J. Rubb. Res., **16(4)**, 227-242

A Comparable Study of Low Temperature Dynamic Behaviour of Natural Rubber: In-house versus *Commercial Environmental Test Chamber*

H.F. WONG*#, N. AHMAD* AND K.C. YONG*

An economical in-house insulated chamber was developed (coupled with MTS 830 servo-hydraulic machine). This chamber was used to carry out double shear dynamic tests at various temperatures in order to study the effect of crystallisation on natural rubber from –20ºC to room temperature. Dry ice was mixed with solvent inside this insulated chamber to produce cold air so that it can be channelled to the test chamber. The cold air channelled to the test chamber was proven to be able to cool the double shear sample up to –30ºC for half an hour to achieve a steady state condition. The commercial environmental test chamber was used to cool down the said sample to a similar condition. Subsequently, a shear deformation was also applied onto it at various temperatures between –20ºC to room temperature. Shear modulus of all natural rubber based test samples were found by increasing the temperature gradually between the studied temperature ranges. An approximately 20% difference in shear modulus was observed at room temperature and –20ºC. The thermo mechanical effect of cold crystallisation in natural rubber was successfully proven through this comparison study.

Keywords: Thermo mechanics; cold crystallisation; shear modulus; natural rubber; environmental test chamber

Natural rubber is widely used in engineering applications, for instance seismic application[1]. Typically, rubber is very sensitive to environmental conditions and its physical properties are dependent upon temperature changes. Cold crystallisation can occur when rubber is cold soaked for a period of time and properties such as tear strength, tensile strength and modulus[2–3] can be readily affected. Furthermore, cold crystallisation has a strong effect on the elastic modulus of natural rubber by a factor of several hundreds[4–6]. Nevertheless, cold crystallisation of rubber is an undesirable phenomenon in common practice.

There are two phenomena which can affect the property of rubber at low temperatures *i.e.* glass hardening and low temperature crystallisation. Glass hardening results in stiffening of rubber which becomes apparent at about –60ºC (close to the glass transition temperature, T_g) and rubber turns brittle[7]. The second of the two phenomena is crystallisation which occurs at low temperatures, typically

*Rubber Research Institute of Malaysia, Malaysian Rubber Board, P.O. Box 10150, 50908, Kuala Lumpur, Malaysia
Corresponding author (e-mail: hfwong@lgm.gov.my)

–20ºC. As the rubber crystallises, it gradually stiffens[4].

Cold crystallisation creates lamellar-type crystals slowly, which are stable whereas stretched natural rubber forms unstable micelle-type crystals[8]. Goppel *et al*.[9] reported that cold crystallisation of rubber can create a maximum of 48% crystallisation and stretched rubber at 400% can only form 5% of crystallisation and more than 30% of crystallisation at 800% extension. Thus, only cold crystallisation of natural rubber in the rubbery stage will be discussed in this paper as influences being most critical between –20ºC and room temperature[7].

The effect of frequency and strain amplitude also play an important role in determining the modulus of natural rubber. The effect of frequency is inversely proportional to the effect of temperature[10] and modulus of natural rubber decreases with increasing strain amplitude[11]. Only a fixed value of frequency and strain amplitude will be used throughout this experiment at various temperatures.

Trabelsi *et al*.[12] studied the crystallisation of natural rubber in static and dynamic deformation by using simultaneous force and wide angle x-ray solution scattering (WAXS) measurement. The orientation of stretched natural rubber was also investigated by his team using Fourier transform infrared (FT-IR) spectroscopy technique. It was reported that the stretching of natural rubber produced crystals in an orientation parallel to the direction of the applied stress while cold crystallisation produced crystals in a random fashion.

The main objective of this work is to develop a simple yet practical test chamber in order to test the stretched natural rubber at various temperatures. This insulated chamber was custom-fabricated in order to determine the properties of stretched natural rubber. This kind of in-house test chamber was also much cheaper than the commercial one and also able to produce cold air in room temperature to about –30ºC.

EXPERIMENTAL

Materials

This work was conducted using a total of six double shear samples of designated engineering Standard Malaysian Rubber (SMR) based compound[13] with conventional accelerated sulphur vulcanising systems. All of these SMR based compounds were cured at 110ºC for 300 minutes. Three of the samples were tested with an in-house test chamber while another three samples were tested with a commercial test chamber. The designated SMR based compound was chosen for this study due to its common usage in engineering applications (particularly seismic application) at various temperatures. *Table 1* shows the formulation of this natural rubber (supplied by Chip Lam Seng) based compound.

In-House Test Chamber

Essentially in the design of the in-house test chamber, dry ice was used as the cooling agent because of the ease with which it can be converted to gas by direct sublimation without residue. Dissolved dry ice using methanol had been used to produce cold air to crystallise natural rubber. The schematic preliminary experimental setup is shown in *Figure 1* where the in-house test chamber (1) was assembled with the servo-hydraulic MTS 830 elastomeric test machine (3). For the in-house test chamber (1) which consisted of two fans, an insulated pipe was used to assist or direct the sublimed dry ice into the test chamber (4) where the double shear test specimen (13) was placed with a jig (14). The test chamber (4) was

TABLE 1. COMPOSITION OF DESIGNATED SMR BASED COMPOUND[13]

Composition	p.h.r.
Natural rubber	100.0
Processing oil (Shellflex 250 MB supplied by Prima-Inter)	2.0
Carbon black (N220 supplied by Cabot (M))	40.0
Stearic acid (PH-80 supplied by Luxchem)	2.0
Antidegradant (Santoflex 13 HPPD supplied by Luxchem)	2.0
Sulphur (Supplied by Lin Ho (M) S)	2.5
Accelerator (Santocure CBS supplied by Luxchem)	0.7

supported by a steel support (5) and hence they were attached on a table (8). A confined volume (11) with certain temperature can be achieved by adjusting the speed of fans (2) with the power supply (9). In *Figure 2*, the schematic drawing shows the transport of sublime dry ice (10) from in-house test chamber (1) to the test chamber (4). Temperature of the confined volume (11) was recorded by a pair of K-type thermocouples (12) and a data logger (6) was used to capture the temperature profile. A computer (7) was utilised to record the force-deflection data of the double shear specimen. A soak period of 30 min was employed at each elevated temperature of 25ºC, 0ºC, –10ºC and –20ºC in order to ensure a steady-state condition could be achieved inside the test chamber (4). Subsequently a shear deformation was also applied onto the rubber specimen at each elevated temperature. Based on the requirement[12], the test was performed at 25 ± 2ºC and ± 1ºC at non-ambient temperature.

