Dynamics Heterogeneity in Silica filled Nitrile Butadiene Rubber

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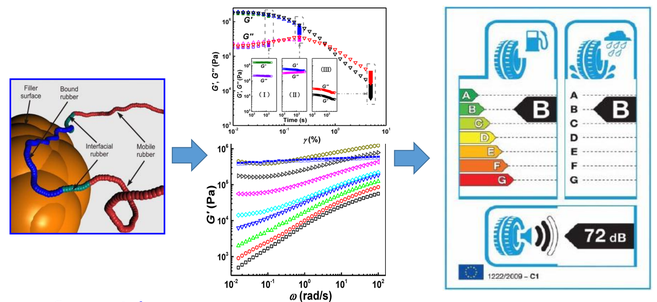
Abstract: Nanoparticles play an important role in improving the mechanical properties of polymers, but the underline mechanism of the impact of nanoparticle on polymer chain dynamics is far from being well understood. Many works focusing on segmental relaxation give contradictory interpretations. The picture about structured interfacial phase does not reach an agreement. Quantifying the filler effect on the heterogeneous polymer dynamics remains still a quite charming and challenging topic.

In present study, dynamics of nitrile butadiene rubber (NBR) filled with silicas of varying loading, specific surface area and surface chemistry are comprehensively investigated. We compare the difference in compounds (before extraction)and filler gels (after extraction) for providing a general understanding of the heterogeneous dynamics of polymer around filler.



Segmental Dynamics *Rheology* *Application*

Results and Discussion

1. Bound Rubber

Table 1. Content of rubber in filler gels

Filler Gel	Content of Rubber (*w* %)	Volume Fraction	Content of Bound Rubber (φ_{BdR})
E-A200(0.15)	28.4±0.6	0.48±0.01	0.17±0.02
E-A200(0.21)	33.1±0.5	0.53±0.01	0.31±0.02
E-A200(0.26)	41.6±1.5	0.62±0.03	0.54±0.03
E-A200(0.30)	40.0±0.8	0.60±0.02	0.66±0.01
E-A380(0.30)	43.9±0.4	0.64±0.01	0.71±0.01
E-R974(0.30)	33.4±0.5	0.54±0.01	0.54±0.02

A200(x), A380(x) and R974(x) are Compounds with A200, A380 and R974. x is volume fraction of filler.

2. Segmental Dynamics: Glassy Layer

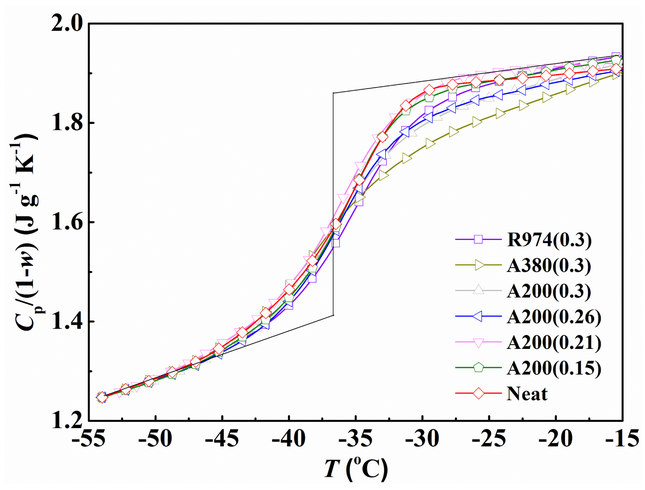


Figure 1. Normalized reserved capacity $C_p/(1\text{-}w)$ of neat NBR and its compounds as a function of temperature *T* in modulated differential scanning calorimetry **(**MDSC) testing.

MDSC allowing detection of relaxation of segments except for those totally immobilized on the surface of filler is employed to investigate polymer dynamics near *Tg*.

