Dynamics Heterogeneity in Silica filled Nitrile Butadiene Rubber

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Introduction

Nanoparticles play an important role in improving the mechanical properties of polymers, but the underline mechanism of the impact of naonparticle 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 and after extraction for providing a general understanding of the heterogeneous dynamics of polymer around filler.

Results and Discussion

1. Before Extraction

Segmental Relaxation ***Glassy Layer***

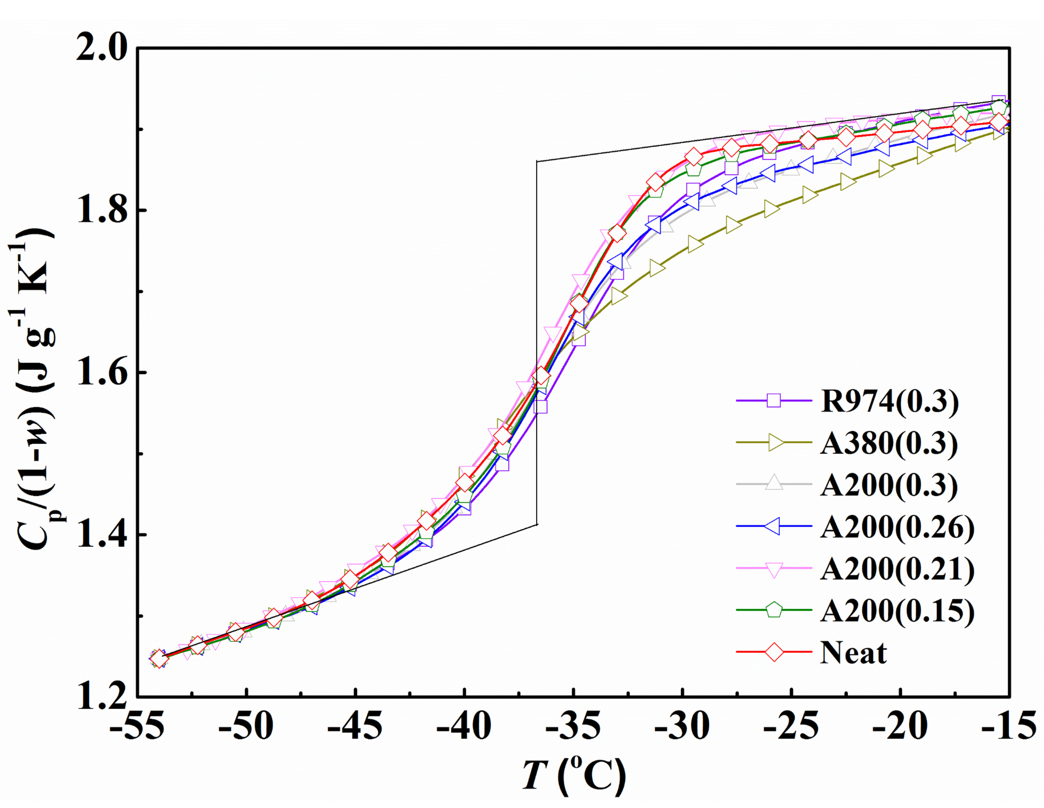
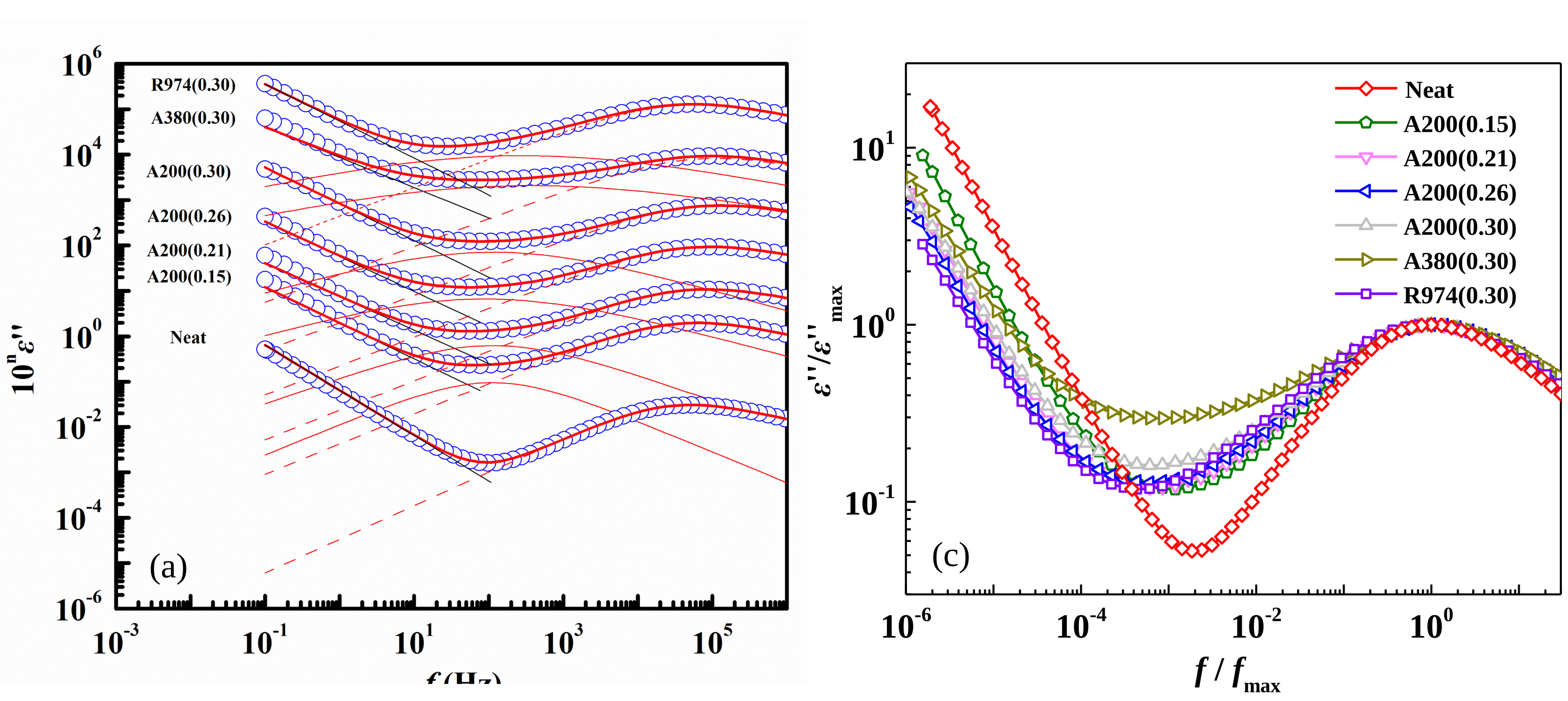