Commercial Environmental Test Chamber

This thermo mechanic test was continued by using the commercial environmental test chamber (Thermotron, model SE-300-4-4-RC, manufactured in Holland) (15). The in-house test chamber was removed and it was replaced by a single stage environmental test chamber. K-type thermocouples (12) and data logger (6) were also removed and the capture of temperature profile of confined volume (11) inside the test chamber (1) was recorded by this commercial test chamber. *Figure 3* shows the experimental setup of the thermo mechanic test with a commercial test chamber. It was also possible to programme the desired test temperature and cooling period using this commercial test chamber.

RESULTS AND DISCUSSION

In-House Test Chamber (Temperature Profile)

The in-house test chamber was used to create a cold confined environment in this part of the study. *Figure 4* shows the temperature profile of the confined volume inside the test chamber at ambient temperature while Figures 5 to 7 show the temperature profiles at non-ambient temperature by using the same test chamber. It was observed that the temperature profile at –20ºC was quite difficult to achieve within the specification limit at ±1ºC.

Commercial Test Chamber (Temperature Profile)

The commercial test chamber was used to create a cold confined environment in this part

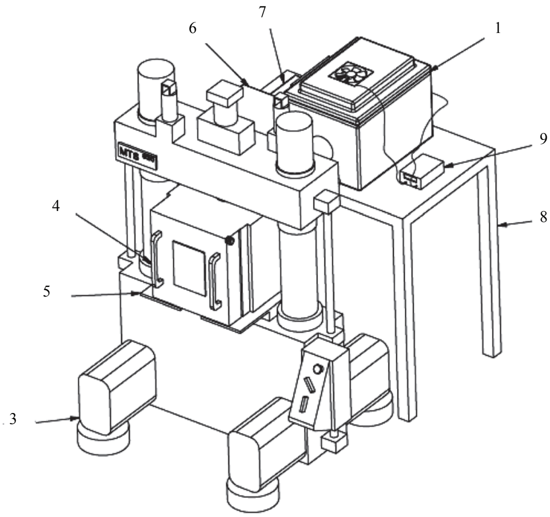

Figure 1. Schematic drawing of experimental setup using in-house test chamber.

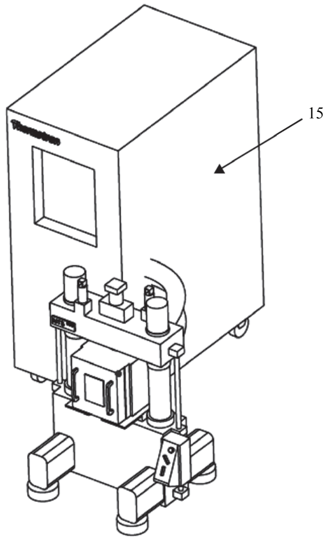

Figure 3. Experimental setup with commercial test chamber.

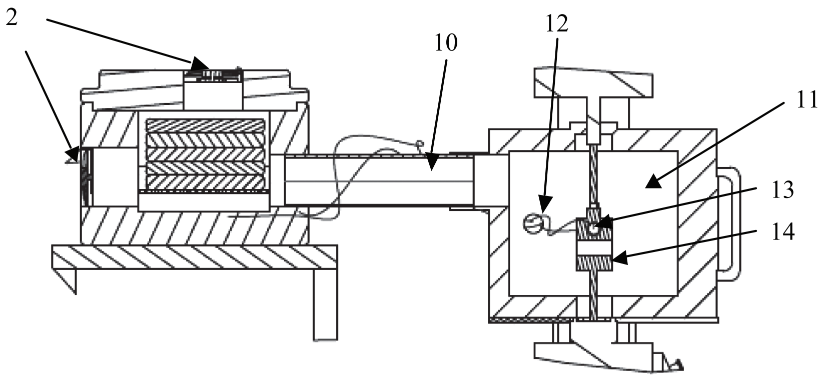

Figure 2. Schematic drawing of transport of sublimed dry ice.

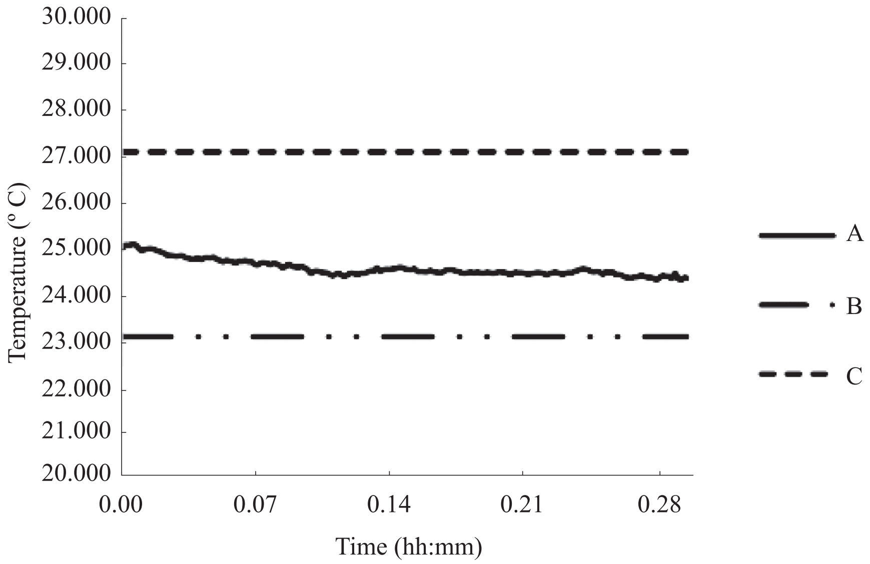

Figure 4. Temperature profile at ambient temperature (25°C) as obtained by using in-house test chamber (A: Temperature profile, B: Lower limit at 23°C, C: Upper limit at 27°C)

