

Thermal Analysis of Natural Rubber Hevea Brasiliensis Latex

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Thermal analysis of the natural rubber Hevea brasiliensis latex (NRL) with different moisture content was characterised using differential scanning calorimeter. The analysis was done between -100°C to 150°C . The thermal characteristics investigated are the glass transition temperature T_g , the boiling point of free-water T_f and bound-water T_b . Results showed that T_g for both dried concentrated rubber latex and dried NRL are similar, i.e. -56.84°C , and -56.57°C , respectively while T_g for diluted NRL was not detected. The existence of moisture shifted the T_f in diluted NRL towards a higher temperature which was similar to the thermogram of de-ionised water.

Natural rubber is a natural polymer that consists of repeated units of isoprene. Liquid or latex of natural rubber is an isotropic substance consisting of rubber molecules, water, protein, resin, carbohydrates and sugar. Water occupied more than half of the latex content and thus the latex very much follows the characterisation of de-ionised water. To determine the influence of water on the thermal properties of rubber latex, the relationship between heat flow against temperature for latex with different moisture content (MC) is determined using the differential scanning calorimeter (DSC).

DSC technique is commonly used for the study of structure-property relationship of polymers. It is defined as a technique in which the difference in the energy inputs into a sample and a reference is measured as a function of the temperature or time while they are subjected to a controlled temperature programme¹. The DSC

curve represents the specific heat of a sample as a function of the scanning temperature. If the sample undergo physical changes, there will be a corresponding change in the enthalpy, appearing as an exothermic or endothermic peak in the curve. Such peaks are attributed to the crystallisation or melting in the sample.

This study reports the measurement of thermal properties of natural rubber latex (NRL) as a function of MC. The thermal properties are the glass transition temperature (T_g) the boiling point of free-water (T_f) and bound-water (T_b). Fresh NRL normally consists of approximately 55% – 80% water, 50% rubber hydrocarbon and 2% – 4% non-rubber constituents². The standard concentrated rubber latex (CRL) supplied by the Rubber Research Institute of Malaysia (RRIM) has a dry rubber content of about 60% with 39% MC. Rubber particles and non-rubber constituents are considered as a single solid

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phase or solid content of NRL and the mixture of this solid phase and water are assumed isotropic and randomly dispersed.

Although the maximum rate of rubber crystallisation is in the range³ of -25°C , this crystallisation temperature was not observed in this study. This is due to the fact that the latex rubber particles which are very small (0.5 μm in diameter) crystallise more than one hundred times slower than solid rubber. This is because, for a single particle to contain crystal nuclei is relatively remote in rubber; with a chance of finding less than one nucleus in fifty latex particles or in 10^6 rubber molecules⁴. Since crystallisation only occur after long periods at -29°C , the lower degree of crystallisation means the polymer is difficult to crystallise. The degree of maximum crystallisation which can be obtained by rubber is $\sim 23\% - 30\%$. The melting temperature of rubber crystal is in the region of -4°C to 6°C , which means that if there is any water in the sample, it would overlap with the thermal transition that is due to the melting of the water crystal.

The variation of the dielectric properties of NRL has been reported over a range of $30\% - 98\%$ MC⁵. This study has shown that for the various range of MC, the thermal properties not only depend upon it but is also strongly dependent upon the optimum MC that formed the latex mixture. An interesting feature of the melting and boiling point of water diluent from 40.10% MC to 91.51% MC of NRL are presented.

METHODOLOGY

Sample Preparation

The samples used in this work consist of as-received freshly tapped NRL and low

ammonia CRL supplied by RRIM. Percentage of MC in the sample is determined by the following procedure: Approximately $1.5\text{ gm} - 2.5\text{ gm}$ of latex sample is spread out uniformly in 3 petri dishes. The wet weight (m_w) is obtained before heating in an oven at 70°C until it loses its whiteness and becomes transparent. After heating, the sample is cooled in a dessicator for 10 min – 15 min before obtaining the dry weight (m_d). Subsequent heating is repeated until constant dried-sample weight (*i.e.* 0% MC) is obtained. The average of three final dried-sample weights is considered as the weight of the dried sample (m_d). The percentage of initial MC in the sample is equivalent to the percentage of water loss *i.e.* $[(m_w - m_d)/m_w] \times 100$. The percentage of initial MC in CRL and NRL are 40.10% and 50.35% , respectively.

