

Conductivity of Polyolefins Filled with High-Structure Carbon Black

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Received 11 January 2005; accepted 28 February 2005

DOI 10.1002/app.22238

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The electrical conductivities of various polyolefins filled with a high-structure carbon black (CB) were studied. Typical percolation behaviors were observed in all of the materials studied. At a critical CB content, which defined the percolation threshold, CB formed conductivity pathways, and resistivity fell sharply from a value characteristic of an insulator into the range of 10–100 Ω cm. The dependence of the percolation threshold on the matrix viscosity was understood in terms of competing effects on CB dispersion during blending and CB flocculation during compression molding. For the conditions used in this study,

polypropylene with a melt flow index of about 50 was optimum. Flocculation in the quiescent melt was studied directly by atomic force microscopy. Conductivity pathways formed over time by CB agglomeration. The temperature dependence of the percolation time was described by an Arrhenius relationship. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1799–1805, 2005

Key words: conducting polymers; polyethylene (PE); polyolefins; poly(propylene) (PP)

INTRODUCTION

Most polymers have excellent electrical insulating properties. However, some level of electrical conductivity is required for antistatic, semiconductive, and electromagnetic interference applications.^{1,2} This need is usually satisfied by the filling of a polymer matrix with conductive particles. It is characteristic of polymers with conductive fillers that resistivity (ρ) falls sharply at a critical filler concentration. The critical concentration is usually interpreted as the filler concentration required to achieve a three-dimensional conductive network. The phenomenon is described by percolation concepts, and the critical concentration is defined as the *percolation threshold*.³

Carbon black (CB) is the most widely used conductive filler for polymers. A high-structure CB consists of many primary nanoparticles fused together in a grape-like aggregate. Macroagglomerates of these ag-

gregates constitute the original millimeter-size CB particle.⁴ During blending, shear forces break up the agglomerates and disperse the CB aggregates. The level of CB dispersion depends on the process parameters and matrix polymer viscosity.^{5,6} If mixing is stopped, the high surface tension of CB aggregates leads to flocculation in the quiescent melt.⁷ Flocculation promotes the formation of a conductive network. The closer the surface tension of polymer is to that of CB, the more compatible they are and the more CB is needed to form a conductive network.^{8,9} Flocculation is a diffusion process and, thus, also depends on the viscosity of the matrix polymer. Because of flocculation, CB is usually not homogeneously distributed in the melt. As a result, conductive behavior may deviate from the classical lattice percolation theory.

The role of matrix crystallization on the distribution of filler and conductivity is not clear from the literature. One can anticipate that matrix polymer crystallization during cooling from the melt will cause CB to segregate to the noncrystalline interlamellar and interspherulitic regions and thereby lower the percolation CB concentration.¹⁰

Polyolefins are widely used in applications that require some level of electrical conductivity. They offer excellent mechanical properties and good chemical resistance and are readily processed by extrusion, injection molding, and compression molding. However, all polyolefins are insulators. Typically, ρ is reduced into the desired range by blending with a conductive

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Contract grant sponsor: PolyOne Corp, Avon Lake, OH 44012.

TABLE I
Characteristics of the Matrix Polyolefins

Property	EO86	EO88	EO90	LLDPE	LDPE	HDPE	PP
Density (g/cm ³)	0.86	0.88	0.90	0.92	0.92	0.96	0.90
MFI (g/10 min)	1.5	2.5	3.2	0.9	2.8	25.0	3.6
Crystallinity (wt %)	4	19	29	40	40	62	44

filler. In this study, a high-structure CB was compounded with various commercial polyolefins, and the effects of the matrix polymer properties and process history on dispersion and conductivity were investigated.

EXPERIMENTAL

The polyolefin matrix materials used in the study were three ethylene–octene copolymers (Affinity EG8180, XUR1567-48562-6A, and PL1880, Dow Chemical Co., Freeport, TX), which are identified as EO86, EO88, and EO90, where the digits refer to density; linear low-density polyethylene (LLDPE; Innovex LL0209AA, BP Chemicals, Warrenville, IL); low-density polyethylene (LDPE; PE586A, Dow Chemical); high-density polyethylene (HDPE; Rigidex HD6070, BP Chemicals); and five polypropylene (PP) resins that differed in melt flow index (MFI; P4G2Z-073A, P4G3Z-039, P4G4Z-011, P4C5B-080, and P4C6Z-059, Huntsman Corp., Marysville, MI). The conductive filler was a high-structure CB (Conductex 975 Ultra, Columbian Chemical Co., Marietta, GA) with a mean particle size of 21 nm, a nitrogen surface area of 242 m²/g, and a dibutyl phthalate absorption of 169 cc/100 g, and a density of 1.8 g/cm³, as given by the manufacturer.