Figure 1. Normalized reserved capacity $C_p/(1-w)$ of filled and unfilled NBR as a function of temperature T.

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

The content of glassy fraction is estimated by $w_g=1-\Delta C_p/[(1-w)\Delta C_{p,NBR}]$.

Segmental Relaxation ***Restricted Layer***



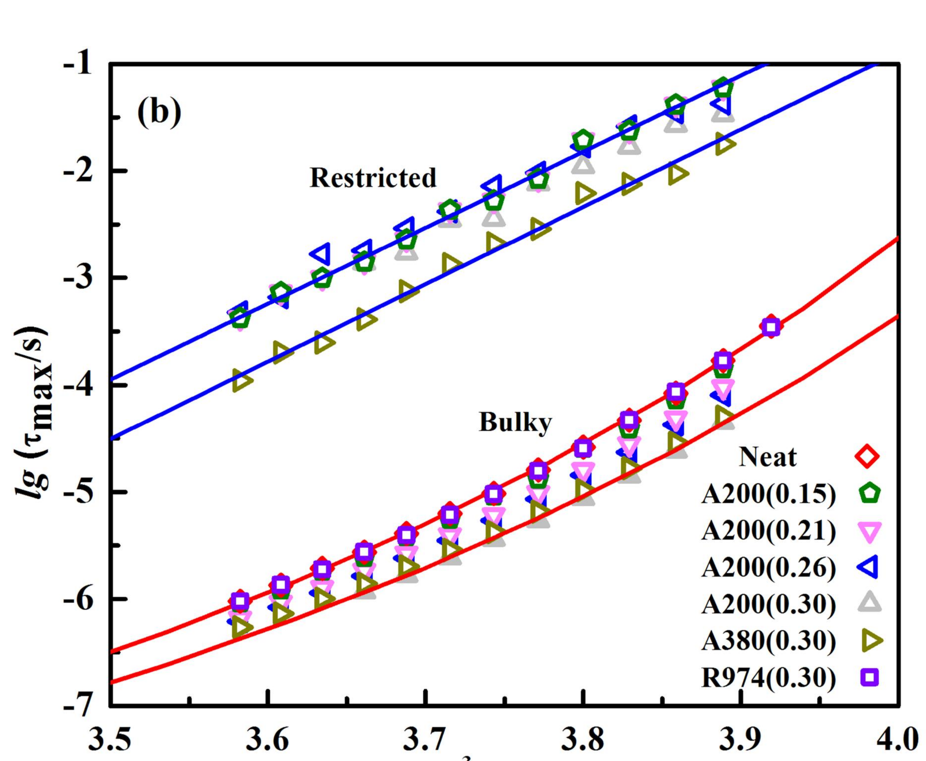


Figure 2. (a) Dielectric loss ε'' as a function of frequency f for net NBR and compounds at 0 °C, and (b) relaxation times of bulky segmental relaxation and Arrhenius-like interfacial phase as a function of reciprocal temperature 1/T. (c) normalized dielectric loss vs normalized frequency. In (a), the black line, red curve and dash red curve represent the contribution of dc conduction, restricted layer and bulky layer, respectively. In (b), the lines and curves are drawn according to VFT and Arrhenius equations, respectively.

The addition of filler can broaden the relaxation spectrum of segmental dynamics. The segments in restricted layer show relaxation time about two orders of magnitude slower than in matrix. The percentage of the Arrhenius-like restricted phase is estimated by $w_{rs}=\Delta\varepsilon_\alpha/[\Delta\varepsilon_{\alpha,NBR}(1-\varphi)]$.