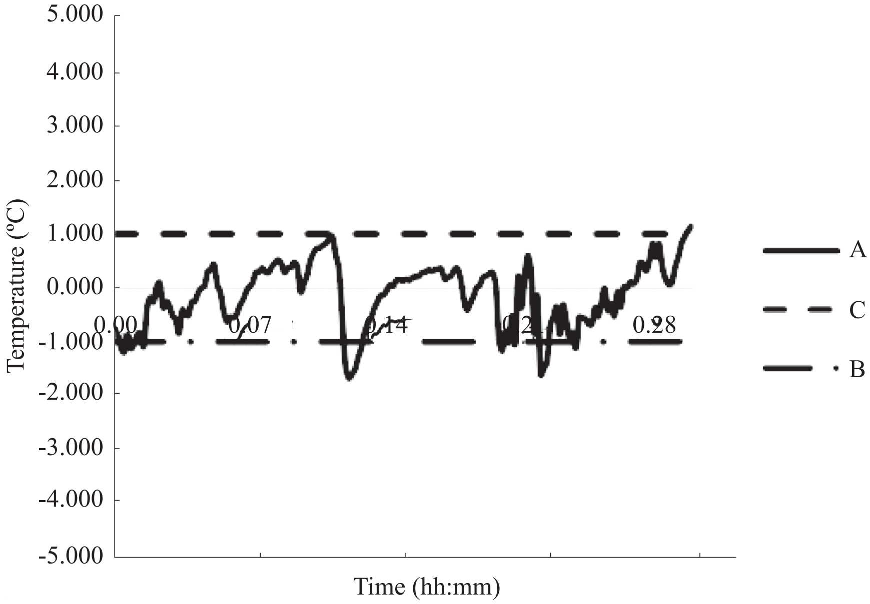

Figure 5. Temperature profile at 0°C as obtained by using in-house test chamber (A: Temperature profile, B: Lower limit at -1°C, C: Upper limit at 1°C)

of the study. *Figure 8* shows the temperature profile of the confined volume inside the test chamber at ambient temperature while *Figures 9* to *11* show the temperature profile at non-ambient temperature by using the commercial test chamber. All the temperature profiles produced by using the commercial test chamber were convincing.

Effect of Soak Period

Cold crystallisation was carried out on this SMR based compound at temperatures of 25ºC, 0ºC, –10ºC and –20ºC. A soak period of 30 min was carried out for each temperature to ensure that a steady state condition within the rubber specimen was achieved. A shear deformation of 100% at frequency of 0.5 Hz with 5 cycles was also applied at different temperatures, *i.e*. 40ºC, 25ºC, 0ºC, –10ºC and –20ºC as shown in *Figure 12*.

A soak period of 30 min was applied, longer than the original requirement at 25 min in this case[14] (at least to the square of the rubber thickness in mm). This was to ensure that the entire rubber test sample was at the test temperature before the shear test was carried out. The temperature profile at the centre and surface of rubber test sample at time, t could be obtained by considering the cylindrical shaped rubber test sample and spatial effect[15] was used in order to calculate the steady state time for rubber to achieve the test temperature. In this study, the rubber was initially at room temperature and surrounded with cold air at a temperature of about –20ºC. Schematic drawing of the rubber test sample which was exposed to the cold air is shown in *Figure 13*.

Hence, time dependence of the temperature at the centre of the rubber test sample was derived from one-term approximation[15] in *Equation 1*.

$$T(0,t) = C_1 \exp\left(\frac{-t\alpha\zeta_1^2}{r_o^2}\right)(T_i - T_\infty) + T_\infty \qquad \ldots 1$$

The surface time-dependent temperature of rubber is given by *Equation 2*.

$$T(r_o,t) = C_1 \exp\left(\frac{-t\alpha\zeta_1^2}{r_o^2}\right)(T_i - T_\infty)J_o\zeta_1 + T_\infty \quad \ldots 2$$

where C_1 = 1.11 and ζ_1 = 0.94, J_o is the Bessel functions of the first kind, r_o is radius of the rubber test sample, T_o is centre temperature, T_∞ is ambient temperature and T_i is initial temperature. Taking the initial temperature as room temperature *i.e.* 25ºC and subjected to cooling air with temperature of –20ºC, the temperature profile could be plotted versus time. The entire rubber test sample achieved the test temperature of –20ºC in about 10 minutes.

Effect of Cold Crystallisation

Cold crystallisation was carried out on the rubber test sample at 25ºC, 0ºC, –10ºC and –20ºC respectively for 30 minutes. Three samples were tested with the in-house test chamber and another three samples were tested with the commercial test chamber. *Figures 15* and *16* show the average force-deflection curve from the three samples which were tested with the in-house test chamber and commercial test chamber respectively. The loop of the force-deflection curve became bigger and steeper from 25ºC to –20ºC for experiments carried out using both the in-house and commercial test chamber.