Dilution of CRL and NRL is done by adding de-ionised water gradually. Dilution of the latex *i.e.* amount of de-ionised water added depend on the initial MC of the latex. Based on the following formula, the amount of water added $m_w' = m_w(C_f - C_i)/(1 - C_f)$ *i.e.* the percentage of water added can be obtained for the required final MC. C_i = initial MC and C_f = required final MC.

Thermal Analysis

The equipment used was a heat flux Polymer Laboratory Differential Scanning Calorimeter (PL-DSC). In a heat flux DSC the instrument signal is derived from the temperature difference between the sample and the reference⁶. The equipment was calibrated using indium. Approximately 4 mg of as-received or diluted CRL and NRL were scanned over the range -100°C up to 150°C at 10°C per min. All T_g , T_f and T_b reported are mid-point values.

RESULTS AND DISCUSSIONS

De-ionised Water

To understand the effect of MC in the latex, the relationship between heat flow against temperature solely for de-ionised water must be scanned with the DSC. Scanning the solidification of de-ionised water alone by liquid nitrogen was done for reference. The liquid

nitrogen changed the physical properties of de-ionised water from the liquid to solid state at -100°C . The thermogram of de-ionised water in *Figure 1* showed two endothermic peaks occurring at 9.41°C and 96.71°C .

The continuous heat flow increases the molecular energy of the de-ionised ice and the endothermic reaction of melting commences at 1.18°C . Since this temperature is equivalent

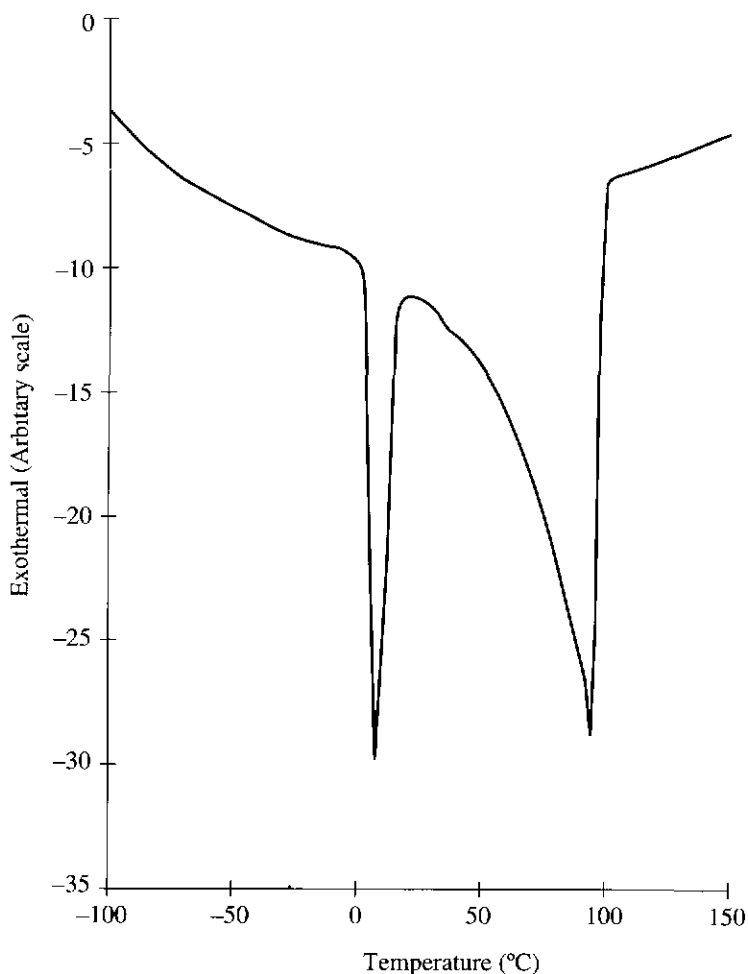


Figure 1 Thermogram of de-ionised water

to the melting temperature of pure ice, it is concluded that the whole ice melted totally at 9.41°C.

