

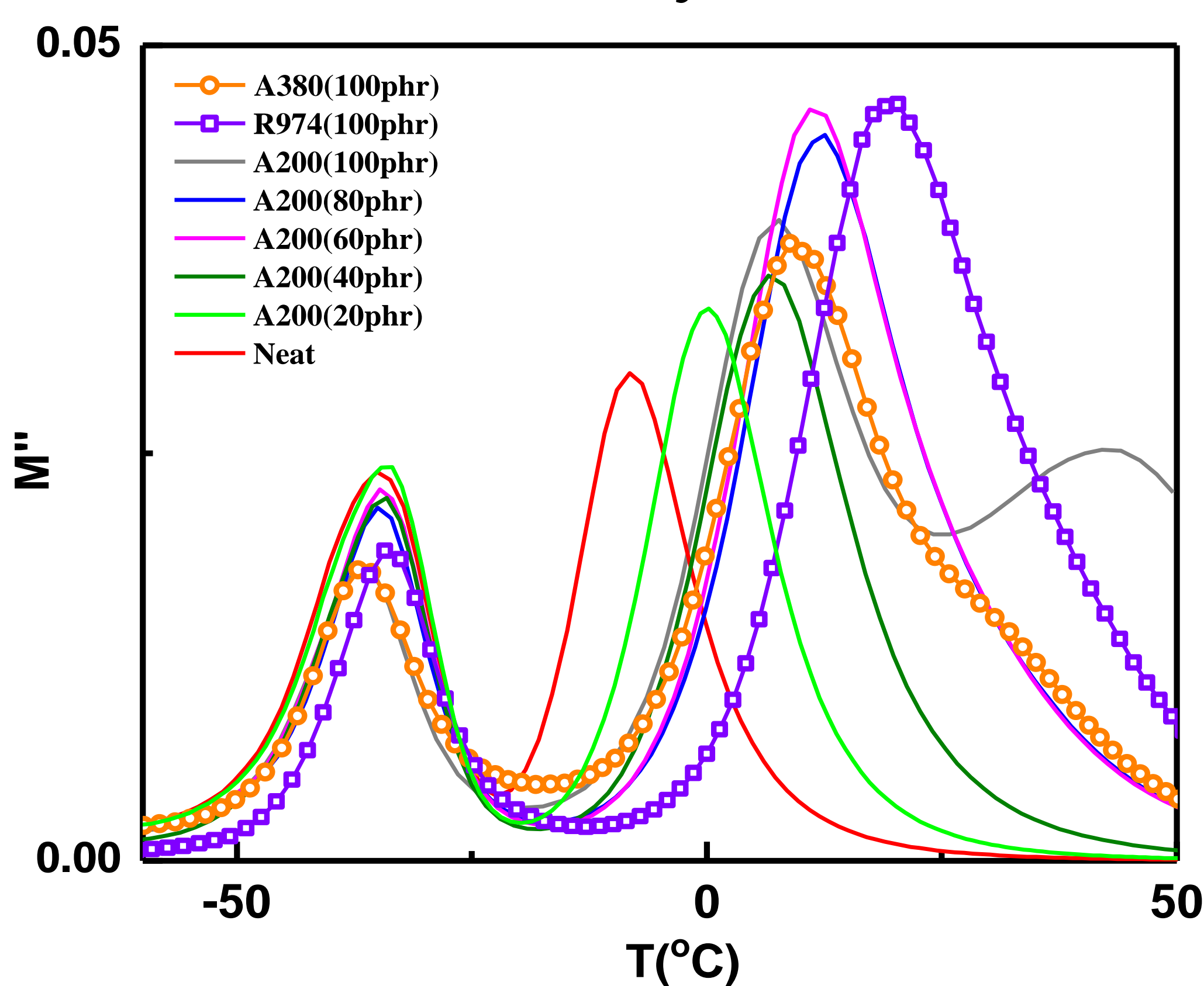
## Introduction

Filled rubber are used in a wide range of applications. Nanoparticles plays an important roles in improving the mechanical properties, but the underline mechanism is far form being well understood. Many works concerning polymer dynamics can be found in literature. Most of them focus on segmental relaxation, giving less attention to global chain dynamics.

In this study, the segment and global chain dynamics of NBR with SiO<sub>2</sub> are investigated by BDS(broadband dielectric spectroscopy ) combined with MDSC(modulated deferential scanning calorimetry ). The effect of loading, surface chemistry(hydrophinic A200 and hydrophobic R974), surface area on molecular dynamics are included.