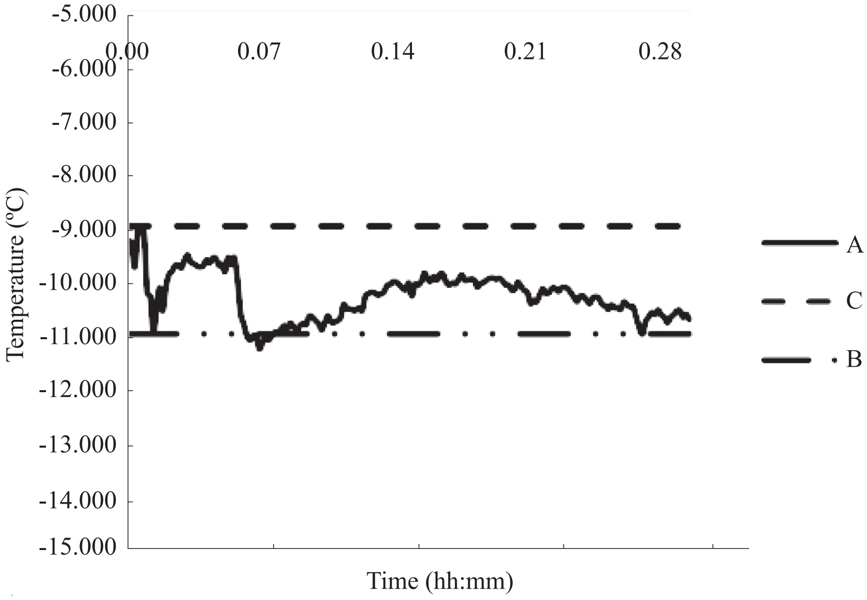

Figure 6. Temperature profile at -10°C as obtained by using in-house test chamber (A: Temperature profile, B: Lower limit at -11°C, C: Upper limit at -9°C)

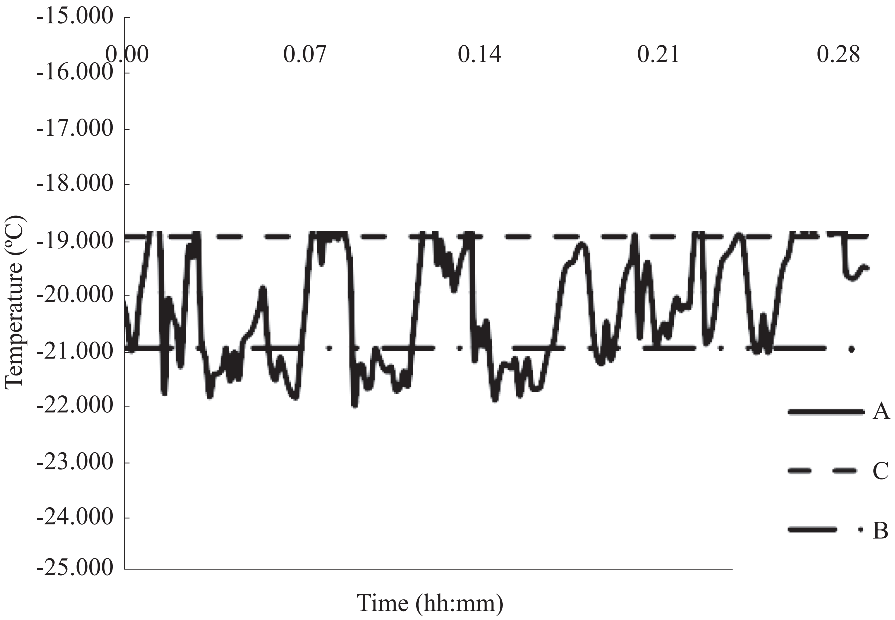

Figure 7. Temperature profile at -20°C as obtained by using in-house test chamber (A: Temperature profile, B: Lower limit at -21°C, C: Upper limit at -19°C)

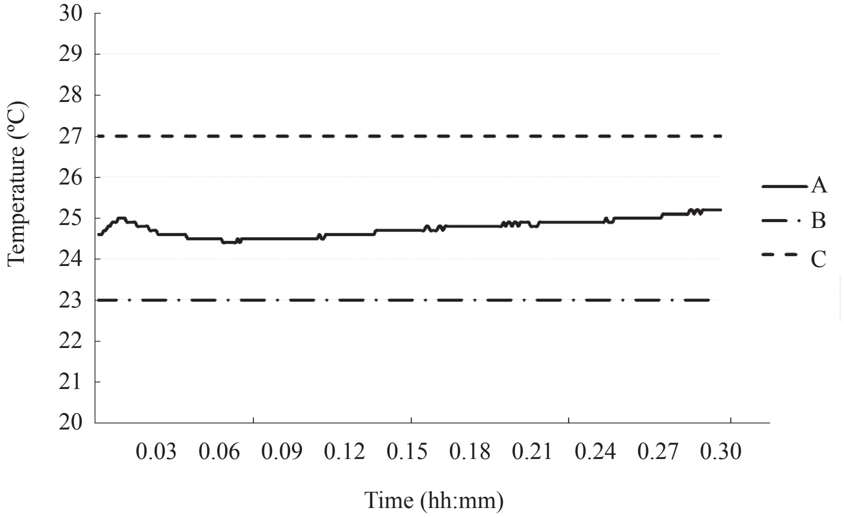

Figure 8. Temperature profile at 25°C as obtained by using commercial test chamber (A: Temperature profile, B: Lower limit at 23°C, C: Upper limit at 27°C)

