

Effect of Soluble Non-rubber Elements and Preliminary Processing on Water-rubber Balances

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Natural rubber comprises around 90% cis-1,4 polyisoprene and 10% various substances (non-rubber elements). These non-rubber elements (proteins, metal ions, etc.) can affect the quality of rubber articles by increasing their water absorption capacity and decreasing their resistance to ageing. The effect of non-rubber elements on water-rubber thermodynamic equilibrium was examined by comparing the desorption isotherms for rubbers from two clones (AF 261 and GT 1), after various types of processing.

The study revealed a significant difference in the water content at equilibrium depending on the treatment and the clone; the major role of soluble proteins extractable by simple washing, in the water retention process; and the lack of any correlation between nitrogen and water content at equilibrium.

Today natural rubber is used in the manufacture of numerous consumer products. Its elasticity, resistance to wear, low internal heat build-up and its adhesive capacity make it an irreplaceable product in certain industrial fields such as aeronautics, the motor industry (aircraft and HGV tyres), the paramedical field (gloves, condoms, etc.) and mechanics (belts, seats for telephone lines and electric cables).

Natural rubber contains about 10% non-rubber elements (proteins, metal salts, etc.) which affect the water content at equilibrium at the end of drying and modify certain characteristics of the end product.

Water uptake by polymers has been covered by numerous studies since the turn of the century.

The major telephone and electricity companies were concerned by the problem of ageing under-sea cables. For instance, Lowry and Kohman¹ demonstrated the importance of water vapour pressure in the air surrounding rubber and the role of impurities in rubber that constitute veritable water traps. Daynes² used a modified version of Fick's law to model water absorption and take into account relative humidity in equilibrium with wet rubber. He also revealed the major role of non-rubber elements, whose composition may vary depending on chemical or bacteriological actions. Crank and Park³ showed that desorption rates were faster than sorption rates and that the anomalies observed could be attributed to variations in the concentration of impurities on the product surface. Gale⁴ studied the effect of relative humidity on the water content

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at equilibrium of rubber sheets dried under carefully controlled conditions. Cousin⁵ plotted the desorption isotherms for samples of sheets manufactured from latex with an ammonia content of 9 g/l, aged for several months and acidified to pH 4.8.

Other authors like Loncin⁶, Brunauer *et al.*⁷ and Anderson⁸, tried to explain the desorption isotherms by developing theoretical models.

All in all, the role played by non-rubber elements has not been sufficiently investigated; likewise the effect of the origin of the matter has virtually remained uninvestigated, though non-rubber elements play a major role in water diffusion during drying and affect the water content of the end product. They, therefore, govern the natural rubber drying process.

The work described in this article concentrates primarily on the effect of soluble non-rubber elements and of the origin of the matter on water-rubber thermodynamic equilibrium, by determining the desorption isotherms. It then goes on to describe the isotherms using existing mathematical models.

MATERIAL AND METHOD

The samples studied were from the experimental plantation at the Centre National de la Recherche Agronomique (CNRA), Bimbresso Research Station, in Côte d'Ivoire.

An experimental design with two factors and three replicates was chosen. The first factor was clone type (AF 261 and GT 1). Clone AF 261 is known for its high nitrogen content; GT 1 is the reference clone in Côte d'Ivoire.

The second factor was the processing system, as may be encountered in the industry, *viz*:

- Natural coagulation at d.r.c. 30%, matured for 20 h
- Natural coagulation at d.r.c. 30%, matured for 4 h
- Controlled coagulation at d.r.c. 30% at pH 4.8 with formic acid at 3%, matured for 18 h, unwashed
- Controlled coagulation at d.r.c. 30% at pH 4.8 with formic acid at 3%, matured for 18 h, washed
- Controlled coagulation at d.r.c. 30% at pH 4.8 with formic acid at 3%, matured for 18 h, heated in a saturated atmosphere at 100°C for 10 min
- Natural coagulation at d.r.c. 30% of a partially deproteinized latex with trypsin at 0.1%, matured for 20 h and washed.