Table 2. MDSC results for NBR and the filler gels

Sample	T_g (ºC)	δT_g (ºC)	ΔC_p (J/g/K)	w_{eg} (%)	$w_{eg}\cdot\varphi_{BdR}$ (%)	ξ (nm)
E-A200(0.15)	-30.4± 0.8	12.7±0.9	0.1255	10.5±0.6	1.7±0.1	0.98±0.03
E-A200(0.21)	-33.9±0.8	12.4±1.0	0.1454	11.1±0.7	3.5±0.2	0.87±0.02
E-A200(0.26)	-35.3±0.4	10.7±0.5	0.1749	14.8±1.2	8.0±0.6	0.96±0.04
E-A200(0.30)	-35.7±1.0	11.5±0.6	0.1672	14.6±1.6	9.6±1.0	1.09±0.05
E-A380(0.30)	-36.5±0.4	11.2±0.4	0.1454	23.6±2.5	16.8±1.3	0.99±0.07
E-R974(0.30)	-30.1±0.5	12.3±0.3	0.1655	11.9±0.6	6.4±0.4	0.94±0.03
NBR	-35.1±0.6	9.1±0.5	0.494	-	-	1.18±0.09

The content of glassy fraction is estimated by $w_g=1-\Delta C_p/[(1-w)\Delta C_{p,NBR}]$
w_{eg} is the content of glassy fraction in filler gels
ξ is the size of cooperativity rearrangement regions

2. Segmental Dynamics: Arrhenius-like Restricted Fraction

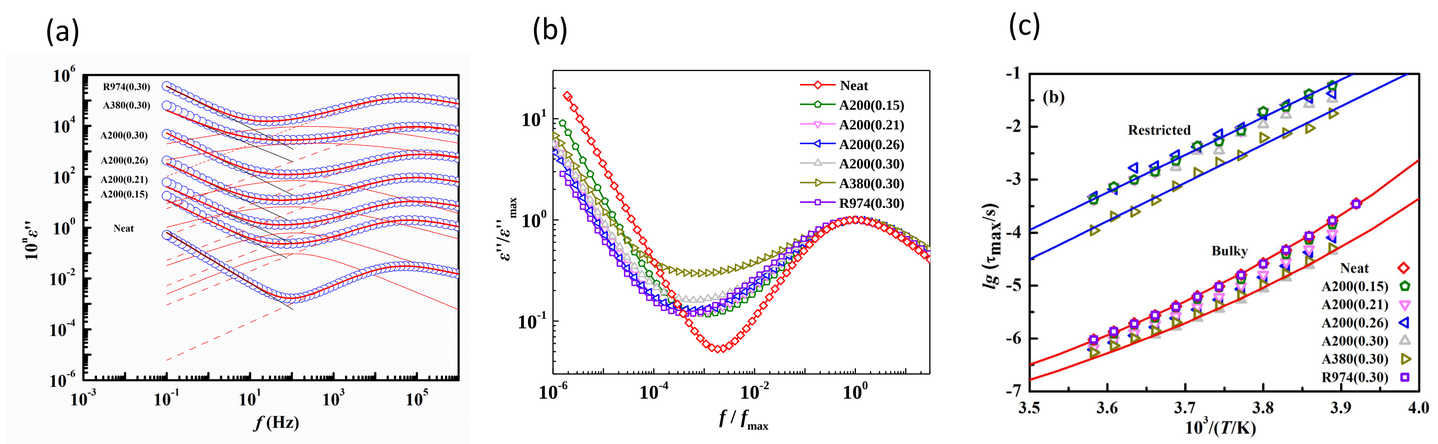


Figure 3. (a) Dielectric loss ε'' as a function of frequency f for neat NBR and compounds at 0 ºC, and (b) relaxation times of bulky segmental relaxation and Arrhenius-like interfacial phase as a function of reciprocal temperature 1/*T*. (c) normalized dielectric loss vs normalized frequency. In (a), the black line, red curve and dash red curve represent the contribution of dc conduction, restricted layer and bulky layer, respectively. In (c), the lines and curves are drawn according to VFT and Arrhenius equations, respectively.

