Carbon Black as a Self-Diagnosing Probe To Trace Polymer Dynamics in Highly Filled Compositions

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ABSTRACT: A new technique for in situ studies on polymer dynamics in highly filled compositions was developed using carbon black (CB) as a self-diagnosing probe. It is based on the fact that CB particles dispersed in the polymer matrix are easy to aggregate and gradually form three-dimensional networks. Real-time monitoring of the dynamic process of the interparticle network formation was realized by tracing the time dependence of electrical resistivity during isothermal treatments. We investigated the influence of time, temperature, concentration, and the molecular weight of the polymer matrix on the dynamic percolation behavior and concluded that the percolation time when the electrical resistivity starts to decrease drastically is directly related to the zero-shear-rate viscosity of the polymer matrix. We also estimated the terminal relaxation time of polymer matrices from the dynamic percolation curves so as to eliminate the effect of CB concentrations. It is expected that the dynamic percolation measurements may provide an incisive method to study the influence of particle−polymer interactions on the relaxation and viscoelastic properties of a polymer matrix.

Introduction

It has been known for long time that addition of an inorganic filler like carbon black (CB) can remarkably change the polymer dynamics due to interfacial adsorption.[1−3] To study the structure and molecular dynamics of polymer chains, especially the organization of macromolecular aggregates and chain entanglements, rheological measurements are widely used.[4] However, for CB-filled polymer composites, the existence of CB aggregates and CB networks often strongly distorts the viscoelastic behavior in the terminal zone,[5,6] causing various ambiguous controversies. So far, the polymer dynamics surrounding the carbon surface is mostly deduced from theoretical analysis based on NMR, dielectric, FTIR, and other atomic/molecular scattering measurements.

In this research, we attempted to measure the polymer dynamics using CB as a self-diagnosing probe. This is based on the fact that CB particles in molten polymers are easy to agglomerate by Brownian movement. During the movement, the particles are thought to sense their environment; therefore, the mobility of CB should incisively reflect the mobility of the polymer layer surrounding the CB surface. The problem is how to determine the mobility of CB particles. Dynamic light scattering (DLS) has been utilized to determine the diffusion coefficient of colloidal particles.[7−11] However, it is only available for a polymer solution with concentrations of both polymer and probe particles lower than a semidilute regime, which is not the practical case with CB highly filled in the polymer matrix.

We noticed that the agglomeration of CB in polymer melts would finally develop to form three-dimensional networks. At this moment, percolation accompanying drastic changes in electrical resistivity arises. Real-time monitoring of the mobility of particles can thus be carried out by in-situ tracing of the time dependence of electrical properties during isothermal treatment of the composite at molten temperatures. The percolation time is characterized at a certain annealing time when the electrical conductivity starts to increase drastically. We call this phenomenon dynamic percolation. It should be pointed out that percolation is a well-defined phenomenon, and the percolation threshold is universally correlated to a mean contact number of filled particles.[12,13] This characteristic provides an essential access for relating the fraction of the contact number to the percolation time and is therefore able to quantitatively estimate the mobility of a filler in polymer melts.

Experimental Section

Raw Materials and Sample Preparations. Ten kinds of polymers having the characteristics listed in Table 1 were used in this study. CB (Seast 300 CB: diameter 28 nm, N_2 surface area 86 m^2/g, Tokai Carbon Co., Japan) was used as filler. The surface tension of CB was determined by the adsorption heat of CB at equilibrium[14] with values $\gamma^d = 94.5$ mJ/m^2 and $\gamma^p = 3.6$ mJ/m^2 at 20 °C. The surface tension for both polymer and CB will be calculated to an experimental temperature by the relation $-d\gamma/dT = 0.06$, which is a general value for polymers.[15] Each polymer was mixed with a certain amount of CB in a two-roll mill for 10 min at a given temperature (see Table 1). Prior to mixing, both the polymers and the carbon particles were dried at 80 °C for 24 h under vacuum. Films with thickness of about 1.0 mm were compression-molded from the polymer−carbon mixtures at the temperatures listed in Table 1 for 5 min under a pressure of 20 MPa, followed by quenching in water.

