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Stress Relaxation Behaviour of Natural Rubber Vulcanisates Containing Non-rubber Constituents

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Natural rubber (NR), which is derived from latex of Hevea brasiliensis *tree, contains about 3%–5% of non-rubber constituents. The presence of these non-rubber constituents, which are mostly proteinaceous materials, affect the sensitivity of rubber to water, thereby affecting properties such as elastic modulus and stress-relaxation.*

Studies using vulcanised unfilled NR showed that changes in relative humidity of the sample gave variations in elastic modulus and stress-relaxation of vulcanisates. The variability was due to the presence of certain types of amino-acid; their presence increases the elastic modulus and reduces the rate of relaxation of NR vulcanisates. These were due to the formation of ionic crosslinks; drying the rubber intensifies the ionic interactions and effectively increases the apparent crosslink density, thereby reducing the rate of relaxation.

Commercial natural rubber is produced in different grades; this arises from the different sources of latex coagulum and different methods of handling rubber. Conventional grades (*e.g.* Standard Malaysian Rubber) are processed by coagulating the latex using acids followed by washing and drying the rubber, whilst the processing of deproteinised rubber (DPNR) involves an extra step whereby the naturally occurring proteins are largely removed prior to coagulation[1,2]. Hence, DPNR contains lower amounts of nitrogenous non-rubber constituents than conventional grades.

It has been reported that rubber which has been processed in different ways show a marked variation in properties due to the presence of different types and/or amount of non-rubber constituents. For instance, proteins are believed to affect creep; Smith observed that the removal of proteins from DPNR reduces the rate of creep[3]. Knight and Tan[4] reported that the presence of proteins caused the modulus of rubber vulcanisates to increase, while amino-acids affect the storage hardening of the raw rubber[5]. Storage hardening is also affected by inorganic materials[6]. Certain nitrogenous bases and fatty acids take part in the sulphur vulcanisation reaction which subsequently affects the properties of rubber vulcanisates[7]. The presence of non-rubber constituents also affect the sensitivity of the rubber to water, thereby properties such as elastic modulus and stress relaxation[8].

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The change in modulus with humidity has been reported in earlier publication[9]. This paper gives further experimental results and discusses the effect of some non-rubber constituents, particularly proteins and hydrolysed components (amino-acids) on the stress relaxation behaviour (physical) of unfilled NR vulcanisates. The discussion of the effect of water/humidity on the elastic modulus preceded stress relaxation because the latter is known to be strongly influenced by humidity[10].

EXPERIMENTAL

Natural rubber containing different types and proportions of naturally occurring non-rubber constituents was used for this study. They were purified rubber containing different types of non-rubber constituents; total solid rubber (TSR or generally known as latex film); centrifuged latex fractions; commercial grade Standard Malaysian Rubber (SMR) and deproteinised natural rubber (DPNR). All tests were carried out in duplicate (unless otherwise indicated) and the average readings were taken.

Preparation of Rubber

Total solid rubber (TSR). Total solid rubber was obtained by film drying the fresh latex onto glass plates at room temperature (21°C). The latex film was about 1 mm to 2 mm thick and the drying process took about 24 h – 48 h. A fan was used to speed up the drying process to overcome the problem of bacterial action that would occur in the latices if they were exposed unnecessarily long in an open environment.

Centrifuged fractions. Fresh latex was ultracentrifuged at 19 500 r.p.m. for about an hour in a Beckman centrifuge to give four main fractions: a white rubber fraction (*i.e.* rubber phase); a yellowish-orange layer containing the Frey Wyssling particles; a serum fraction and a grey-yellow gelatinous bottom fraction *(Figure 1)*. They were manually separated to give fractions containing different types and proportions of non-rubber constituents. The rubber phase (RP) was redispersed in distilled water and film dried at room temperature in a similar manner to the TSR. Rubber phase containing bottom and serum fractions were prepared by mixing it with those fractions before the filming and drying process.

Purified rubber (PR). Purified rubber was obtained from the rubber fraction. This was first isolated and then redispersed in 5% aqueous sodium dodecyl sulphate for about 24 h before being recentrifuged to remove the remnants of the serum fractions. The treated rubber phase was rewashed with aqueous sodium dodecyl sulphate followed by water before it was finally redispersed in water to give a purified latex. The purified latex was subsequently film dried on glass plates at room temperature (21°C) to give PR.

SMR L and DPNR

Standard Malaysian Rubber grade L (SMR L) and deproteinised natural rubber (DPNR) were commercial rubber grades.

Isolation of Non-rubber Constituents

Isolation of bottom protein (β-serum protein). The β-serum protein (later termed bottom protein) was obtained from the bottom fraction of the ultracentrifuged fresh latex. The bottom fraction was first freeze-thawed three times, recentrifuged and the clear serum collected. Ammonium sulphate was added to the serum to a saturation level and the mixture was left in the refrigerator for about 6 h. The

precipitated protein was collected from the recentrifuged mixture, redissolved in water and dialysed against water to remove any ammonium sulphate remnants. The dialysed mixture was then freeze-dried to give a powdered form of ammonium sulphate precipitated bottom protein.

Isolation of serum protein. The serum protein was obtained from the serum fraction of the ultracentrifuged latex in a similar manner to the bottom protein, through precipitation with ammonium sulphate.

Isolation of proteolipid. The proteolipid was obtained from the rubber phase of the NR latex according to the procedure reported by Hasma[11]. The rubber phase was redispersed in water, filtered and added drop-wise to about five volumes of a continuously stirred chloroform/methanol (2:1, volume/volume) mixture. The extract was separated from the rubber coagulum and washed with salt solution. A lower layer of the chloroform fraction and a thin whitish interfacial layer were isolated. The chloroform layer was concentrated on a rotatory evaporator. The insoluble portion containing proteolipids was collected.

Amino-acids and natural rubber serum powder (NRSP). Amino-acids were of commercial grade and the NRSP was obtained from the Rubber Research Institute of Malaysia pilot plant.

Re-incorporation of Proteins and Amino-acids

Proteins and amino-acids were dissolved in water and then added to the purified latex. The mixture was thoroughly mixed before film drying on glass plates at room temperature. Dried latex films were then blended by using a two-roll mill to give rubbers containing the required proportion of the non-rubber constituents.

Compounding and Vulcanisation

Dried films of purified rubber containing *non-rubber constituents*, *total solid rubber*, different fractions of centrifuged latex and commercially processed rubbers (SMR L and DPNR) were mixed in accordance with the formulation given in *Table 1*.

All purified rubbers were mixed in accordance with ACS-1 formula while the commercial grade and total solid rubbers were mixed using the CBS/S systems.

The mixing process was carried out using a laboratory two-roll mill. Moulding of rubber test pieces (1 to 2 mm thick) was carried out using a steam-heated press at 150°C for a period required to fully vulcanise the rubber (*i.e.* t_{100}) measured by a rheometer. Extra care was taken during handling and storage of vulcanisates to reduce degradation since antioxidant was not incorporated.

