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LETTER

Simultaneous measurement of rheological and conductive properties of carbon black filled ethylene–tetrafluorothylene copolymer

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Composites composed of carbon black (CB) filled polymers have been widely applied in many areas such as electromagnetic/radio-frequency interference shielding, electrostatic discharge, conductive adhesives for die attachment in electronic packaging applications, and electroactive polymeric sensors in hand prostheses [1, 2]. It is well known that the morphology and properties of filled polymer composites are greatly influenced by the state of filler dispersion [3]. Due to the small size and high specific surface, the filler particles are favorable to form a three-dimensional flocculation structure [4]. Even though scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations can give us a lot of information on structure and morphology involving fillers, they only reflect the dispersion localized within a two-dimensional microscopic site and thereby are easily misinterpreted with respect on the correlation of the information to the real dispersion space and its contribution to the target properties [5, 6].

It is accepted that dynamic rheological measurements are effective for dealing with the structure and morphology of filled polymers as well as the filler dispersion because the structure of samples tested is indestructible under small strain (γ) amplitudes [7]. The rheological properties of highly filled polymer composites may provide essential information about the flocculation structure of the filler that contributes to the physical properties such as mechanical strength, electrical resistivity, and heat conductivity [8]. Much work has been performed on the rheological behavior of various filled polymers. Krishnamoorti and Giannelis [9] observed nonterminal low-frequency rheological behavior in nanocomposites containing layered silicates. Zhang and Archer [10] reported a transition to solid-like response at low oscillation frequencies due to the presence of a filler network in poly(ethyl oxide)/silica nanocomposites.

Simultaneous measurement of rheological and conductive behaviors under γ has been made on CB-filled natural rubbers [11] or vulcanizates [12] to study the carbon black structure inside these materials. It was found that shear moduli and electrical conductivity vary in an approximately similar way as the amplitude of dynamic oscillation increases. In the aforementioned literatures, small strain oscillation was achieved by using spring while the large one is controlled using machine driving or hand wheel. Recently, Pan and Mckinley [13] studied viscoelasticity and conduction behaviors of an electrorheological fluid suspension using simultaneous measurement technique. To our knowledge, few work has been reported to study filled semicrystalline polymers at temperatures above melting point (T_m) using simultaneous measurement of rheological and conductive behaviors.

In a previous paper [14], we examined the conductive behavior of ethylene–tetrafluorothylene (ETFE) copolymer/CB composites and found that the switching characteristic show a reproducible stability at the upper limit of the percolation transition. Here we present some unique results from simultaneous measurements of the dynamic storage modulus (G') and electrical resistance (R) for ETFE/CB melt. It is noted that the modified rheometer allows us to obtain the data of measuring G' and R for ETFE/CB composites in a relative wide strain range in one mode.

The composites were prepared by mixing ETFE (ETFE-750 from DuPont, density 0.942 g cm^{-3}, melting point

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250 °C, and melt flow index 700 g/10 min) and CB (VX_c-605 from Shanghai Cabot Chemical Co., Ltd., particle size 25 nm, density 1.85 g cm^{-3}, nitrogen absorption special surface area 63 m^2 g^{-1}, and dibutyl phthalate absorption 1,480 mm^3 g^{-1}) on a two-roll mill at 280 °C and 60 rpm for 10 min. The blended samples were then thermo-molded at 280 °C and 14.7 MPa for 10 min to form sheet specimens. After being naturally cooled to room temperature, the sheets were cut into discs of 7.9 mm in diameter and 1.2 mm in thickness.

The experimental setup for simultaneous measurements of G' and R is schematically illustrated in Fig. 1. Dynamic rheological measurement was performed on an advanced rheometric expanded system (ARES, Rheometrics Co., USA) in the mode of strain sweep by using a stainless steel parallel-plate geometry. The isothermal dynamic strain sweep was conducted at frequency 10 rad s^{-1} by varying strain γ from 0.002% to 160%. Two thin copper guides were bound to the torque transducer rod and the motor rod, respectively. The weight of the copper guides was too small to influence the measurement accuracy of the rheological parameters. The in-situ resistance change under shear strain was pursued by a computer controlled system based on a digital multimeter (Escort-3146A, Schmidt Scientific Taiwan Ltd., China) connecting to the copper guides. The measurements were performed at 260 °C higher than T_m of ETFE.

Figure 2 shows R as a function of time (t) for the composite containing 13 vol% CB at strain zero, and also with increasing strain. For the composite at strain zero, R decays with t, which indicates an intrinsic resistance relaxation involved in the rearrangement and agglomeration of CB particles in the melt. For the composites upon straining, R drops as the same manner as the intrinsic resistance relaxation at $t < 53$ s (strain $\gamma < 0.007\%$). The R decay becomes slower at $53 \text{ s} < t < 402$ s ($0.007\% < \gamma < 0.4\%$) while faster at $402 \text{ s} < t < 562$ s ($0.4\% < \gamma < 2.5\%$) in comparison with the intrinsic resistance relaxation. On the other hand, R increases dramatically more than 10 orders of magnitude at $t > 562$ s ($\gamma > 2.52\%$), corresponding to a conductor-to-insulator transition. To account for the particular R variation under strain, it seems necessary to invoke the postulate that to some extent there are both structural reformation and breakdown of the percolation network. At very small strains at $t < 53$ s, the structural reformation and breakdown are in balance so that the time dependent R is identical to the intrinsic resistance relaxation. The breakdown process dominates at $53 \text{ s} < t < 402$ s, which decelerates the resistance relaxation. Subsequently, the reformation process dominates at $402 \text{ s} < t < 562$ s, which accelerates the resistance relaxation. The conductor-to-insulator transition might be ascribed to the predominated breakdown of conducting pathways at $t > 562$ s at extremely large strains. The resistance plateau on the upper part of the curve is due to the limited measurement range of the multimeter.