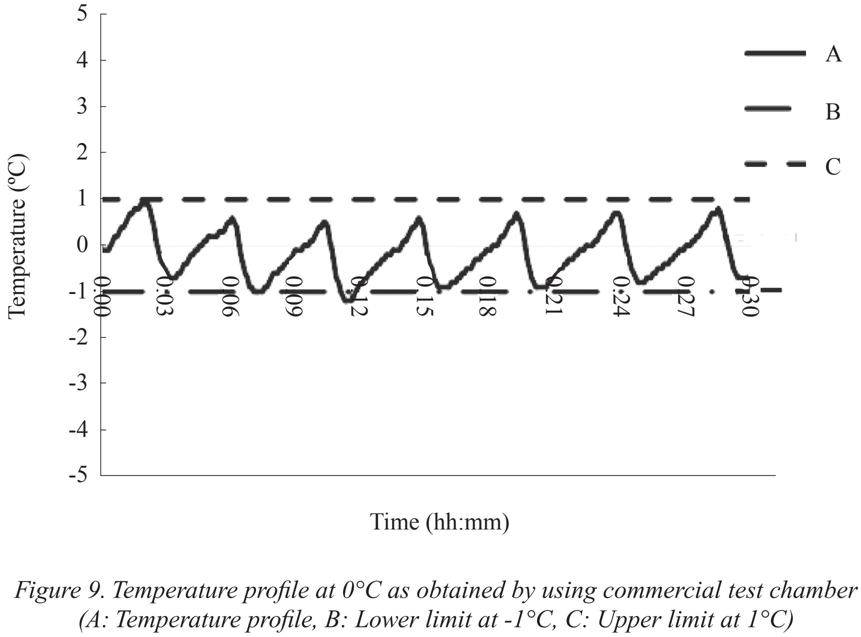

Figure 9. Temperature profile at 0°C as obtained by using commercial test chamber (A: Temperature profile, B: Lower limit at -1°C, C: Upper limit at 1°C)

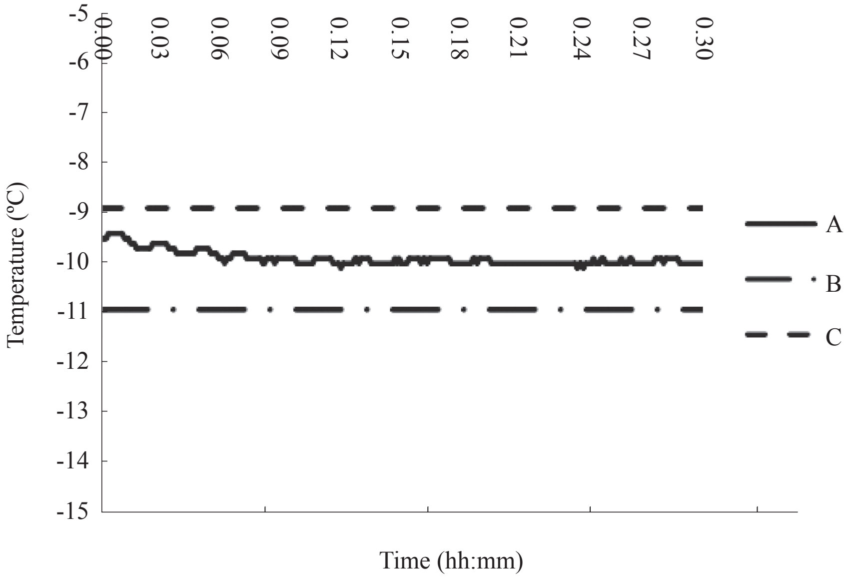

Figure 10. Temperature profile at -10°C as obtained by using commercial test chamber (A: Temperature profile, B: Lower limit at -11°C, C: Upper limit at -9°C)

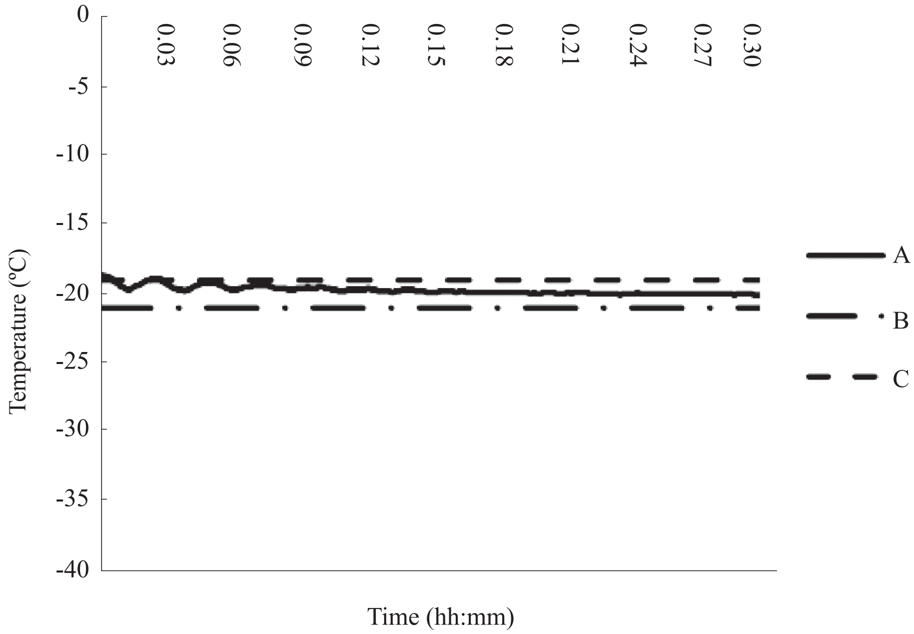

Figure 11. Temperature profile at -20°C as obtained by using commercial test chamber (A: Temperature profile, B: Lower limit at -21°C, C: Upper limit at -19°C)