Test Methods

Relaxed modulus test. The relaxed modulus test (MR 100) was carried out by extending a square-end dumb-bell test piece to 100% extension and measuring the load after one minute. The test was carried out on the rubber conditioned under three different environments.

Stress relaxation measurements. Stress relaxation tests were carried out under tensile deformation. Sample strips (1.0 to 2.0 mm thick) were die-stamped from moulded sheet. Two techniques were employed for this study: a conventional technique and the 'bow string' technique.

TABLE 1. RUBBER FORMULATIONS (P.H.R.)

Vulcanising systems	ACS-1	Conventional[d]	Semi-EV[d]	EV[d]
Rubber[a]	100.0	100.0	100.0	100.0
Zinc oxide	6.0	5.0	5.0	5.0
Stearic acid	0.5	2.0	2.0	2.0
Sulphur	3.5	2.5	1.5	0.6
MBT[b]	0.5	–	–	–
CBS[c]	–	0.6	1.5	2.5

[a]The non-rubber constituents were added at 1% wt. of NR. The nitrogen and ash contents were determined in accordance with *ISO 1656* (1988) and *ISO 247* (1980), respectively

[b]2-Mercaptobenzothiazole

[c]N-cyclohexyl benzothiazole-2-sulphenamide

[d]$\sqrt{(\text{CBS})\times(\text{sulphur})}$ was kept constant to obtain the same crosslink density

The conventional technique uses modern tensile equipment. Samples were held firmly in screw-tight grips and pulled to a required extension at 100% per minute. The change in stress with time at constant strain was monitored using the output facilities available (*i.e.* a portable computer).

The 'bow string' technique is a new technique of measuring stress relaxation of rubber and detail procedures has recently been published[12]. This technique allows the change in stress, under different environments, to be monitored for longer period of time (>2 weeks).

The new technique of measuring stresses involve pushing/pulling vertically an extended piece of rubber strip at the mid-point to give a three-point bending or 'bow-string' configuration. The stresses at three different angular displacements, namely (about) 4, 6, 8 degrees were calculated and the average value taken.

With both techniques, the sample used were die-stamped from moulded sheet of about 1.0 to 2.0 mm thick and 10 mm wide. Most of the relaxation tests were performed at 30% elongation and extension rate was 100% per minute, unless otherwise stated. At low strain (<50%), the rubber is within the so-called 'affine deformation' region, where the bulk deformation of the sample is considered to be a good approximation to the infinitesimal deformation of the rubber network. Thus, at this low extension, the possible effects due to non-affine deformation will be minimised.

The results were either presented as a plot of relative stress, which is the ratio of stress to the reference stress, against log(time) or as relaxation rate. The rate was calculated from the stress *versus* log(time) plot and expressed as percent stress relaxation per decade of time.

Conditioning samples at different relative humidities. The relaxation test was carried out at three different relative humidities, namely low humidity (7% to 25%RH), room humidity (50% to 60%RH) and high humidity (100%RH). Prior to the test, the sample strips which were die-stamped from moulded sheet, were conditioned at the respective humidity for about 14 days.

The low humidity environment was achieved by placing phosphorus pentoxide (P_2O_5) in a desiccator. Samples were placed in the desiccator and taken out only during testing.

The higher humidity condition was obtained by immersing the sample in water. It was carried out by placing the sample in water for between 14 to 30 days. The change in weight of the sample due to absorption of water into the rubber was measured prior to testing.

Equilibration of samples at room humidity was carried out by placing the rubber strip in a dark cupboard. The relative humidity varied from about 48%RH to about 60%RH, depending on the outside weather.

Crosslink density measurement. The crosslink density of rubber was determined from equilibrium swelling data using the Flory-Rehner equation[13]. Samples of about 2 mm thickness were cut into 25 mm squares and swollen in toluene in the dark for several days, during which their weights were regularly monitored. At equilibrium swelling, the weights were recorded and sample dried in a vacuum oven at 60°C. The difference between the weight of the swollen and dried samples was taken as the true weight of the solvent imbibed.

RESULTS AND DISCUSSION

Physical (or primary) relaxation has been associated with movement taking place amongst the following: rubber network; the side groups on the rubber chain; chain entanglements and filler structures/particles. This type of relaxation is dominant in the early stages of the relaxation process ($<10^4$ min), particularly at ambient or low temperatures and the changes in stress has been observed to be linear with log(time)[8,14].

Effect of Non-rubber Constituents

It has been reported that DPNR has greater resistance to relaxation than conventional grades of SMR[3]. The current work which was carried out using three different types of rubber containing different proportions of natural non-rubber constituents is in agreement with those results. They were the unfilled DPNR, a conventional grade NR (SMR L) and TSR vulcanised using a semi-EV system; TSR has a higher proportion of non-rubber constituents than SMR L and DPNR has the lowest content.

The results, presented as a plot of relative stress, f/f_0 against log t are given in *Figure 2*. DPNR was observed to have a lower rate of physical stress relaxation than SMR L or TSR. The stress relaxation rate of TSR was marginally higher than that of SMR.

The lower rate of stress relaxation of DPNR compared to SMR and TSR is presumably due to the removal of non-rubber constituents during the deproteinisation process. The non-rubber constituents removed during the production of DPNR include proteins and amino-acids. A study was carried out to relate the presence of these individual non-rubber constituents to the relaxation rates of the rubber. Initially, tests were carried out by using three different centrifuged fractions of latex, namely the rubber phase (RP), the RP+bottom fraction, and the RP+serum fraction. Results showed that the magnitudes of the rates of relaxation of those rubbers are as follows (*Figure 3*):

(RP=RP+bottom fraction) < (RP+serum fraction) < TSR

The relaxation rate of the RP containing added serum fraction is about 2.7% per decade, which is approximately the same as the TSR.