Washing consists of soaking in a crystallisor for one hour in 100 ml of water (temperature 30°C), replaced three times then passed through the rollers of a small spin-dryer to wring out the water.

The measuring principle involves placing the samples in a sealed environment whose atmosphere is perfectly regulated in terms of temperature and relative humidity, then the quantity of water retained by the material at equilibrium is measured.

In practice, the study was carried out in 1000 ml 'preserves type' jars, in which the relative humidity was controlled by saturated salt solutions (*Table 1*).

The jars with their contents were placed in a water bath and completely submerged (to prevent condensation on the lid). The temperature

TABLE 1. EQUILIBRIUM WATER CONTENTS FOR DIFFERENT SATURATED SOLUTIONS

Salt type	Relative Humidity at 35°C
Magnesium chloride	32%
Sodium nitrite	62%
Sodium chloride	75%
Potassium nitrate	89%

was monitored and regulated ($35 \pm 0.1^\circ\text{C}$) by a circulation thermostat as shown in *Figure 1*. The samples were weighed twice a day to monitor weight loss over time. Once equilibrium was reached (negligible variation in weight), the volatile matter content was measured as per standard *ISO 248*. It was expressed as a percentage of water in relation to dry rubber weight.

The amount of protein substances contained in the rubber sample was obtained by measuring the nitrogen content as per standard *ISO 1656*. It was expressed as the percentage of nitrogen in relation to dry rubber weight.

Given the experimental results obtained, Levenburg-Marquardt's direct curvilinear regression was used to find a mathematical model applicable to our desorption isotherms.

RESULTS

Desorption Isotherms

The water content results obtained for the different treatments are shown in *Tables 2 and 3*.

The figures (*Table 2 and 3*) reveal similar values; the differences seen are due to the water contents at equilibrium of the different samples:

- The washed sample had water content values at equilibrium lower than those of the heated (unwashed) and unwashed samples.
- The partially deproteinised sample also had water content values at equilibrium lower than those of the samples matured for 20 h and 4 days.
- There was no significant difference between the water content values at equilibrium for the samples matured for 20 h and 4 days.
- Likewise, the washed sample had a water content virtually equivalent to that of the deproteinised and washed sample.

Nitrogen Content

The results for nitrogen content measured at equilibrium obtained for the different treatments are given in *Table 4*.

Statistical analysis of the results shown in *Table 4* was carried out with *Statitcf* software. The analysis of variance did not enable any distinction to be made between the two clones (AF 261 and GT 1). However, the treatments were significantly differentiated into four uniform groups ($F = 23.4$ for a probability of less than

