Cooperatively rearranging regions for rubbers with carbon black concentration and under large deformation by TMDSC

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Abstract

Recently the dynamic heat capacity of various polymers has been measured by TMDSC (Temperature-Modulated Differential Scanning Calorimetry). Especially, the glass transition of polymer has much interest since the microscopic behaviors of molecules can be understood via the relaxation phenomena. The dynamic heat capacity of Chloroprene rubber (CR), Natural rubber (NR), Styrene Butadiene Rubber (SBR) and Isobutene Isoprene Rubber (IIR) reinforced various carbon black concentration has been measured in the glass transition region for various frequencies by TMDSC. Moreover, the rubber under pressure has been measured as well. From complex heat capacity, we calculated the volume of Cooperatively Rearranging Region (CRR) V_α. As a result, we found the frequency and temperature dependence of CRR. Further, we will discuss about influence of carbon black and pressure on CRR.

Cooperativity

Molecular chain movement had been freezing below glass transition region. With increase of temperature, molecular chains begin to move at glass transition region. The concept of dynamic heterogeneity and cooperativity due to fluctuation of molecular mobility at glass transition are introduced by recent researches.

Area with same mobility is defined to Cooperatively Rearranging Region (CRR) and molecular units in a CRR behave cooperatively. The volume of CRR V_α, the number of molecular units in a CRR N_α and the characteristic length ξ are calculated from complex heat capacity at glass transition region measured by TMDSC.

CRR of rubbers ➡
- Frequency and temperature dependence
- Influence of carbon black concentration
- Influence of large deformation (pressure)

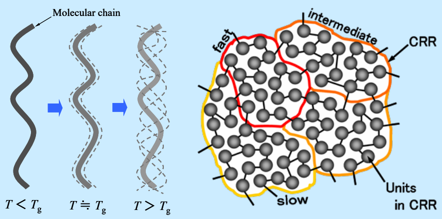
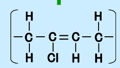


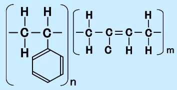
Fig.1 Dynamic heterogeneity at glass transition region.

Experimental

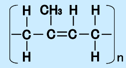
Samples



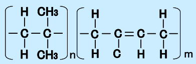
Chloroprene Rubber (CR)



Styrene Butadiene Rubber (SBR)



Natural Rubber (NR)



Isobutene Isoprene Rubber (IIR)

Table1 Properties of all samples

Sample	Hardness	Carbon black concentration (%)	Density (g/cm^3)	Moleculer weight (g/mol)
CR	45	0	1.262	88.53
	55	19.486		
	65	25.056		
	75	27.207		
NR	40	0	0.923	68.114
	55	22.997		
	65	30.983		
	75	39.598		
SBR	55	27.774	0.787	158.232
	65	32.484		
	75	38.043		
IIR	27	0	0.825	124.218
	55	22.73		
	65	29.433		
	75	36.387		

Hardness is controlled by carbon black concentration only.

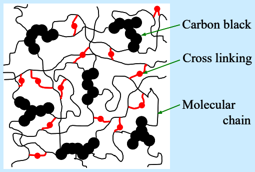


Fig.2 The mechanism of rubber reinforcement by carbon black.

TMDSC

Instrument : Mettler Toledo DSC822^e/400

Temperature program

Amplitude : 0.5K

Scanning rate : 0.2K/min

Range : 213K～253K (CR series)

193K～233K (NR, SBR and IIR)

Period : 42,48,54,60,90,120,150180,210, 240,270,300,600,900sec

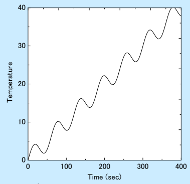


Fig.3 The temperature program.

Compression pan

Material	Stainless
Plate thickness	0.5mm
Mass	300mg
Maximum pressure	5MPa

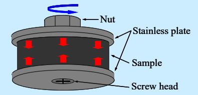


Fig.4 Handmade compression pan

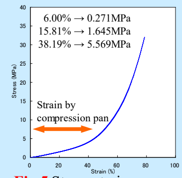


Fig.5 Stress-strain curve of CR65 on compression test.

Dynamic glass transition temperature and Fragility

VFTH equation

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

Fragility at T_g

$$m(T_g) \approx 15 \frac{T_g}{T_g - T_\infty}$$

ω : Angular frequency (rad/s)

T : Temperature (K)

A : Constant

B : Activation energy of appearance

T_∞ : Vogel temperature (K)

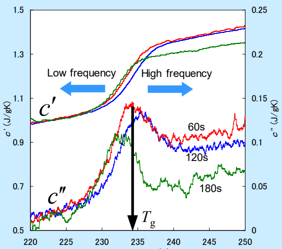


Fig.6 The complex heat capacity of rubber at glass transition region measured by TMDSC

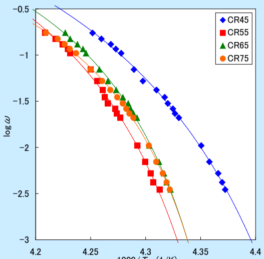


Fig.7 The frequency dependence of T_g fitted by VFTH equation.