## Results and Discussion

### 1. Temperature sweep of filled rubber with varying loading, different surface chemistry and surface area

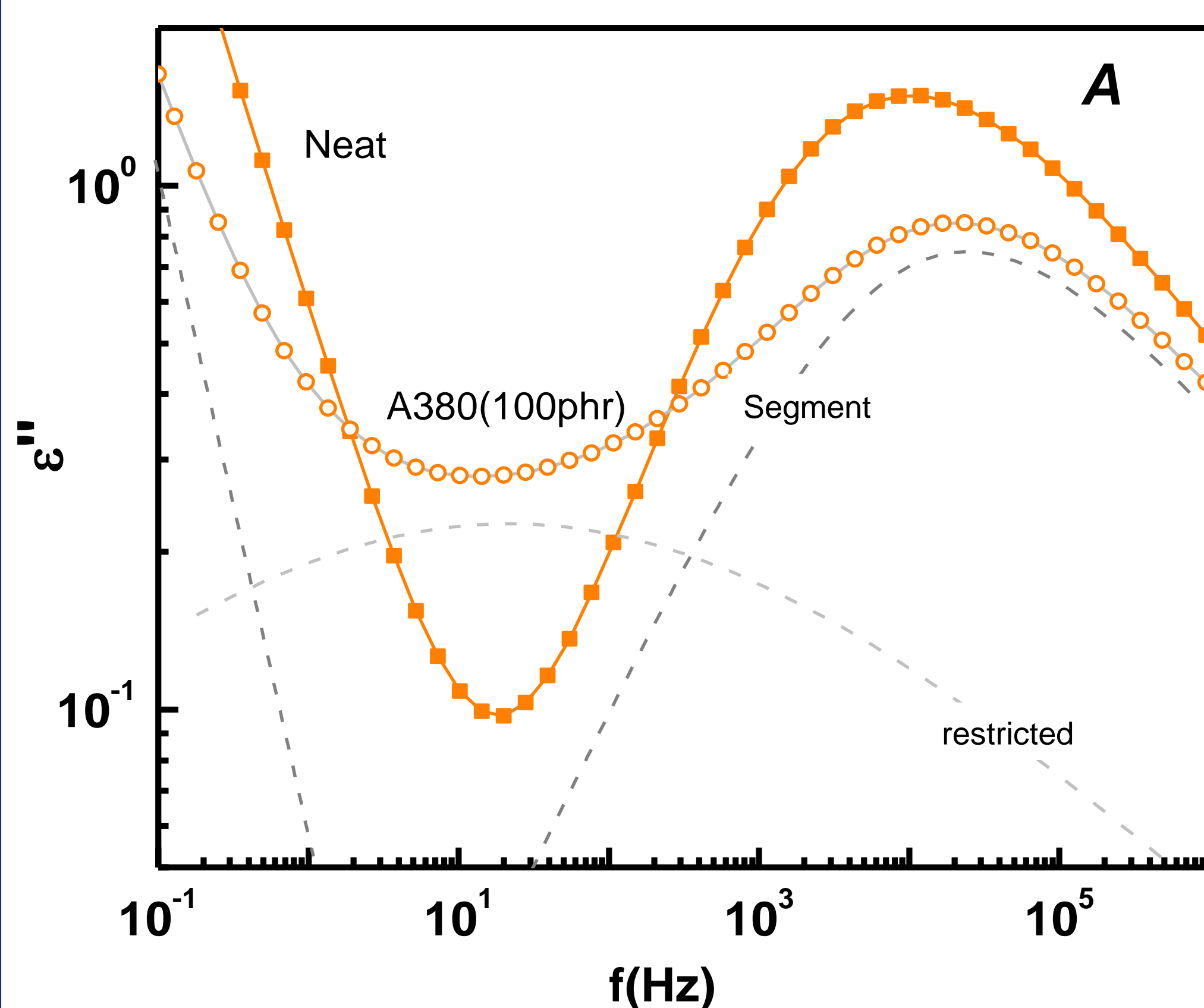


M'' is said to be unaffected by ion conductivity. Loss peak located at lower temperature comes from the segmental relaxation, the other is connected with normal mode process, which related to global chain relaxation.