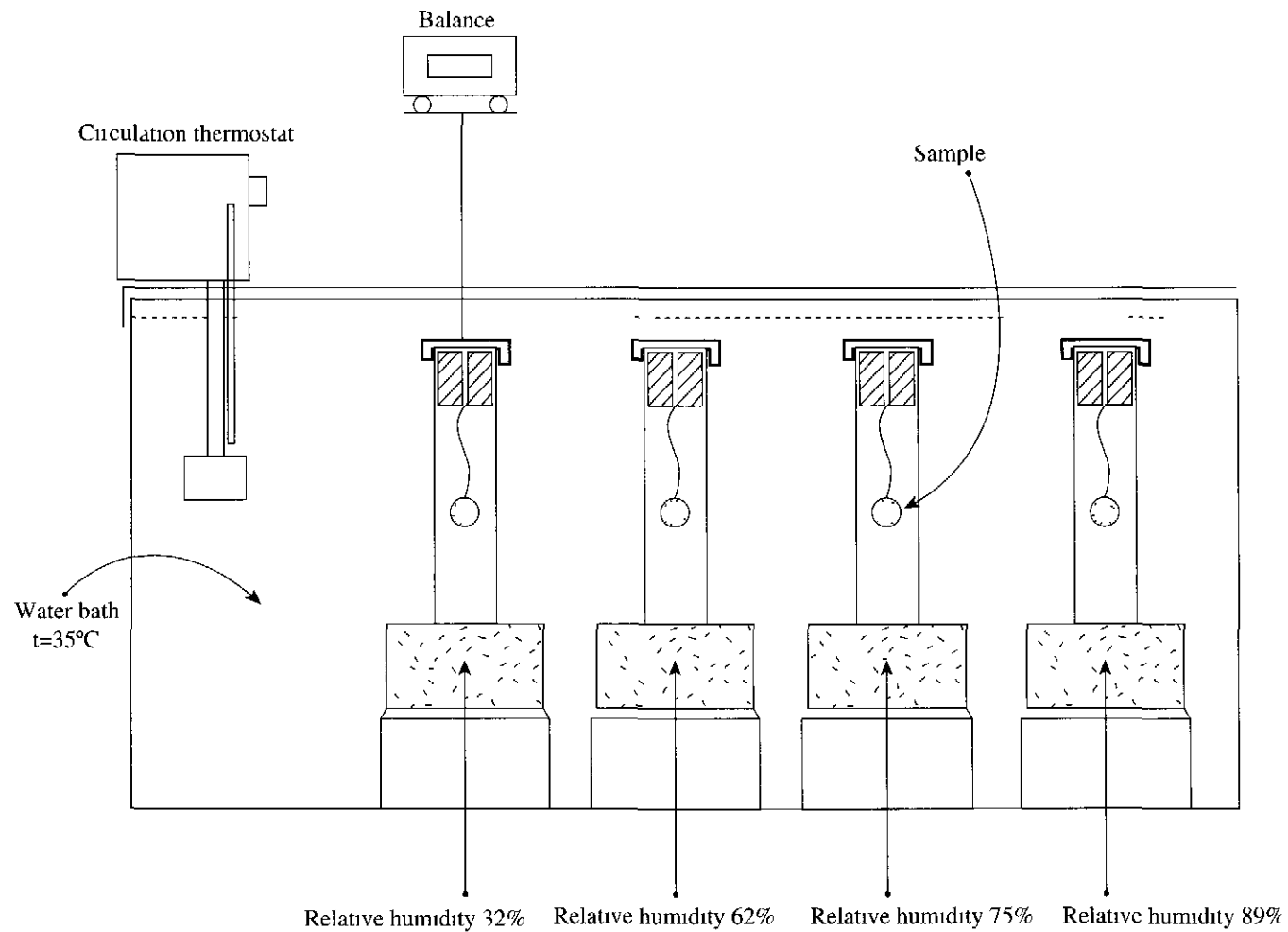


Figure 1 Experimented design

TABLE 2 WATER CONTENT AT EQUILIBRIUM (%) – MEAN OF 3 REPLICATES,
T = 35°C (CLONE AF 261)

Relative humidity (%)		32	62	75	89
Natural coagulation	$\bar{x}$	0.89	1.50	1.82	3.09
(matured for 20 h)	σ	0.25	0.20	0.38	0.31
Natural coagulation	$\bar{x}$	0.86	1.38	1.63	3.59
(matured for 4 days)	σ	0.05	0.10	0.07	0.86
Controlled coagulation	$\bar{x}$	1.00	1.80	2.72	3.18
(unwashed)	σ	0.29	0.20	0.63	0.04
Controlled coagulation	$\bar{x}$	0.34	0.66	1.13	2.77
(washed)	σ	0.09	0.08	0.20	1.27
Controlled coagulation	$\bar{x}$	0.72	1.61	2.92	3.81
(heated, unwashed)	σ	0.04	0.29	0.17	0.24
Natural coagulation	$\bar{x}$	0.42	0.62	1.60	2.45
(deproteinised, washed)	σ	0.12	0.08	0.35	0.53

$1 \cdot 10^{-5}$), the residual variance being 0.06 for a coefficient of variation of 15.6%)

