DYNAMIC GLASS TRANSITION OF CHLOROPRENE RUBBER UNDER STRESS BY TEMPERATURE-MODULATED DSC

- *Masayoshi Murata*

Masanori Iijima

Takeshi Osada

Masaru Minagawa

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Introduction

Recently dynamic heat capacity of various polymers has been measured by using TMDSC (temperature-modulated DSC).

One of main aims of such measurements

In the glass transition region

- vitrification
- relaxation process

Experimental

The dynamic heat capacity in the glass transition region for various frequencies ⇐ TMDSC

relaxed and stressed rubbers

- Sample : Chloroprene rubber (+ 35per Carbon black)

  (Engineer use typical synthetic rubber)

- DSC : DSC822e/400 (METTLER TOLEDO)
- Experimental condition :

  Amplitude = 0.5 K
  Heating rate = 1 K/min
  Period = 60,75,90,105,120,135,150,165,180,210,240,300s
  (But stressed rubber are 60, 90, 120, 150,180,210,240s)

relaxed and stressed rubbers

The heat capacity spectroscopy in the glass transition region

- the real part : c'
- the imaginary part : c''

↓

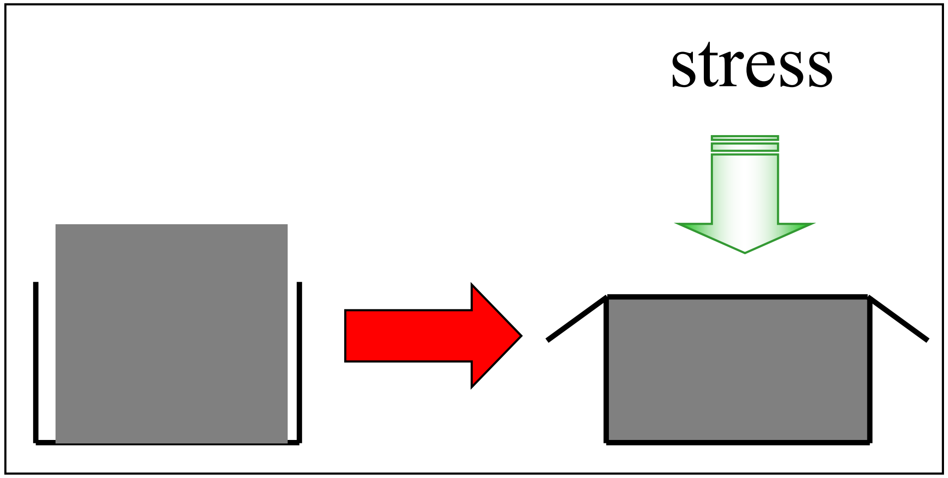
The frequencies dependence of the dynamic glass transition temperature Tg

We understood by well known non-Arrhenius type VFTH (Vogel-Fulcher-Tamman-Hesse) equation

↓

The temperature dependent on the glass transition cooperativity N_{α} from the fluctuation approach

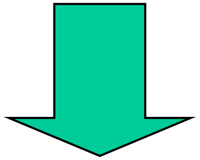
Sample preparation for the stressed rubber



The stressed rubber is compressed by the lid with screw.

About 5MPa pressure is given for the sample around Tg temperature.

When the rubber is compressed by the stress, the free volume is reduced due to the compression of the phase space.