Measurements. The time dependence of electrical resistivity was measured using a Keithley 487 picoammeter equipped with a direct current voltage source at a given annealing temperature. The specimen with width and length of 18 × 18 mm was cut from the center area of the molded film and fixed on a glass slide using polyimide tapes. Silver paste was used to ensure good contact between the sample surface and the copper electrodes. The sample was then placed in a temperature-controlled chamber. Nitrogen gas was introduced during measurements in order to prevent oxidation of the samples. The applied voltage for measurements was 1 V.

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Table 1. Characteristics of Matrices Used: Polystyrene (PS), *trans*-Polyisoprene (TPI), High-Density Polyethylene (HDPE), Low-Density Polyethylene (LDPE), Polypropylene (PP), and Poly(methyl methacrylate) (PMMA)

			surface tension[a] (mJ/m^2)			
matrices (manufacturer)	M_w ($\times 10^3$)	density (g/cm^3)	γ^d	γ^p	mixing temp (°C)	press temp (°C)
PMMA1 (Aldrich)	15	1.15	33.2	7.9	150	150
PMMA2 (Aldrich)	89	1.15	33.2	7.9	200	200
PMMA3 (Aldrich)	120	1.15	33.2	7.9	220	220
PMMA4 (Aldrich)	350	1.15	33.2	7.9	240	220
PMMA5 (Aldrich)	996	1.15	33.2	7.9	240	240
PS (Aldrich)	250	1.05	37.0	3.7	200	180
TPI (Kuraray)	140	0.96	29.0	0	160	90
PP (Mitsubishi)	MFR[b] = 5.0	0.90	29.7	0.4	180	170
HDPE (PO, Japan)	MFR = 0.05	0.95	35.7	0	170	140
LDPE (Toso, Japan)	MFR = 0.6	0.92	35.7	0	160	120

[a] γ^d and γ^p are the surface tension of the polymer in dispersive and polar component, respectively. Data obtained from ref 15 at 20 °C. [b] Melt flow rate of polymer; data obtained from manufacturers.