- Coagulated with acid, unwashed and heated, unwashed
- Coagulated naturally, matured for 20 h, and coagulated with acid, washed
- Coagulated naturally, matured for 4 days
- Coagulated naturally, partially deproteinised, washed

Figure 2 gives the nitrogen content and water content at equilibrium for clone GT 1 in the different treatments

As regards the nitrogen content, it was higher in the samples matured for 20 h than in the samples matured for 4 days and deproteinised the samples coagulated with acid and unwashed and those heated and unwashed were identical, but differed very little from the washed samples

For water content at equilibrium, it was higher in the sample matured for 20 h than in the samples matured for 4 days and deproteinised

Modelling

The tendency of the data given in Tables 2 and 3 during the desorption isotherms can be explained by the application of the GAB model. Fitting the model to the observed data gave the results which were converted into graph form, as shown in Figures 3 and 4

$$W = \frac{W_m C K a_n}{(1 - K a_n)(1 - K a_n + C K a_n)} \quad 1$$

where, a_n = water activity (dimensionless)

w = weight of water in relation to weight of water of the anhydrous compound (g/100 g) of dried basis

W_m = weight of adsorbed water by the monolayer (g/100 g of dried basis)

TABLE 3. WATER CONTENT AT EQUILIBRIUM (%) – MEAN OF 3 REPLICATES;
T = 35°C (CLONE GT 1)

Relative humidity (%)		32	62	75	89
Natural coagulation	$\bar{x}$	1.13	1.87	2.01	3.41
(matured for 20 h)	σ	0.15	0.28	0.32	0.48
Natural coagulation	$\bar{x}$	0.90	1.64	2.30	3.95
(matured for 4 days)	σ	0.11	0.25	0.79	0.59
Controlled coagulation	$\bar{x}$	1.24	2.04	3.03	4.03
(unwashed)	σ	0.49	0.16	0.44	0.21
Controlled coagulation	$\bar{x}$	0.34	0.86	1.18	2.05
(washed)	σ	0.09	0.30	0.33	0.12
Controlled coagulation	$\bar{x}$	0.57	1.98	2.59	3.30
(heated, unwashed)	σ	0.06	0.34	0.13	0.54
Natural coagulation	$\bar{x}$	0.60	0.52	2.64	3.22
(deproteinised, washed)	σ	0.12	0.18	0.42	0.39

TABLE 4. NITROGEN CONTENTS FOR SAMPLES SUBJECTED TO DIFFERENT
TREATMENTS – MEAN OF 3 REPLICATES

Treatment	Nitrogen content (weight %)				
	Group	GT 1		AF 261	
		$\bar{x}$	σ	$\bar{x}$	σ
Controlled coagulation (unwashed)	1	0.53	0.05	0.46	0.01
Controlled coagulation (heated, unwashed)	1	0.54	0.05	0.58	0.09
Natural coagulation (matured for 20 h)	2	0.43	0.05	0.48	0.05
Controlled coagulation (washed)	2	0.47	0.10	0.41	0.06
Natural coagulation (matured for 4 days)	3	0.34	0.02	0.34	0.02
Natural coagulation (deproteinised, washed)	4	0.20	0.02	0.19	0.02

C = Guggenheim's constant (dimensionless)
 $-C \exp (H - Hm)/RT$

H = total sorption heat of the water in the monolayer (kJ. kg⁻¹)

Hm = total sorption heat of the water (kJ. kg⁻¹)

K = correlation factor (dimensionless) — $K' \exp (H_1 - Hm)/RT$

K' = entropy contribution (dimensionless)