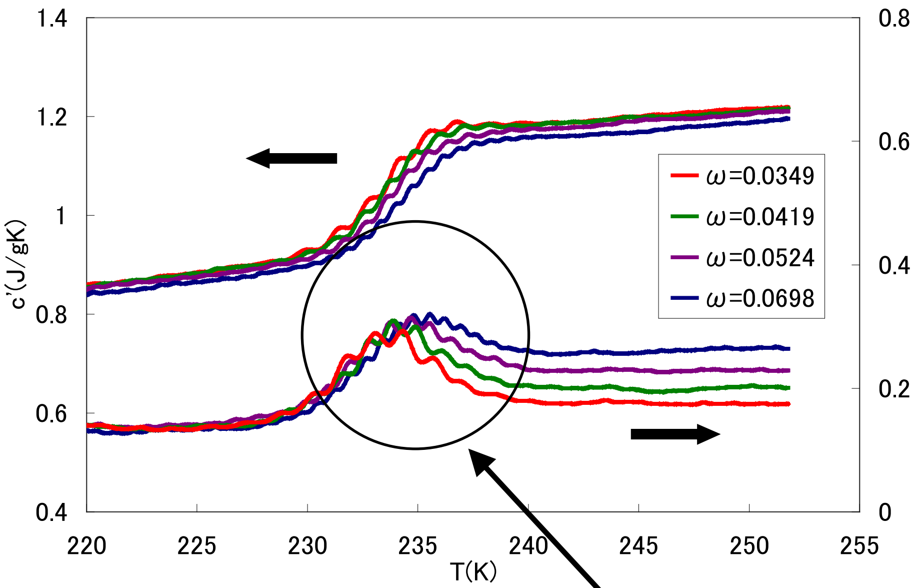
How VFTH parameters and cooperativity for stressed rubber change.

Results

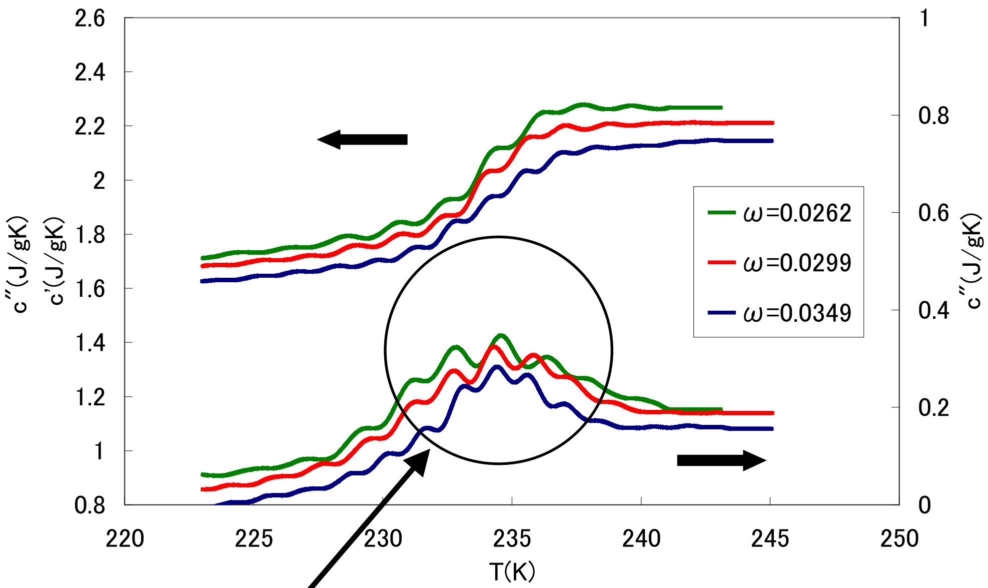
The heat capacity spectroscopy in the glass transition region

- the real part : *c'*
- the imaginary part : *c"*

Relaxed rubber



Stressed rubber



The dynamic glass transition temperature ***Tg***

Analysis

We used well known non-Arrhenius type
Vogel-Fulcher-Tamman-Hesse (VFTH) equation.

