Effect of Natural Coagula Maturation on the Processability, Cure, and Mechanical Properties of Unfilled Vulcanizates of *Hevea* Natural Rubber

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ABSTRACT: Fresh latex from different *Hevea brasiliensis* clones was naturally coagulated, subjected to different durations of maturation, processed into solid rubber, and compounded into pure gum stocks and vulcanized. Coagula maturation had clone-specific effects on the processability of the raw rubber: reduced for some clones, while others was less sensitive. The cure and mechanical behaviors of the compounded stocks and vulcanizates, respectively, were not sensitive to the clonal origin of coagula and their duration of maturation. Although coagula maturation could be associated with leaching, deactivation of inherent antioxidants in *Hevea* latex, as well as crosslinking and/or oxidation of polyisoprene chains, these results show that compounding with a standard pure gum recipe compensates for the *Hevea* latex constituents affected by maturation. Hence, extended maturation of *Hevea* coagula, for economic or other reasons, would influence much more the bulk behavior of raw rubber and have insignificant effects on the compounded stocks and vulcanizates. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2359–2363, 2007

Key words: *Hevea brasiliensis*; natural rubber; coagula; maturation; vulcanization; crosslinks

INTRODUCTION

Raw natural rubber from the *Hevea brasiliensis* is employed in a wide range of applications mainly because of its excellent dynamic properties such as elasticity, green strength, and resistance to heat build-up.[1,2] The flow behavior of natural rubber depends largely on the length of its constitutive poly(*cis*-isoprene) chains and to a smaller extent on the relative quantities of its nonrubber components, which at times participate in chain crosslinking.[3] In effect, during the vulcanization process, crosslinks are introduced between polyisoprene chains, thereby converting the rubber matrix from a weak thermal mass into a strong and highly elastic three-dimensional network structure.

Latex from the *Hevea* is normally subjected to several treatments before the dry marketable products are obtained. Traditionally, rubber is rapidly coagulated from latex, treated to eliminate serum, and appropriately dried. The end products in such cases constitute premium technically-specified and conventional sheet grades. The scarcity of raw rubber at times impels middle-level dealers and factory processors to accumulate coagula over extended and uncontrolled durations before processing (maturation periods). Despite the cost savings associated with such practices, these practices are progressively being abandoned because of the very dark undesired color that develops, high Mooney viscosity, and low resistance to thermal oxidation.[4,5]

Despite the literature on thermal ageing of natural rubber, much less work has been done with respect to its light-induced ageing, probably because the material is mostly used in black mixes, which are little affected by solar radiation. The photochemical reactions involved could be generated from reactions involving oxygen, from the action of light alone in air (photolysis) as well as under vacuum (isomerization).[6] Indeed, olefinic photo-oxidation is reported to proceed (initiation, propagation, and termination) in accordance with a radical reaction mechanism identical to that of thermal oxidation.[7] Consequently, certain C—H or C—C bonds in the structure of natural rubber breakdown under the influence of light[8,9] or temperature.[10] The free radicals formed either react with one another, with irradiation under limited oxygen concentration, or initiate a photo-oxidative process in the presence of oxygen. Even the effects of some agronomic traits of the *Hevea* plant on the bulk behavior of its rubber have been postulated. Indeed, significant relationships have been confirmed between some relevant bulk properties of

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raw rubber and some physiological parameters of *Hevea* latex (inorganic phosphorus and total solids content),[11] as well as on the effects of coagula maturation and storage on the macromolecular chain length of raw natural rubber of different clonal typologies.[12] This study was undertaken to investigate the contribution of coagula maturation prior to factory processing (washing and drying) on the flow behavior of natural rubber, the cure behavior of its pure gum (ACS 1) compounded stocks, and the mechanical properties of its vulcanizates.

EXPERIMENTAL

Materials and coagula treatment

Latex from trees belonging to three *H. brasiliensis* clones of different metabolic levels were used in this study: PB 235 clone of relatively high metabolism, GT 1 of intermediate metabolism, and PB 217 of slow metabolism.[13] The trees were of similar ages, planted around 1983 in the humid forest zone of South West Cameroon.

The trees were opened for tapping in 1990 and had been in exploitation for 9 years at the start of this study. The trees were stimulated following local industrial recommendations and tapped once every 4 days on a half spiral (d/4, ½S). On tapping, fresh latex was left to coagulate naturally in the cups and the coagula were subjected to various extents of maturation prior to factory processing: 3 days of maturation in cups and 15 days of storage in the factory (total of 18 days); 3 days in cups, 3 days on barns, and 15 days in the factory (total of 21 days); and 3 days in cups, 27 days on barns, and a further 15 days in the factory (total of 45 days).