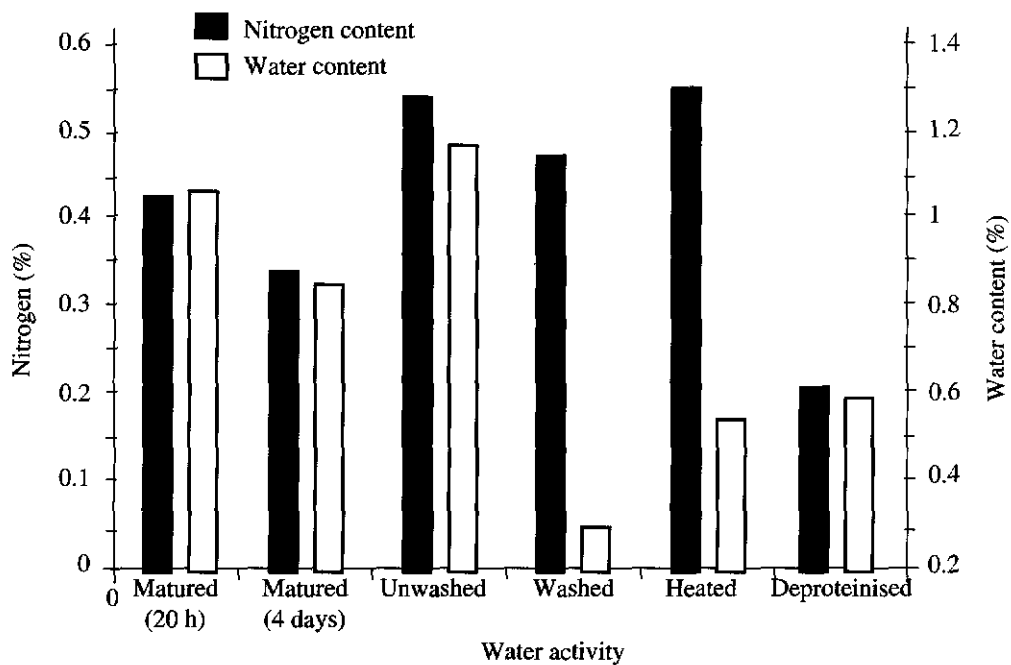


Figure 2. Water content and nitrogen content at equilibrium for clone GT 1 in the different treatments.

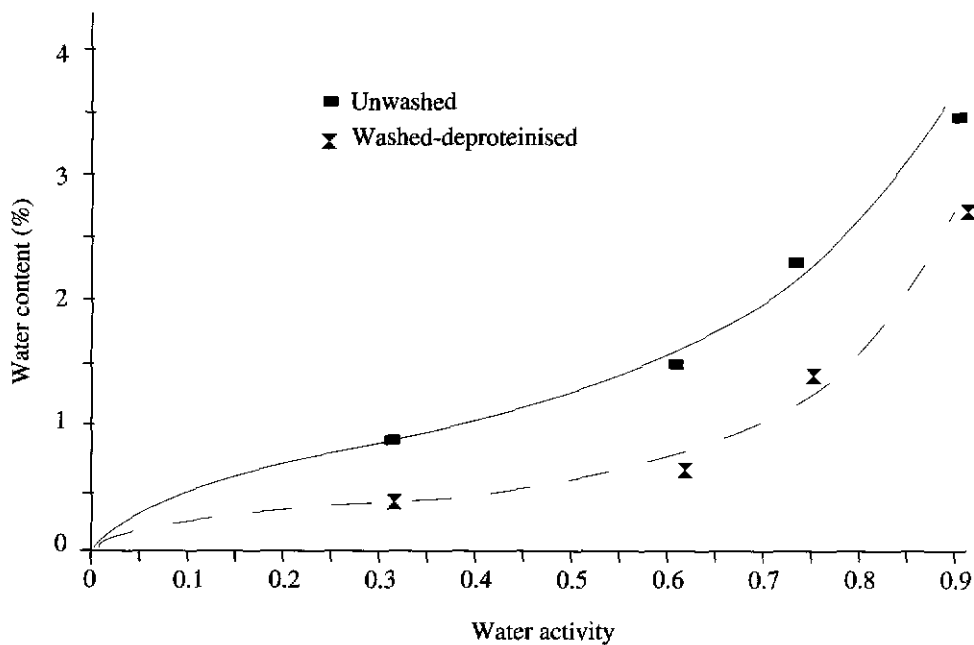


Figure 3. Desorption isotherms at 35°C (Clone AF 261).

