

Change in Filler Network and Nonlinear Viscoelasticity of Filled Rubber

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Abstract さまざまなせん断歪で、カーボンブラック充填ゴムの緩和弾性率と電気抵抗を同時測定した。低充填試料では非線形粘弾性に対応する歪範囲でも電気抵抗は変化しなかった。しかし、高充填試料において、線形歪範囲では電気抵抗が平衡状態での値から変化しないが、非線形歪範囲で増加することが明らかとなった。これは、高充填試料中にはカーボンブラック・フィラー網目が存在し、その非線形粘弾性はフィラー網目の破壊によることを明確に示す。

1. Introduction

It is well known that rubber materials filled with carbon black show clear nonlinear viscoelasticity even in moderate strain such as strong strain amplitude dependence of dynamic modulus [1]. In rubber materials, there are various interactions; polymer-polymer, polymer-filler, and filler-filler interactions [2]. The first is so-called entanglement effect [3] and the second filler gel [4]. Due to the third interaction, there may be filler network in filled rubbers. The second interaction is considered to be strong enough. Hence nonlinear behaviors in uncross-linked, filled rubber may come from strain-induced chain anisotropy, disentanglement/re-entanglement, and filler network rupture. However, chain anisotropy may disappear shortly with relaxation of stress. So we should focus our concern on the latter two effects. However, the two effects occur simultaneously. Therefore, we cannot distinguish the one from the other using viscoelastic function such as relaxation modulus. We need another probe.

Polymers are non-conductive materials. However, carbon black (CB) shows high electric conductivity. It is well known that rubbers filled with enough amount of CB show low electric resistivity [5]. This may mean formation of CB-filler network. Therefore, if filler network ruptures in large deformation, electric resistance should increase.

The purpose of this work is to discuss the change in filler network and nonlinear viscoelasticity of uncross-linked, CB-filled rubber by simultaneous measurements of electrical resistivity and relaxation modulus in large shearing deformations.

2. Experimental

2.1 Samples The rubber used was styrene-butadiene copolymer (SBR). CB used was N330 (primary particle size 28 nm). Four rubber samples having 0-50 phr (0-33 wt%) of CB and small amount of additives. All the samples have no cross-linking.

2.2 Methods Relaxation modulus was measured using high-precision Rotational Rheometer RDA-3 (Rheometric Scientific) and disk shaped sample having 19.8 mm diameter at various values of shear strain γ ranged from 0.001 to 1.0. Electrical resistivity was measured using Digital Electrometer R8340A (Advantest). ρ was calculated from the electrical resistance R by $\rho = RA/L$, where A is the sectional area, and L the distance between two parallel plates. Both the relaxation modulus and electric resistivity were measured simultaneously at 353K.

3. Results and Discussion

The unfilled SBR showed linear-nonlinear transition in viscoelasticity at shear strain

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$\gamma=0.1$ due to disentanglement. The upper panels in Figs. 1 and 2 show the relaxation modulus $G(\gamma, t)$ curves for the samples 1 (having 20 phr of CB) and 2 (35 phr of CB) at various shear strains, respectively. The filled SBRs show linear behaviors at very small strains, but show clear nonlinear behaviors at high strains.

The lower panels in Figs. 1 and 2 show the change in electrical resistivity $\rho(\gamma, t)$ observed simultaneously with the measurements of relaxation modulus for the two samples at various shear strains, where broken lines denote the values of electrical resistivity measured before straining $\rho_{initial}$. The value of $\rho_{initial}$ for the sample 1 was very high and almost no change was found in straining, indicating that filler network was not formed in the sample 1. However, much different behaviors in electrical resistivity can be found for the other sample 2 having 35 phr of CB. The sample 2 showed very low values of $\rho_{initial}$, 420 Ωm . In addition, no change of the values of $\rho(\gamma, t)$ was observed in the range of strain where linear behaviors in $G(t)$ were found, but increased with strain corresponding to nonlinear viscoelasticity. Quite similar results have been obtained for the sample having 50 phr of CB, too. The results clearly show that there exist CB filler network in the rubbers having CB of 35 phr or higher, and the nonlinear viscoelasticity for the rubbers is due to rupture in CB filler network.

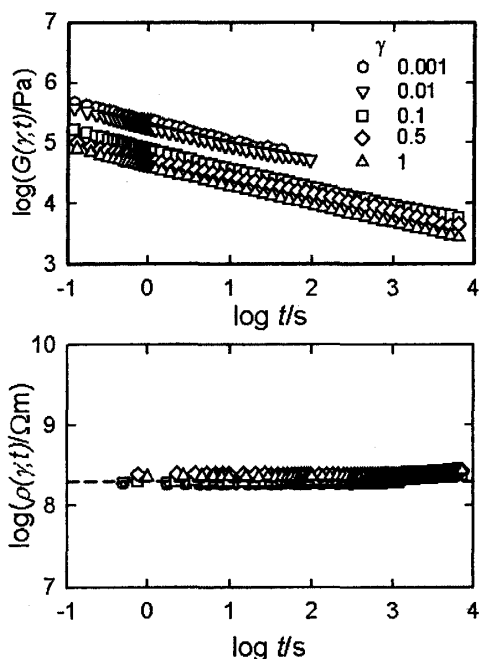


Fig.1 Relaxation modulus and electric resistivity vs. time curves for the sample 1 (20 phr) at various shear strains. $T=353\text{K}$.

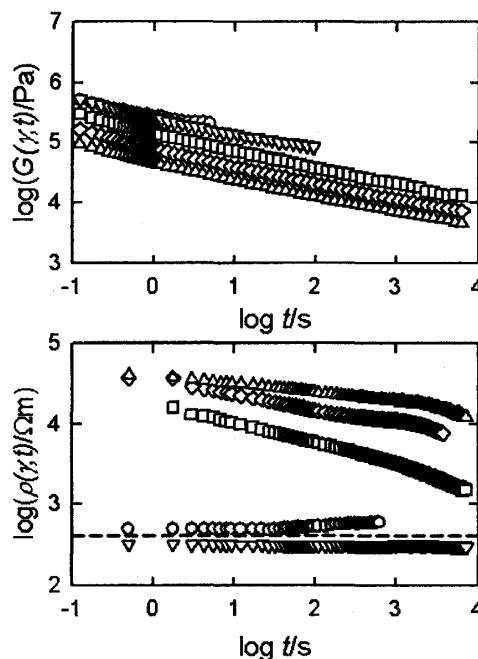


Fig.2 Relaxation modulus and electric resistivity vs. time curves for the sample 2 (35 phr) at various shear strains. $T=353\text{K}$.

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