Effect of Maturation on the Bulk Viscosity and Molecular Chain Length of Cuplump Natural Rubber

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ABSTRACT: The effects of the maturation and storage of naturally coagulated latex, generally termed *cuplumps*, on some bulk rheological properties and on parameters characterizing the macromolecular chain length were investigated for natural rubbers of different clonal typologies. The sensitivity of the clonal material to the degradative effects of cuplump maturation increased with the level of tree energetic metabolism, with the most metabolically active plant materials (e.g., PB 235) being most sensitive, whereas the less active clone PB 217 was less sensitive. A definite relationship evolves between *Hevea* tree metabolism and the stability of the structure of the biosynthesized rubber. The results presented here highlight at a macromolecular level the effects of maturation previously demonstrated on bulk processing parameters. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 703–708, 2002

Key words: bulk viscosity; cuplumps; *Hevea brasiliensis*; maturation; molecular chain length; molar mass distribution; degradation; crosslinking; natural rubber

INTRODUCTION

A significant factor contributing to the flow behavior of latex and the deformation behavior of solid raw rubber is the length of its polyisoprene chains.[1,2] However, most bulk properties, such as the Mooney viscosity and Wallace plasticity number, that are generally adopted to describe flow behavior do not provide enough information to assess the fundamental properties.[3] This is mainly because freshly coagulated *Hevea* rubber (natural) is variable in its size and molecular structural arrangement with respect to the origin of vegetative materials (clones), crop collection methods, and methods of processing.[4]

After being tapped, *Hevea* latex is normally subjected to several treatments before the crop is marketable. Conventionally, rubber is rapidly coagulated from latex and subjected to operations that eliminate most of the serum and nonrubber constituents. The crumb is then dried appropriately and baled, with the product constituting premium technically specified and conventional sheet grades. The practice of collecting latex directly into plastic bags and accumulating several tappings before processing has been abandoned despite the cost savings associated with this collection system. This has been due to the development of some undesired properties, such as the very dark color that develops, high viscosity, low nitrogen content, and low resistance to thermal oxidation.[5] A more commonly adopted practice today is coagulating the rubber naturally in cups, collecting it at variable frequencies, and storing it for extended periods before factory processing. The scarcity of raw rubber further impels middle-level dealers and factory processors to adopt this practice. In a previous study,[6] significant relationships were found between certain physiological parameters of latex from some selected Hevea clones and some relevant bulk technological properties of raw rubber. These relationships, although greatly influenced by ecoclimatic conditions, illustrated the effect of latex physiological parameters such as inorganic phosphorus and total solid content and identified some of these as early markers of properties of processed crumb. The objective of this study was to investigate the influence of the adopted exploitation practices of extended cuplump maturation before processing on the flow behavior and length of polyisoprene chains of processed rubber.

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EXPERIMENTAL

Materials

Cuplumps were collected and pooled (from January to June 1999) from 300 trees of each of three *Hevea bra-*

siliensis clones, PB 235, GT 1, and PB 217, which showed high, intermediate, and slow metabolic activity, respectively.[7] These clones were the most cultivated and were reference materials for large-scale planting in Cameroon. The trees were planted in 1984 (i.e., they were 15 years old at the beginning of the experiment), were opened in 1990, and had the same panel history (virgin BO-1, 90 cm above the union). They were regularly tapped on ½S d/4, ET2.5%, Pa 11/y (clones GT1 and PB 217) and ½S d/4, ET2.5%, Pa 4/y (clone PB 235).

Latex from the first tapping of each month was subjected to various durations of maturation and storage before processing. For the first treatment, which followed typical industrial practice, cuplumps were matured in cups for 3 days and under shade for 15 days more (18 days in all). The second treatment consisted of 3 days of cup maturation followed by 3 days on field barns and 15 days more in the factory (21 days in all). The third treatment, a simulation of small holders' practice, involved 3 days of cup maturation, 27 days on barns, and 15 days in the factory (45 days in all).

All cuplumps were then granulated, washed, and dried in an industrial drier under the same processing conditions to avoid between-batch variations. Other variations observed were, therefore, attributed to the clonal material and extent of maturation. Test portions were cut and homogenized according to the ISO 1795 standard.