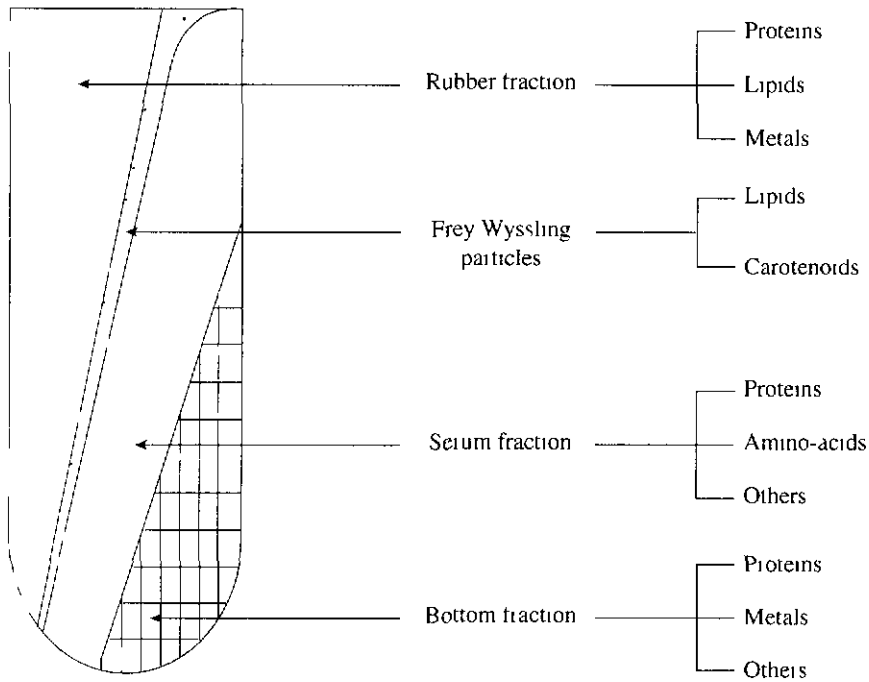


Figure 1 Ultracentrifuged fresh natural rubber latex fractions

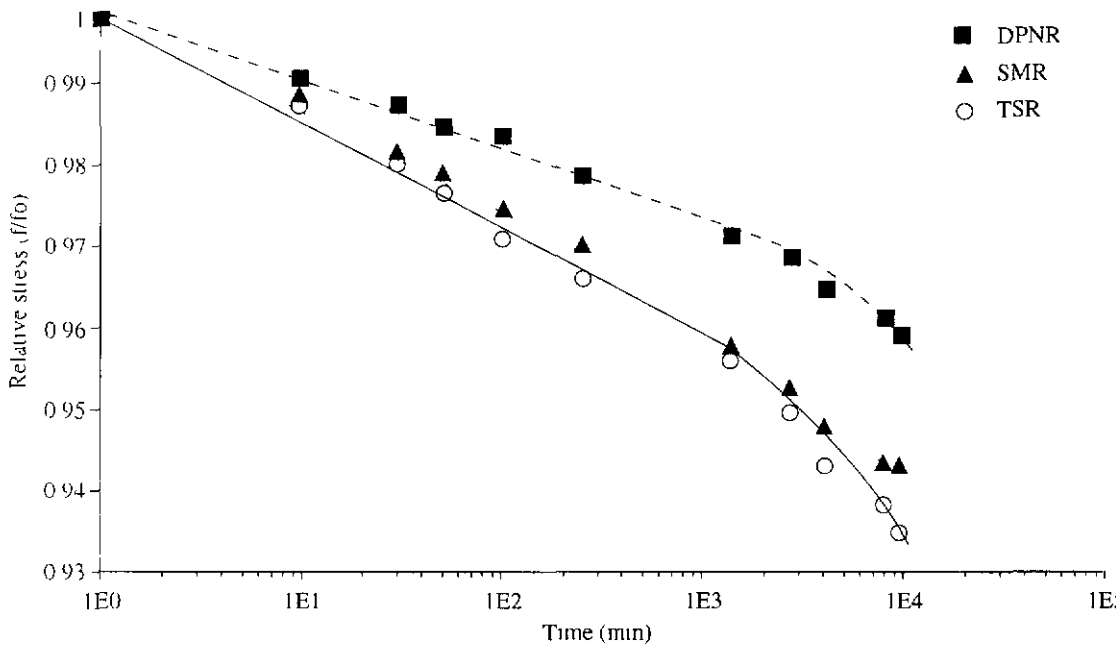


Figure 2 Stress relaxation of different types of natural rubber (Semi-EV formulation, 55%RH)

This shows that most of the non-rubber constituents which increase the stress relaxation of the rubber are in the serum rather than the bottom fraction.

The serum fraction contains several types of non-rubber including proteins and amino-acids. Proteins are the major component of the non-rubbers and amino-acids are their hydrolysis products. Accordingly, the effects of proteins and the amino-acids on stress relaxation were investigated. Results presented as a plot of relative stress against log(time) are shown in *Figure 4*.

The incorporation of 1% protein into the purified rubber did not give any significant change to the relaxation behaviour of the NR vulcanisates. The relative stress of purified rubber containing proteins was approximately the same as for purified rubber. A similar value was obtained with amino-acids such as glutamic acid.

However, the incorporation of amino-acids such as alanine and arginine, gave a different result; their relaxation rates were markedly lower. The presence of 1% wt. alanine and arginine reduces the relaxation rate of purified rubber by about 30% and 60%, respectively.

It may be noted that there are differences in the rate of relaxation between two 'clean' rubbers: purified rubber (*ca.* 0.04% wt. nitrogen) and DPNR (*ca.* 0.08% wt. nitrogen). It would be expected that these two rubbers have approximately similar relaxation rates due to the low amount of nitrogenous materials. However, direct comparisons of the results in *Figures 2* and *4* show the rate of relaxation of DPNR is lower than the rate for purified rubber.

This difference could be due to three possible reasons. Firstly, the two rubbers were processed by different methods, resulting with rubber having different average molecular weight. Purified rubber possesses lower molecular weight than DPNR as reflected by the lower Mooney viscosity values (*Table 2*). This could lead to purified rubber having comparatively higher relaxation rate than DPNR.

TABLE 2. MOONEY VISCOSITY OF RAW RUBBER

Rubber	Mooney viscosity [ML(1+4)@100°C]
Purified rubber	64
DPNR	81

Secondly, the two rubbers were compounded using different formulations–DPNR using a semi-EV and purified rubber with the ACS-1 formulation. This will give rubber having different types of crosslink and give rise to differences in the relaxation rate.

Thirdly, commercial grade DPNR is treated routinely with thiourea after the coagulation and washing processes. Thiourea treatment is carried out to increase the plasticity retention index of raw rubber; an index giving a measure of the oxidisability of rubber. This occurs by the chelation of the pro-oxidants present in the rubber and with the introduction of small amount of crosslinks to the rubber network. This treatment will result in DPNR having higher resistance to physical relaxation. No thiourea treatment was given to purified rubber.

These three different processes give two different types of rubber which could not be compared directly and the differences in the relaxation properties between DPNR and purified rubber could possibly be due to one/ more of these factors.