Prolonged and continuous heating increased the vibration of atom in the water molecule that was eventually released as steam. The boiling point of pure water at 1 atmosphere is 100°C. From *Figure 1*, the energy absorbed totally by all de-ionised water occurred at 96.71°C *i.e.* the peak temperature of the endothermic reaction of boiling point for de-ionised water.

Concentrated Rubber Latex

T_g for natural rubber is -73°C or 200 K⁷. The CRL was tested to confirm the T_g of dried NRL since diluted NRL does not show any T_g because of low rubber concentration in NRL. *Figure 2* showed the thermogram for dried CRL and NRL. Both dried CRL and NRL showed a shift in the base line at the T_g *i.e.* -56.84°C and -56.57°C, respectively.

Figure 3 showed the thermogram for dried, as-received and diluted CRL. As-received CRL with 40.10% MC showed a T_g at -57.78°C and 2 endothermic peak *i.e.* at 1.55°C and 33.68°C. Diluted CRL with 45.05% MC had a T_g at -58.42°C followed by 3 endothermic peaks at 3.91°C, 52.11°C and 144.93°C. The apparent slight decrease in T_g (see *Table 1*) on dilution of CRL is due to the less precise measurement at low rubber content⁸. The peaks at 1.55°C and 3.91°C in as-received and diluted CRL, respectively are associated with the endothermic reaction of melting of the water phase in the latex as showed earlier by de-ionised water. The low boiling temperature of free water (33.68°C and 52.11°C) in CRL is probably because of the evaporation of ammonia. Diluted CRL with 45.05% MC showed T_b at 144.93°C. Although the 45.05% MC of CRL is low compared to 50.35% MC of NRL, the existence of T_b in the 45.05% MC of CRL is also due to the evaporation of ammonia. When the latex is concentrated, *i.e.* as-received CRL with 40.1%

TABLE 1. ENDOTHERMIC PEAKS OBTAINED FROM THE CRL AND NRL THERMOGRAM

% MC	T_g (°C)	T_m (°C)	T_f (°C)	T_b (°C)
Dried (CRL)	-56.84	—	—	—
40.10 (CRL)	-57.78	1.55	33.68	—
45.05 (CRL)	-58.42	3.91	52.11	144.93
Dried (NRL)	-56.57	—	—	—
50.35 (NRL)	—	5.18	79.76	—
53.94 (NRL)	—	4.37	82.45	—
55.98 (NRL)	—	6.91	82.21	114.13
61.24 (NRL)	—	6.31	81.71	106.35
70.82 (NRL)	—	7.29	84.25	107.40
91.51 (NRL)	—	5.84	93.66	—
100 (De-ionised)	—	9.41	96.71	—