Testing of the bulk rubbers

The bulk viscosity was measured on a Mooney shearing viscometer (model MK IV, Negretti Automation, Surrey, United Kingdom) operating at 100°C. The large rotor (Type L, 38.10 mm diam. and 5.54 mm thickness) was used, and the Mooney viscosity (M) was recorded as the torque value after 1 min of preheating and 4 min of shearing [ML(1 + 4) at 100°C]. The initial Wallace plasticity number (P_0) and the plasticity retention index (PRI) were determined per ISO 2007 and ISO 2930 norms, respectively.

Determination of the macromolecular structure

Average molar masses were measured by steric exclusion chromatography with cyclohexane as eluent. Solutions of natural rubber in cyclohexane were centrifuged at 35,000*g* for 1 h to precipitate the insoluble macrogel. The sol fractions were diluted to 0.2 mg/mL and filtered through a 1-μm filter before the injection of 100 μL into the chromatograph. Details of the procedures are as described elsewhere.[8]

RESULTS AND DISCUSSION

Effect of the *Hevea* clone and cuplump maturation on the bulk properties

The evolution of the bulk properties of processed crumb, as shown in Figure 1, revealed significant effects of the cuplump maturation time (18–21 days against 45 days) and clonal-specific behavior (the slow metabolic activity of PB 217 vs the others).

The P_0 and *ML* values of rubber from clone PB 235 decreased on maturation from 18 to 21 days, whereas those of clone GT 1 rubber were less sensitive and were only reduced in a significant manner after 45 days [Fig. 1(A,B)]. At the extreme end was the clone PB 217 rubber, which remained unaltered even after prolonged 45 days of maturation. The PRI, which characterizes the resistance of raw rubber to heat and oxidative aging, decreased progressively with the maturation of clone PB 235 rubber but remained almost constant throughout for the others [Fig. 1(C)].

Coagulation and maturation modify the structure of natural rubber, and this modification could be translated as either an increase (crosslinking) or a decrease (chain scission) in its viscosity. The reduced viscosity favors competing reactions of peroxy radicals and, therefore, oxidation rates.[9] The relationship between the molecular chain breakdown and the decrease in viscosity following maturation and storage could arise from the fact that the slower the metabolism is of the tree, the more efficiently synthesized its rubber will be. However, because the biological environment characterizing natural rubber coagulation and maturation is very complex, a change in the serum activity with maturation should be associated with the selective activation of antioxidants from their less reactive forms. The activation was initially slower but increased progressively with maturation, especially for clone PB 235 with its high metabolic activity.

Effect of the cuplump maturation on the polyisoprene chain length

The number-average (M_n) and weight-average molar masses (M_w) of rubber from clones GT 1 and PB 217 were not affected by 45 days of cuplump maturation and storage [Fig. 2(A,B)]. However, these parameters decreased with the maturation of clone PB 235 rubber. There is little in the literature relating antioxidant activity and *Hevea* metabolism. It is likely that the chain-scission process is more pronounced in clone PB 235 rubber because of insufficient natural antioxidants. Meanwhile, the scission could result in the formation of unstable terminal groups that crosslink the molecular chains.[10,11] The reduction in molar mass we observe for clone PB 235 rubber is the sum of the two antagonist processes, indicating a predominance of chain-scission reactions on prolonged rubber maturation.