VFTH equation

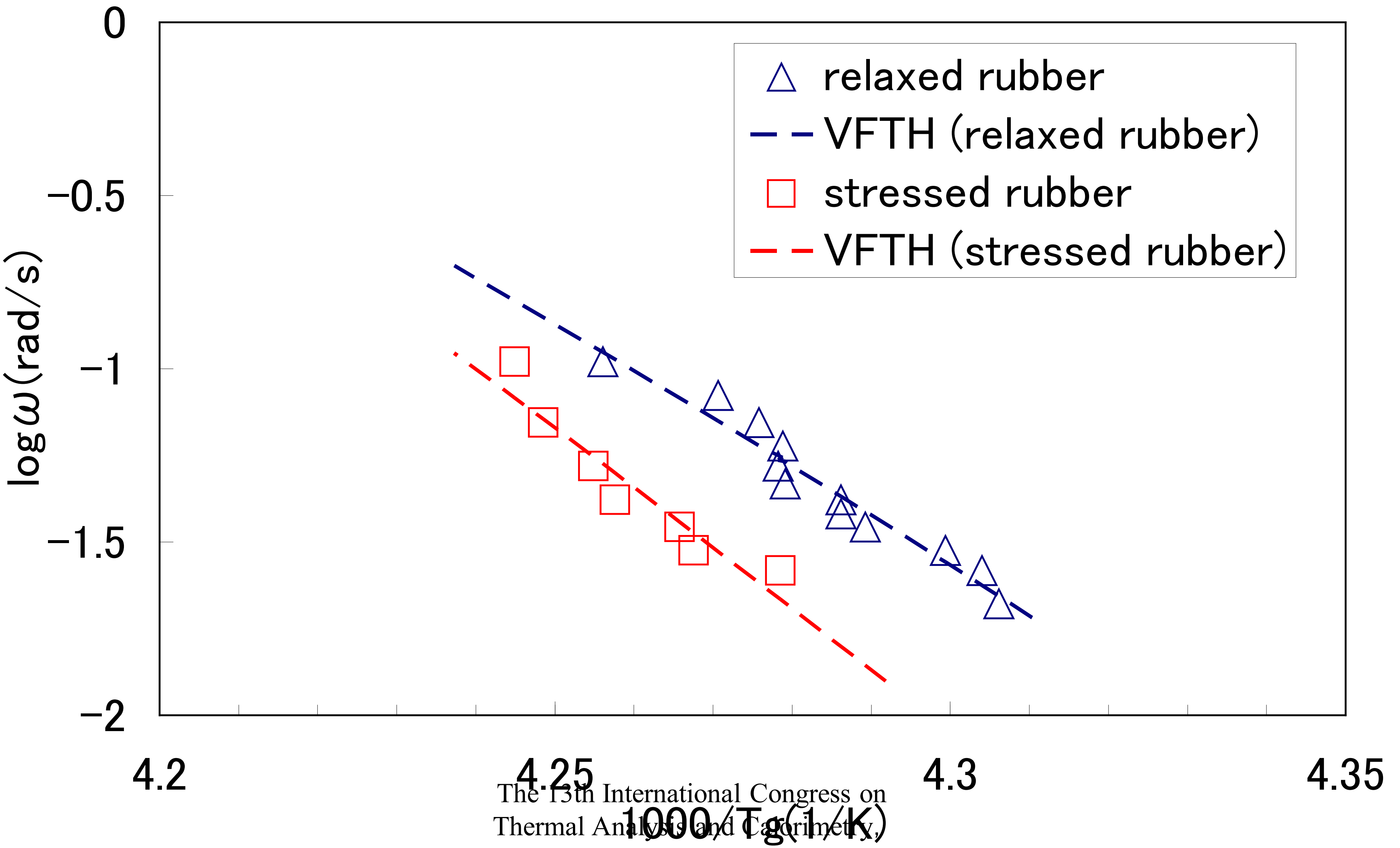
$$\log \omega = A + \frac{B}{T - T_{\infty}}$$

VFTH parameter :

Relaxed rubber	Stressed rubber
$A = 12.03$	$A = 22.12$
$B = -688.88$ K	$B = -1756.17$ K
$T_{\infty} = 181.88$ K	$T_{\infty} = 159.89$ K

The stressed rubber's Tg is lower than the relaxed rubber's Tg.

