminated and quantified by centrifugation. The soluble fraction contains the polyisoprene macromolecules, and a variable quantity of microaggregates, between 1 and 15 μm in diameter,[7] forming the microgel. The microstructure of natural rub-
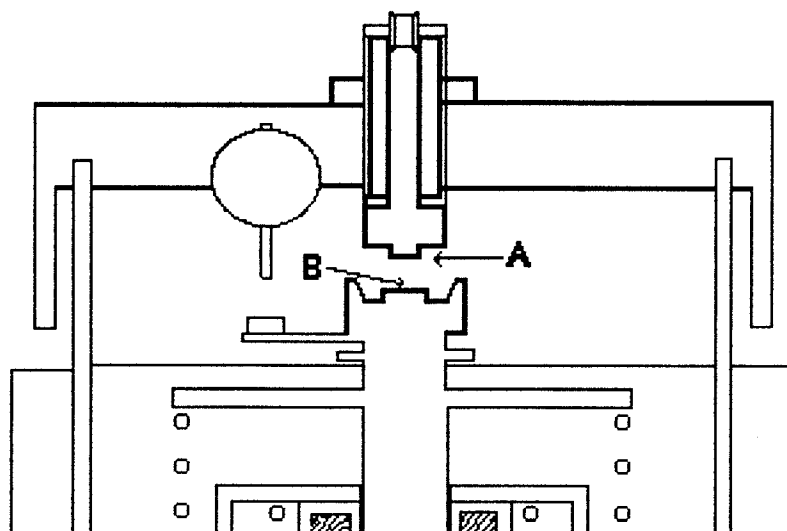
Figure 1 Wallace plastimeter operating diagram. A, upper heated platen; B, lower heated platen.

ber can, therefore, be split into three components: (a) the macromolecular structure including the average chain length, or average molar mass, the molar mass distribution, and the degree of branching along the chains; (b) the microgel; and (c) the macrogel.

Table I   Wallace Plasticities and M_w for PR107, GT1, or PB235 Cup Lump Samples

Clone (Type of Raw Material)	Sample	Initial Values		Values after 30 min Aging at 140°C or 147°C[a]	
		P_0 (1/100 mm)	M_{w_0} ($\times\ 10^{-3}$) (g/mol)	P_{30} (1/100 mm)	$M_{w_{30}}$ ($\times\ 10^{-3}$) (g/mol)
PR107 (Cup Lumps)	R6	55.4	833	39.6	641
	R10A[a]	62	1020	38.8	633
	R10B	59	945	47.6	701
	R10C	60.5	978	43.2	644
	R15A[a]	57.7	858	34.6	549
	R15B	58.4	832	37.2	612
	R15C	58.2	819	37.6	582
	M8[a]	59.6	959	31.3	558
GT1 (Cup Lumps)	40F[a]	57.1	882	11.9	373
	45FA[a]	50.4	739	7.1	274
	45FB	52.5	780	14.2	404
	60FQ5[a]	53.3	821	11.1	357
	33F	48.6	744	7.5	348
PB235 (Cup Lumps)	12F[a]	44.7	804	7.9	336
	16FQ5[a]	42.4	771	7.4	328
	6FQ5[a]	49.1	863	17.3	479
	20FA	46.8	771	16.6	440
	20FB	47	782	12.6	420
	20FC	46.6	755	13	388
	13F	47.7	820	20	494
	17F	44.2	769	11.4	421
	3FQ10	42.7	732	12.2	393
	11F	46.3	793	19.3	478

[a] Thermo-oxidized, in a PRI oven, at 147°C rather than 140°C.

Table II   Molecular Parameters and Wallace Plasticities for Off-Latex or CV Samples

Clone (Type of Raw Material)	Sample	Initial Values		Values after 30 min Aging at 140°C or 147°C[a]	
		P_0 (1/100 mm)	M_w ($\times 10^{-3}$) (g/mol)	P_{30} (1/100 mm)	M_w ($\times 10^{-3}$) (g/mol)
GT1 (Off-Latex)	13CEA[a]	55.3	1033	45.4	805
	13CEB	51.2	991	43.1	840
	16CEA[a]	51.5	1011	45.4	819
	16CEB	47.1	953	40.6	803
	17CE	39.1	781	26.5	567
	20LBA[a]	53.2	993	33.8	647
	20LBB[a]	53.1	852	32.3	—
Mixture (Off-Latex Industrial)	301LA[a]	53.7	1075	39.3	699
	301LB	51.8	1018	46.5	795
	5WF1	49	925	—	—
	5WF2	45.8	864	—	—
	5WF3	52	1055	—	—
	L	46	959	—	—
Mixture (Off-Latex CV-Industrial)	5CVIA[a]	33.4	874	28.2	—
	5CVIB	35.7	905	33.4	753
	5CVIC	34.6	877	31.7	692
	Y149A[a]	31.3	731	26.1	—
	Y149B[a]	31.1	725	25.3	556
	7G3922	18.6	447	11.7	381
	7G1287	35.9	727	27.1	594
	7G1280	29.3	655	23.2	544
Mixture (CL CV-Industrial)	10VA[a]	28.9	617	13.4	—
	10VB	28.7	568	17.4	430

[a] Thermo-oxidized, in a PRI oven, at 147°C instead of 140°C. CL: cup lumps, CV: constant viscosity.