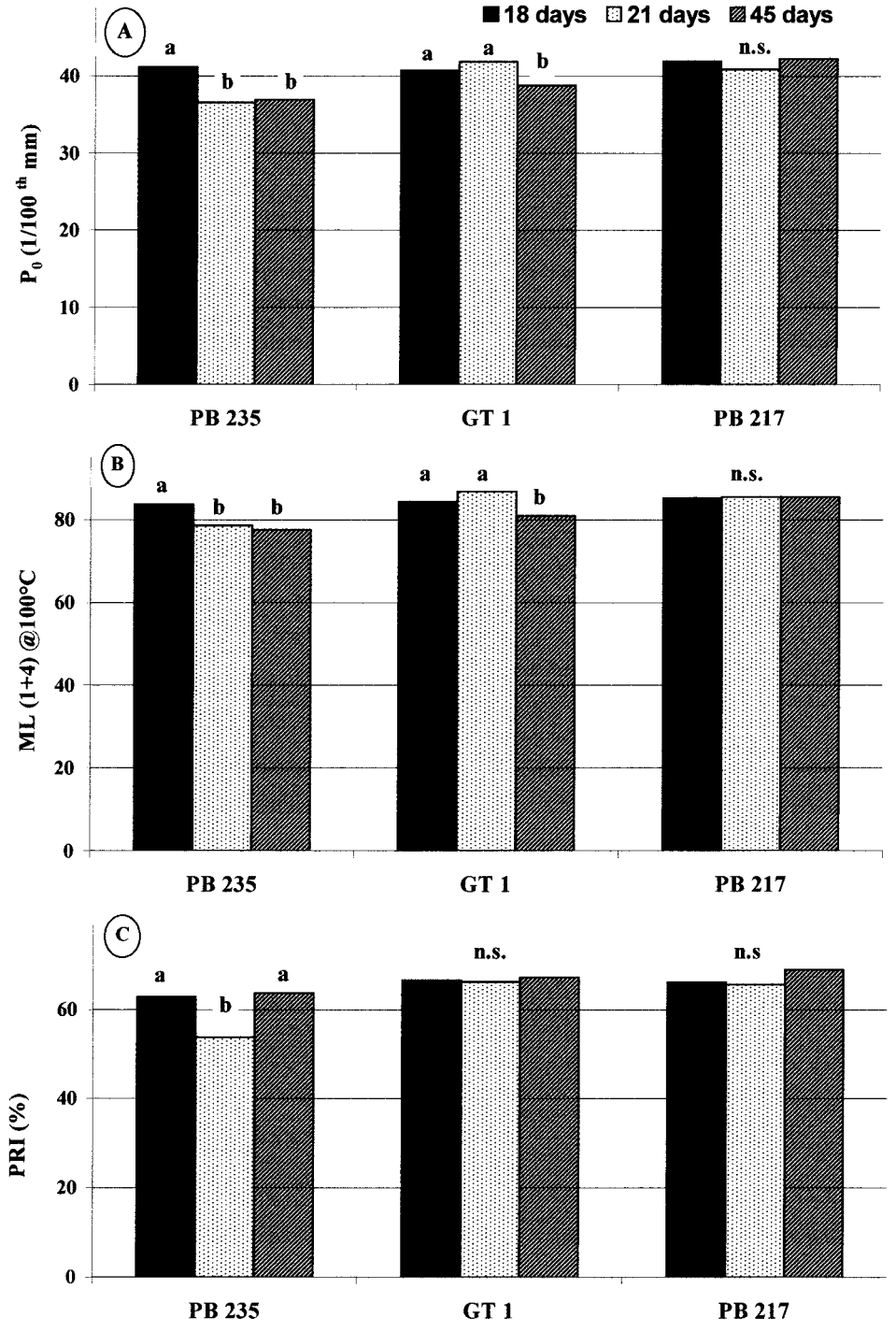

Figure 1 Effect of the clonal typology and cuplump maturation on (A) P_0, (B) *ML*, and (C) PRI for the raw processed natural rubber. Maturation times for the same clones bearing the same letters were not significantly different ($P = 5\%$). *ns* indicates that maturation effects were not significant for a particular clone.

The polydispersity index, although always highest for clone GT 1 (≥4 units), varied in the same manner for the three clones [Fig. 2(C)], reducing on maturation from 18 to 21 days but increasing with further maturation to 45 days. The molar mass distributions for clone PB 235 and PB 217 rubber remained unchanged after 21 days of maturation [Fig. 3(A,C)]. After 45 days, however, the intensity of the very long chains decreased, and shorter ones were produced. The molar mass distribution of clone GT 1 was different from that of the other clones, as a significant reduction in the intensity of the very long chains was observed earlier, just after 21 days of maturation and storage [Fig. 3(C)].