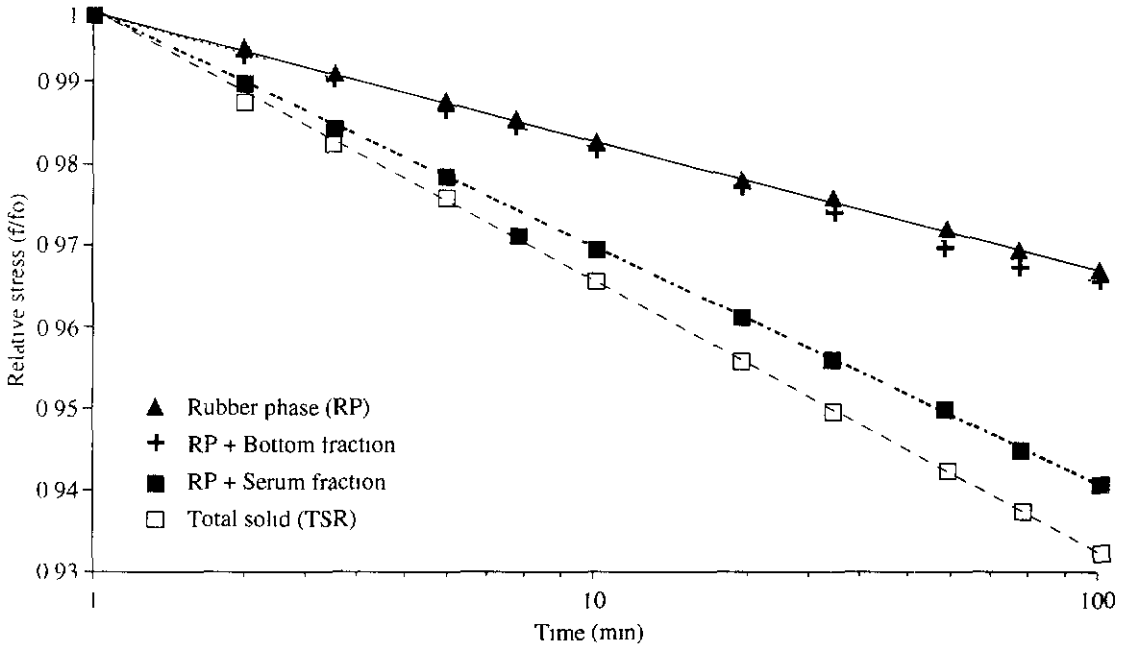


Figure 3 Stress relaxation of centrifuged natural rubber latex fractions (ACS-1 formulation, 55%RH)

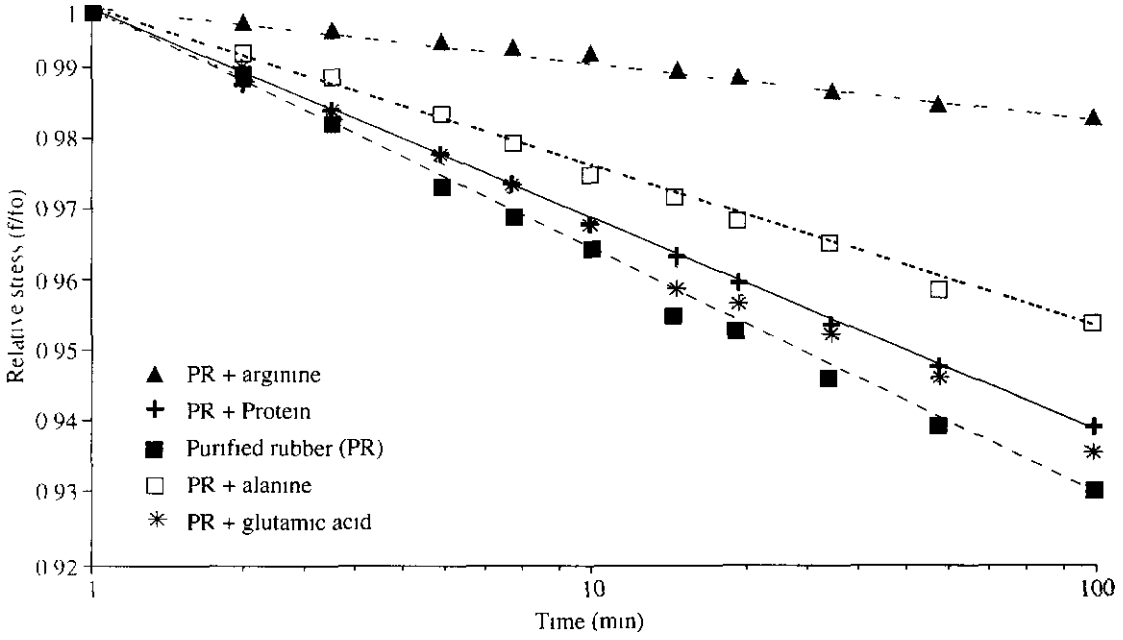


Figure 4 Stress relaxation of purified rubber (PR) containing proteins and amino-acids (ACS-1 formulation 55%RH)

Physical stress relaxation is due to physical realignment and chain slippages. Any factor which influences chain mobility will affect the rates of physical relaxation. This includes internal lubricants, molecular chain modifications and/or changes in the crosslink density.

Previously[9], it was shown that the presence of alanine and arginine increases the crosslink density of rubber. The presence of these amino-acids was shown earlier to give rise to rubber having a good resistance to physical relaxation. Thus it is likely that the good resistance to stress relaxation of these rubbers could be due to the increase in the crosslink density and/or decrease in the polysulphidics rank; that is, the presence of those non-rubber constituents resulted in rubber having a higher crosslink density, thus better resistance to relaxation.

The dependence of relaxation rate on crosslink density was clearly shown when the rate was presented as a function of molecular weight between crosslinks, M_c , which is inversely proportional to crosslink density.

Results showed that the relaxation rates of several purified rubbers containing proteins and amino-acids were linearly related to the M_c (*Figure 5*). This linear relationship shows that the relaxation rate decreases as the crosslink density of the rubber increases. This is consistent with published results which showed a linear decrease in relaxation rates as the crosslink density increases[10].

Thus, it is most likely that the improvement in the relaxation behaviour of purified rubber is due to the increase in crosslink density and/ or reduction in polysulphidics rank. This occurs, possibly, during the vulcanisation reaction due to the presence of amino-acids such as alanine and arginine. The presence of these extra crosslinks reduces the ability of the chain movement and slippages, thus lowering the relaxation rates.

Effect of Humidity

Types of rubber. In this study, the effect of humidity on the stress relaxation rate of different types of NR was demonstrated. Rubber containing different amounts and types of non-rubber constituents was used. They include TSR, SMR, DPNR and purified rubbers containing added proteins and amino-acids.

Results obtained on tests carried out with various rubbers are given in *Figure 6*. Generally, it was observed that rubber containing higher non-rubber constituents (TSR) gave larger changes in relaxation rates than 'cleaner' rubber (DPNR). Hence, the presence of non-rubber constituents can cause the larger variability in the relaxation rates of TSR compared to DPNR due to changes in relative humidity.