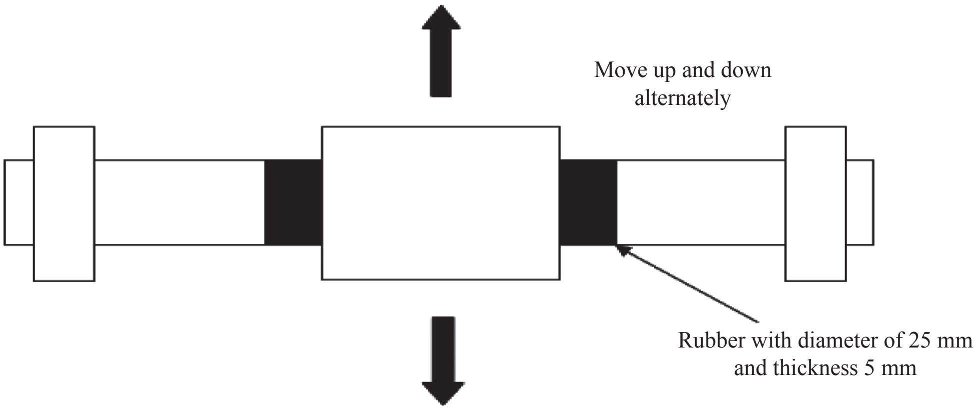

Figure 12. Shear deformation

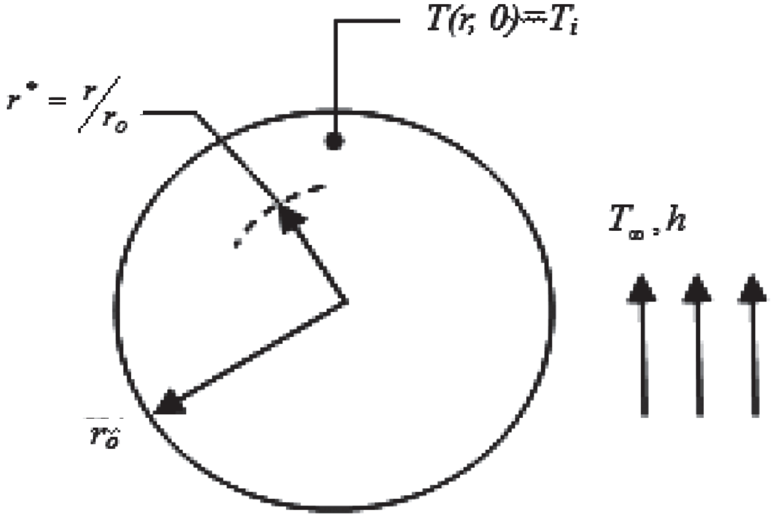

Figure 13. Schematic drawing of rubber test sample exposed to cool air[15]

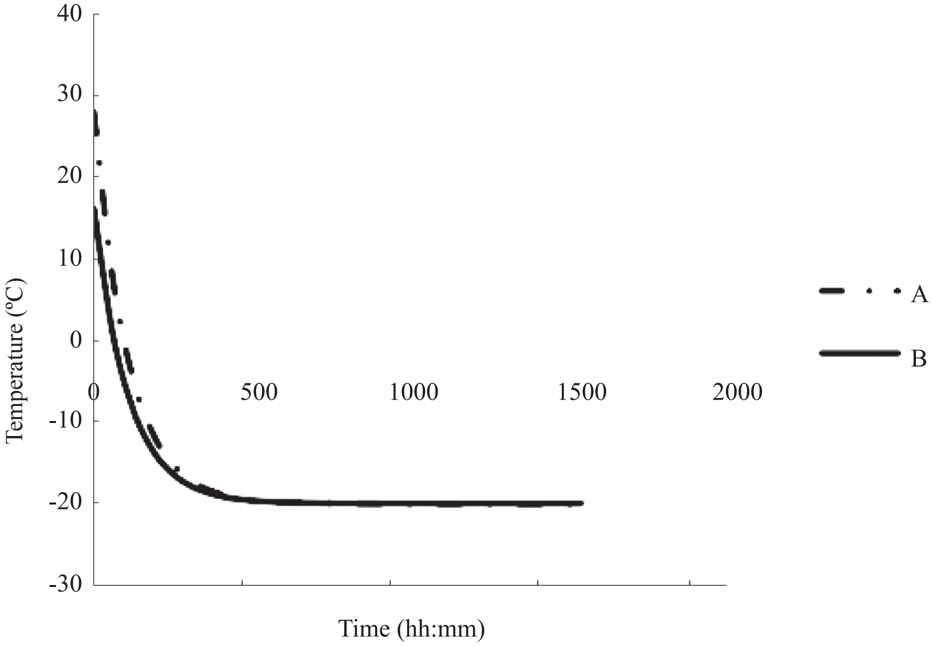

Figure 14. Temperature profile of cylindrical rubber test sample
(A: Surface temperature, B: Centre temperature)

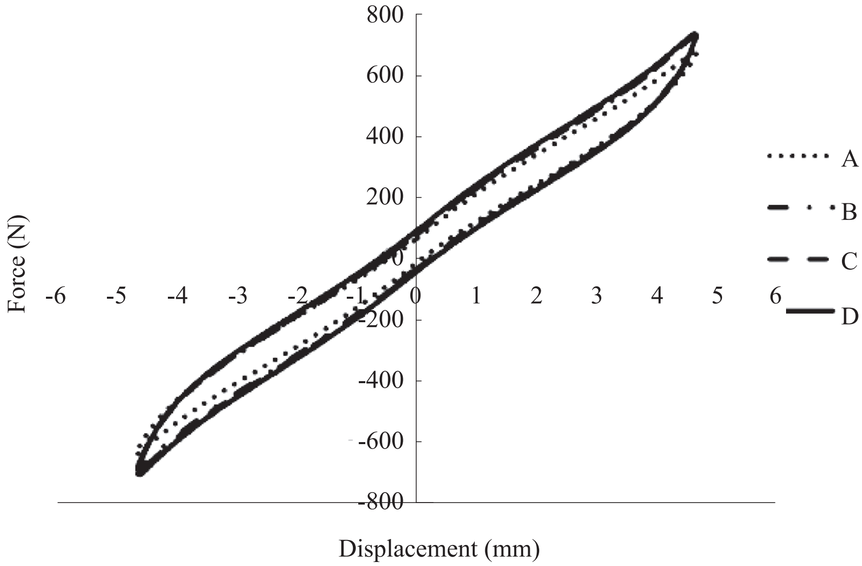

Figure 15. Force deflection curve as obtained by using in-house test chamber
(A: 23°C, B: 0°C, C: -10°C, D: -20°C)