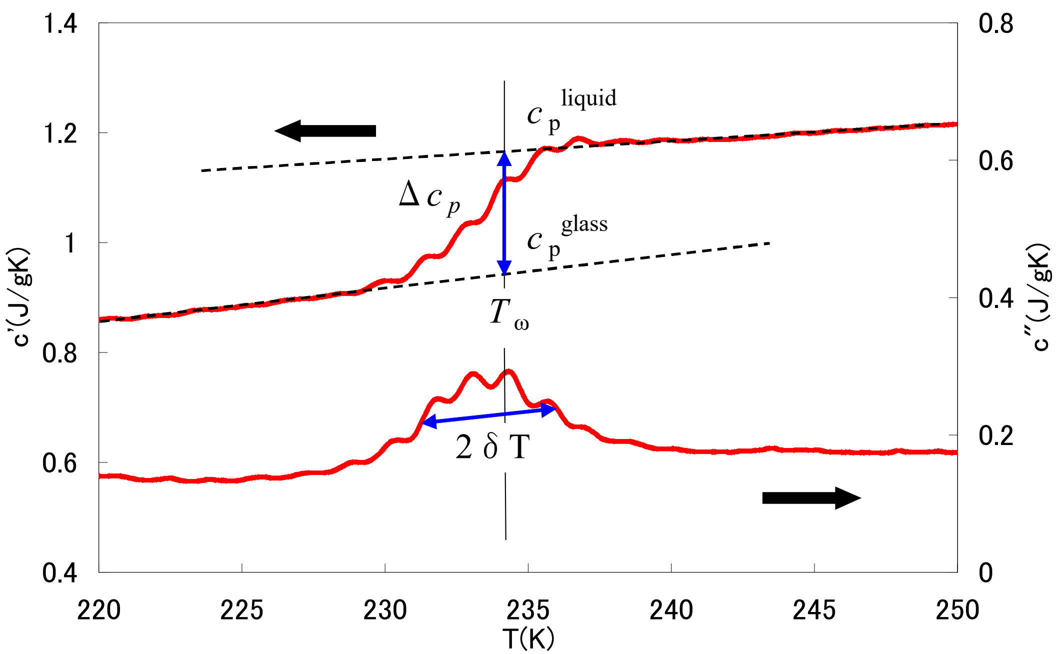
Relaxed and stressed rubber can be fitted by the VFTH.



We used the fluctuation approach to obtain the temperature dependent on the glass transition cooperativity N_α.

$$N_\alpha \cong \frac{RT_\omega^{\,2}\Delta(1/C_p)}{M_0\delta T^2}$$

[2] S.Weyer et al



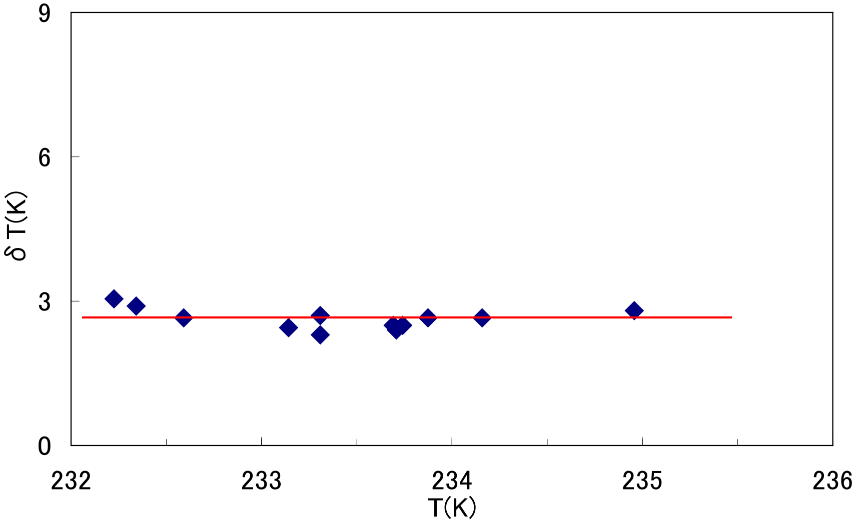
$$\Delta(1/C_p) = 1/C_p^{glass} - 1/C_p^{liquid}$$