TABLE 5. CONSTANT VALUES FOR THE G.A.B. MODEL DEPENDING ON CLONAL ORIGIN

CLONE	K	C	W_m (g/100 g of dried basis)
AF 261	0.0085	11.99	0.91
GT 1	0.0087	23.56	0.99

TABLE 6. CONSTANT VALUES FOR THE G.A.B. MODEL DEPENDING ON THE TREATMENTS

CLONE	Treatment	K	C	W_m (g/100 g of dried basis)
AF 261	Unwashed	0.0089	11.74	0.75
	Washed-deproteinised	0.0099	30.86	0.35
GT 1	Unwashed	0.0088	113.36	0.81
	Washed-deproteinised	0.0098	50.72	0.29

H_1 = steam condensation heat (kJ. kg⁻¹)

T = temperature (°K)

R = perfect gases constant (kJ. kg⁻¹ . °K⁻¹)

The constant values calculated according to clone and treatment type are given in *Tables 5* and *6*.

The constant K (representing the difference in energy between condensation and absorption phenomena) and W_m (representing the quantity of water absorbed by the monolayer) virtually did not vary with clonal origin.

On the other hand, constant C (total heat sorption) for clone AF 261 was clearly lower than for clone GT 1.

The G.A.B. model tallied well with the observed data. Irrespective of the clone, the curves had identical trends, but the water content at equilibrium for the deproteinised washed rubber was always lower than that for the unwashed rubber; clone GT 1 had the higher

water content at equilibrium, irrespective of the relative humidity of the surrounding air.

As regards the treatments, irrespective of the clone, constant K of the unwashed treatment was lower than that for the deproteinised, washed treatment, but constant W_m for the unwashed treatment was higher than that for the washed treatment.

The treatments had opposite effects on the value of constant C depending on the clone.

DISCUSSION

The desorption isotherms obtained had trends that complied with those in the literature^{1,2}.

The effects of the type of treatments on water contents at equilibrium were assessed by an analysis of variance. The difference found between the matured treatments (20 h and 4 days) and the unwashed and heated treatments

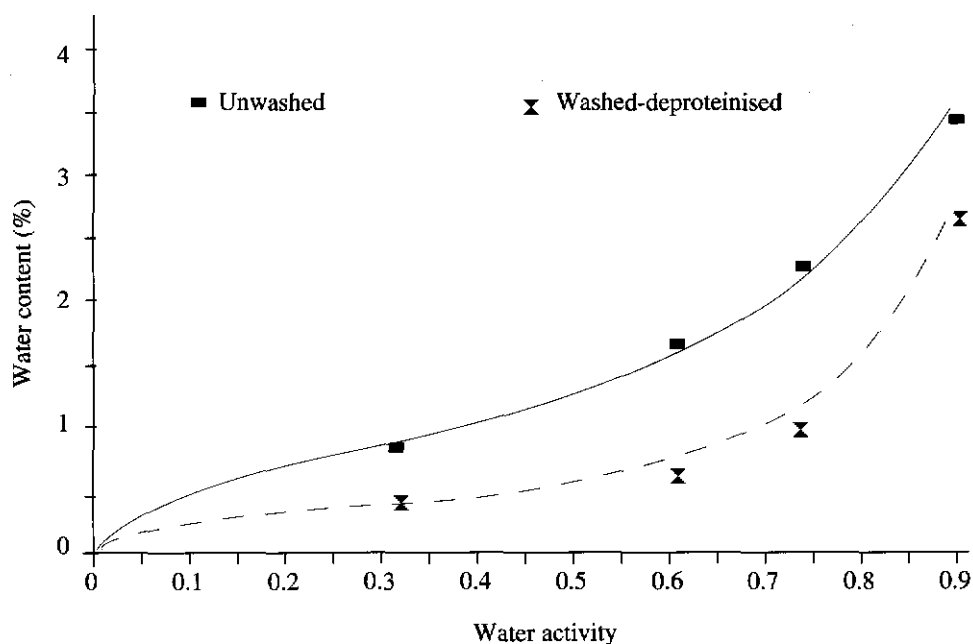


Figure 4. Desorption isotherms at 35°C (Clone GT 1).

was not significant. Irrespective of the relative humidity value, there was no difference between the washed and deproteinised treatments; they formed part of the same uniform group according to the Newman-Keuls test at 5%.