Although numerous studies on synthetic poly(*cis*-1,4-isoprenes), reviewed by Fuller,[8] have revealed the essential effect of the macromolecular structure (a) of the polymer on viscoelastic properties, few people have taken an interest in the relations between the P_0 of natural rubber and its macromolecular structure. Nair[9] showed that there was a linear relation ($r^2 = 0.79$) between the Wallace plasticity (P) and intrinsic viscosity ([η]) of natural rubber. Sambhi[10] discovered that this relation (P − [η]) was different from one family of samples to another, samples that differed depending on the type of processing. Li et al.[11] have shown that the P_0 was correlated to the M_w for an NR sample after accelerated storage.

Given the above facts, it seems important to know and understand the relations existing between the Wallace plasticity of natural rubber and the different components of its microstruc-

ture. This article looks at just one aspect of this vast problem, i.e., the relations obtained between Wallace plasticity and the weight-average molar mass (M_w) of natural rubber determined by SEC. The correlations obtained show that numerous factors affect the parameters of the model, notably clonal origin, the collection method, and the type of processing.

MATERIAL AND METHODS

Materials

Two types of raw material were studied, the first collected in cup lump form (natural latex coagulation in the field), the second collected in latex form and coagulated artificially with acid (off-latex rubber). For processing, only one parameter was analyzed—the treatment of crumbs with hy-
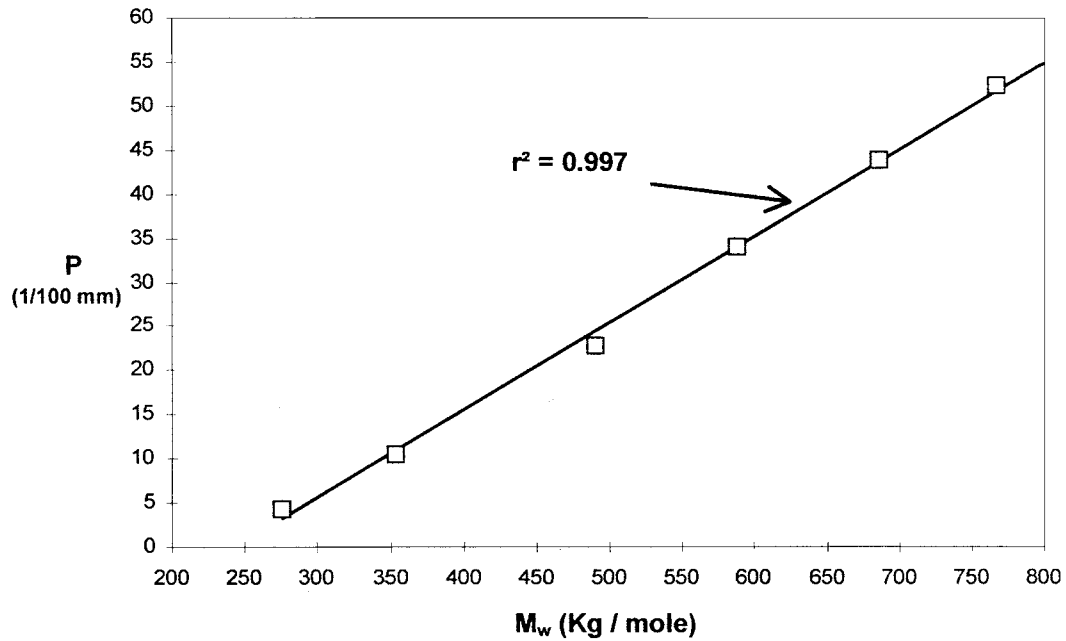
Figure 2   Relation between Wallace plasticity and M_w for a sample thermo-oxydized in a PRI oven (140°C) at different times.