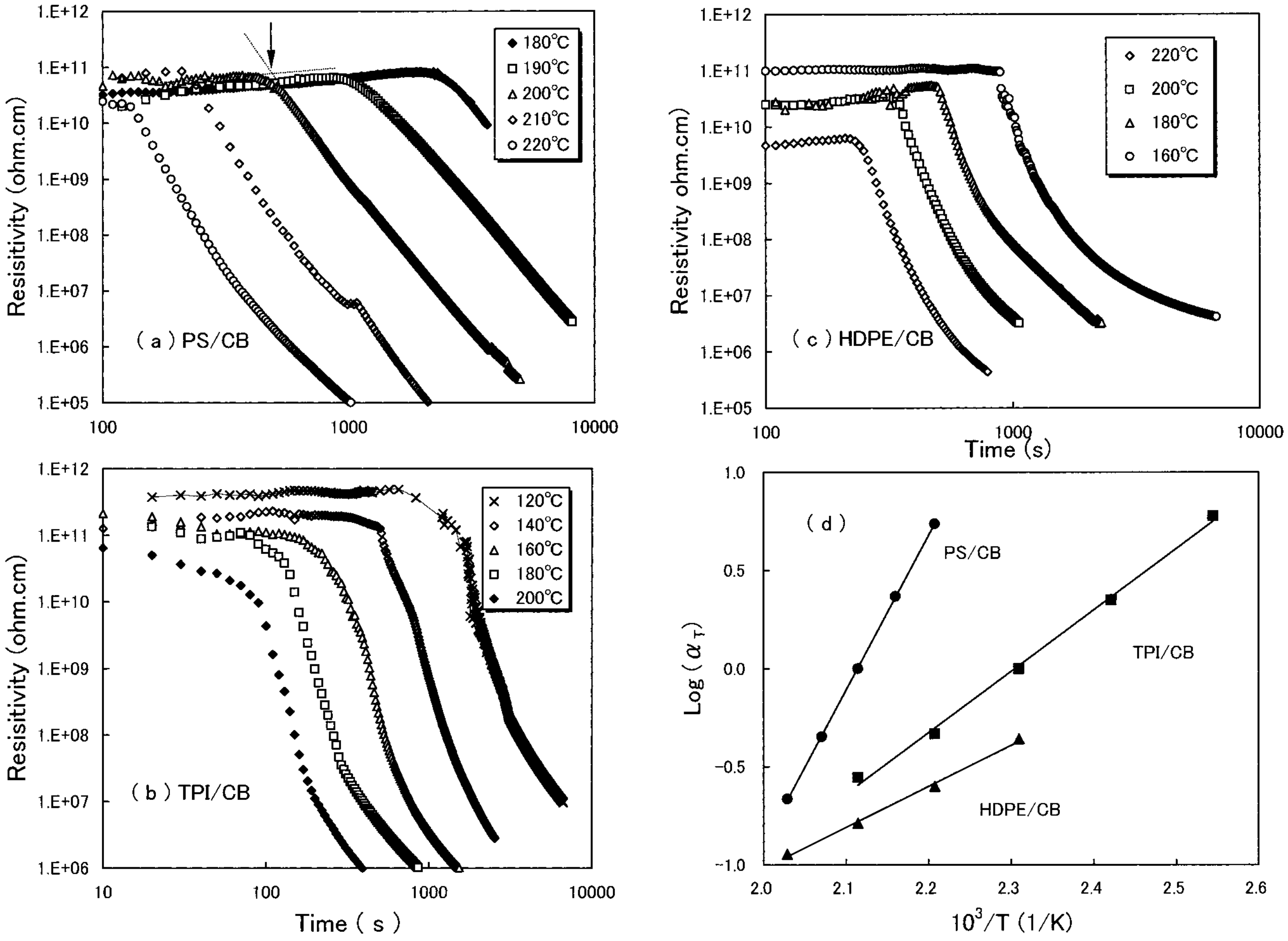

Figure 1. Time dependence of the resistivity for (a) polystyrene (PS)/CB, (b) *trans*-polyisoprene (TPI)/CB, and (c) high-density polyethylene (HDPE)/CB mixtures filled with the same concentration of CB (15 phr) and annealed at various temperatures. (d) Arrhenius plots of the shift factor against annealing temperatures for the above mixtures. The arrow pointing to a cross point of dash lines in (a) indicates the percolation time of PS/CB at 200 °C. This method has been used to determine the percolation time for all of the dynamic percolation curves in the present study.

The zero-shear-rate viscosity, η_0, for various pure polymers was determined by dynamic rheological measurements using a universal dynamic spectrometer (Physica UDS200, Physica Messtechnik) at a sufficiently low shear rate such that the viscosity approaches a constant value. For those that did not show the Newtonian plateau, η_0 was estimated from the Cross equation by extrapolation.[16]

Results and Discussion

Time−Temperature Dependence. Parts a, b, and c of Figure 1 show typical plots of time dependence of the resistivity for polystyrene (PS)/CB, *trans*-polyisoprene (TPI)/CB, and high-density polyethylene (HDPE)/CB mixtures, respectively, annealed at various temperatures. All of the samples were filled with the same concentration of CB [15 phr (per hundred matrix)]. As shown in these figures, the dynamic percolation is a function of time and temperature. The resistivity decreases as the annealing time increases, slightly at first and then rapidly when a critical time is reached; that is, a transition from an insulator to a conductor takes place. The critical annealing time is defined as the

Table 2. Activation Energy (in kJ/mol) of Polymer Viscosity ($E_{\eta 0}$), Percolation Time (E_{tp}), Retardation Time of Percolation ($E_{\tau 0}$), and the Deviation ($E_{tp} - E_{\eta 0}$) for Various CB-Filled Mixtures; the Terminal Relaxation Time Calculated from the Dynamic Percolation Measurements (τ_0) Is Also Listed

mixtures	$E_{\eta 0}$	E_{tp}	$E_{tp} - E_{\eta 0}$	τ_0[a] (test temp, °C)	$E_{\tau 0}$
PMMA1/C	160	170	10	1.62×10^3 (150)	173
PMMA2/CB	158	168	10	1.16×10^3 (220)	178
PMMA3/CB	165	180	15	7.03×10^3 (220)	181
PMMA4/CB	171	182	11	5.92×10^4 (220)	181
PMMA5/CB	171	181	10	1.44×10^5 (260)	182
PS/CB	110	150	40	1.81×10^3 (220)	151
TPI/CB	33	54	21	4.70×10^3 (140)	55
PP/C	37	39	2	1.24×10^3 (180)	40
HDPE/CB	21	36	15	4.32×10^3 (180)	34
LDPE/CB	49	65	16	2.23×10^3 (150)	69
PVDF/CB[b]	49	75	26		