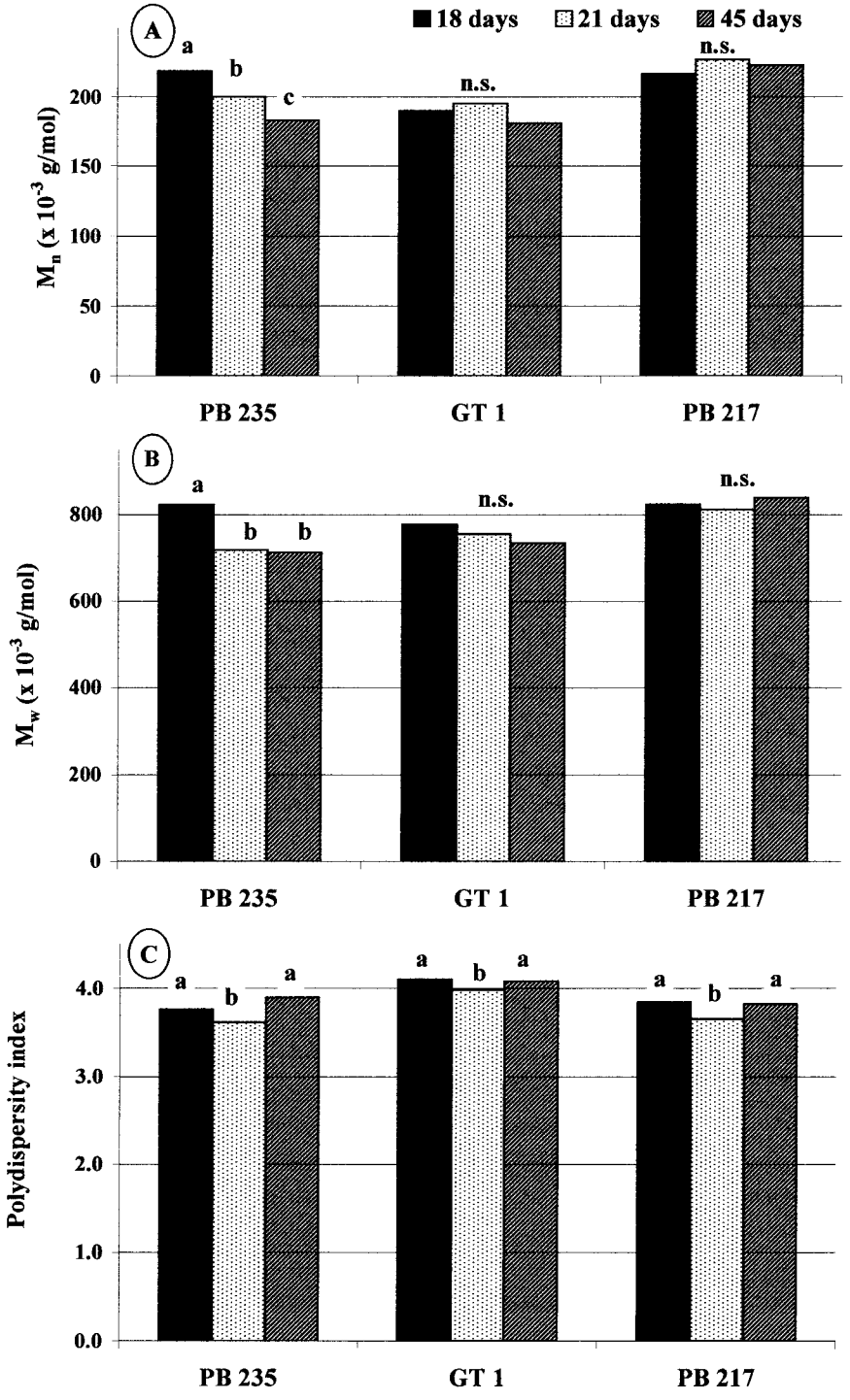

Figure 2 Effect of the clonal typology and cuplump maturation on (A) M_n, (B) M_w, and (C) the polydispersity index for raw natural rubber. Maturation times for the same clones bearing the same letters were not significantly different (P = 5%). *ns* indicates that maturation effects were not significant for a particular clone.

Relationships between the bulk properties and macromolecular chain length

With consideration of the interactions between the clonal origin of the rubber and the cuplump maturation with respect to the rubber chain lengths, Pearson correlation coefficients were determined between bulk properties and molecular parameters for the different extents of maturation (Table I).