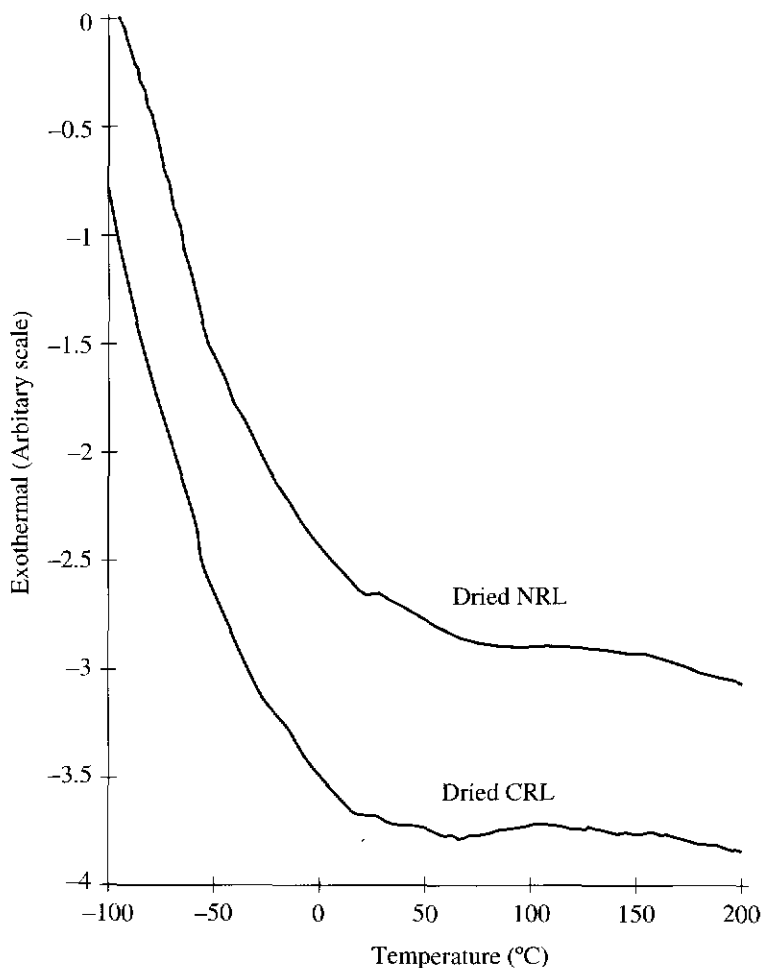


Figure 2. Thermogram of dried CRL and NRL.

MC, T_b was not detected due to the fact that high concentration of rubber hold more bound-water.

A thermogravimetry analysis (TGA) was done on 25 mg solid rubber sample between 40°C and 960°C. A 100% weight loss occurred at 500°C, where at this stage all the hydrocarbon elements of rubber changes to carbon and

gas *i.e.* indicative of total degradation. This degradation process starts at 270°C and it is possible that thermal characteristic changes are still present above this degradation temperature. In other words, TGA confirmed that below 270°C all thermal tests done on the rubber samples in this range are still true and any changes on the thermal characteristic does not cause degradation to the sample.

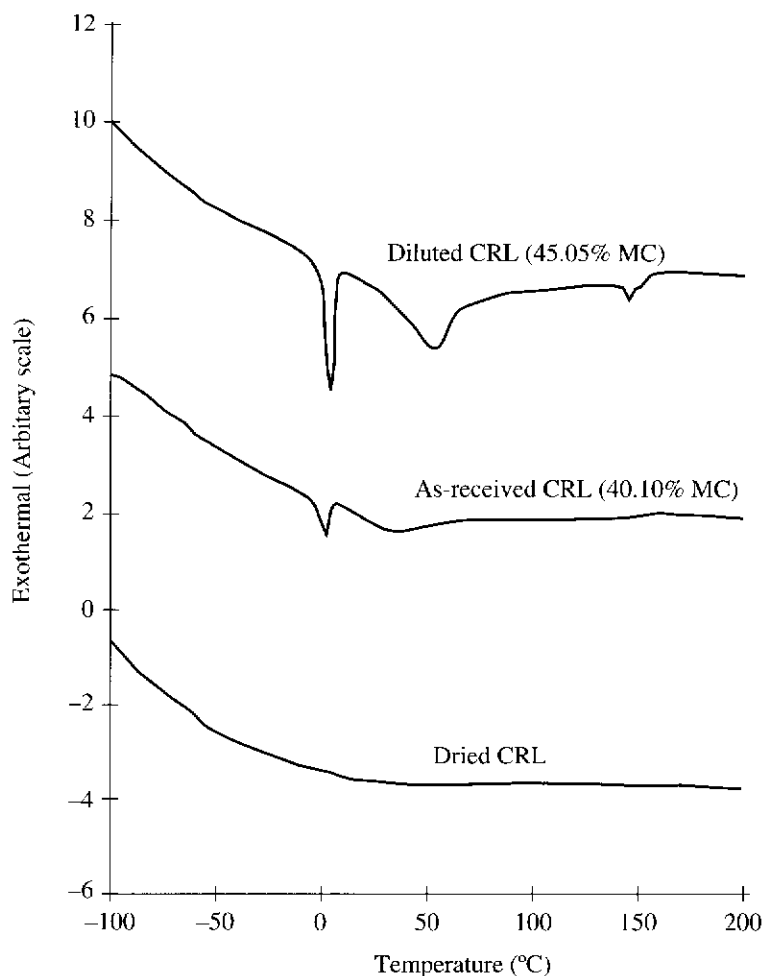


Figure 3. Thermogram for dried, as-received and diluted CRL.