Bulk characterization of raw rubber

The coagula were processed under industrial conditions at the Tiko rubber factory of the Cameroon Development Corp. (CDC). Test pieces were cut from dried crumbs and homogenized in conformity with the ISO 1795 norm. The normalized Mooney viscosity [ML(1 + 4) at 100°C], Wallace rapid plasticity (P_0), and the plasticity retention index (PRI) were equally determined, according to the ISO 2000 norm.

Compounding of gum stocks and characterization of cure behavior

Compounded natural rubber stocks were prepared on the basis of the standard ACS1 gum stock recipe: natural rubber (100 phr), mercaptobenzothiazole (0.5 phr) as accelerator, elemental sulfur (3.5 phr) as vulcanizing agent, stearic acid (0.5 phr), and zinc oxide (6 phr) as activators. Compounded stocks were
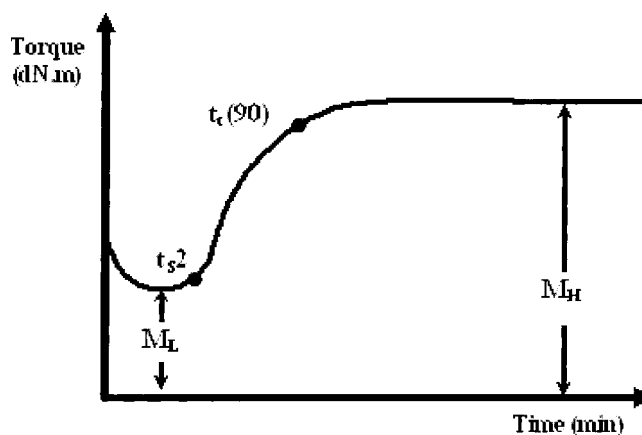
Figure 1 Typical cure curve (rheograph) to equilibrium obtained during curing of a natural rubber gum stock on an oscillating disk rheometer. The parameters t_s2, t_c (90) M_L, and M_H are described in the text.

prepared in a two-batch process on a laboratory two-roll mill, following standardized procedures (ISO 3417) and characterized for their cure behaviors on an oscillating disc rheometer (Model 100, Monsanto) oscillating at an amplitude of 3° and a frequency of 1.67 Hz. Cure curves as shown in Figure 1, were obtained isothermally at 160°C, from which some cure characteristics were estimated:[14,15]

full or maximum cure (M_H), a measure of the shear modulus of the vulcanizate;
scorch time (t_s2), time required for the torque to increase by two units above its minimum;
optimum cure, $t_c(90)$ is the time required for the torque to reach 90% of full cure;
the reaction rate constant at 90% of full cure, K_{90}, [eq. (1)];

$$K_{90} = \ln 10/t_c(90) \quad (1)$$

the cure rate index, CRI [eq. (2)] or slope of the cure curve in the steep region:

$$\text{Cure rate index, CRI} = 100/[t_c(90) - t_s2] \quad (2)$$

Characterization of vulcanizates

The compounded stocks were vulcanized in an electrically-heated hydraulic press (model T100, Pinette Emidecau, France) at 140°C and 3.5 MPa for 40 min. The vulcanizates were stored in the dark at 25°C and only retrieved for eventual determination of their tensile properties. These were done on Type 2 dumb-bell test pieces (25 mm long, 4 mm wide, and 4 mm thick) using a dynamometer (DY 22 Adamel Lhomargy, France) operating at a crosshead speed of 50 mm/min. From the stress-strain data, the following were calculated:

The ultimate stress, expressed as the ratio of the breaking force (in N) to the initial cross-sectional area (in mm^2);

The ultimate elongation (percentage elongation at break), estimated as the change in length over the original length;

The 300% modulus or ratio of the stress at 300% elongation to the corresponding strain.

Statistical analysis

Mean and standard deviations were computed for all data recorded. The significance of the treatments (extent of maturation and clone type) was analyzed on a randomized complete block design using the JMP software (version 5, SAS Institute). Treatments were ranked in groups of homogeneous means using the Student's *t*-test at the 5% level of significance. Where necessary, linear correlation analyses were conducted to determine the degree of the linear relationships between the parameters studied.

RESULTS AND DISCUSSION

Effect of maturation on the bulk properties of processed crumb

Characterization of some bulk properties of the processed natural rubber samples in terms of their initial Wallace plasticity values (P_0), Mooney viscosity (ML1 + 4 at 100°C), and plasticity retention index (PRI) showed, on the whole, significant effects of the duration of coagula maturation (18–45 days) and clone specific behavior. That is, a different trend for clones PB 217 and GT 1, of slow and intermediate metabolism, respectively, and another for clone PB 235 of relatively higher metabolism (Fig. 2).