The material characteristics of the matrix polymers are given in Table I. Density was given by the manufacturer. MFI was determined at 185°C with a melt flow indexer (model D7054, Kayeness, Inc., Honey Brook, PA). A 5-kg plunger was used in all of the measurements. Thermal analysis was performed with a PerkinElmer DSC-7 (Boston, MA). The heating/cooling rate was 10°C/min. The crystallinity of the polyethylenes was determined with a heat of melting of 277 J/g, and the crystallinity of the PPs was determined with a heat of melting of 209 J/g.¹¹

Blending was carried out in a Haake Rheomix 600 mixing head (Haake, Karlsruhe, Germany). After the polymer was melted for 1 min, the CB was slowly added. The total blending process took 10 min at 185°C, and the mixing speed was maintained at 40 rpm. The material was cooled in air after blending and compression-molded into 2 mm thick plaques. The blended materials were preheated in a compression molder for 5 min under minimum pressure at 185°C, subjected to five pressure–release cycles to remove air

bubbles, and kept under a pressure of 4.8 MPa for an additional 5 min. All specimens were immediately quenched in cold water unless otherwise specified. Some CB-filled PP (MFI = 3.6) specimens were cooled from the melt at different rates, which was achieved by quenching into a dry ice–acetone mixture at –40°C, removing the specimen from the compression molder, and cooling it in air or slowly cooling the specimen in the compression molder at a rate of about 2°C/min. Other CB-filled PP (MFI = 3.6) specimens were held in the melt under pressure for longer periods of time up to 4 h before quenching. Other CB-filled PP (MFI = 3.6) specimens were molded at various temperatures between 185 and 240°C.

Two specimen geometries were used for conductivity measurements. To measure in-plane resistivity (ρ_{\parallel}), a 70-mm strip with width (W) of 10 mm and a thickness (H) of 2 mm was used. Gold electrodes about 200 nm thick were deposited on one surface; the separation of the electrodes (L) was 22 mm. ρ_{\parallel} was obtained from the resistance (R) as

$$\rho_{\parallel} = R \frac{WH}{L} \quad (1)$$

To measure the through-thickness resistivity (ρ_{\perp}), 200 nm of gold was deposited on both surfaces of a disc specimen with a diameter (D) of 2.5 mm and a H of 2 mm. Then

$$\rho_{\perp} = R \frac{\pi D^2}{3H} \quad (2)$$

All surfaces were cleaned with ethanol to remove dust and any other contaminants and dried in air before the electrodes were deposited. R was measured with the four-terminal technique described previously.^{12,13} A Keithley model 220 (Keithley Instruments, Cleveland, OH) was used as a current source, and a Keithley model 619 was used for voltage and current measurements.

A tapping-mode atomic force microscope (Nanoscope IIIa Multimode head, Digital Instruments, Santa Barbara, CA) was used to study the distribution of CB in PP. Specimens were sectioned with an ultramicrotome (MT 6000-XL, RMC, Tucson, AZ) to obtain a smooth surface and were etched for 10 min in a po-

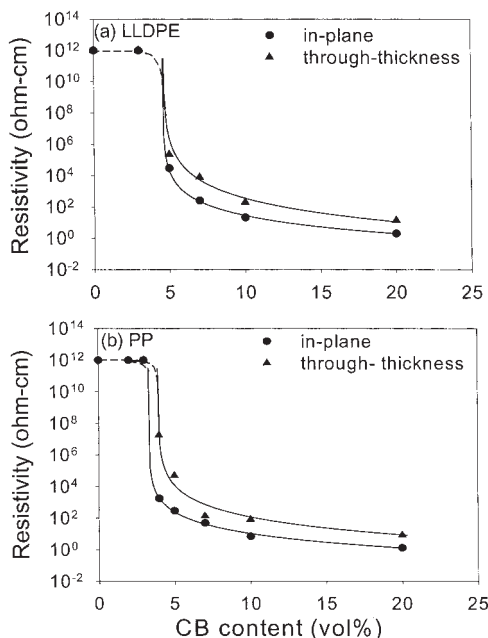


Figure 1 Comparison of ρ_{\parallel} and ρ_{\perp} for CB-filled (a) LLDPE and (b) PP.

tassium permanganate solution at ambient temperature. The solution contained 0.7 wt % potassium permanganate in a 2:1 v/v mixture of concentrated sulfuric acid (95%) and orthophosphoric acid (85%).