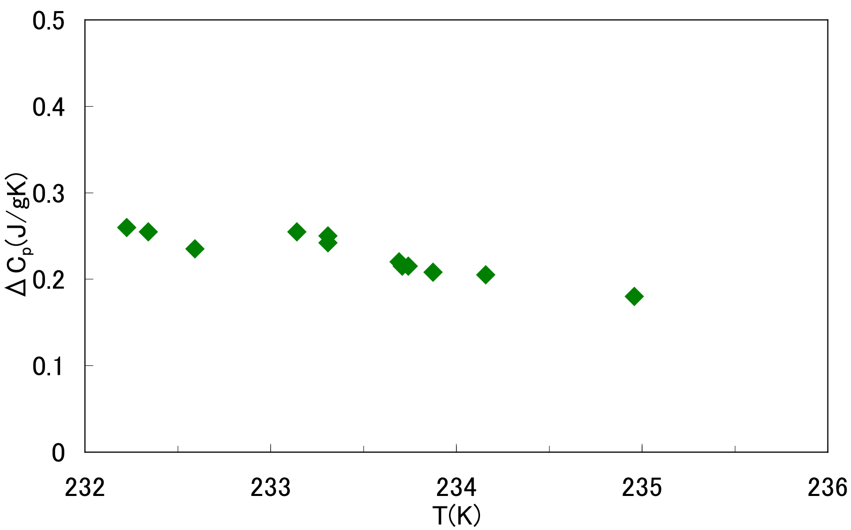
R : the gas constant

T_ω : the dynamic glass transition temperature for the frequency ω

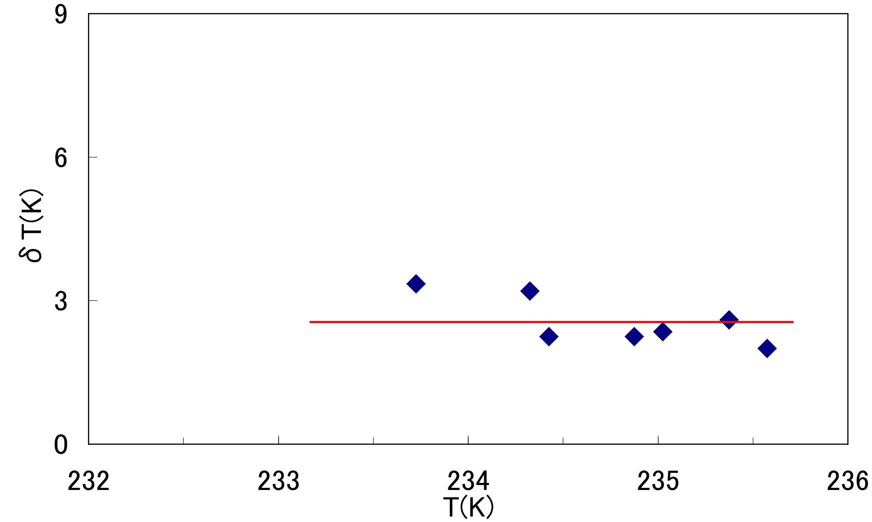
M_0 : the molecular weight of the relevant particle