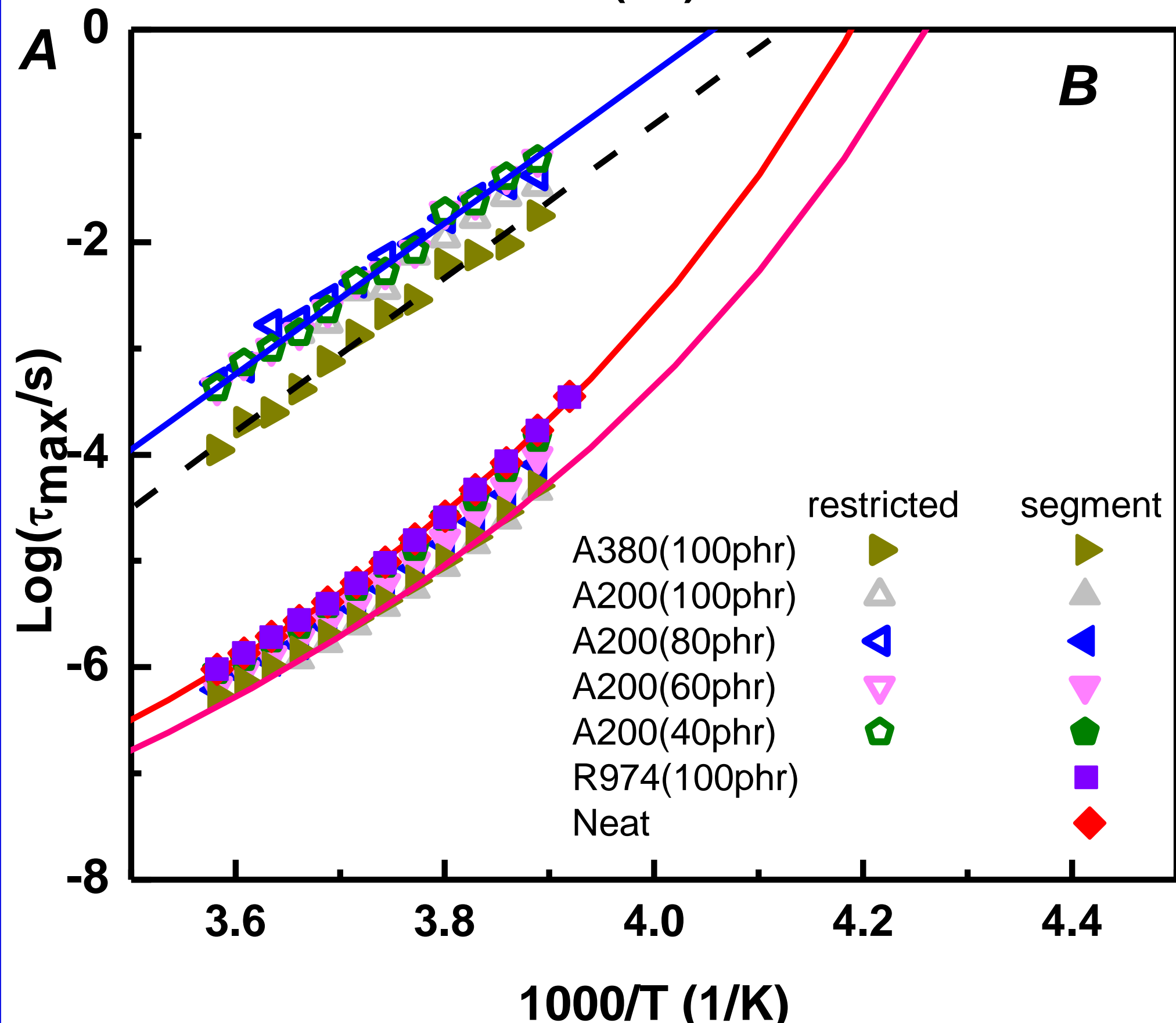
The addition of SiO<sub>2</sub> can reduce both the dynamics of global chain.

$$M'' = \frac{1}{\omega} \frac{1}{\epsilon'' - j\epsilon'} = \frac{\epsilon''}{\epsilon''^2 + \epsilon'^2} + j \frac{\epsilon'}{\epsilon''^2 + \epsilon'^2} = M'' + jM'''$$