The Wallace rapid plasticity [Fig. 2(i)] and Mooney viscosity values [Fig. 2(ii)] of rubber from clones GT 1 and PB 217 decreased as the duration of maturation increased (from 18 to 45 days), whereas rubber from clone PB 235 was less sensitive to the effects of maturation. The hydroperoxidation of polyisoprene chains and the competing reactions of peroxy-radicals during the maturation process could either lead to degradation or crosslinking, depending on the temperature and humidity conditions prevailing, as well as the presence of amines.[16] The rather continuous decrease in these bulk properties with maturation would indicate that conditions characterizing the maturation process would favor the degradation of the long polyisoprene chains.[16] However, this did not seem to be the case when the susceptibility to thermo-oxidation of the macromolecular chains as the PRI did not evolve in the same manner for the three clones studied [Fig. 2(iii)]. Although the PRI of rubber from clones PB 235 and PB 217 remained almost constant throughout, those from clone GT 1
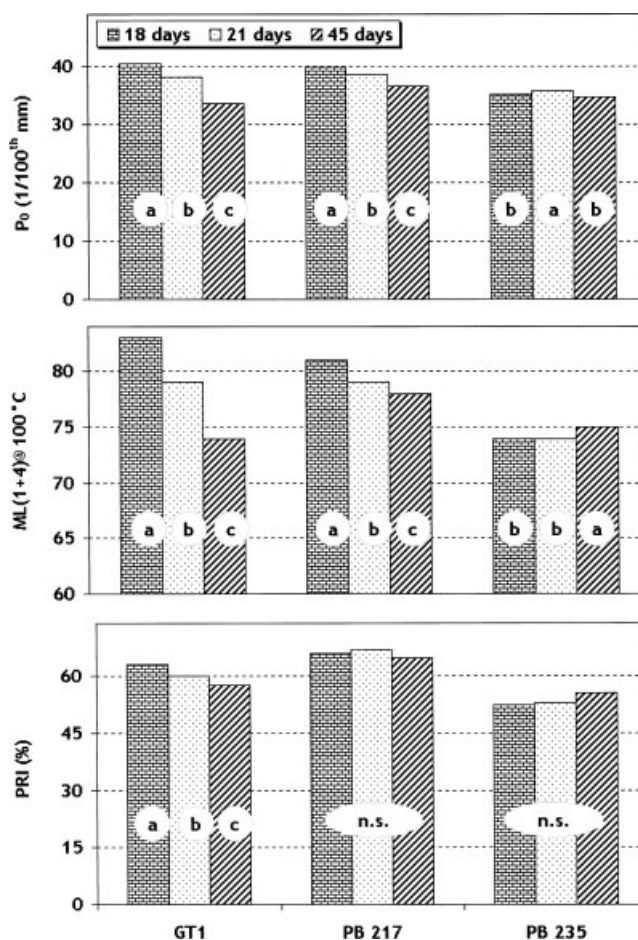

Figure 2 Effect of the duration of maturation of coagula from different *Hevea* clones on their bulk rheological properties: (i) Wallace rapid plasticity, (ii) Mooney viscosity and (iii) plasticity retention index. Maturation times for same clones bearing same letters were not significantly different ($P \leq 5\%$).

decreased significantly following prolonged maturation and storage for 45 days. The differences observed for the various clones would indicate some inherent differences in the nonrubber constituents of the clones studied and/or a discriminatory effect of maturation (leaching, denaturing, and deactivation), depending on the clonal origin of the rubber.[12]

Effect of maturation on the cure of compounded stocks

The cure kinetics of compounded ACS 1 stocks were characterized at 160°C for their scorch time (t_s2), cure rate index (CRI), and reaction rate constant at 90% of full cure (K_{90}). At this temperature, little or no reversion behavior was noted even at prolonged cure (data not shown), indicating that the created polysulfidic crosslinks ($-C-S_x-C$), common in conventional-sulfur cured compounds, were rather stable with little or no rearrangement.[17] The effect of

maturation on the duration for onset of crosslinking (Scorch time) of compounded stocks was not clear [Fig. 3(i)], with no effect on some clones (GT 1) and increasing the scorch of others (clone PB 235). Although our results could indicate that leaching and/or deactivation of cure activators in *Hevea* rubber could be clone-specific, the nature of such compounds is unclear. Indeed, it has been observed that photolytic reactions associated with the storage of raw rubber would provoke random breaking of the α-methylenic C—H bonds and main chain C—C bonds adjacent to the double bond.[6] The radicals so formed initiate an auto-oxidation process, producing oxidative cleavage of the chain in the termination step.