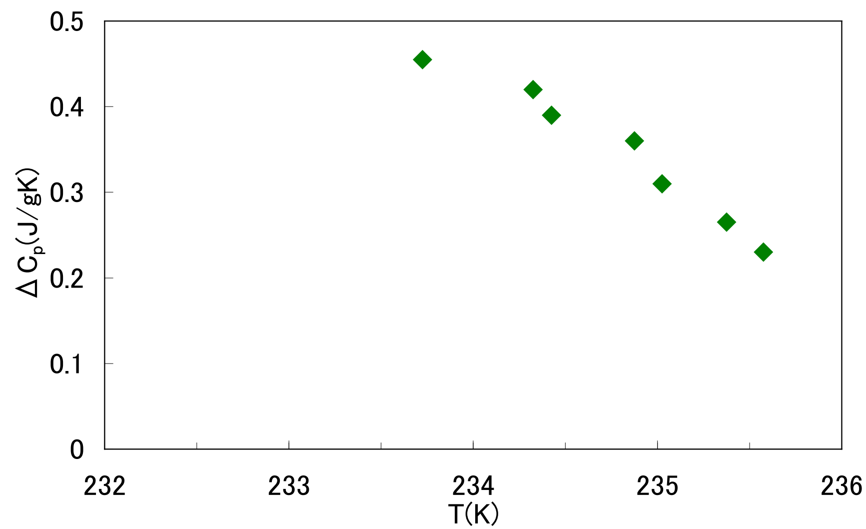
Relaxed rubber





Stressed rubber



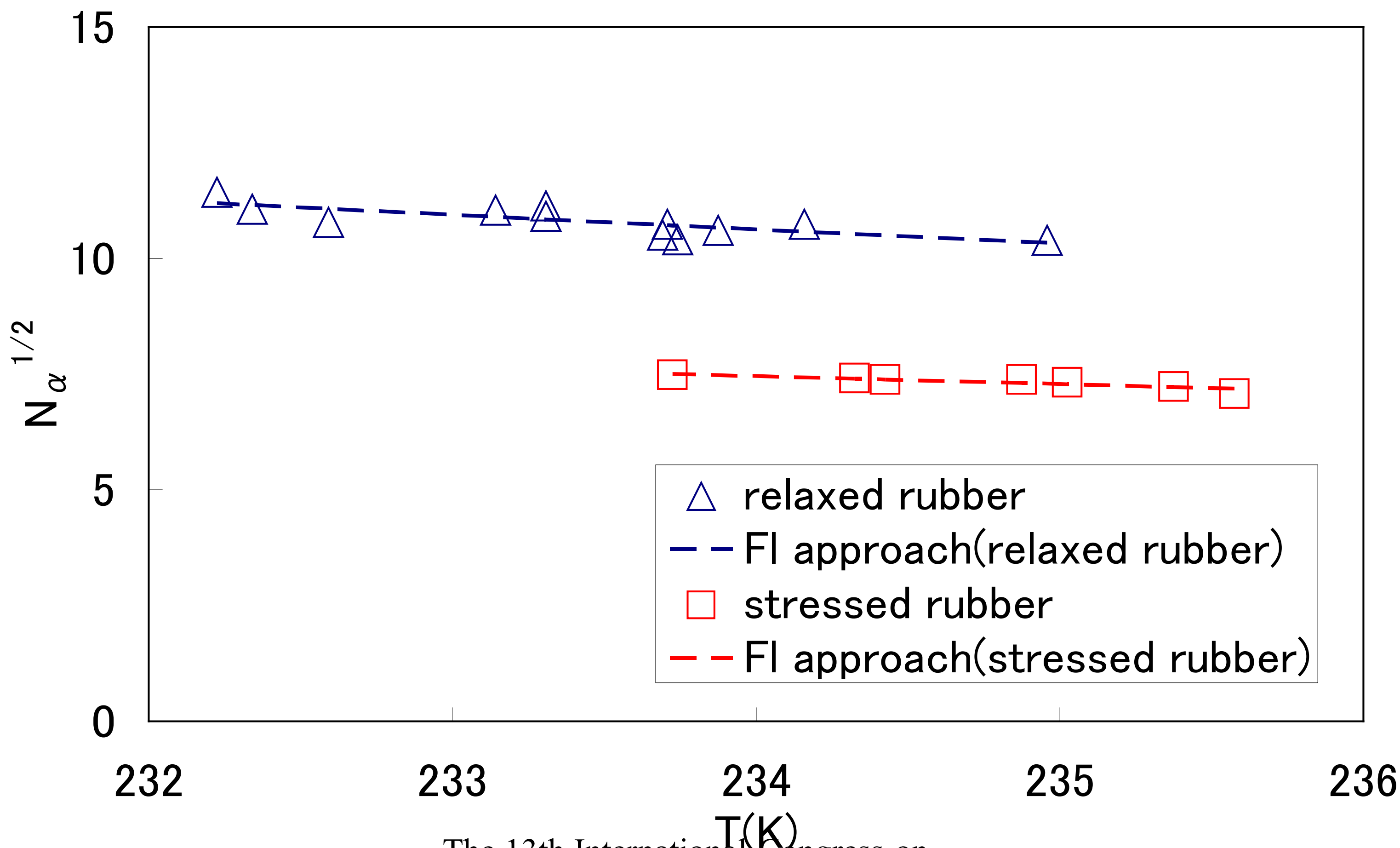


Fluctuation approach

$$N_{\alpha}^{1/2}(T) = A\left(\frac{T_{on} - T}{T - T_{\infty}}\right)$$

T_{∞} : the Vogel temperature by VFTH equation

[2] S.Weyer et al



The thick lines are fits by the fluctuation approach.

Discussion

Cooperativity parameter :

	A	T_{on}(K)
relaxed rubber	5.45	335.6
stressed rubber	5.37	337.0
Other materials		
polystyrene	10.9	429
styrene butadiene rubber	6.8	275