Segmental Relaxation ***Highly Restricted Layer***

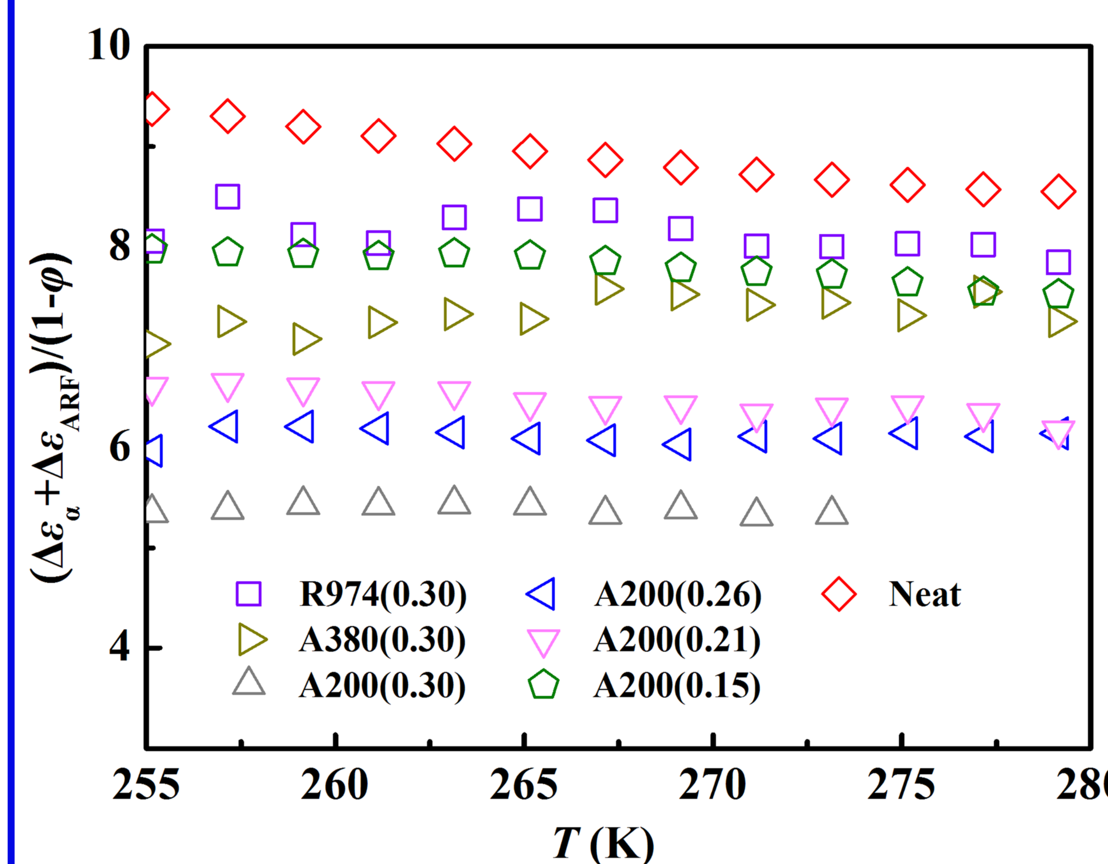


Figure 3. Normalized total dielectric strength of segmental and Arrhenius-like interfacial processes, $(\Delta\varepsilon_\alpha+\Delta\varepsilon_{rs})/(1-\varphi)$, at different temperature T for NBR and its compounds.

$(\Delta\varepsilon_\alpha+\Delta\varepsilon_{rs})/(1-\varphi)$ decreases markedly with increasing A200 loading, 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 $w_{hrs}=1-(\Delta\varepsilon_\alpha+\Delta\varepsilon_{rs})/[\Delta\varepsilon_{\alpha,NBR}(1-\varphi)]-w_g$.

Table 1. The content and estimated thickness of glassy and restricted layer determined by MDSC and BDS.

Sample	MDSC		BDS				
	Glassy layer		Highly restricted layer		Restricted layer		Total thickness of bound layer
	Content w_g (%)	Thickness Δ_g (nm)	Content w_{hrs} (%)	Thickness Δ_{hrs} (nm)	Content w_{rs} (%)	Thickness Δ_{rs} (nm)	(nm)
A200(0.15)	1.05±0.35	0.13	11.25	1.19	3.26	0.29	1.61
A200(0.21)	2.65±0.54	0.22	24.85	1.62	3.55	0.19	2.03
A200(0.26)	7.91±1.94	0.48	23.39	1.14	5.42	0.22	1.84
A200(0.30)	11.45±2.63	0.55	28.75	1.10	6.03	0.20	1.85
A380(0.30)	18.00 ±4.42	0.44	0	0	22.92	0.45	0.88
R974(0.30)	1.92±0.20	0.12	3.8	0.11	5.06	0.28	0.51

2. After Extraction

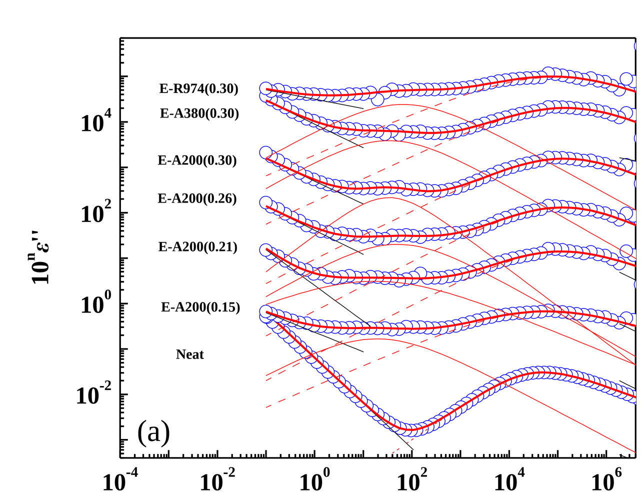


Table 2. The content of bound rubber in compounds after extraction.