When the effects of proteins and amino-acids were studied, small variation (<8%) in the relaxation rates was observed (*Figure 7*). For instance, with purified rubber containing 1% wt. arginine, the relaxation rate varies from about 1.26% to 1.33% per decade when the relative humidity was changed from 25% to 100%. The presence of proteins gave a slightly larger change in relaxation rates with humidity.

These results suggest that the non-rubber constituents which give a large variation in relaxation rates with humidity are not amino-acids; amino-acids increase the crosslink density, and improves the resistance to physical relaxation, thus reducing the variability at

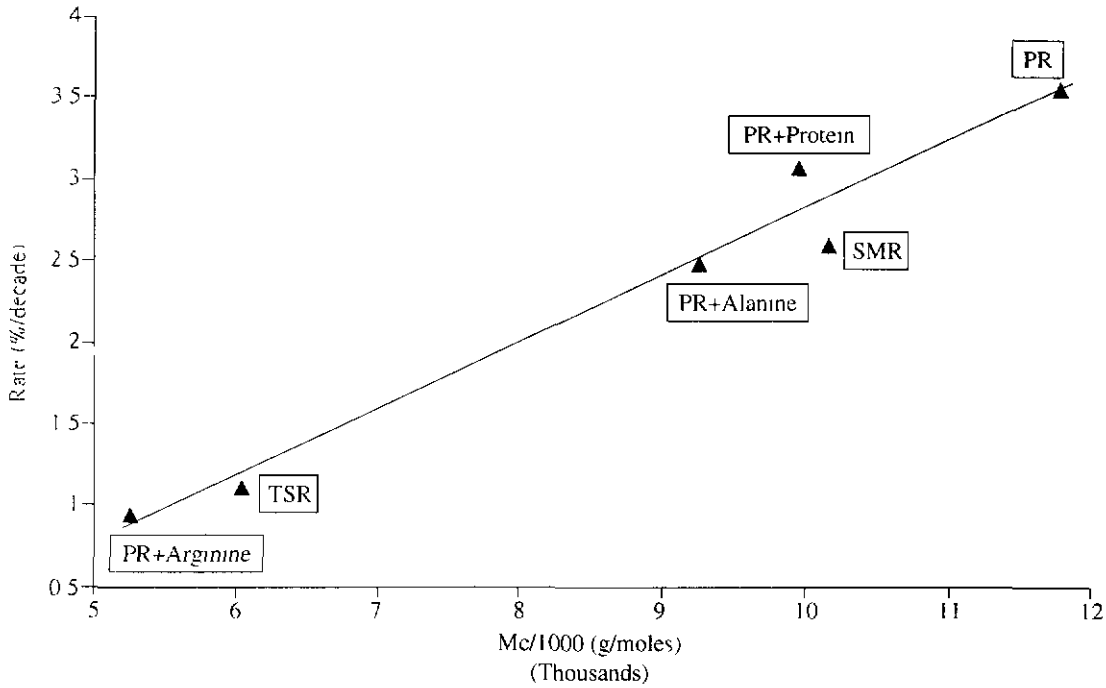


Figure 5 Stress relaxation rates as a function of molecular weight between crosslink (M_c).

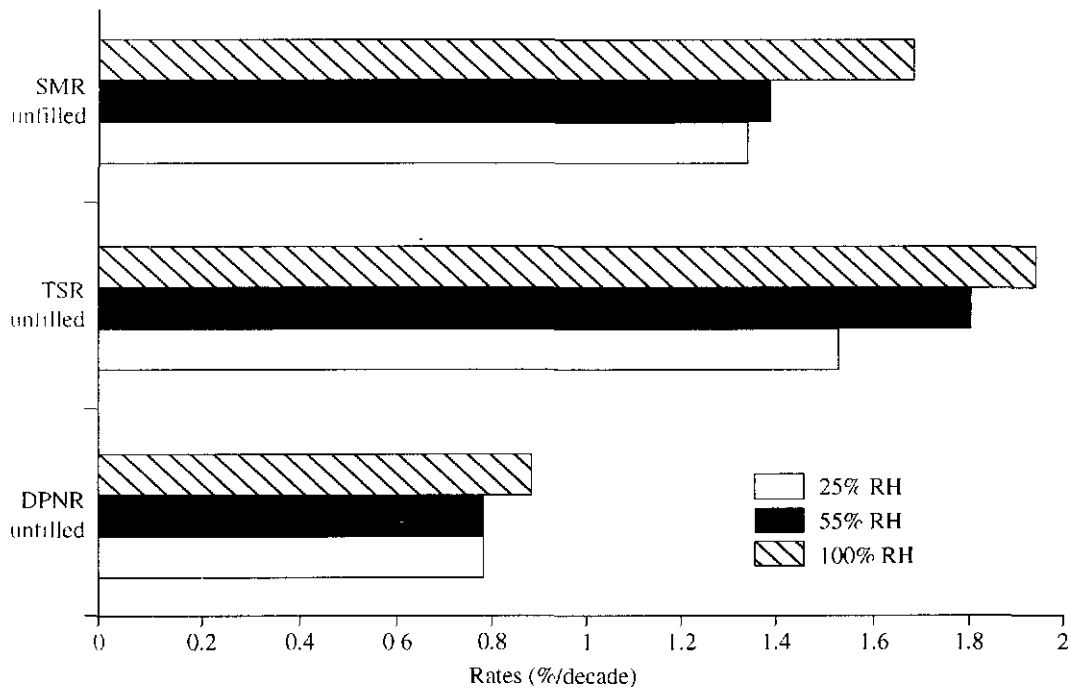


Figure 6 Stress relaxation rates of different types of rubber (Semi-EV formulation).

different humidities. So some other factors must be causing the changes

It is possible that the non-rubber constituents in TSR which cause the large variation in relaxation rates are the materials which are chemically inactive and behave as inert fillers Protein is one such material. In this study, the variation observed with purified rubber containing proteins was small; though larger than the change observed with the presence of amino-acids. The amount of proteins added (1% wt) may be too low to give a more significant variation If we were to assume that the increase in rate with humidity is linearly related to the amount of proteins, then when the humidity changes from 25%RH to 100%RH, we would obtain about 21% increase in rates when the protein content is increased to 3% wt , the approximate amount present in TSR However, we do not have any evidence for linearity to date so it would be wise to consider what else could have caused the changes in relaxation due to moisture uptake.

Muniandy and Thomas[15] reported that the presence in rubber of low molecular weight inorganic materials increased the affinity to water Low molecular weight/hydrophilic materials, (which are inorganic salts) are known to be present in TSR and commercial grades rubber, but not in purified rubber. Thus it is likely that the large changes in relaxation rates obtained with those rubbers are due to the presence of those inorganic materials.