The cure rate index (CRI) of the compounded stocks evolved differently as maturation progressed [Fig. 3(ii)]: increasing with maturation from 18 to 21 days and then remaining unchanged thereafter for clone GT 1 rubber, staying constant and decreasing in magnitude on prolonged maturation for clone PB 235 rubber. For clone PB 217 rubber, the CRI increased on maturation from 18 to 21 days, and then reduced slightly on prolonged maturation for

Figure 3 Effect of the duration of maturation of coagula from different *Hevea* clones on the cure behavior of their compounded stocks: (i) Scorch time, (ii) cure rate index, and (iii) reaction rate constant at 90% of full cure. Maturation times for the same clones bearing same letters were not significantly different ($P \leq 5\%$).

45 days. As concerns with the reaction rate constant at 90% of full cure (K_{90}), only compounded stocks from clone GT 1 seemed to have been affected by changes in the duration of maturation [Fig. 3(iii)]. Considering that the kinetics of crosslink formation during sulfur vulcanization follows a first-order mechanism,[3] these results would indicate that a much greater portion of the reactant species, whose concentration conditions the reaction rate constant, come from ingredients in the gum formulation as the coagula contains very small quantities of this species.

Effect of maturation on some mechanical properties of vulcanizates

The effect of the duration of coagula maturation seemed to have different effects on the tensile stress at break (ultimate stress), the ultimate elongation, and the modulus at 300% elongation depending on the clonal origin of the coagula (Fig. 4). The ultimate tensile stress of vulcanizates from coagula from clones GT1 and PB 217 were not affected by even prolonged coagula maturation for up to 45 days, whereas those of vulcanizates compounded from clone PB 235 rubber increased significantly with maturation from 18 to 21 days, and then decreased with further maturation [Fig. 4(i)]. Such trends were not observed with respect to the ultimate elongation of vulcanizates as they were not affected to any significant degree by the conditions and durations of maturation experimented [Fig. 4(ii)]. Based on the magnitudes of the moduli at 300% elongation, all the clonal vulcanizates behaved similarly on maturation from 18 to 21 days, but a bit differently on further maturation from 21 to 45 days [Fig. 4(iii)]. The trends obtained on further maturation enabled the vulcanizates to be classified in two groups; one for clone GT 1 coagula, whose moduli remained rather constant on further maturation, and the other for coagula from clones PB 235 and PB 217 rubber, whose moduli reduced significantly [Fig. 4(iii)]. Increases in modulus could be associated with higher crosslink densities in the vulcanizates, and *vice versa*.[18] Hence, changes in the tensile properties of vulcanizates should be associated with changes in the number of crosslinkable sites along the constitutive polyisoprene chains as well as the lengths of these chains.[12]