### 2. Segmental relaxation



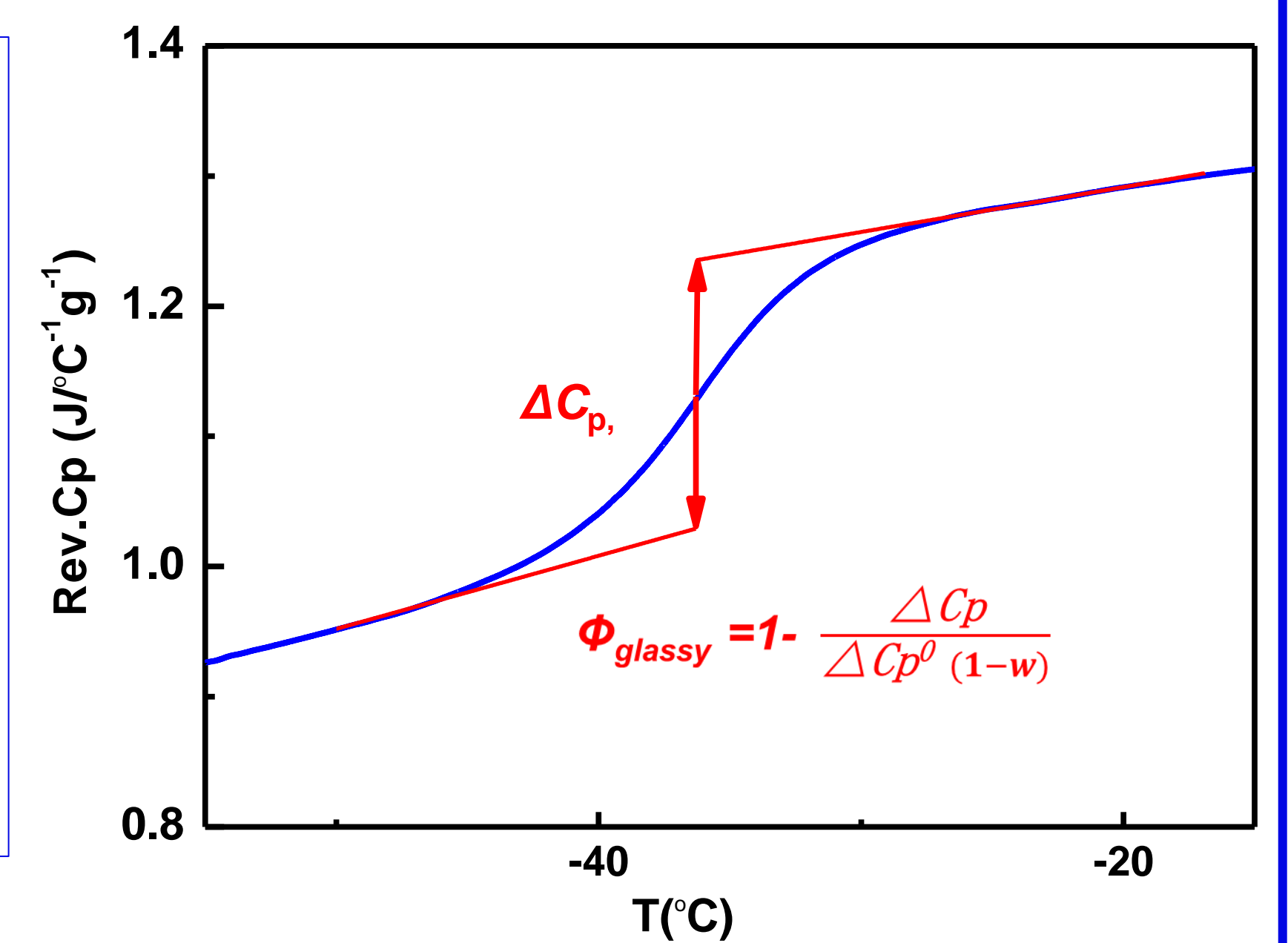
A. Comparison of frequency sweep of neat NBR and 100 phr A380(with surface are of 380 m<sup>2</sup> /g) filled NBR at -8°C. A slower segmental relaxation peak can be observed, which corresponding to the restricted fraction of segment. The dash line represents the result of HN fitting.



B. Maximum relaxation time of all the filled system investigated as a function of temperature. The temperature dependence of segmental relaxation is VFT like, the restricted layer can be fitted with Arrhenius function. The ratio of dielectric intensity of the two relaxation process can reflect the content of restricted segment. The results is listed in the table below.