The change in modulus with humidity was found to be independent of the type of crosslink present This is shown by TSR vulcanised using conventional, semi-EV, EV and peroxide systems, in which the modulus of the rubber consistently decreased by about 22% when the relative humidity was changed from 7% to 55% (*Figure 8*)

Correlation was observed between the increase in crosslink density and the changes in modulus with humidity. That is to say, the *presence of the non-rubber constituents which* cause the increase in the crosslink density of the vulcanisates gave the biggest change in the modulus with the change in the relative humidity. Thus, certain types of amino-acids such as arginine and alanine gave a larger reduction in modulus with humidity changes compared to the presence of other non-rubber constituents These amino-acids are present in the serum fraction of NR latex[16].

The reduction in modulus when the rubber is being equilibrated at higher relative humidities is reversible. This is clearly shown by unfilled TSR which was subjected to a series of humidity cycles from 55% through 7%, 100% and back to 55% (*Figure 9*). The initial modulus obtained at 55%RH was observed to remain approximately the same at the end of *the humidity cycles*

The change in modulus was observed to be very marked when the sample was exposed to moisture The variation was observed to be significant in the presence of alanine and arginine, the two amino-acids present in the serum fraction of the NR latex There was no change in the mass water uptake between rubber equilibrated at low (7% to 25%RH) and room humidity (55%RH) A similar effect was observed with the physical stress relaxation behaviour of the rubber equilibrated at different relative humidities.

The reduction in modulus and increase in rates of relaxation due to the presence of water could be explained by the plasticising effect of the water, an effect similar to the presence of oily plasticiser in rubber[17]. The plasticising effect of water lowers the modulus because the rubber network structure approaches a more

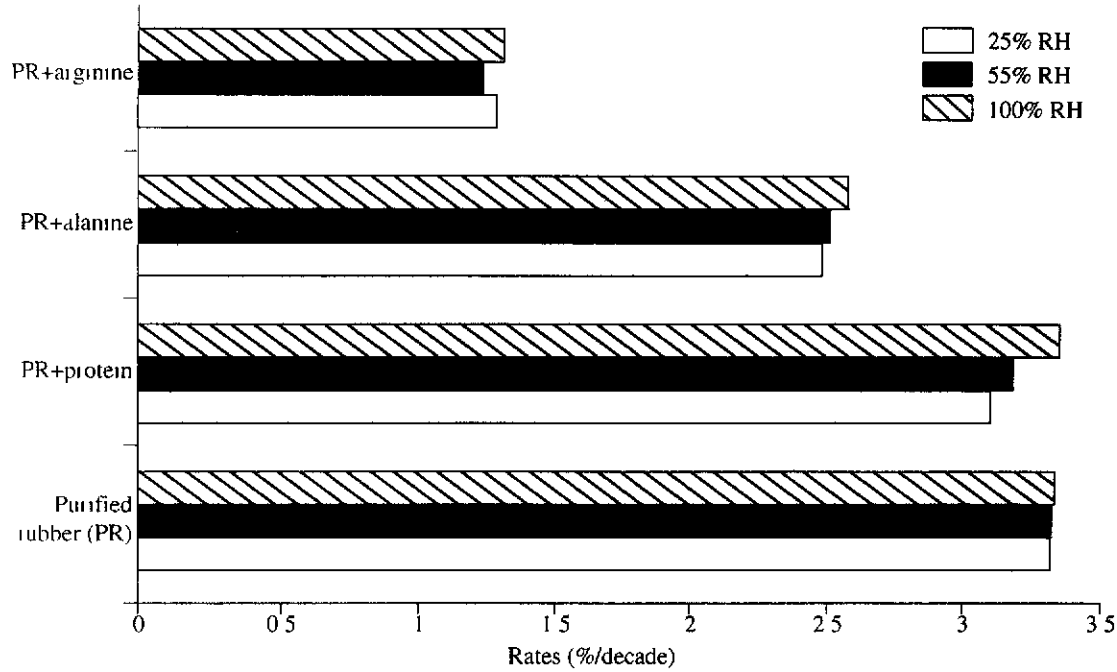


Figure 7 Stress relaxation rates of purified rubber (PR) containing non-rubber constituents (ACS-1 formulation, 55%RH)

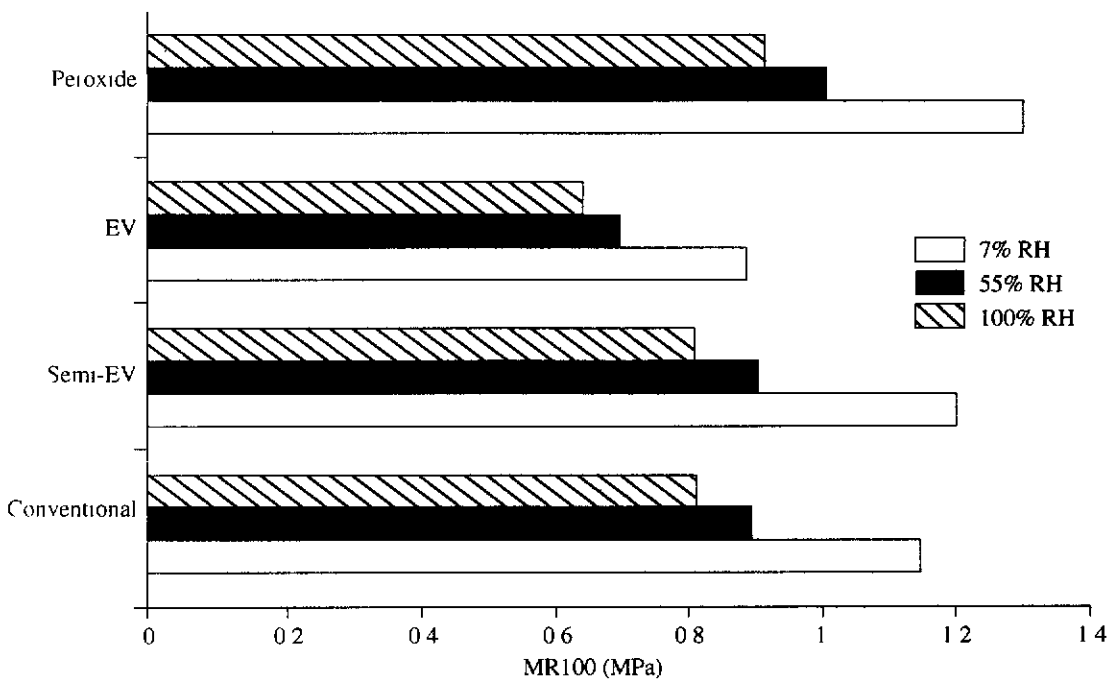


Figure 8 Change in modulus with humidity for TSR

nearly equilibrium configuration. This being so, it would be expected that the subsequent rate of the 'wet' rubber would be lower. However, it was observed that the rate of relaxation of unfilled NR increases as the amount of water imbibed increases. This is shown in *Figure 10* where the relaxation rates of NR (SMR L) vulcanisate swollen in water is presented as a function of applied strain. The rates of relaxation clearly increased as the water content in the rubber increased.