Indeed, hardening is a common feature with the behavior of raw natural rubber following the condensation of α-methylenic groups present in the polyisoprene main chain.[16] Differences between the various clonal rubber could be accounted for by their inherent differences in natural antioxidants as well as the propensity of their molecular chains to degrade during the maturation and storage process, as de-
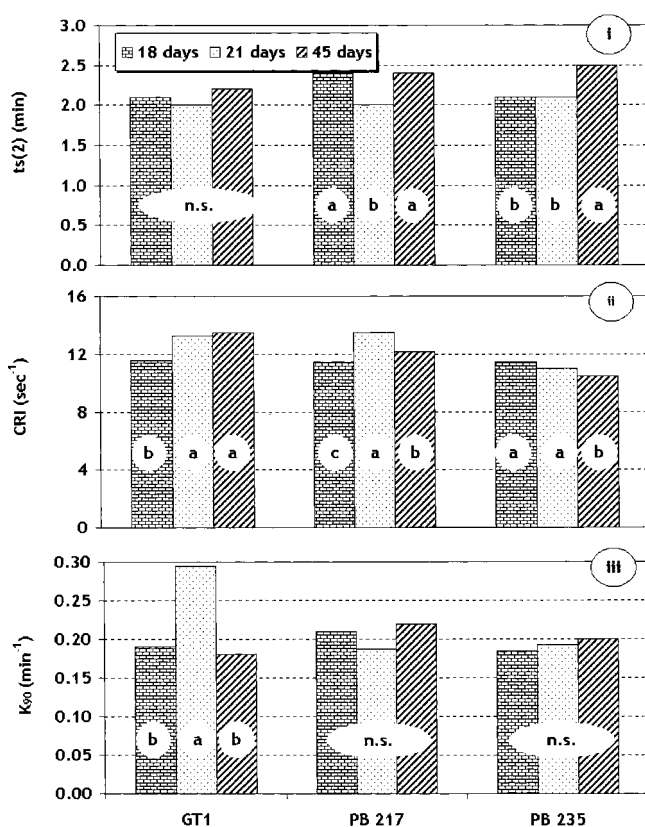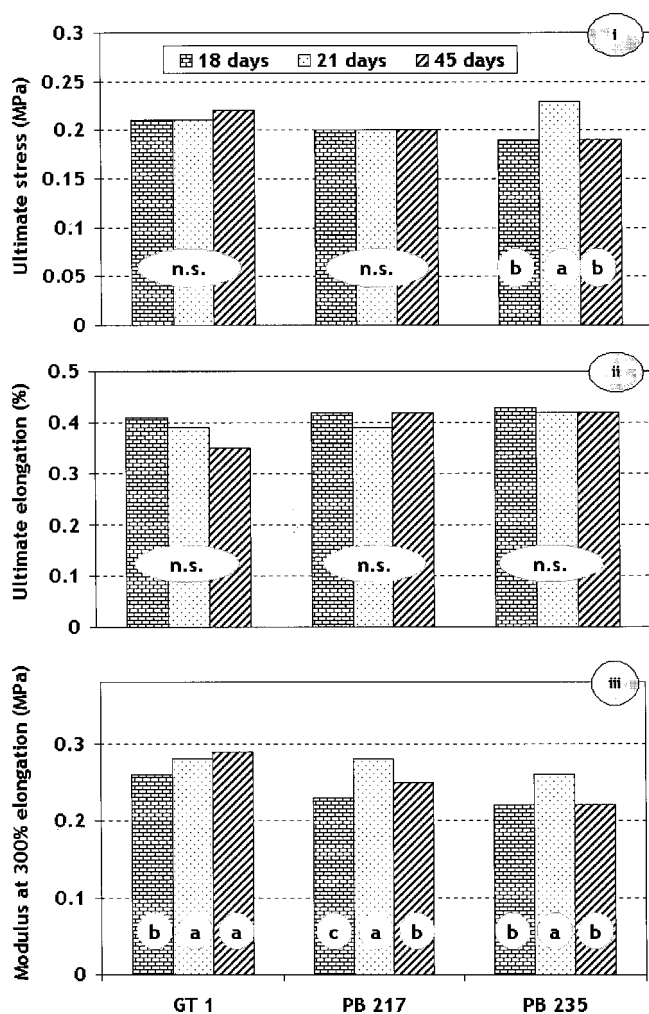
Figure 4 Effect of the duration of maturation of raw rubber from different *Hevea brasiliensis* clones on the mechanical properties of unfilled vulcanised stocks: (i) ultimate stress, (ii) ultimate elongation, and (iii) modulus at break. Maturation times for the same clones bearing the same letters were not significantly different ($P \leq 5\%$).

picted by their PRI values [Fig. 2(iii)]. The variable trends observed with the different tensile properties following maturation from 18 to 45 days could indicate the absence of consistency in molecular chain degradation or their crosslinking during the maturation process, or the rather minor influences of the nonrubber constituents in the unprocessed coagula. Indeed, it has even been demonstrated that although the nonrubber constituents in natural rubber display a protective effect, other vulcanization ingredients like mercaptobenzothiazole and sulfur could slow down solar ultraviolet-induced degradation.[6]

From the results obtained, no consistent and significant linear correlations were observed between the rheological properties of the raw processed rubber crumb, the cure behavior of compounded pure gum stocks, and the tensile properties of their vulcanizates (data not shown).

CONCLUSIONS

This study was undertaken to investigate the contribution of the duration of maturation of *Hevea* coagula on the flow of natural rubber, the cure of its compounded stocks, and the mechanical properties of its vulcanizates. The bulk properties (Wallace plasticity, Mooney viscosity, and plasticity retention index) decreased significantly as maturation progressed, indicative of the prevalence of conditions that favor degradation of long polyisoprene chains. These changes were often clone-dependent because of the differences in their nonrubber constituents and/or the propensity of their molecular chains to degrade under such conditions. The cure of compounded stocks showed no consistent trends attributable to the coagula maturation, probably because the rate-limiting species in the cure process were from the vulcanization ingredients and not the coagula. The tensile properties of the vulcanizates were not maturation-dependent either indicating the random nature of changes in the length of the constitutive polyisoprene chains as well as the number of crosslinkable sites along each of them.

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