[a] Units of τ_0: seconds. [b] Data from ref 21.

percolation time, t_p, at which the first conductive network is constructed throughout the polymer matrix. With increasing annealing temperature, the dynamic percolation curves shift to a lower percolation time. It is found that, for a given composite, the shape of the dynamic percolation curves does not change with the change in annealing temperature, indicating that the primary characteristic of the conductive network structure does not change with the annealing temperature. This characteristic reminds us that the dynamic percolation curves for the given system could be shifted to form a master curve.

Figure 1d shows Arrhenius plots of the shift factor against the annealing temperature for the respective systems. Despite the different slopes, each system displays a linear Arrhenius plot, suggesting that the effect of annealing temperature can be converted to that of annealing time. From the slope of the plots, the activation energy is calculated to be 150, 54, and 36 kJ/mol for PS/CB, TPI/CB, and HDPE/CB composites, respectively.

Time−Temperature−Concentration Dependence. The CB concentration dependence of the dynamic percolation for low-density polyethylene (LDPE)/CB, polypropylene (PP)/CB, and poly(methyl methacrylate) (PMMA4)/ CB mixtures is presented in Figures 2a, 3a, and 4a, respectively. It is clear that the percolation time decreases with increasing the CB concentration while the shape of the curves remains similar for the respective systems. Figures 2b, 3b, and 4b show their Arrehenius plots of the percolation time against the annealing temperature at various CB concentrations. Here, the percolation time was determined at an inflection point of the resistivity vs time curves. (See the indicated arrows. We have noticed that the percolation time determined from this approach is well reproducible among different samples within an error of 5%.) A family of parallel straight lines for each system is obtained, suggesting that the activation energy of the dynamic percolation is not dependent on the CB concentration. Accordingly, it is possible to obtain a reduced dynamic percolation curve for a given system by time−temperature−concentration superposition.

To compare the dynamic percolation results with viscoelastic behavior in the terminal zone, zero-shear-rate viscosity of pure polymer matrices were measured. Table 2 summarizes the activation energy of zero-shear-rate viscosity and the activation energy of the percolation time for various composite systems. The activation energies of the viscosity for various pure polymers were determined at the same temperature range of dynamic percolation measurements. One can find that the two activation energy values are close to each other for a given system. The result strongly indicates that the dynamic percolation is related to the mobility and the structure of polymer matrix. It shows that the contact process between two CB particles can be equivalent to the excluding process of polymer molecules between two particles; thus, the mobility of CB particles in the matrix could reflect the mobility of the polymer layer between CB particles. Since the particle−particle interaction force is very weak, the shear stress and shear rate in the polymer melts are so weak that the movement of the polymer layer between CB particles can be regarded as a state of zero-shear rate.