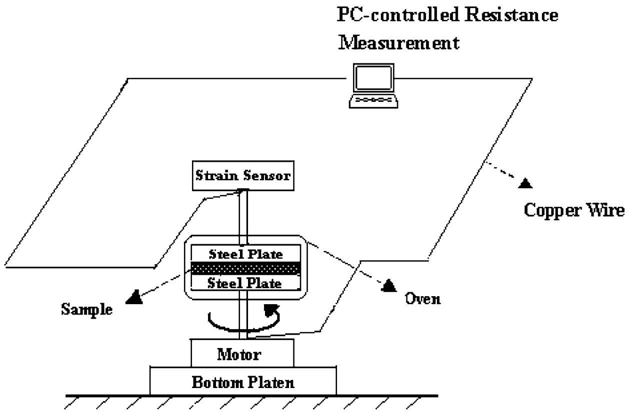

Fig. 1 Scheme of simultaneous measurement of storage modulus G' and resistance R

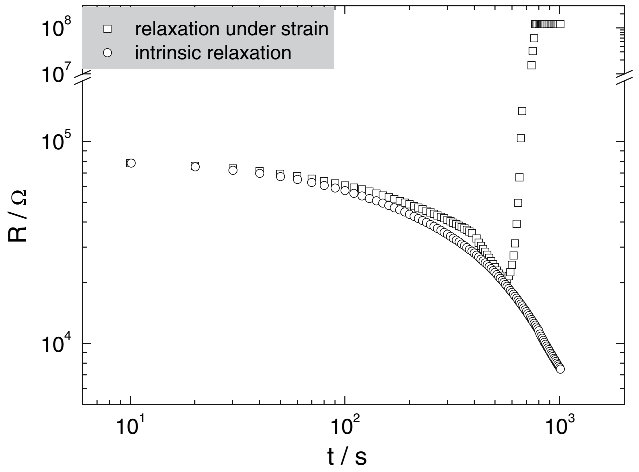

Fig. 2 Resistance R as a function of time t for the ETFE/CB composite containing 13 vol% CB at 260 °C

Figure 3 shows G' and R as a function of γ for the composites containing different amount of CB. It is clear that G' remains constant at small γ while it decreases at large one. On the other hand, R decreases first to a minimum and then increases dramatically, which indicates that the nonlinear viscoelasticity is related to mechanical breakdown of percolation network. The critical strain (γ_c) for the linearity-to-nonlinearity transition of G' is defined as γ_{CG} and that for the conductor-to-insulator transition is defined as γ_{CR}. The values of γ_{CG} and γ_{CR} obtained from Fig. 3 are listed in Table 1, together with the corresponding critical storage modulus (G'_c) and the critical resistance (R_c). It can be seen that γ_{CG} decreases with increasing CB concentration, which is common for filled polymers,

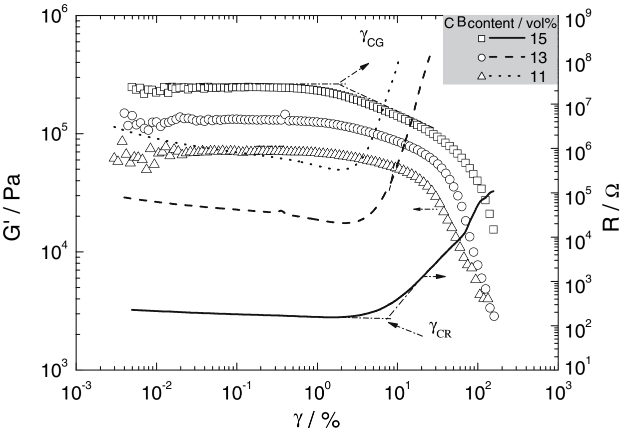

Fig. 3 Storage modulus G' and resistance R as a function of shear strain γ for the ETFE/CB composites containing different amount of CB at 260 °C

Table 1 Critical strains γ_c and corresponding storage modulus G' and resistance R for the ETFE/CB composites at 260 °C

ϕ	11 vol%	13 vol%	15 vol%
γ_{CG} (%)	2.79	2.34	1.85
G'_c (kPa)	79.1	144.9	260.0
γ_{CR} (%)	3.07	5.12	7.22
R_c (kΩ)	45.09	15.96	2.74

especially for the Payne effect of filled elastomers. It is widely accepted that filler agglomeration and network formation are responsible for the reinforcement while deagglomeration and network breakdown account for the rheological nonlinearity with respect to γ [15]. However, the reformation and breakdown of the filler network under γ have been seldom validated experimentally in previously studies. The γ dependence of R in the recent investigation gives the first direct evidence because the variation of conduction only reflects the structural evolution of the percolation network. γ_{CR} corresponding to the conductor-to-insulator transition increases with increasing CB concentration, which is opposite to the variation of γ_{CG}. It is suggested that the dense percolation network at higher CB concentrations is mechanically stable in comparison with that at lower concentrations.

Simultaneous measurement of G' and R was performed to ETFE/CB composites at 260 °C. At small shear strains (γ), G' is almost independent of γ while R decreases with increasing γ. However, G' decrease whereas R increases remarkably at large γ. These phenomena indicate that the mechanical breakdown of percolation network is essential for the nonlinear viscoelasticity. It is interesting that increasing CB concentration causes a decrease in the critical strain (γ_c) for the linear-to-nonlinear rheological transition, and an increase for the conductor-to-insulator transition.

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