droxylamine sulphate (HAS) usually used to block aggregation phenomena and thereby obtain constant viscosity (CV) rubbers. The clonal effect was considered solely for cup lumps, which is the most common collection method used by small holders, comparing three clones: PR107, GT1, and PB235. The same applied for the maturation time, i.e., the interval from tapping to processing.
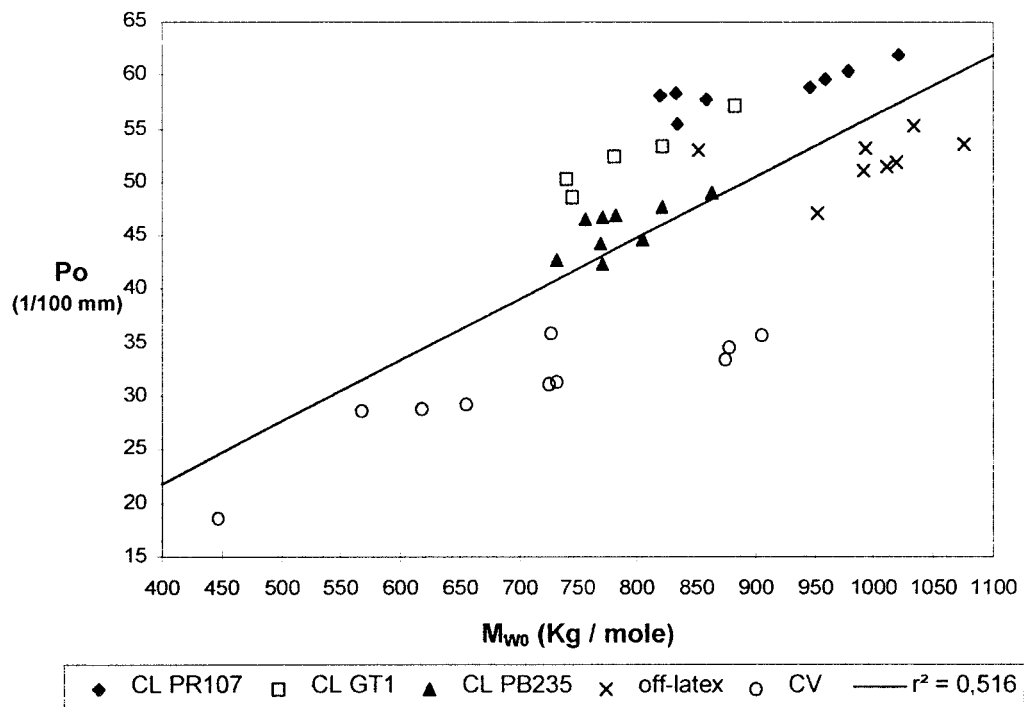

Figure 3   Relation between P_0 and M_{w0} for all the samples analyzed.
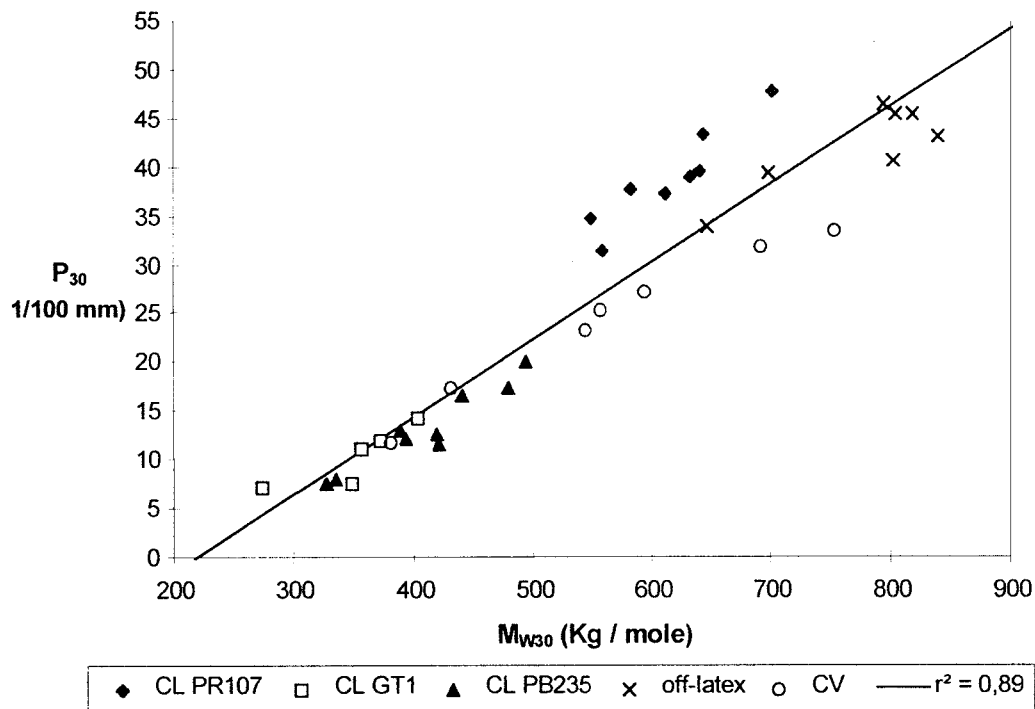
Figure 4   Relation between P_{30} and M_{w30} for all the samples analyzed.