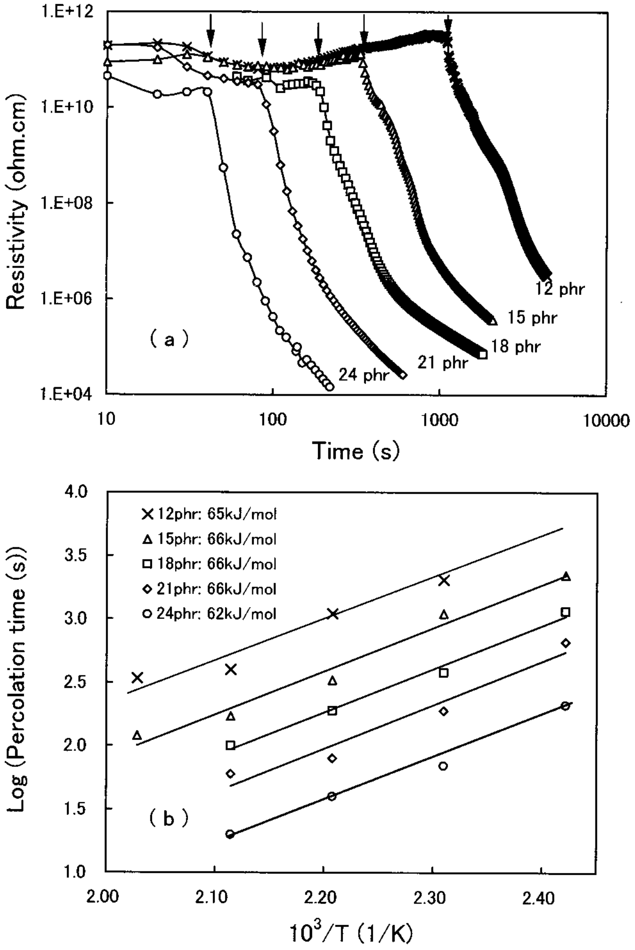

Figure 2. Dynamic percolation of LDPE/CB with various CB concentrations: (a) measured at 180 °C; (b) Arrhenius plots of the percolation time.

It is worth noting that for most composites filled with Seast 300 CB the activation energy of the percolation time is about 10−20 kJ/mol higher than that of viscosity. This should be mainly attributed to the difference between the mobility of pure polymer melts and the mobility of those filled with CB. Because of the thermodynamic interactions between the CB surface and the polymer matrix, generally, the polymer chains are absorbed on the CB surface, resulting in changes in the molecular dynamics of polymer chains.[1−3,17] The increase in the activation energy of the percolation time might reflect the restricted mobility of polymer molecules (see Table 2). Besides, we should also point out

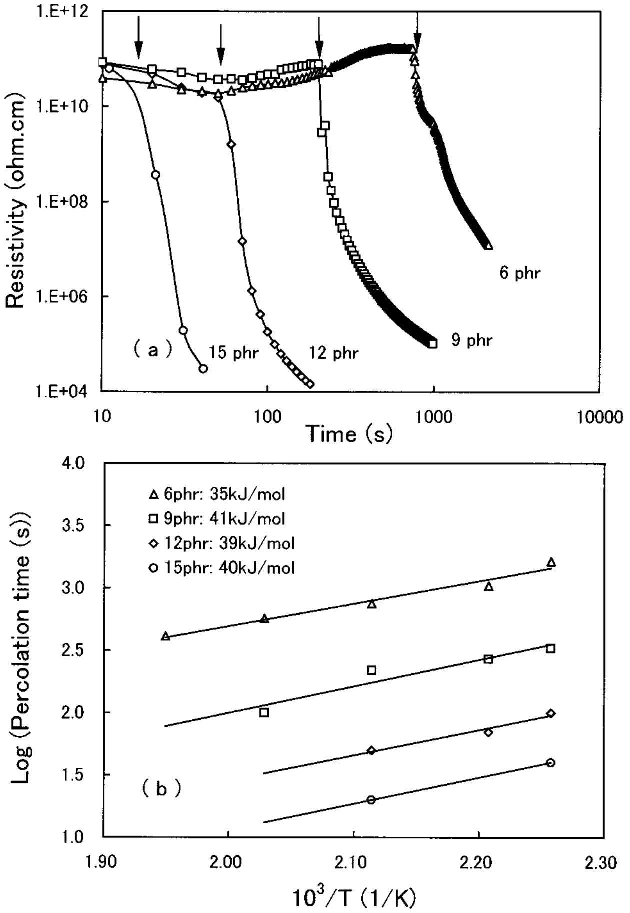

Figure 3. Dynamic percolation of PP/CB with various CB concentrations: (a) measured at 200 °C; (b) Arrhenius plots of the percolation time.