<u>Both rubbers have nearly same parameter.</u>

Conclusion

• Measurement of the rubber under stress can be performed in TMDSC by using normally optioned pressure pan.

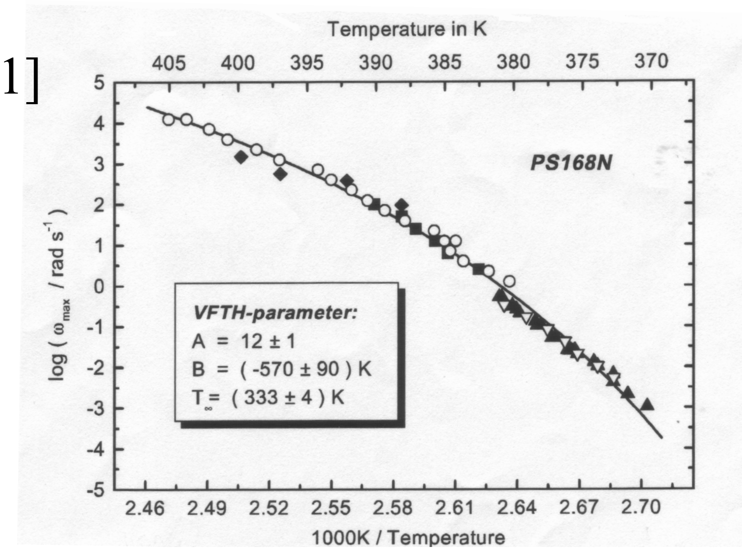
• The relaxed and stressed rubber can fit by the VFTH equation similarly.

• Although N_α value is different between both of rubbers, their temperature dependencies are same.

• Glass transition behavior for the stressed rubber can be explained cooperativity.

Reference

[1]



