A Study on Multilayer Microstructure of Nanosilica filled Carboxylated Styrene-Butadiene Rubber

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Abstract

Carboxylated styrene-butadiene rubber/nanosilica (XSBR/A200) composites with an extraodinarily wide range of A200 loading (0~300 phr) have been prepared by absorption mixing and the composites with 0~60 phr A200 have also been fabricated by latex mixing plus extra open-milling methods. Temperature modulated differential scanning calorimetry (TMDSC) was used to investigate glass-transition behavior of composites prepared by both methods while dynamic mechanical tests were carried out to investigate the reinforcement of the compounds prepared by the latex mixing plus extra open-milling methods. TMDSC results show that the content of the glassy layer immobilized in the close vicinity of A200 nanoparticles increases proportionally with silica loading regardless of mixing methods. Comparision between TMDSC and rheology results indicates that there exists an outer absorption layer besides the glassy layer in compounds. The glassy layer corresponds to the XBSR fraction surrounding nanosilica that does not undergo glass transtion. On the other hand, the outer layer is able to undergo glass transition together with the bulky rubber phase but it behaves rigid at high frequencies. Both these two layers contribute to the reinforcement effect. Assuming equivalent A200 spheres of 6.8 nm in radius, equivalent thicknesses of the glassy and outer layers are estimated as 1.0 nm and 1.6 nm, respectively.

Introduction

Glassy layer has been widely measured in many nanoparticle-filled systems using different methods, such as DMA, NMR-H, BDS, TMDSC, FTIR. Unfortunately, none of these methods can be applied to all nanoparticle-filled systems. TMDSC is a relatively common method, but signal in TMDSC tests is not sensitive enough for nanosilica-filled rubber. We used a new absorption mixing method preparing samples to improve signal strength and compared the results with regular open-milling mixing method. High similarity was found between two sample systems. TMDSC gave stable glassy layer information. Rheology behavior at high frequency of nanosilica-filled system was futher researched. Hydrodynamic reinforcement theory was applied to the reinforcement data at high frequency, which generated a concept of outer absorption layer together with glasy layer.

Results and discussion

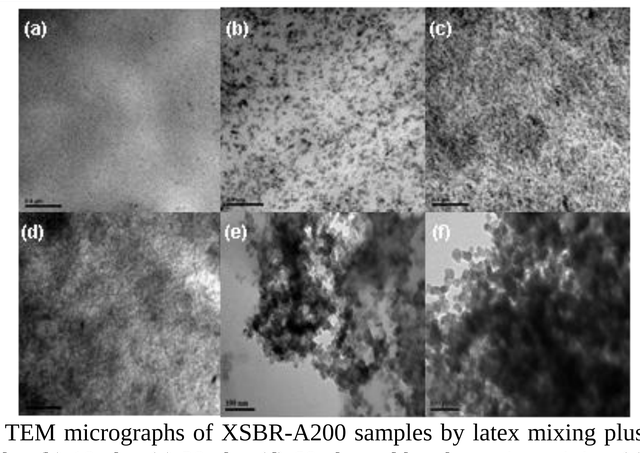

Fig. 1 TEM micrographs of XSBR-A200 samples by latex mixing plus milling (a) 0 phr; (b) 10 phr; (c) 30 phr; (d) 60 phr and by absorption mixing (e) 50 phr; (f) 200 phr

As seen from the TEM graphs in Figure 1, A200 was almost homodispersed in XSBR matrix, which is especially clear in 10 phr XSBR/A200 composite. Particle size was close to the size of primary aggregates of A200 in Figure 1 (b). This indicates few A200 primary aggregates futher aggregated into agglomerates of larger size.

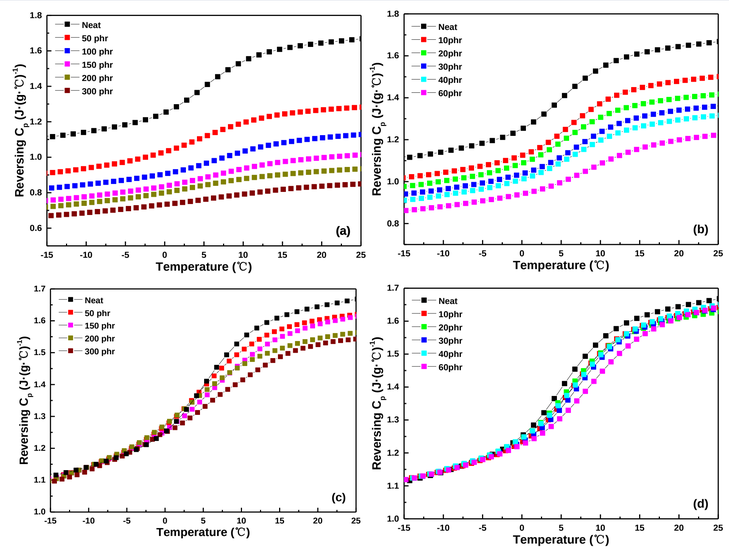

Fig. 2 Reversing capacity curves of compounds (a and b) and their XSBR parts (c and d) prepared by absorption mixing (a and c) and latex mixing plus milling methods (b and d)

Reversing capacity curves of samples from both systems were recorded as shown as Figure 2 (a) and (b). Original curves can be transferred into curves of reversing capacity of XSBR parts in composites shown as (c) and (d). If glassy layer did not exist, there should be no decrease in reversing capacity step of XSBR parts with increasing A200 loading, which was exactly contrary in (c) and (d). We can calculate the amount of glassy layer on the basis of the decrease of reversing capacity step of XSBR .