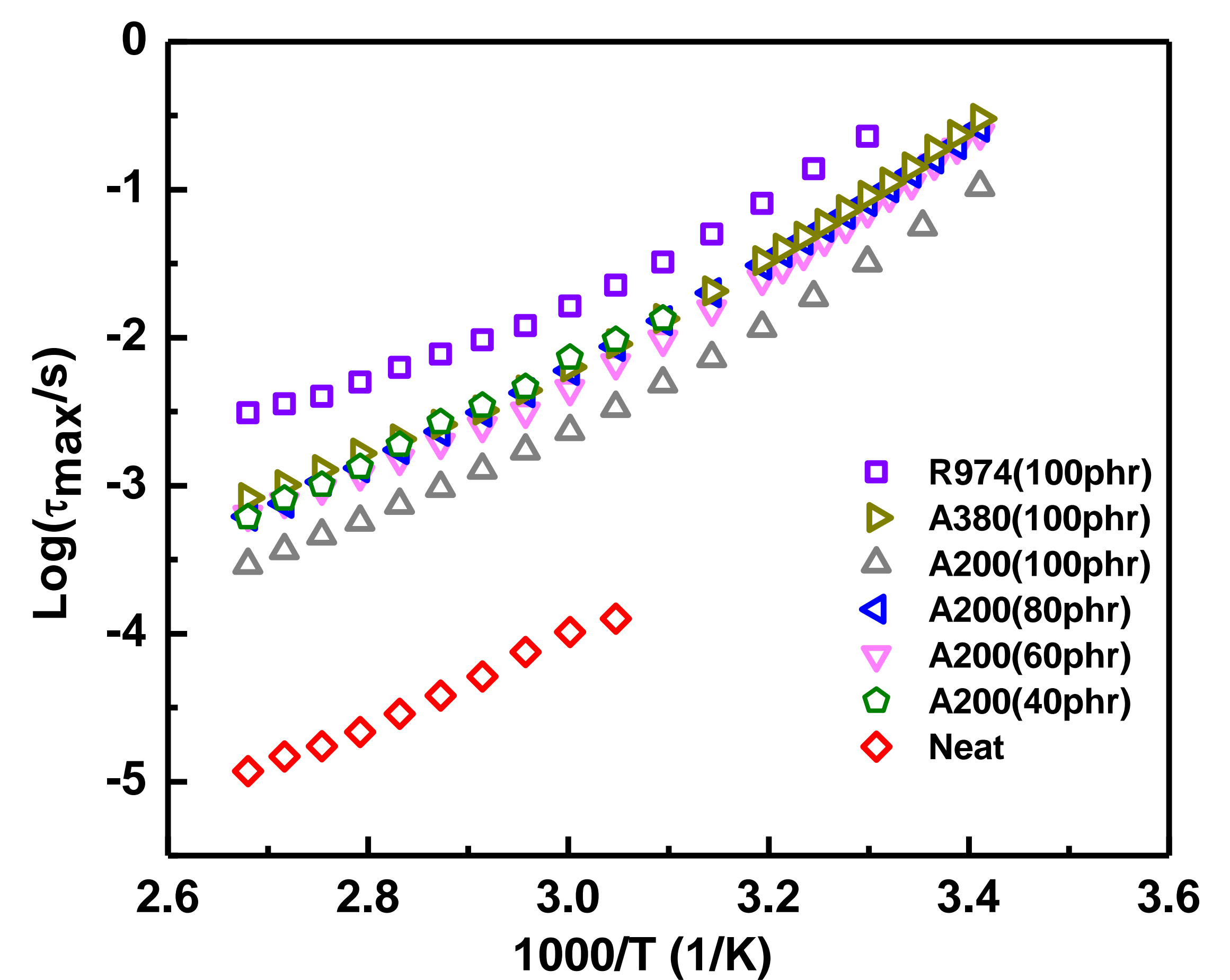
► Reserved capacity of filled NBR with 80 phr A200 as a function of temperature. The glassy layer can not contribute to reserved capacity, so the loss of  $\Delta C_p$  determines weight fraction of glassy layer.

▼ The content of restricted layer and glassy layer determined by MDSC and BDS is listed in the table. Glassy layer detected by MDSC may differ from BDS.



Sample	MDSC		BDS		glassy layer content (%)	glassy layer thickness (nm)	Interparticle distance (nm)
	glassy layer content (%)	glassy layer thickness (nm)	restricted layer content (%)	restricted layer thickness (nm)			
A200(60phr)	3.9±2.4	0.33	3.33	0.28	32.09	2.68	5.21
A200(80phr)	11.4±3.4	0.74	5.09	0.33	35.58	2.32	4.14
A200(100phr)	13.5±2.0	0.71	5.61	0.30	44.26	2.32	3.32
A380(100phr)	18.3±3.9	1.05	21.48	0.65	22.69	0.68	2.73
R974(100phr)	3.5±3.1	0.09	-	-	14.27	0.37	3.32

### 3. Global chain dynamics



Compared with neat rubber, the inclusion of high loading of filler can significantly retard the raption of rubber chains, regardless of surface chemistry and surface area. This result consistent with what observed in temperature sweep.

## Conclusions

### Schematic presentation



1. Hydrophinic SiO<sub>2</sub> (A200 and A380) can reduce both segment and global chain dynamics, Higer surface area will restrict more fraction of segment.

2. The relaxation behavior of restricted layer and global chain do not vary with loading.

3. Hydrophobic SiO<sub>2</sub>(R974) retard global chain relaxation more significantly, compared with A200 and A380.

## References

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