The bulk rheological properties (e.g., P_0 and *ML*) and molar masses remained positively correlated for the three clones, regardless of the extent of maturation, confirming, in part, earlier reports on unaged styrene–butadiene rubber[12] and unaged natural rubber.[13] However, with respect to M_n, the P_0–M_n and ML–M_n correlations were slightly different. The more metabolically active clone (PB 235) was sensitive to maturation effects,

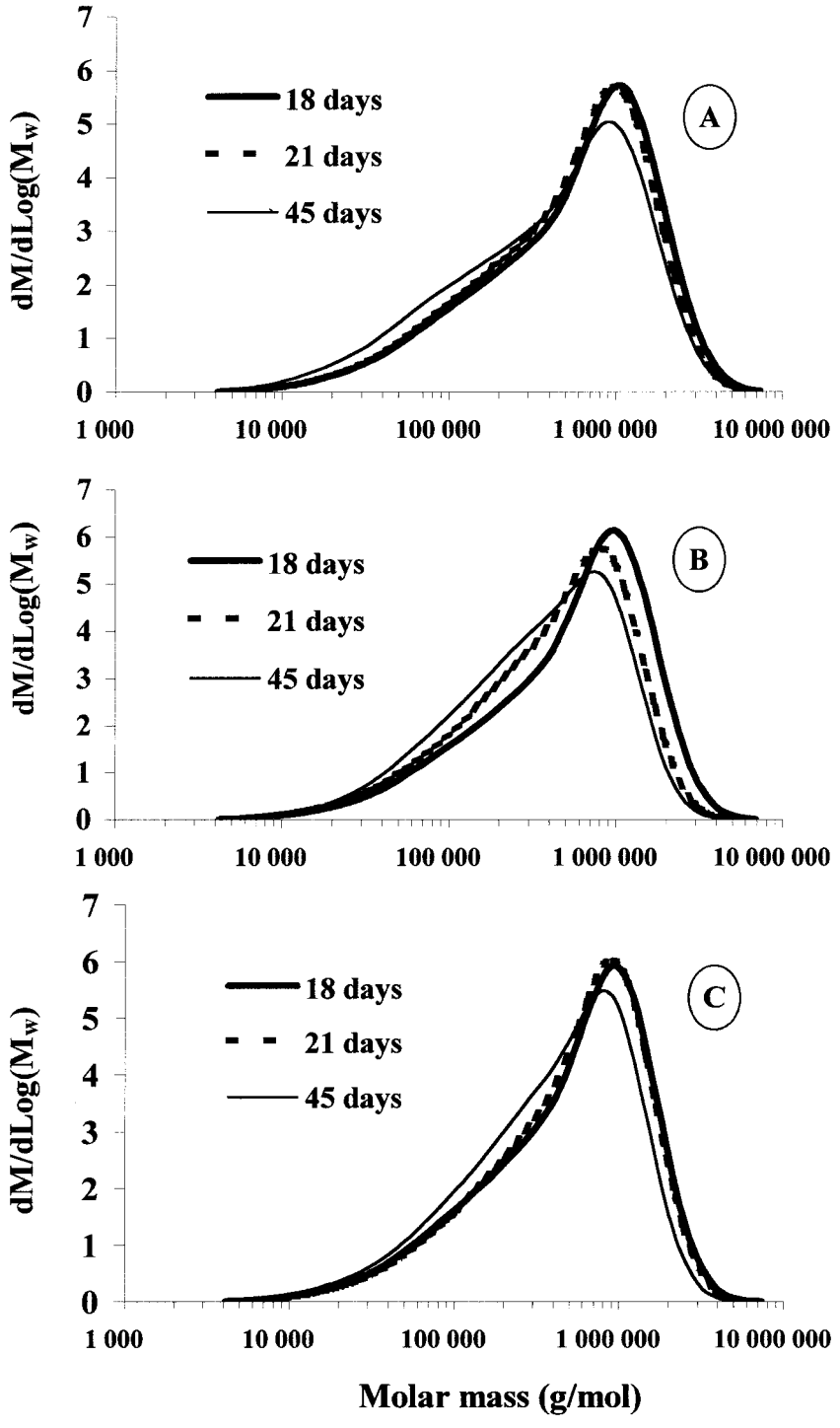

Figure 3 Effect of the clonal typology and cuplump maturation on the molar mass distribution of raw processed natural rubber from (A) clone PB 235, (B) clone GT 1, and (C) clone PB 217.

whereas rubbers from the less active GT 1 and PB 217 clones were not sensitive. The coefficients characterizing the relationship between PRI and M_w or M_n were negative or nonsignificant for clone PB 235 rubber but positive for the others, confirming further that the latter clones would contain more natural antioxidants.