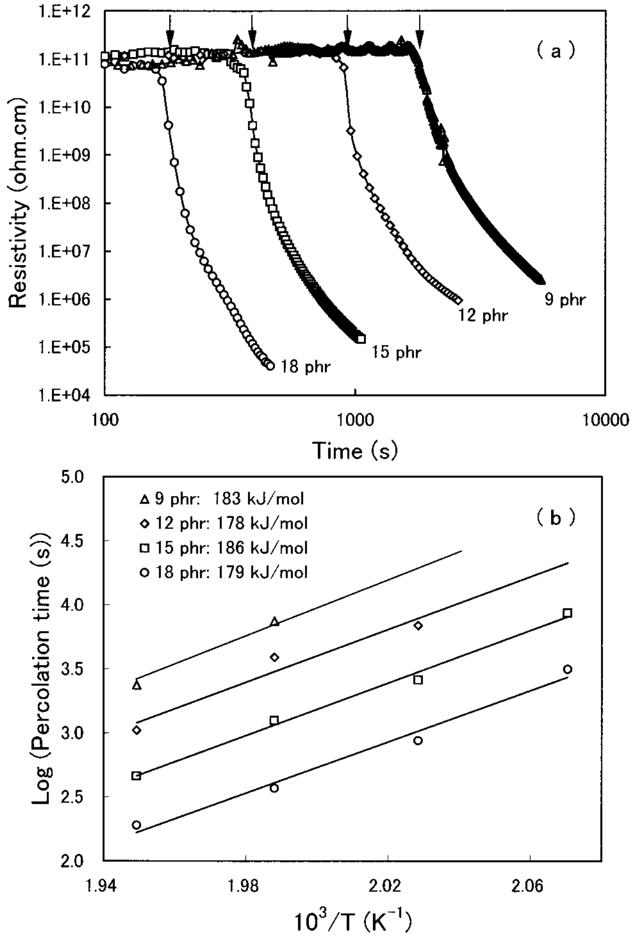

Figure 4. Dynamic percolation of PMMA4/CB with various CB concentrations: (a) measured at 240 °C; (b) Arrhenius plots of the percolation time.

that for some polymers like PS the temperature dependence of viscosity (or chain dynamics) follows the WLF form, not the Arrhenius form; therefore, the activation energy obtained is only an apparent form. A deviation may arise from the different measurement approaches.

Effect of Molecular Weight. Five types of PMMA with molecular weights of 15 × 10^3, 89 × 10^3, 120 × 10^3, 350 × 10^3, and 996 × 10^3 were used as matrices. They are designated as PMMA1, PMMA2, PMMA3, PMMA4, and PMMA5, respectively. The time–temperature–concentration dependence of the dynamic percolation for these PMMA/CB mixtures was investigated. A comparison in the dynamic percolation curves among these systems is presented in Figure 5a for mixtures filled with 15 phr CB and annealed at 220 °C. From these curves, one can observe that (1) the percolation time increases with increasing the molecular weight of PMMA under the same measuring conditions, (2) the shape of the dynamic percolation curves does not change a lot, and (3) the activation energy of the percolation time is in a normal range from 168 to 182 kJ/mol for mixtures with different molecular weight of PMMA matrices (see Table 2). It should be noted that a fluctuation in the dynamic percolation behavior might correspond to a different interfacial adsorption behavior for polymers with different molecular weight.[3]

Since the zero-shear-rate viscosity is directly related to the molecular weight of a polymer, the increase in the percolation time with increasing the molecular weight can be considered as an effect of increasing polymer viscosity. Figure 5b shows the relationship between the percolation time and the zero-shear-rate viscosity. Two groups of data are presented. One is the influence of PMMA molecular weight. The other is the influence of measuring temperature. As shown, all of the data are well correlated, suggesting that the influence of molecular weight on the percolation time has the same effect as the influence of temperature in terms of viscosity. These results further confirm the conclusion that the percolation time is directly related to the zero-shear-rate viscosity of polymer matrix.

A Terminal Relaxation Time. The terminal relaxation time, τ_0, is a parameter essential for quantitative estimation of polymer dynamics. According to definition,[4] it is a measure of the time required for internal stresses of polymer melts to relax during an annealing process and also of the time required to attain steady-state flow under constant stress. In the present case, the stress comes from Brownian force driving CB particles to agglomerate. τ_0 is related to the zero-shear-rate viscosity η_0 in a formula as[18]

$$\tau_0 = c\frac{\eta_0}{kT} \qquad (1)$$

where c is a constant relating to the entanglement molar mass and the distribution of the molecular weight of the polymer matrix. T is temperature, and k is Boltzmann's constant.