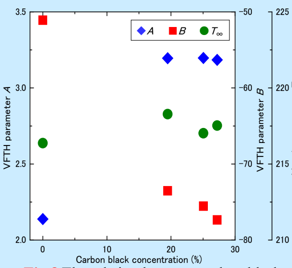


Fig.8 The relation between carbon black concentration and VFTH parameter.

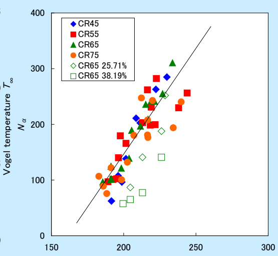


Fig.9 The relation between fragility at glass transition $m(T_g)$ and N_α.

The volume of Cooperatively Rearranging Region

The volume of CRR V_α

$$V_\alpha = \frac{k T_\omega^2 \Delta c_p^{-1}}{\rho \delta T^2}$$

$$\Delta c_p^{-1} = 1/c_p^{glass} - 1/c_p^{liquid}$$

k : Boltzmann constant

T_ω : T_g measured by frequency ω

ρ : Density of sample

δT : Half width of c''

c_p^{glass} : The value of c' at glassy state

c_p^{liquid} : The value of c' at rubber state

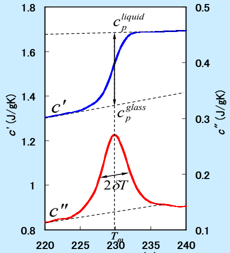


Fig.10 The definition of values used for calculation.

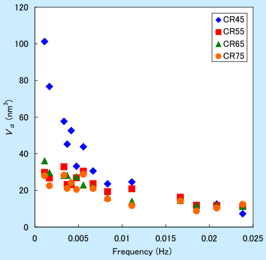


Fig.11 Frequency dependence of V_α for CR series.

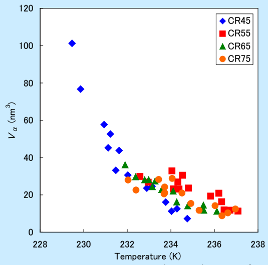


Fig.12 Temperature dependence of V_α for CR series.

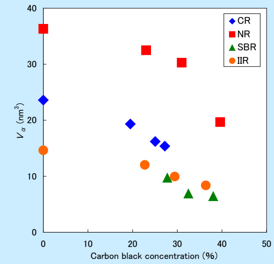


Fig.13 The effect of carbon black concentration on V_α for four rubbers.

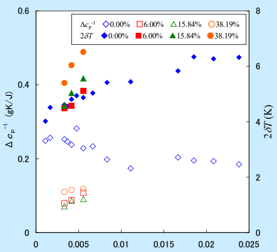


Fig.14 Frequency dependence of Δc_p^{-1} and $2\delta T$ for CR65.

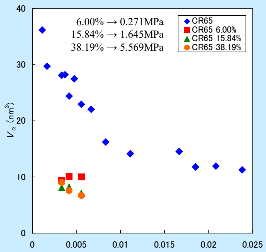


Fig.15 The effect of deformation on V_α for CR65.

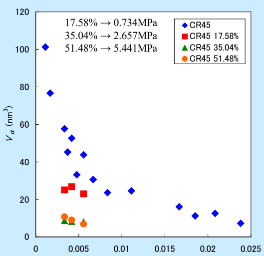


Fig.16 The effect of deformation on V_α for CR45.

Conclusion

Dynamic glass transition and Fragility

◎Frequency dependence of T_g can be fitted reasonably by VFTH equation.

◎VFTH parameters (A, B and T_∞) strongly depend on carbon black concentration.

◎Fragility at T_g can be calculated from T_g and Vogel temperature T_∞.

◎The number of molecular units in a CRR N_α is proportional to fragility at T_g.

Cooperativity

◎The volume of CRR V_α can be calculated from complex heat capacity.

◎V_α increases with frequency and temperature decreases.

◎V_α decreases with carbon black concentration and deformation increases.

◎In case of rubber reinforced by carbon black, rubber has weakly frequency dependence of V_α compare with un-reinforced rubber.

◎In case of rubber under large deformation, rubber has weakly frequency dependence of V_α.

Reference

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