Prior to any analysis, the samples were homogenized in accordance with standard ISO1796, and sheeted by three passes through the mill rollers at 27°C.

SEC Analysis

The samples were dissolved in cyclohexane stabilized with 2,6-di-*tert*-butyl-4-methylphenol (BHT),
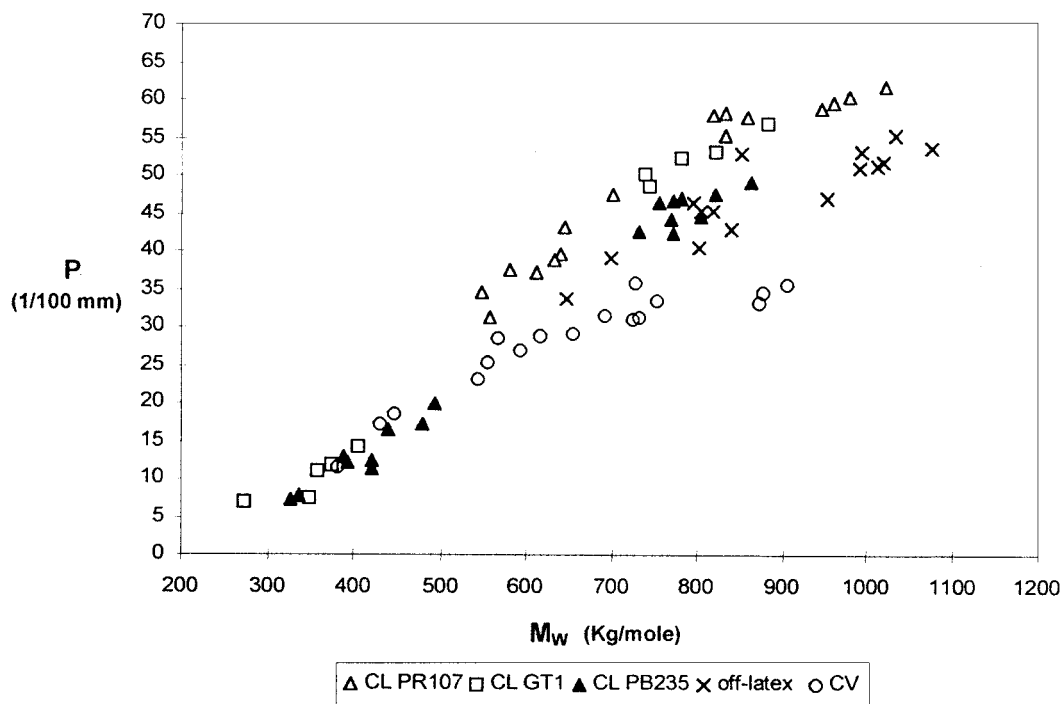

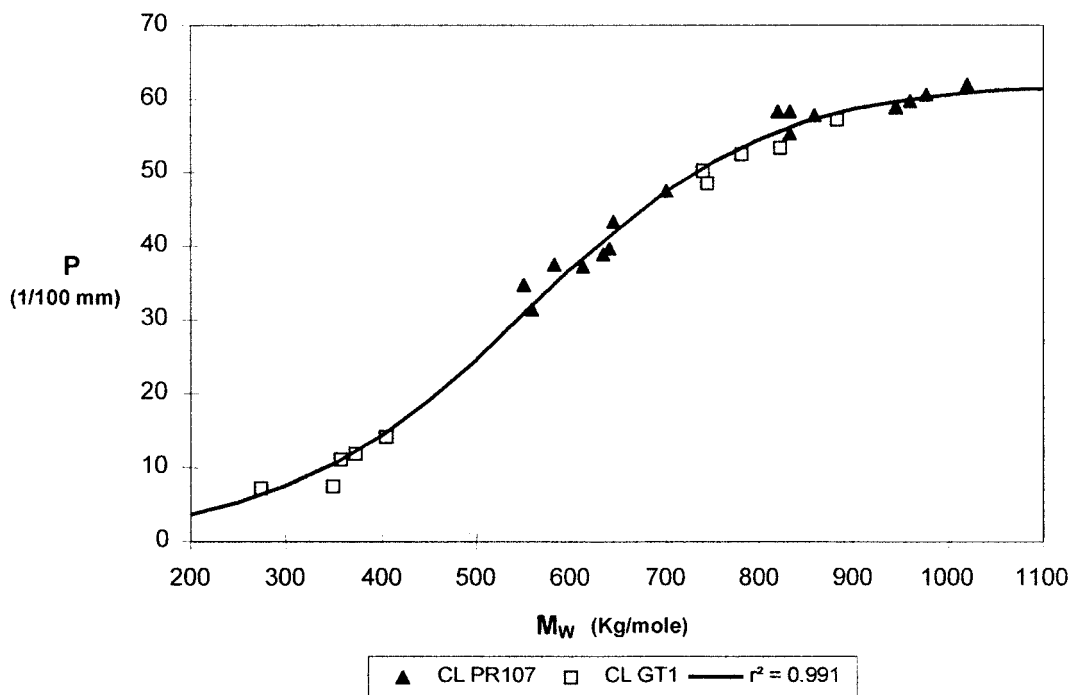**Figure 5**   Relation between P and M_w for all the samples analyzed.