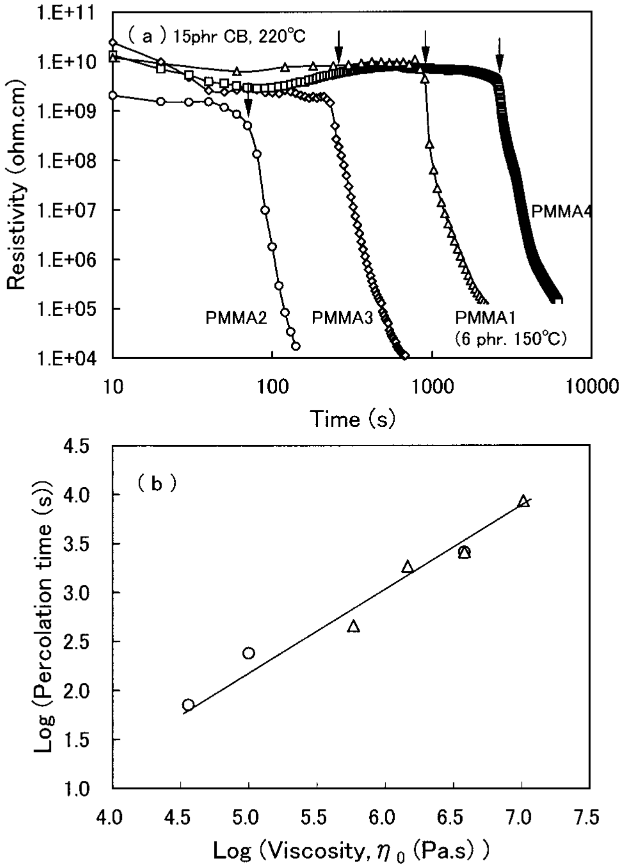

Figure 5. (a) Effect of molecular weight of PMMA on dynamic percolation for PMMA/CB (15 phr CB, 220 °C). (b) Effect of PMMA viscosity on the percolation time: (○) influence of molecular weight for PMMA/CB (15 phr CB, 220 °C); (△) influence of temperature for PMMA4/CB (15 phr).

Kinetic analysis of CB agglomeration[11,19] in polymer melts has shown that τ_0 can be calculated from the following equations:[20]

$$P(t_p) = P(\infty) - (P(\infty) - P(0)) \exp(-t_p/\tau_0) \qquad (2)$$

where

$$\frac{P(t_p)}{P(\infty)} = \frac{\Delta g^* R}{3K} \frac{1-\phi}{\phi} \qquad (3)$$

Here, $P(0)$ is the fraction of contact CB particles at $t = 0$, $P(t_p)$ at $t = t_p$, and $P(\infty)$ at equilibrium states. ϕ is the volume fraction of spherical CB particles with a radius of R. Δg^* is a "universal value" relating to the total interfacial free energy between CB and a polymer at equilibrium percolation. K is the interfacial energy per unit area, which can be calculated from the equation given in ref 15:

$$K = \gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p}$$

where subscript 1 indicates a CB particle and 2 a polymer, while d and p represent the dispersive and polar components of the surface energy of CB, respectively. A detailed derivation of these equations can be found in our previous paper.[20]

The terminal relaxation time τ_0 was estimated as follows. The fraction of the number of particles in contact at percolation time, $P(t_p)$, was calculated from eq 3, where the interfacial free energy, K, was determined by eq 4 using the data presented in Table 1. Δg^* is 5.1×10^4 J/m^3, which has been determined previously.[21] The percolation time dependence of $\ln(1 - P(t_p)/P(\infty))$ for LDPE/CB and PMMA4/CB composites is shown in Figures 6 and 7, respectively. A linear relationship was found for both systems, confirming that eq 2 sufficiently agrees with the experimental results. It is also observed that some data at high percolation time deviated from the straight line, as indicated by an arrow in Figure 6. This may be ascribed to the first approximation assumption of eq 2.