Sample	After Extraction (w%)	Before Extraction (w%)	Content of Bound Rubber (w%)
E-A200(0.15)	28.37	70.33	16.71
E-A200(0.21)	33.12	61.16	31.45
E-A200(0.26)	41.55	56.76	54.15
E-A200(0.30)	39.62	49.99	65.64
E-A380(0.30)	43.86	52.27	71.34
E-R974(0.30)	33.43	48.26	53.84

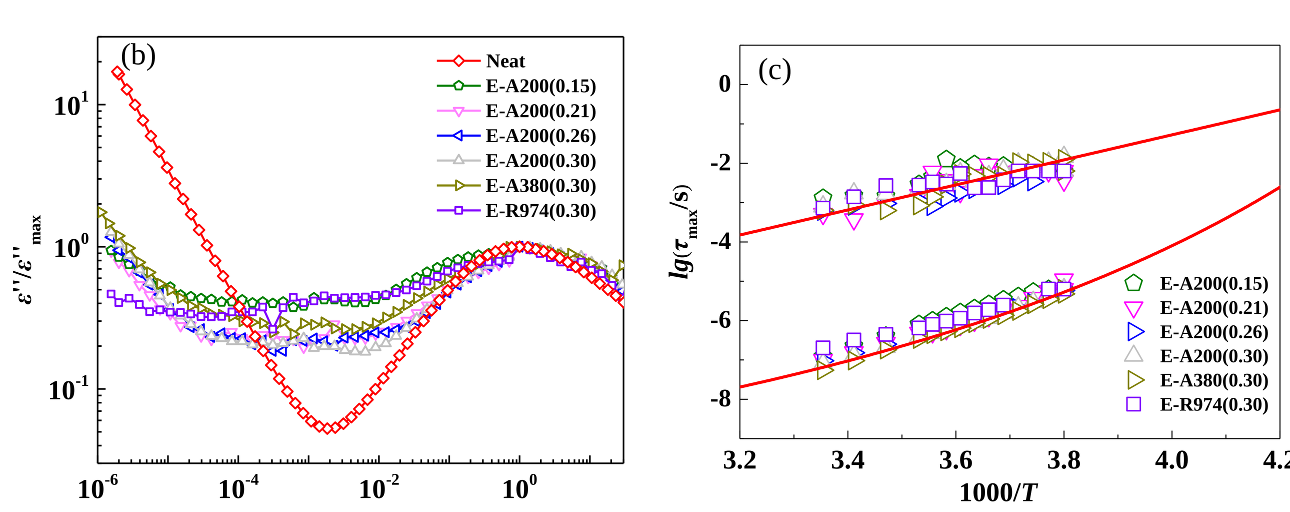


Figure 4. (a) Dielectric loss ε'' as a function of frequency f for net NBR and compounds after extraction and (b) normalized dielectric loss vs normalized frequency. (c) relaxation times of bulky segmental relaxation and Arrhenius-like interfacial phase as a function of reciprocal temperature 1/*T*.

Sample	MDSC				BDS
	Tg	ΔTg	Content of Glassy layer	Correlation to compound before extraction	Ratio of restricted layer and bulky segments
E-A200(0.15)	-30.4± 0.8	12.7±0.9	10.5±0.6%	1.7±0.1%	16.3%
E-A200(0.21)	-35.1±0.8	12.4±1	11.1±0.7%	3.5±0.2%	18.9%
E-A200(0.26)	-36.1±0.2	10.7±0.5	14.8±1.2%	8.0±0.6%	15.8%
E-A200(0.30)	-36.9±1.0	11.5±0.6	14.6±1.6%	9.6±1%	12.7%
E-A380(0.30)	-38.2±0.4	11.2±0.4	23.6±2.5%	16.8±1.3%	18.8%
E-R974(0.30)	-30.1±0.5	12.3±0.3	5.7±0.6%	3±0.4%	16.3%
Neat	-35.1±0.6	9.1±0.5	-	-	-

Table 3. The results of MDSC and BDS testing on compounds after extraction.

The content of glassy layer in compounds after extraction is in agreement with compounds before extraction

The restricted layer is even more obvious in compounds after extraction.

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.

References

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