Nevertheless, two groups were evident: the group comprising the washed and/or deproteinised treatment, the group comprising the naturally coagulated treatments (20 h and 4 days), the treatments coagulated with acetic acid and unwashed, and lastly the heated and unwashed treatments.

It was in fact the washing stage that enabled a distinction to be made between these two groups. The removal of hydrophilous elements during washing determined the future equilibrium, but differently depending on the clones: GT 1 seemingly less susceptible than clone AF 261. Enzyme treatment smoothed out this difference.

A clonal difference appeared during the analysis of variance, except for the heated and deproteinised treatments; clone GT 1 always had a higher water content at equilibrium than clone AF 261. Likewise, clone/processing interaction, *i.e.* the effect of processing on the clone, did not occur, but seemed to change its nature for the heated and deproteinised treatments.

As regards the nitrogen content, the experiment conducted did not enable a distinction to be made between clones GT 1 and AF 261, though the later is known for its high nitrogen content. On the other hand, the treatments differed significantly from each other and could be split into four uniform groups according to the Newman and Keuls test. For a relative humidity of 32%, little difference was found between a sample coagulated with acid that was washed (0.47%) and unwashed (53%), indicating a relatively

small quantity of soluble proteins; on the other hand, a substantial difference was found for water retention in the same samples. That, therefore, seems to indicate that there is no correlation between the nitrogen rate and the water content at equilibrium. Moreover, among the naturally coagulated treatments, it was the deproteinised washed treatment that had the lowest nitrogen content; that might have been due to the fact that deproteinisation causes hydrolysis of proteins into soluble amino acids, which would then be removed during washing at the same time as the solutes; it should be noted that deproteinisation did not alter the water content at equilibrium compared with a washed treatment. Non-soluble proteins would therefore not seem to be involved in the water retention problems, unlike nitrogenous or non-nitrogenous substances (potassium, sodium in ionic form, sugar, *etc.*) which we could not distinguish under the operating conditions of our experiment.

The sigmoidal trend obtained by fitting the G.A.B. model to the observed data indicates multilayer type absorption usually encountered with agri-food products rich in polar polymers. The model clearly confirmed that water contents at equilibrium closely depended on the background of the rubber.

An unwashed treatment, possessing the majority of its hydrophilous groups, will absorb much more water than a deproteinised washed treatment, devoid of a proportion of its hygroscopic elements. That undoubtedly explains the fact that the W_m constant for the unwashed treatment was higher than for the deproteinised washed treatment and why the K constant of the unwashed treatment was lower than for the deproteinised washed treatment.

As regards total sorption energy (represented by the constant C), it was linked to both the clone and the treatments.

CONCLUSIONS AND PROSPECTS

The trend of the desorption isotherms obtained was independent from clonal origin, but the level of equilibrium reached was not. The water content at equilibrium varied with the treatment undergone by the sample; significant differences existed between unwashed latexes (acidified or not) and washed latexes (treated or not with a protease type enzyme). Soluble proteins (non-rubber elements) extracted by washing were involved in the water retention process. It seems that there was no correlation between nitrogen content and water content at equilibrium. The G.A.B. model tallied well with the observed data; it confirmed that water content at equilibrium was closely connected with the treatment undergone by the sample. The water retention phenomenon may also depend on the solutes (potassium, sodium, sugar, *etc.*); a study is required to show the contribution of each of them.

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