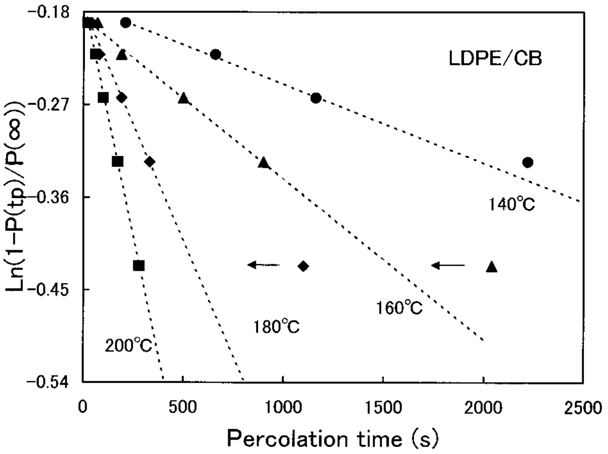

Figure 6. Determination of the terminal relaxation time for LDPE/CB.

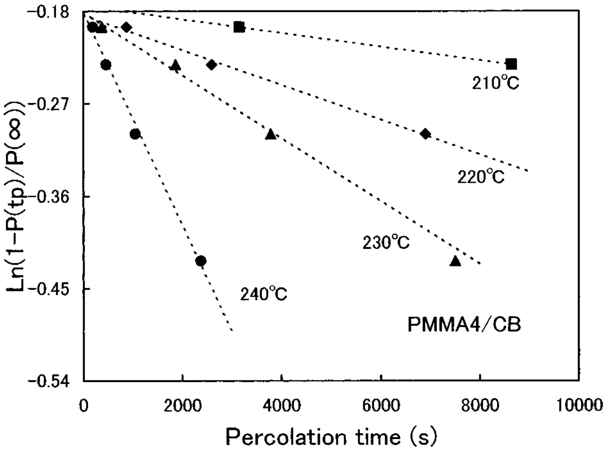

Figure 7. Determination of the retardation time for PMMA4/CB.

τ_0 can be calculated from the reciprocal of the slope value. The data for various polymer composites at a given temperature are listed in Table 2. Obviously, τ_0 is no longer dependent on CB concentration but dependent on temperature and molecular weight dependence. As shown in Figures 6 and 7, the slope value increases with the increasing annealing temperature, suggesting a decrease of τ_0 with temperature. The activation energy of τ_0 for various systems is presented in Table 2. One can find that the activation energy of τ_0 is close to the activation energy of η_0 and the percolation time t_p. Figure 8 shows the terminal relaxation time of PMMA/CB as a function of PMMA molecular weight measured at 220 °C. It is found that τ_0 is directly correlated to the molecular weight of PMMA as $\tau_0 \sim M_w^{3.46}$, which is the same as the result of rheological measurements for nonfilled polymers.[4]

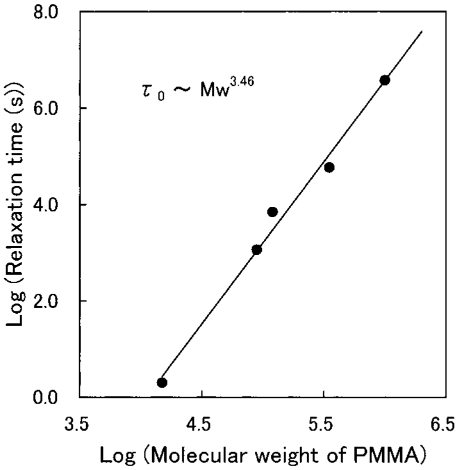

Figure 8. Terminal relaxation time for PMMA/CB mixtures as a function of PMMA molecular weight measured at 220 °C.

Conclusions

The dynamic process of CB network formation for various CB-filled polymer composites was investigated by real-time tracing of the time dependence of electrical resistivity during isothermal treatments at molten temperatures. It was found that the dynamic percolation is a function of time, temperature, filler concentration, and molecular weight of polymers. For a given system, the dynamic percolation curves influenced by these factors could be reduced to form a master curve since their shapes remain similar. The activation energy of the percolation time was found close to the activation energy of the zero-shear-rate viscosity of a polymer, irrespective of CB concentration, molecular weight, and chemical composition of the polymer matrix, suggesting that the mobility of CB is indeed controlled by the bulk mobility of polymer layer surrounding CB particles. We confirmed that the percolation time is directly related to the zero-shear-rate viscosity of polymer matrix.

The terminal relaxation time of polymer matrices, which is independent of CB concentrations, was also determined on the basis of theoretical analysis of the dynamic percolation behavior.

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