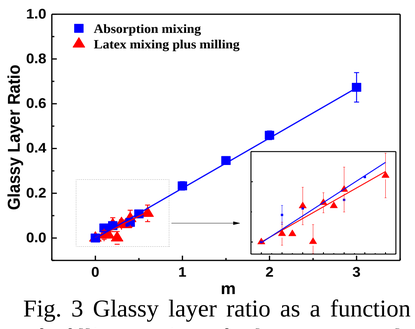

Fig. 3 Glassy layer ratio as a function of filling ratio of the compounds prepared by absorption mixing and latex mixing plus milling methods

Glassy layer ratio can be calculated on the basis of decrease in reversing capacity step of XSBR parts in composites during glass transition region through the following formula:

$$X_{glass} = 1 - \frac{(1+m)\Delta C_p - 0.07887m}{0.37005} \quad (1)$$

Glassy layer ratio as a function of filling ratio of the compounds prepared by absorption mixing and latex mixing plus milling methods was shown as Figure 3. We can see both systems shared a similar slope which can be further transferred into thickness of glassy layer.

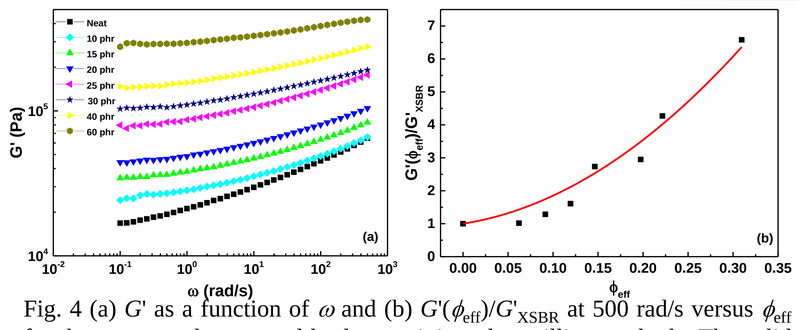

Fig. 4 (a) G' as a function of ω and (b) $G'(\phi_{eff})/G'_{XSBR}$ at 500 rad/s versus ϕ_{eff} for the compounds prepared by latex mixing plus milling methods. The solid curve in (b) is drawn according to Guth-Gold function

Combining glassy layer and practical A200 volume, effective filler volume fraction (ϕ_{eff}) was calculated. $G'(\phi_{eff})/G'_{XSBR}$ at 500 rad/s versus ϕ_{eff} for the compounds prepared by latex mixing plus milling methods was shown in Figure 4 (b). Guth-Gold function fitting generates a factor 1.73 referring to an outer layer behaving rigid at high frequency.

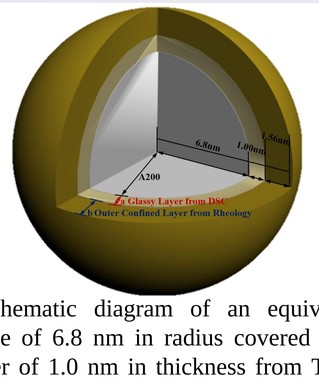

Fig. 5 Schematic diagram of an equivalent A200 nanoparticle of 6.8 nm in radius covered by an inner glassy layer of 1.0 nm in thickness from TMDSC and an outer absorption layer of 1.6 nm from rheology tests

Thickness of glassy layer (a=1 nm) can be calculated according to the slopes in Figure 3 and the following formula:

$$k_{DSC} = \frac{0.94\times[(6.8+a)^3 - 6.8^3]}{2.2\times 6.8^3} = 0.22119 \quad (2)$$

Thickness of outer layer (b=1.6 nm) can be calculated according to Guth-Gold function fitting parameter 1.73 and the formula:

$$k_{Guth-Gold} = \left(\frac{6.8+1.02+b}{6.8+1.02}\right)^3 = 1.73 \quad (3)$$

Schematic diagram of two-layer microstructure of an equivalent A200 nanoparticle was shown as Figure 5.

Conclusion

1. XSBR/A200 composites were prepared by absorption mixing and latex mixing plus milling methods. A stable method to measure the amount and thickness of glassy layer using TMDSC was established.
2. In XSBR/A200 composites inner glassy and an outer absorption layer of 1.0 and 1.6 nm in thickness by the combination of TMDSC and rheology methods, respectively. Immobilized XSBR layer of 2.6 nm in thickness and nanoparticle of 6.8 nm in radius both contributed to the reinforcement effect.

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