CONCLUSIONS

This study highlights the effects that certain exploitation practices related to the collection of raw natural rubber, notably the natural coagulation of latex and the eventual storage of cuplumps, could have on the

TABLE I
Pearson Correlation Coefficients Between Bulk Rheological Properties, Molar Mass, and Molar Mass Distribution of Raw Processed Crumb Subjected to Different Extents of Maturation

Clone	Chain-length parameters	P_0 (1/100 mm)			ML (1 + 4) at 100°C			PRI (%)		
		T_1	T_2	T_3	T_1	T_2	T_3	T_1	T_2	T_3
PB 235: high metabolism	M_w	++	+	+	++	+	O	O	O	O
	M_n	+	O	+	+	O	O	− −	O	−
	M_w/M_n	++	O	O	+	O	++	++	++	O
GT 1: average metabolism	M_w	+	+	+	++	++	+	++	+	+
	M_n	+	O	O	O	O	O	++	O	O
	M_w/M_n	O	O	++	+	O	+	O	+	O
PB 217: slow metabolism	M_w	++	+	++	++	++	++	+	+	++
	M_n	O	O	O	+	O	O	O	O	++
	M_w/M_n	++	+	+	++	O	O	O	++	O

T_1, T_2, and T_3 represent maturation and storage for 18, 21, and 45 days, respectively The double symbols ++ and −− represent highly significant positive and negative correlations, respectively ($p \leq 1\%$). The single symbols + and − represent significant positive and significant negative correlations respectively ($p \leq 5\%$), whereas the symbol O indicates no significant correlation.

molecular structure and rheological behavior of the processed raw rubber. The results indicate that, depending on the metabolic activity of the biological source (the *Hevea* tree), natural rubber could be more or less disposed to degradation after the maturation and storage of cuplumps before processing. The less metabolically active the *Hevea* clone (e.g., PB 217) is, the more stable the molecular structure is of its rubber and vice versa. Furthermore, prolonged maturation of cuplumps for as long as 45 days had a minor influence on the length of the polyisoprene chains and the molar mass distribution of the polymer. Correlation analyses indicated that despite the modifying effects of maturation, the bulk viscosity expressed in terms of P_0 and *ML* remained significantly influenced by the lengths of the rubber chains.

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References

1. Nair, S. J Rubber Res Inst Malaya 1970, 23, 76.
2. Van de Sype, H. Rev Gen Caout Plast 1985, 655, 91.
3. Leblanc, J.-L. Eur Rubb J 1980, 162, 20.
4. Hanower, P.; Chretin, H.; Michel, P.; de Livonnière, H. Caout Plast 1989, 605, 85.
5. Loyen, G.; de Livonnière, H. Rev Gen Caout Plast 1975, 52, 153.
6. Le Roux, Y.; Ehabe, E.; Sainte-Beuve, J.; Nkengafac, J.; Nkeng, G.; Ngolemasango, F.; Gobina, S. J Rubber Res 2000, 3, 142.
7. Jacob, J.-L.; d'Auzac, J.; Prevot, J.-C.; Serier, J.-B. Recherche 1995, 276, 538.
8. Bonfils, F.; Koman, A.; Sainte-Beuve, J.; Sylla, S.; Allet Don, A.; Laigneau, J.-C. J Nat Rubber Res 1995, 10, 143.
9. Norling, P. M.; Tobolsky, A. V. In Thermal Stability of Polymers; Conley, R. T., Ed.; Marcel Dekker: New York, 1970.
10. Shelton, W. Rubber Chem Technol 1972, 45, 359.
11. Li, S.-D.; Yu, H.-P.; Peng, Z.; Li, P.-S. J Appl Polym Sci 1998, 70, 1779.
12. Kramer, O.; Good, W. R. J Appl Polym Sci 1972, 16, 2677.
13. Bonfils, F.; Flori, A.; Sainte-Beuve, J. J Appl Polym Sci 1999, 74, 3078.