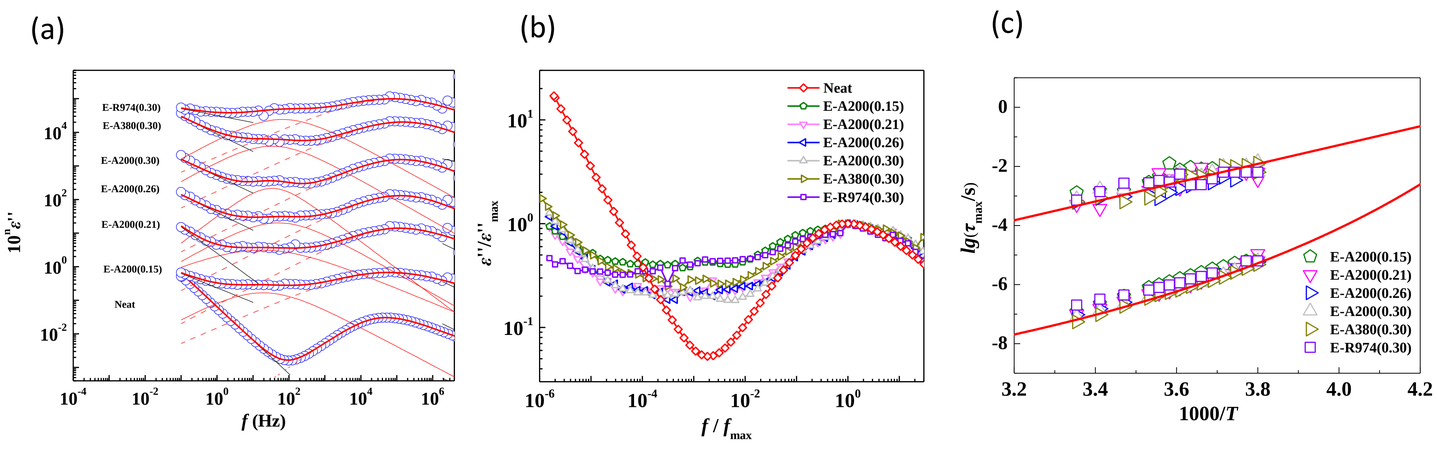


Figure 4. (a) Dielectric loss ε'' as a function of frequency f for neat NBR and filler gels at 0 ºC, and (b) normalized dielectric loss vs normalized frequency. (c) relaxation times of bulky segmental relaxation and Arrhenius-like interfacial phase as a function of reciprocal temperature 1/*T*. In (a), the black line, red curve and dash red curve represent the contribution of dc conduction, restricted layer and bulky layer, respectively. In (c), the lines and curves are drawn according to VFT and Arrhenius equations, respectively.

3. Segmental Dynamics: Highly Restricted Fraction

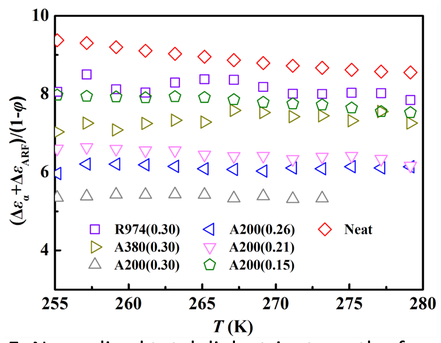


Figure 5. Normalized total dielectric strength of segmental and Arrhenius-like interfacial processes, $(\Delta\varepsilon_\alpha+\Delta\varepsilon_{rs})/(1\text{-}\varphi)$, at different temperature *T* for NBR and its compounds

$(\Delta\varepsilon_\alpha+\Delta\varepsilon_{rs})/(1\text{-}\varphi)$ decreases markedly with increasing A200 loading in compounds, which could be ascribed to the existence of a fraction of highly restricted segments.

The percentage of this highly restricted fraction is estimated according to $w_{hrs}=1-(\Delta\varepsilon_\alpha+\Delta\varepsilon_{rs})/[\Delta\varepsilon_{\alpha,NBR}(1\text{-}\varphi)]-w_g$.

Table 3. Contents and thicknesses of glassy and restricted layers.

Compounds	MDSC		BDS			
	Glassy layer		HRF layer		ARF layer	
	Content w_g (%)	Thickness D_g (nm)	Content w_{HRF} (%)	Thickness D_{HRF} (nm)	Content w_{ARF} (%)	Thickness D_{ARF} (nm)
A200(0.15)	1.05±0.35	0.13	11.25	1.19	3.26	0.29
A200(0.21)	2.65±0.54	0.22	24.85	1.62	3.55	0.19
A200(0.26)	7.91±1.94	0.48	23.39	1.14	5.42	0.22
A200(0.30)	11.45±2.63	0.55	28.75	1.1	6.03	0.2
A380(0.30)	18.00 ±4.42	0.44	0	0	22.92	0.45
R974(0.30)	6.3±1.2	0.37	0	0	4.33	0.24

Conclusions

1.The addition of fillers improves dynamics heterogeneity in nanocomposites.

2.The segments around naonoparticle surface display a gridient mobility from glassy to bulklike. The interfacial structrue depends on filler surface chemistry and specific surface area.

Acknowledgement

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