Figure 6 Relation between P and M_w for all the PR107 and GT1 cup lump samples.

at a rate of 120 mg for 30 mL of solvent. The solutions were gently stirred for 1 h periodically for 14 days, then centrifuged (17,000 rpm, i.e., 35,000 × g for 1 h at 17°C), diluted to 0.2 mg/mL,

filtered (porosity 1 μm), and injected into the SEC apparatus.

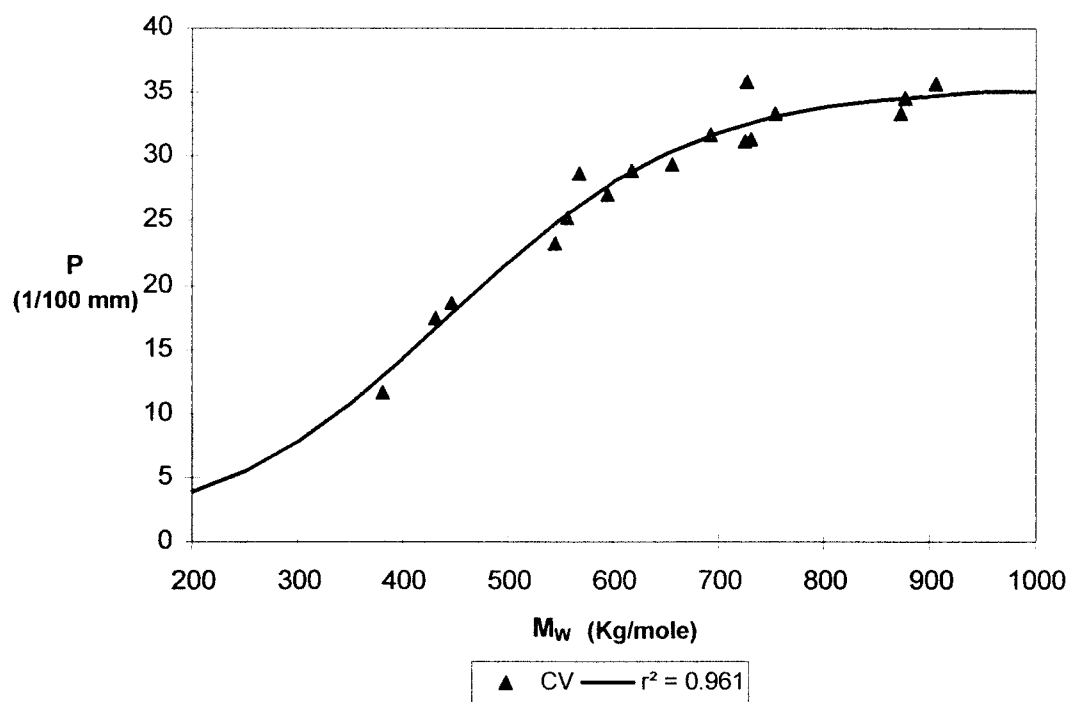The chromatograph used consisted of an ERMA ERC-3112 solvent gas remover, a Waters

Figure 7 Relation between P and M_w for the CV samples.

Table III   Model Used and Parameters Obtained for the Natural Rubber Sample Families Studied

$$\text{Model: } P = \frac{P_{\max}}{1 + \left(\dfrac{a}{M_W}\right)^b}$$

Sample Family	$P_{\max}$	a	b	r^2
CL[a] PR107 or GT1	69.81	575.7	3.667	0.991
CL* PB235	66.43	623.3	3.425	0.992
OL[a] Industrial or GT1	61.02	606.7	3.357	0.872
CV[a]	37.22	453.5	4.013	0.961
All samples	62.33	591.7	3.389	0.867

[a] CL = cup lumps, OL = off-latex, CV = constant viscosity.

510 pump, an automatic injector, a Waters 486 UV detector (220 nm), and two PLGEL 30-cm mixed columns with a porosity of 20 μm (Polymer Laboratories). The entire installation was computer controlled by special software (Maxima-Waters).