Natural Rubber Latex

Figure 2 showed that both dried CRL and dried NRL have similar T_g . The observation of T_g for dried NRL and CRL is indistinguishable from diluted CRL; this has also been observed by Burfield on natural rubber latices⁸. Figure 4 showed the traces obtained from diluted NRL with 50.35%, 53.94%, 55.98%, 61.24%,

70.82%, and 91.51% MC, respectively. Table 1 shows the endothermic peaks obtained from both the CRL and NRL thermograms. From the table, Peak 1 and 2 increases with the percentage of MC i.e. a higher energy and a longer time is needed to change the phase from solid to liquid as well as to boil the free water in the latex. Figure 5 shows the curve of the endothermic peak (T_m , T_f and T_b) plotted

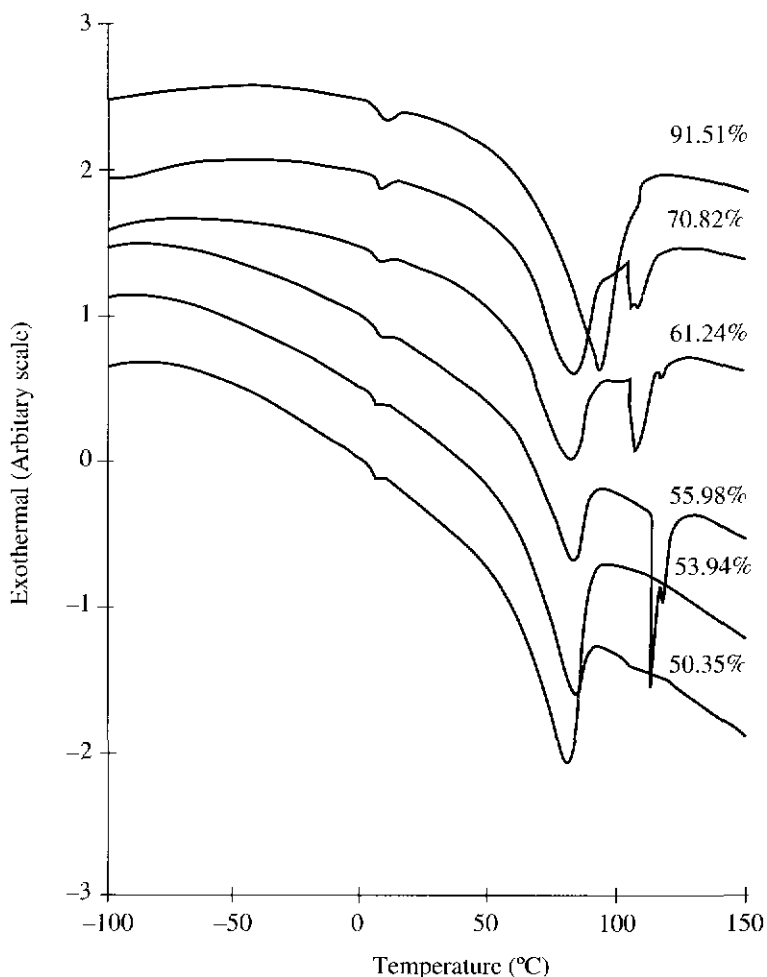


Figure 4. Thermogram for NRL with various MC content.

against the percentage of MC. Due to the similarity of *Peak 1* to ice-melting temperature, *Peak 1* therefore is attributed to the melting temperature (T_m) of water in the latex.

An interesting feature occurs at certain percentage of MC *i.e.* there exists a third peak (T_b) in both diluted CRL and NRL samples but disappears at higher MC. Some water

molecules are trapped and bound with the rubber particle known as bound-water leaving some as free-water. Free-water boils easily as indicated by *Peak 2* and therefore *Peak 2* is attributed to the boiling temperature of free-water diluent (T_f) in the latex.