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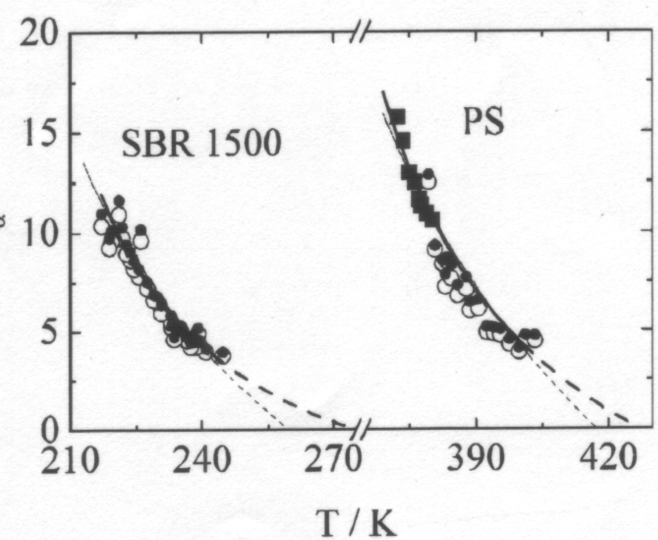

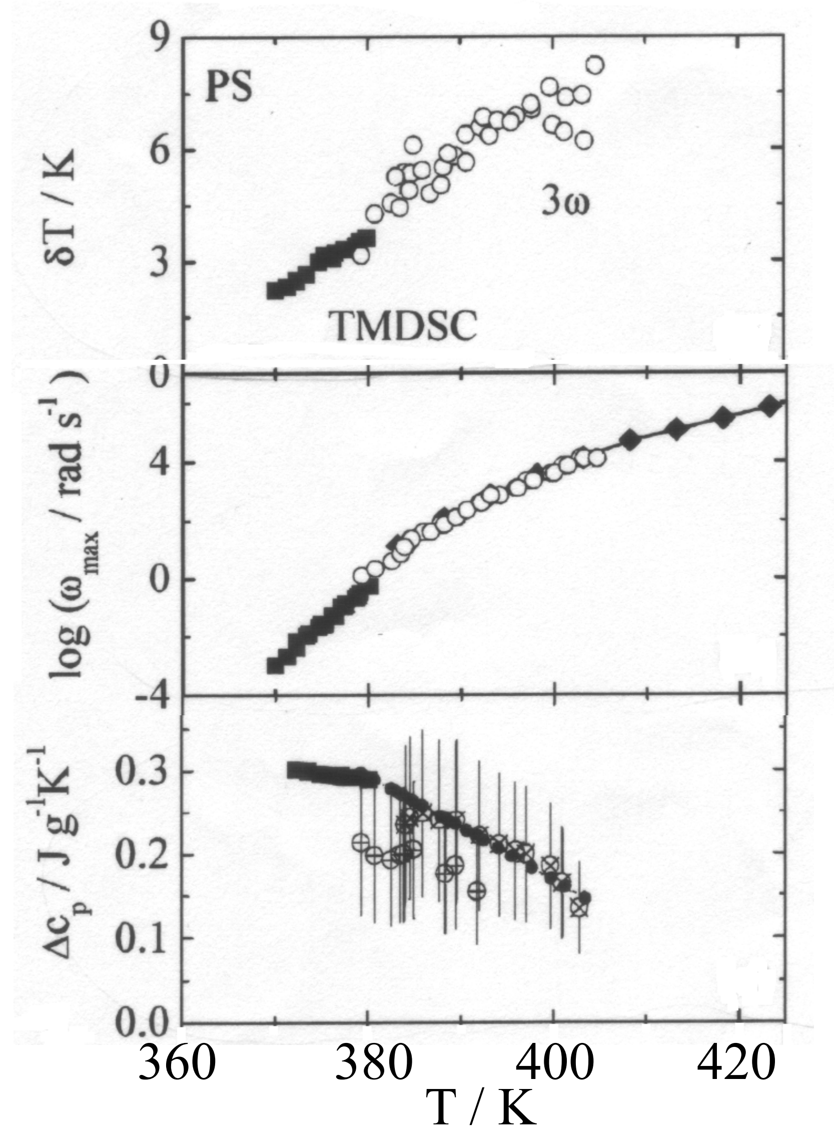

[1] H.Huth et al. / Thermochimica Acta 377 (2001) 133-124
[2] S.Weyer et al . / Thermochimica Acta 377 (2001) 85-96