These results indicate that the explanation for reduction in modulus and increase in relaxation rates with increasing relative humidity is more complicated than the 'plasticisation' theory which suggests that the presence of water 'plasticises' the rubber network. If the 'plasticisation' theory is valid, we would expect the differences in modulus and relaxation at humidities between 7%RH and 55%RH to be negligible since there was no difference in the uptake of water by the rubber at those humidities. However the above results showed that a much bigger effect could be obtained when humidity was reduced from 55%RH to 7%RH; increasing the relative humidity to 100%RH gave a comparatively smaller effect.

Thus the 'plasticisation' theory could not adequately explain the phenomena observed in this study. A possible and more likely process which has taken place is a reaction similar to the phenomenon of storage hardening of unvulcanised raw rubber[18,19]. The presence of certain types of amino-acid may catalyse the formation of active functional groups from the available side or abnormal groups on the rubber chains, namely the epoxide or the carbonyl groups (*Scheme 1*).

The presence of the –OH group and the –COOH groups may result with the following crosslinking esterification reaction[19] (*Scheme 2*).

However, the above esterification process is not reversible and this is not consistent with the current observation whereby the effect of the modulus on humidity is reversible. Thus, a plausible reaction which may give a reversible effect and yet provide a strong linkage may be the ionic crosslink. The crosslink may be catalysed by metal ions (which are present in the rubber) or the amino-acid zwitter ions (*Scheme 3*).

Such systems are known to be sensitive to moisture – this is explicable, for a strong hydrated ion reduces the strength of the crosslink. Conversely, drying the rubber reduces the solvation by water, intensifies the ionic interactions and hence effectively increases the apparent crosslink density and reduces relaxation rate.

An alternative explanation (for S_8-cured rubber) would be the ionic polysulphidic exchange reactions between crosslinks:

$$R_1–S_x–S_y–R_2 + R_3–S_{z-1}–S^- \leftrightarrow R_1–S_x–S_z–R_3 + R_2–S_{y-1}–S^-$$

The relaxation rate would increase with ionic strength. However, since the effect was also observed with peroxide cured rubber, the latter explanation may be unjustified.

CONCLUSIONS

Under ambient conditions, wide variation in the modulus and stress relaxation was observed when non-rubbers were present. Much relates

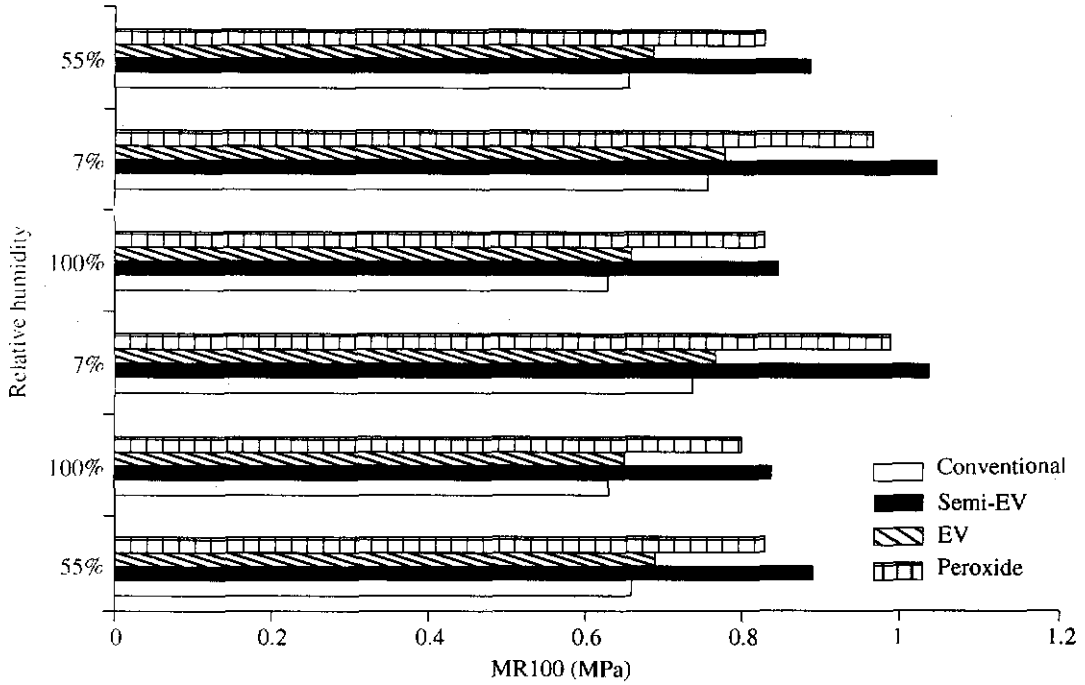


Figure 9. Change in modulus of TSR after a series of humidity cycle.