The column temperature was fixed at 65°C. The cyclohexane flow rate was 0.8 mL/min, the injected volume 100 μL (at a concentration of 0.2 mg/mL before filtration), for the natural rubber samples, and 25 μL for the standard solutions. Calibration was carried out with synthetic poly-(*cis*-isoprenes) with molecular weights of 1310, 3030, 8000, 32,400, 71,950, 97,200, 295,000, 452,000, and 1.2 million (expressed in g/mol).

Wallace Plasticity

A Wallace plastimeter was used to measure plasticity, in accordance with standard ISO2007. Aging was carried out at either 140 or 147°C in a Wallace oven.

RESULTS AND DISCUSSION

Tables I and II list the plasticity results and weight-average molar masses (M_w) before ageing

(index 0) and after aging (index 30) obtained for the samples analyzed. A good relation exists between Wallace plasticity and M_w for a given sample submitted to a specific treatement: storage hardening (Li et al.[11]) or thermo-oxydation (Fig. 2). However, for samples of different origins, Figure 3, which gives initial plasticity (P_0) depending on the initial M_w (M_{w0}), shows a very moderate linear relation ($r^2 = 0.52$) between P_0 and M_{w0}. There is clearly a better relation ($r^2 = 0.89$) between P_{30} and M_{w30} (Fig. 4). In Figure 5, which gives plasticity according to M_w, without making a distinction between initial values and after aging, it is possible to split the performances of the analyzed samples into several families. The samples were, therefore, classed into four families. The first contained cup lump crumbs from PR107 and GT1 clones (Fig. 6), the second concerned cup lump crumbs from PB235 clones, the third contained off-latex crumbs, and the fourth concerned CV crumbs (Fig. 7). A sigmoidal model (Table III) described the performance of each sample family ($0.872 < r^2 < 0.992$). The differences between the four sigmoids are statistically highly significant (Table IV).

For instance, it appears (Fig. 8) that the relation between plasticity and the M_w depends on

Table IV   Test of Model Equality for All the Natural Rubber Sample Families

Source	DF[a]	Sum of Squares	Mean Square	F-Value	$P_r > F$
Total	82	137252.2			
Common model	3	134577.07			
Gain common specific	9	2397.96	266.44	67.289	0.0001
Residual	70	277.17	3.960		

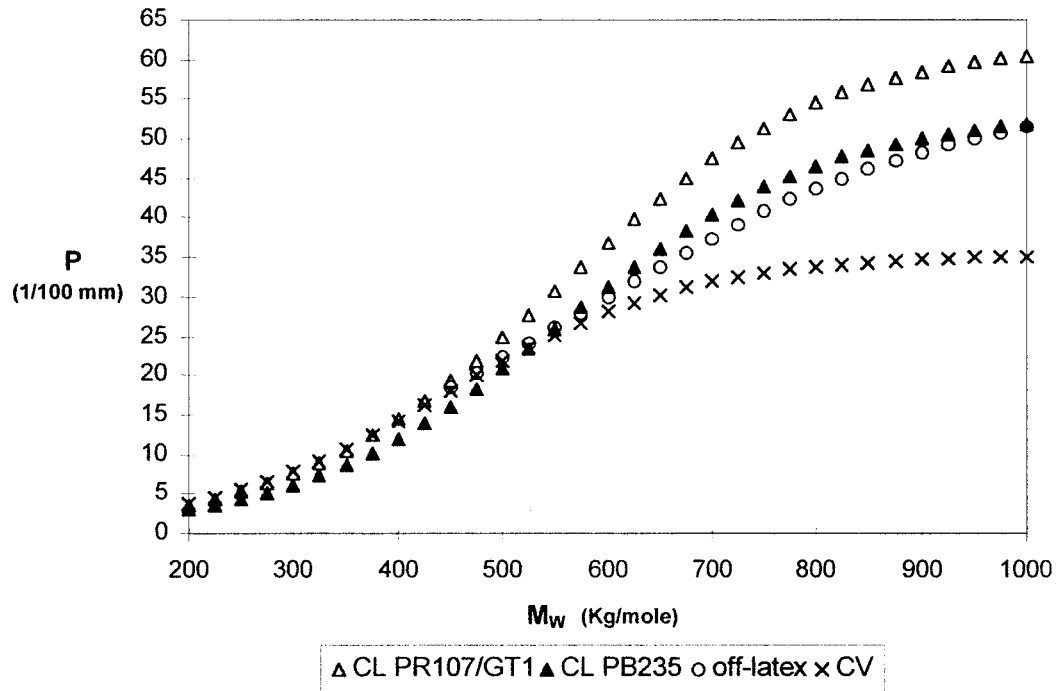[a] DF: degree of freedom.