The transition of water from solid to liquid in the latex solution is a gradual process and it

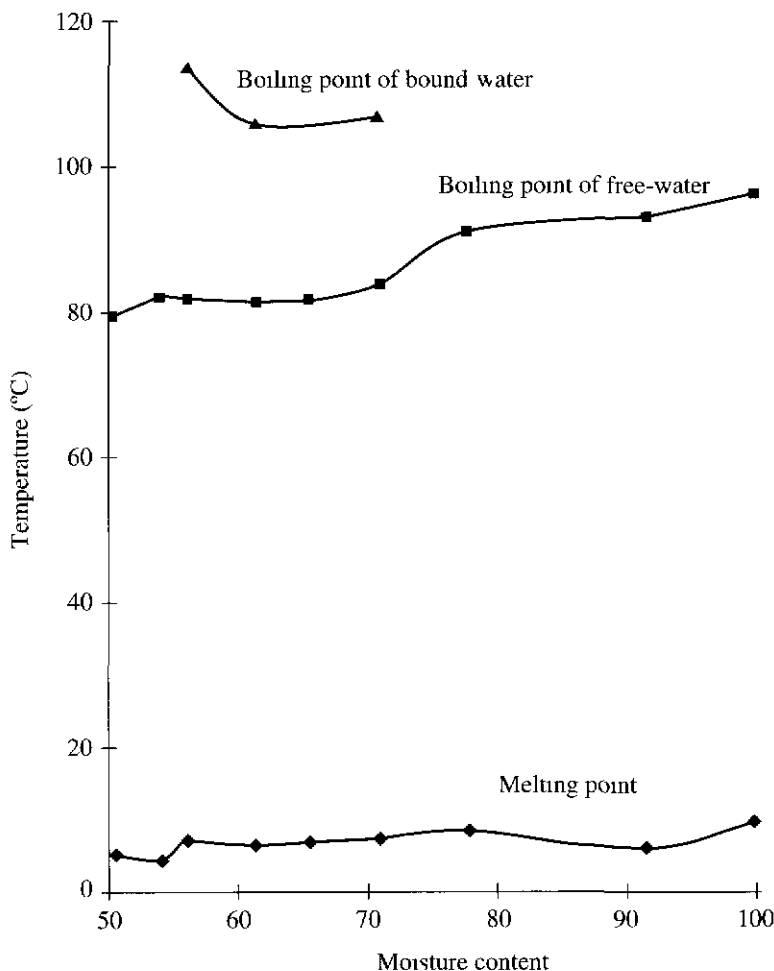


Figure 5 Melting point boiling point of free- and bound water of NRL vs moisture

occurred at a progressively lower temperature when concentration of latex is increased⁹ This has been observed in this study from the results obtained in *Table 1* for the melting peak (T_m) This phenomenon has also been reported¹⁰ in sucrose solution at temperatures -90°C to 20°C Based on these factors and the fact that when the latex is concentrated, there exists more bound-water This can also be seen in

this study where the boiling point of the bound-water, T_b increases with increasing concentration or decreasing MC

The bound-water evaporates almost at constant higher temperature that is shown by *Peak 3* At 53 94% MC NRL, *Peak 3* does not appear due to high concentration of rubber content that holds the bound-water to evaporate

At 55.98% MC, bound-water evaporates and this yields the highest value of *Peak 3* (*i.e.* 114.13°C). The highest value of *Peak 3* indicates that 55.98% is the optimum MC that is easily trapped by the high concentration of latex particles. As MC increases, the concentration of latex particles decreases so that less water is trapped to form bound-water and a lower value for *Peak 3* occurs. Both 61.24% MC and 70.82% MC that yields *Peak 3* values of 106.35°C and 107.40°C, respectively, shows the formation of bound-water. As MC increases up to 91.51%, *Peak 3* totally disappears and occurs as *Peak 2* to yield an endothermic peak similar to that of de-ionised water.

CONCLUSION

The drying of CRL and NRL increases the T_g of natural rubber from -73°C to -56.84°C and -56.57°C, respectively. The T_g for 40.10% MC of CRL is -57.78°C while that for 45.05% MC of CRL is -58.42°C. The T_g for as-received and diluted NRL is not determined due to high MC in the latex. With the diluted latex the melting and boiling of free-water shift towards a higher temperature such that the thermogram is similar to de-ionised water as the MC increases. Above the optimum MC, the bound-water evaporates at lower temperature. This is followed by evaporation of free-water, similar to the de-ionised water.

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