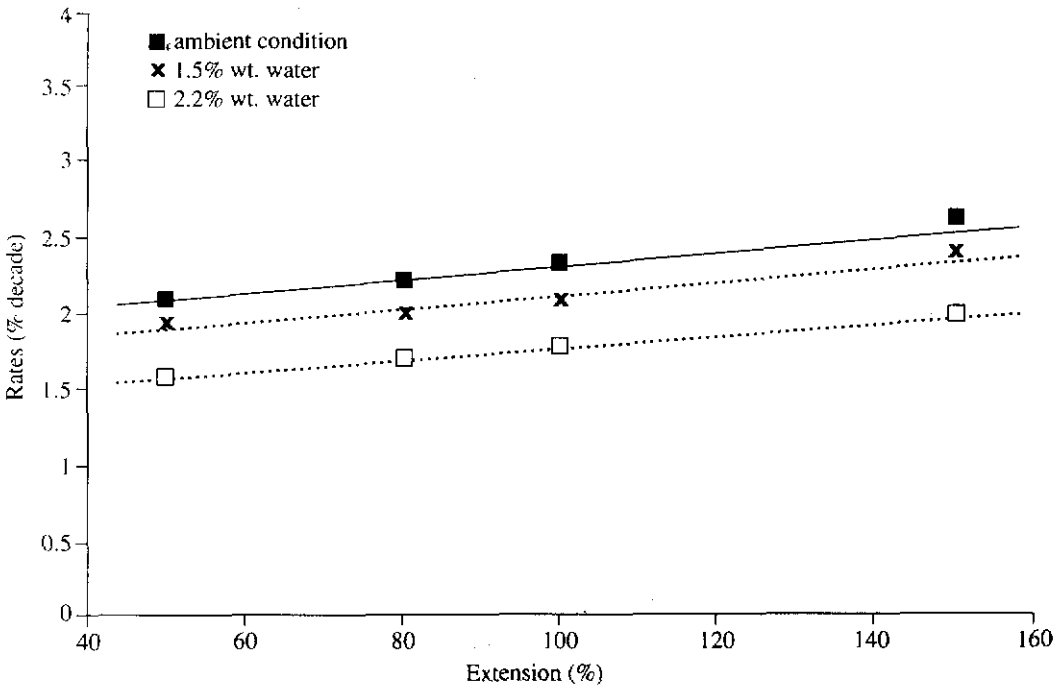
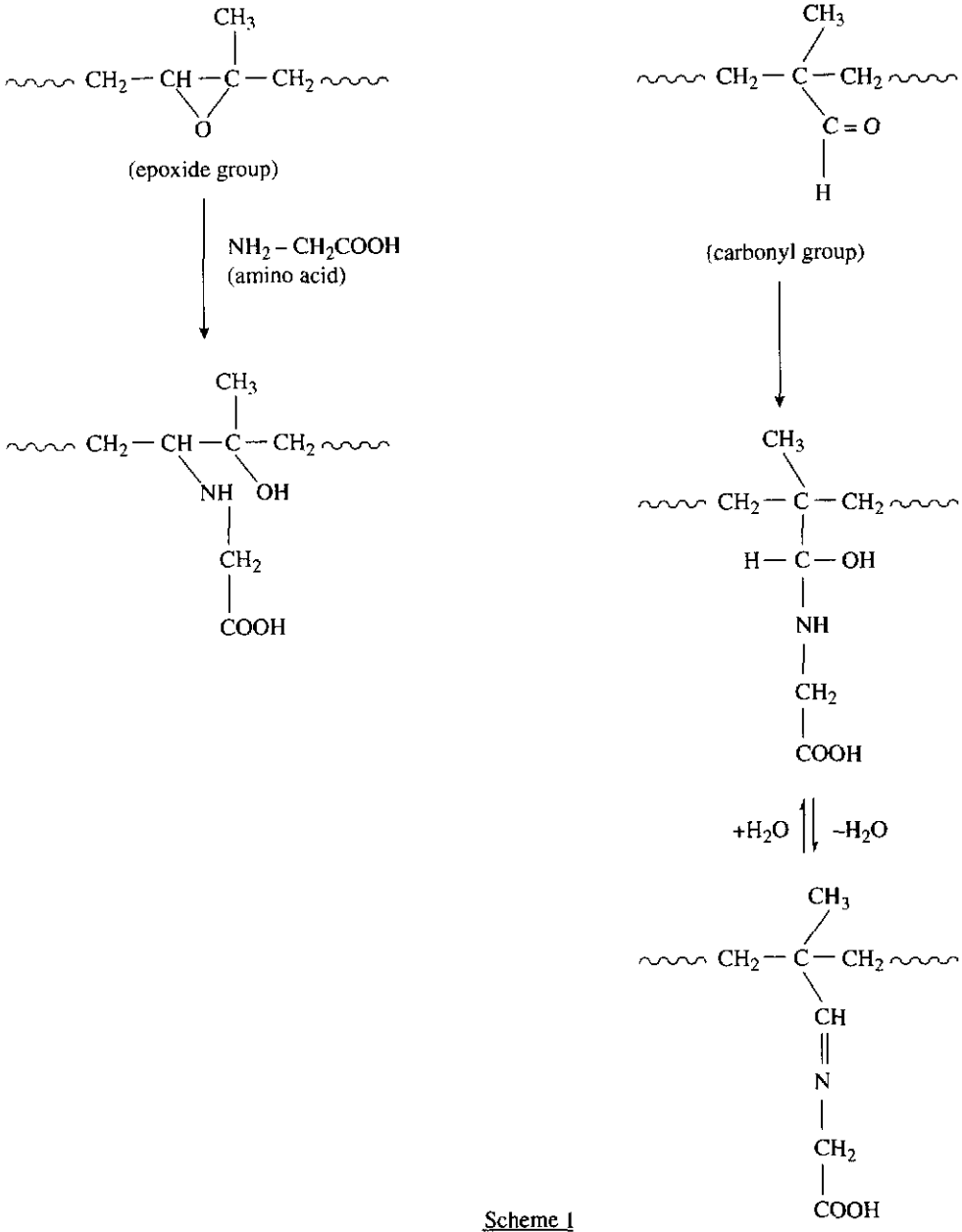
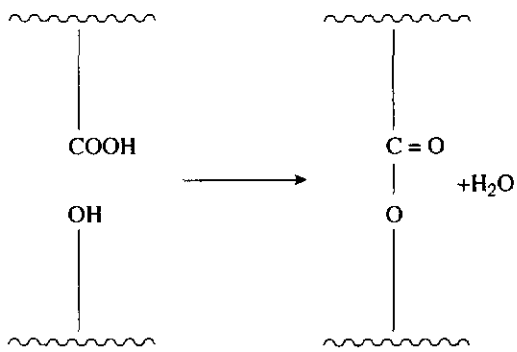


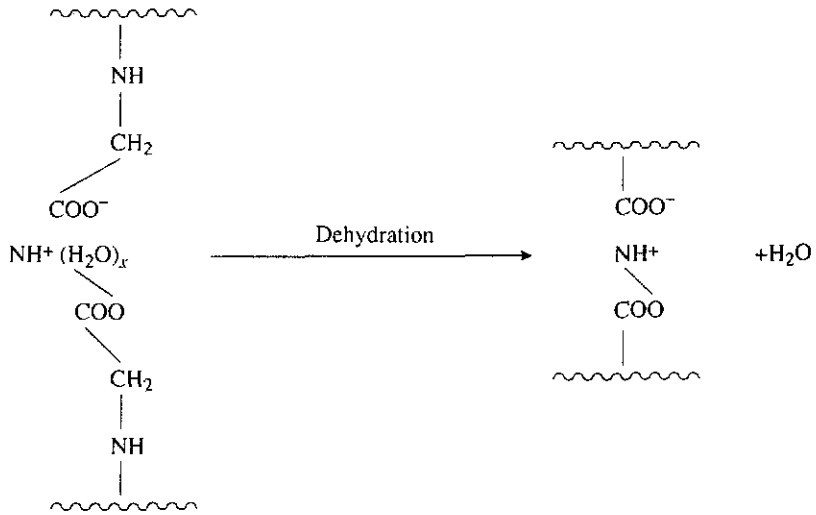
Figure 10. Stress relaxation rates of 'wet' natural rubber (Semi-EV formulation).



Scheme 1



Scheme 2



Scheme 3

to the presence of amino-acids, particularly, alanine and arginine, which resulted in an increase in modulus and reduction in relaxation rates. Proteins did not significantly affect these properties; they acted as inert fillers.

At lower humidity, the relaxation rate is lower than at higher humidity. The modulus is higher at lower humidity.

The largest variation in properties was caused by the presence of amino-acid. It was reasoned that these variations were due to the formation of ionic crosslinks.

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