Figure 8   P = f(M_w) models obtained for the different sample families analyzed.

numerous factors, such as clonal origin, the type of collection (cup lumps or latex), and the type of processing, but also the cup lump maturation time (t_m) (Fig. 9).

As a general rule, the short chains of a polymer tend to plasticize the material. It, therefore, seems reasonable to assume that the molar mass distribution curves for the four sample families
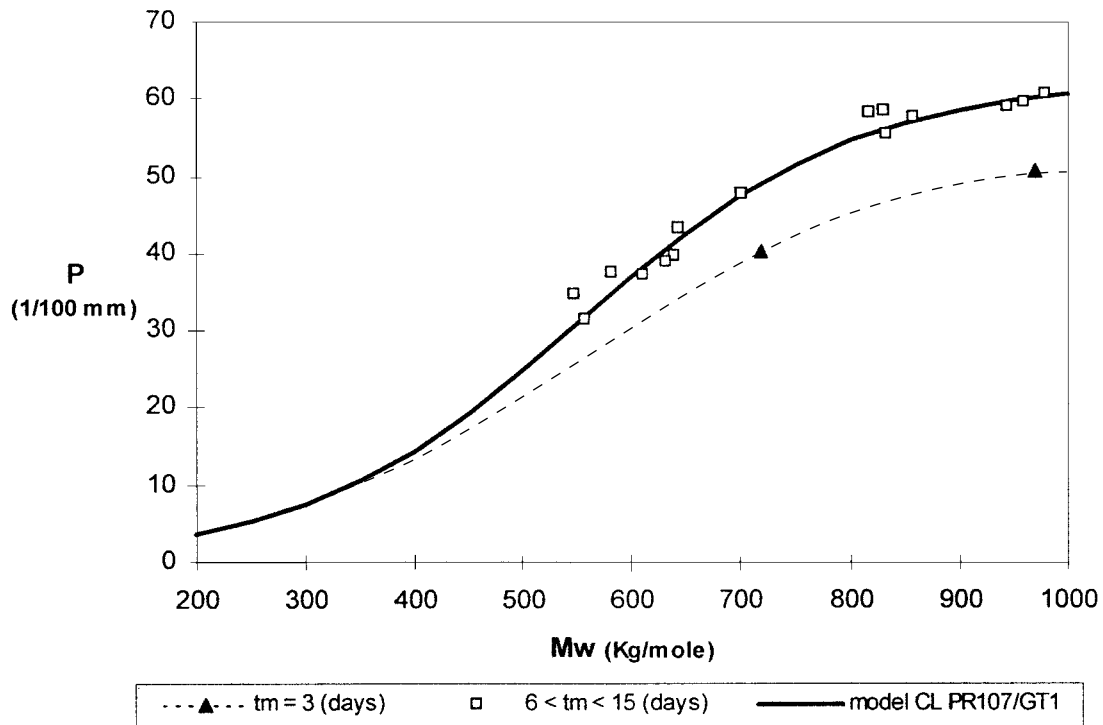

Figure 9   Effect of cup lump maturation time on the relation between P and M_w for clone PR107.
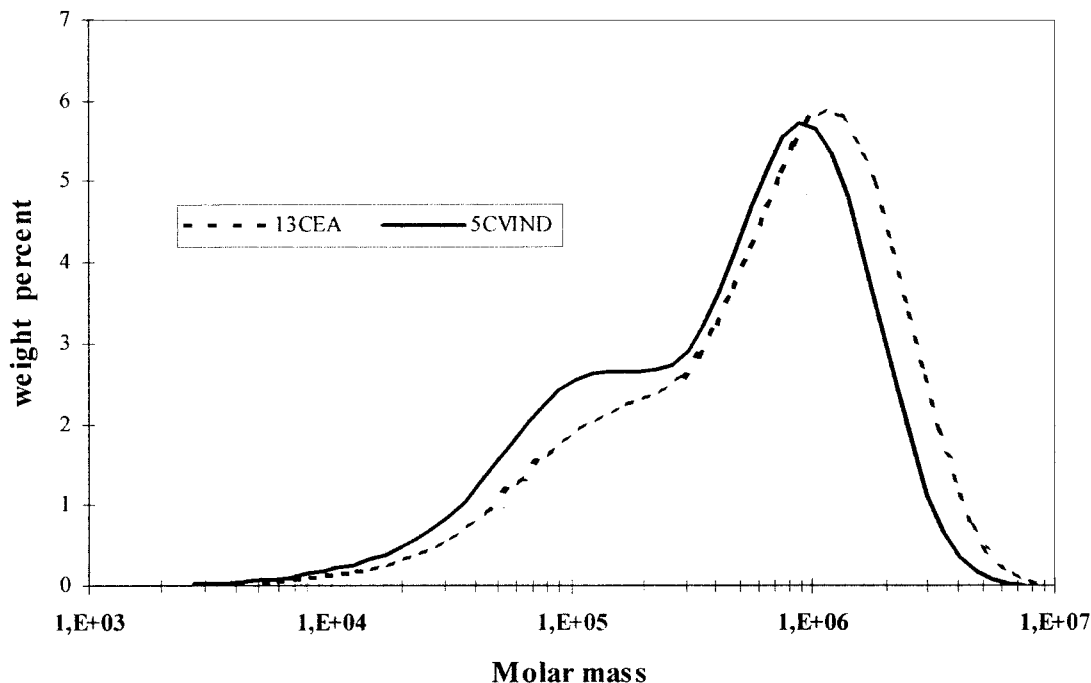
Figure 10 Molar mass distribution curves obtained for a CV off-latex sample (5CVIND) and an off-latex sample (13CEA).