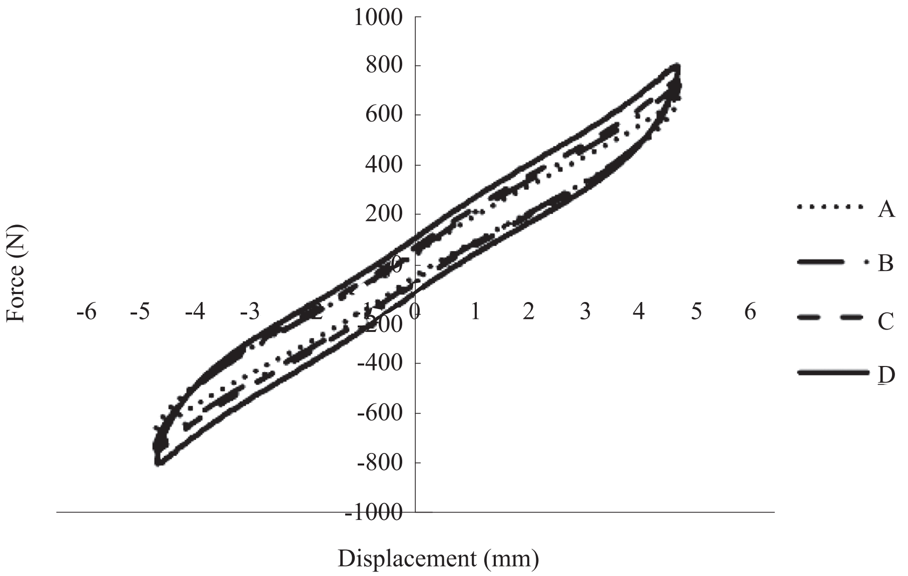

Figure 16. Force deflection curve as obtained by using commercial test chamber (A: 23°C, B: 0°C, C: -10°C, D: -20°C)

Figures 17 to *18* show the average temperature dependent shear modulus and damping ratio of rubber test samples recorded from the experiment by using the in-house and commercial test chamber, respectively. All of them showed a similar trend where the shear modulus and damping ratio decreased with increasing temperature. Shear modulus, *G* could be calculated based on *Equation 3*.

$$G = {k_s t}/{A} \qquad \ldots 3$$

where k_s is the shear stiffness of rubber (obtained from the experiment), *A* is the cross sectional area of the rubber test sample and t is the thickness of rubber test sample.

Damping ratio, ζ could be related to the loop area of the force-deflection curve through *Equation 4*.

$$\zeta = \frac{2 \times loop\_area}{\pi \times k_s \times (d^+ - d^-)^2} \times 100\% \qquad \ldots 4$$

where *loop area* was calculated from the area inside the force-deflection curve (*Figures 15* and *16*) using the trapezoidal integration rule. d^+ is maximum displacement and d^- is minimum displacement.

As observed in *Figure 17*, the difference in value of average shear modulus between 25ºC and –20ºC was about 14.6% with the experimental setup using in-house test chamber and about 18.0% with experimental setup using the commercial test chamber. Similarly, it was observed from *Figure 18* that the difference in value of average damping ratio between 25ºC and -20ºC was about 102% with the in-house test chamber and about 96.2% with the commercial test chamber. Since the studied temperature range falls in

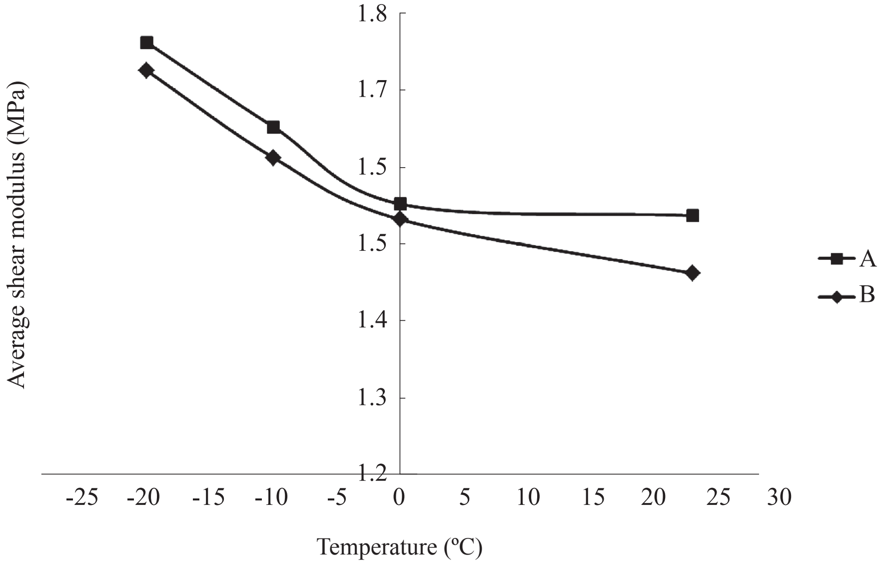

Figure 17. Average shear modulus vs *temperature (A: obtained by using in-house test chamber, B: obtained by using commercial test chamber)*