will have significant differences in the low molar masses section. In fact, only the CV rubbers are really different from the other sample families in terms of molar mass distribution (Fig. 10), by containing a larger proportion of short chains. It is surprising to see that two cup lump samples
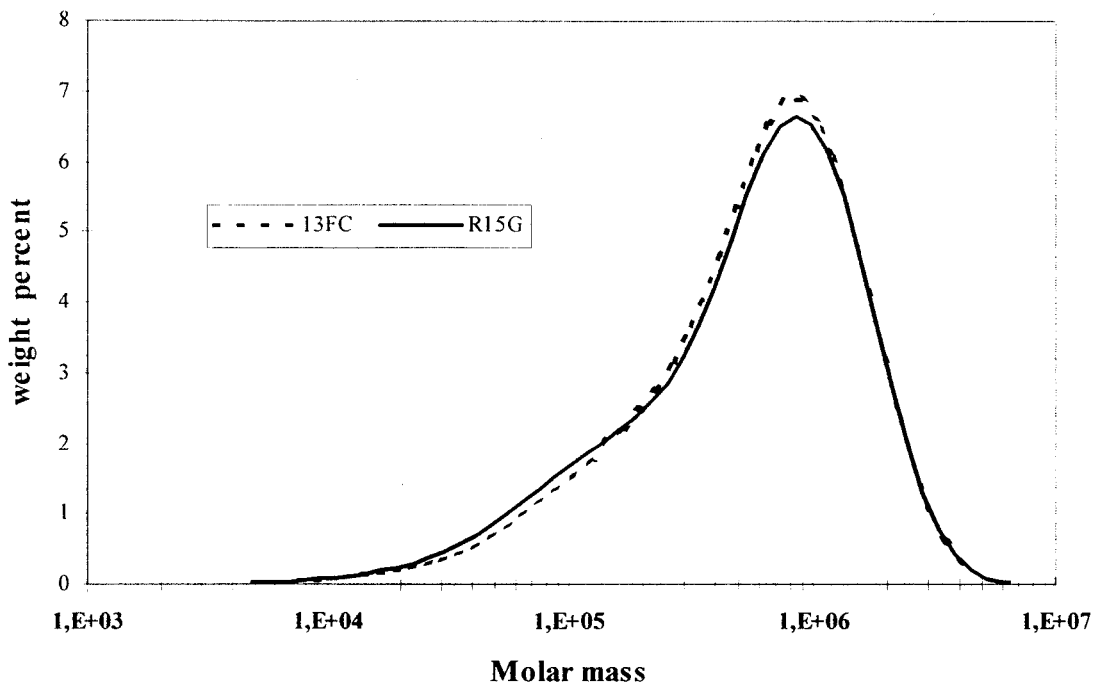

Figure 11 Molar mass distribution curves obtained for a PR107 cup lump sample (R15G) and a PB235 cup lump sample (13FC).

from different sample families (e.g., R15C and 13F) had identical molar mass distributions (Fig. 11) but P_0 values that differed by 10 points (Table I). These results suggest that the degree of branching along the chains and/or gel proportions, which are bound to play an insubstantial role in the plasticity measurement, lie behind these differences in performance. Indeed, the role played by the degree of branching along the chain, and the gel, on the relaxation modulus of natural rubber had already been shown.[12–14]

CONCLUSION

This study showed that there were very clear relations between Wallace plasticity and the M_w of natural rubber, but for given families of samples. The clonal origin, type of collection, maturation time, and type of processing have a highly significant effect on the P = f(M_w) relations observed; hence, in principle, on the technological properties of natural rubber. Given these phenomena, two samples of natural rubber with the same P_0 will have a very different M_w; hence, probably different processing performances and properties.

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