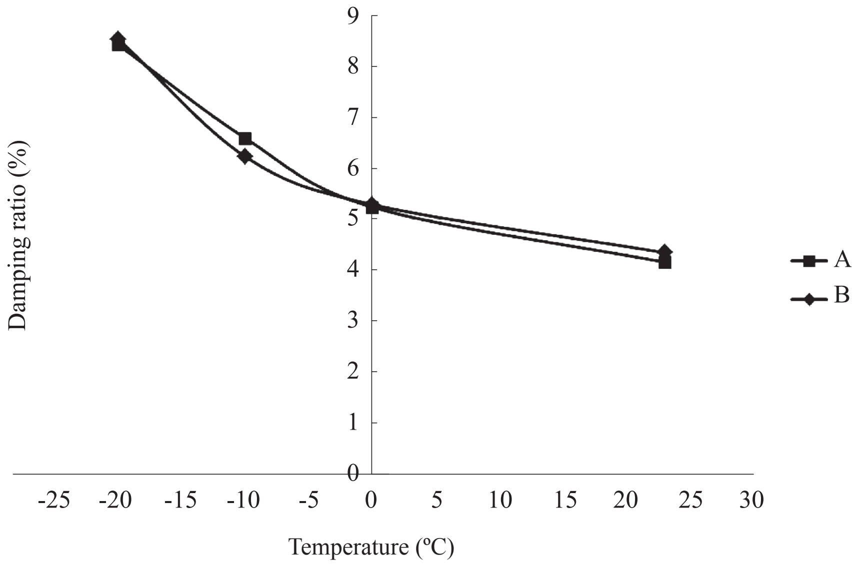

Figure 18. Average damping ratio vs *temperature (A: obtained by using in-house test chamber, B: obtained by using commercial test chamber)*

the rubbery region, both values of damping ratio and shear modulus increased with decreasing temperature[16] due to the formation of lamellar-type crystals[8]. On the other hand, these crystallites in natural rubber can act as reinforcing agents.

The reinforcing agents in crystallisation of rubber are explained in *Figure 19*. In diagram A, all polymer chains are in an amorphous form. When rubber is subjected to cold temperatures, the arrangement of polymer chains become compact and appear in a random orientation as shown in diagram B. However in diagram C, once it is subjected to stretch in a preferred orientation, all the crystals will follow the direction of the applied force and hence these crystallisations act as reinforcing agents and increase the shear modulus of rubber. After the applied force has been released as shown in diagram D, all the polymer chains are back to a random position but slightly more aligned then before the stretching cycle. Since the rubber was stretched in a cyclic manner, the arrangement of polymer chains have enhanced alignment leading to increase in stiffness on each cycle. Consequently the damping ratio increases, causing concomitant energy absorption.

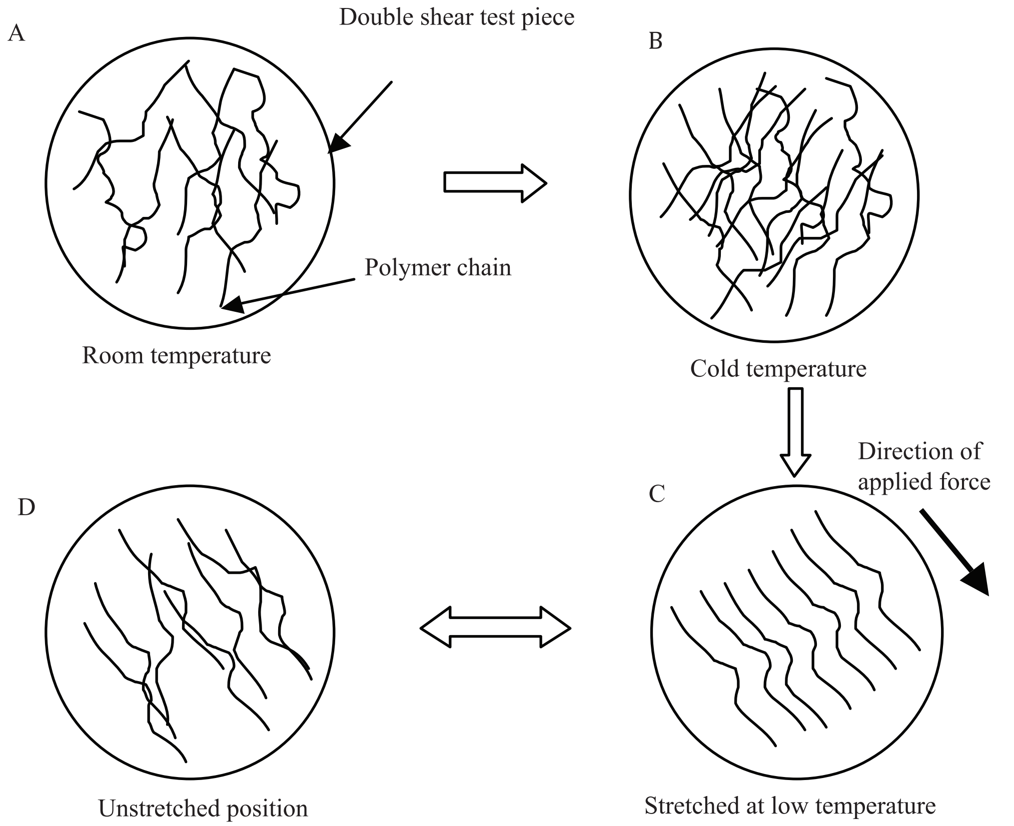

Figure 19. Crystallisation of rubber at low temperature.

CONCLUSION

In this work, the economical in-house test chamber used to produce cold air at low temperatures was successfully designed based on a fundamental heat transfer approach. The thermo mechanic behaviour of natural rubber in the rubbery region was then compared with the experimental setup using a commercial test chamber. Both chambers were coupled with an MTS 830 hydraulic machine in order to perform shear deformation tests and measure thermo mechanical behaviour of natural rubber in the rubbery region. It can be concluded that this newly designed in-house test chamber was able to measure the thermo mechanical behaviour of natural rubber although the produced temperature profile fluctuated more than the one produced with the commercial test chamber. The profile produced using this in-house test chamber fell within the specified limit mostly. As a result, this in-house test chamber was able to prove the low temperature effect due to the thermo mechanic behaviour of natural rubber; where properties of natural rubber are greatly influenced by temperature.

Date of receipt: June 2013
Date of acceptance: August 2013

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