RESULTS AND DISCUSSION

Effect of the specimen geometry

ρ_{\parallel} and ρ_{\perp} as a function of CB content are compared in Figure 1. Typical percolation behavior was observed in all cases. Specimens with low CB contents were insulative. As CB content increased to a critical value, which defined the percolation threshold, ρ fell sharply into the range of 10–100 Ω cm. As CB content increased above the percolation threshold, ρ started to level off. The percolation threshold measured in the in-plane and through-thickness directions was about the same. However, ρ_{\perp} was systematically lower than ρ_{\parallel} . Apparent anisotropy can be caused by contact resistance. The effect arises from the difference in current path length.¹⁴ For an isotropic material, the ratio of the apparent ρ_{\perp} to the apparent ρ_{\parallel} (m) is given by

$$m = \frac{\rho_{\perp}}{\rho_{\parallel}} = \frac{L}{H} \quad (3)$$

For the specimens used in this study, m was about 11. Similarity between m from eq. (3) and the observed ratio of 7–30 indicated that the difference in the apparent ρ_{\parallel} and ρ_{\perp} values was a contact resistance effect and did not reflect anisotropy in the molded specimens.

Effect of crystallinity

ρ as a function of CB content for the different polyolefin matrices is shown in Figure 2 for the in-plane and through-thickness directions. Typical percolation behavior was observed in all cases. ρ of a dispersion of conductive particles in an insulating matrix at and above the percolation threshold is generally described by a power law relationship:¹⁵

$$\frac{1}{\rho} \propto \left(\frac{V - V_c}{1 - V_c} \right)^t \quad (4)$$

where V is the volume fraction of the filler, V_c is the volume fraction of the filler at the percolation threshold, and t is the power law exponent that characterizes the strength of the transition. The fits of eq. (4) are included in Figure 2 as solid lines, and the corresponding parameters are given in Table II. t was assumed to depend only on the dimensionality of the system and for a three-dimensional system is 2 according to classical lattice percolation theory or 3 according to continuum percolation theory.¹⁶ In most cases, t was in the range 2–3.

The percolation threshold was about the same in the two directions for all the filled polymers but depended strongly on the polymer matrix (Table II). Some of the polymers were highly crystalline, which raised the

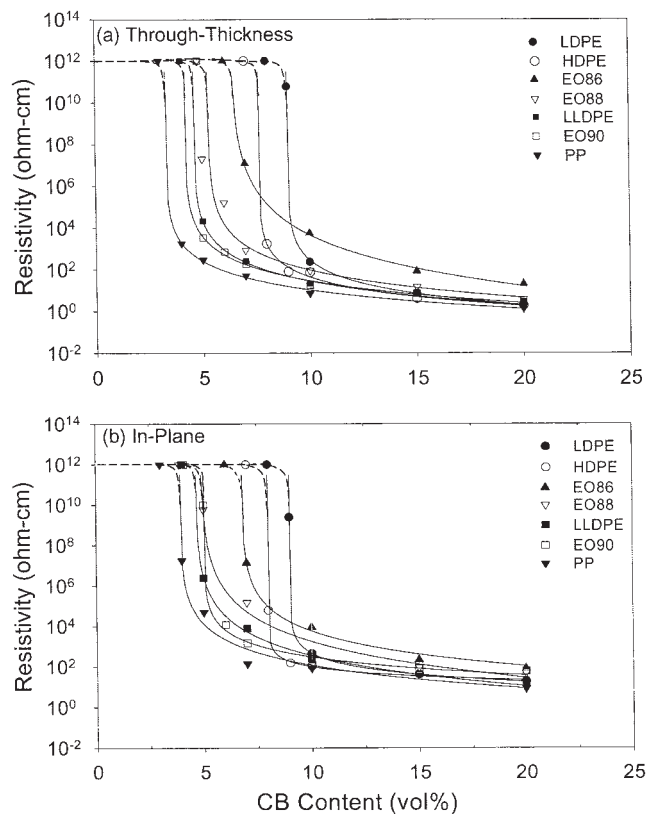


Figure 2 ρ as a function of CB content for various polyolefin matrix polymers: (a) ρ_{\perp} and (b) ρ_{\parallel} .

TABLE II
Power Law Parameters for the Resistivity of CB-Filled Polyolefins

Matrix polymer	t		V_c (vol %)		Matrix crystallinity (wt %)
	In-plane	Through-thickness	In-plane	Through-thickness	
PP	2.3	2.7	3.3	3.9	44
EO90	2.4	1.9	4.2	5.0	29
LLDPE	2.5	3.3	4.6	4.6	40
EO88	2.7	3.8	5.2	4.9	19
EO86	4.3	2.8	6.4	6.8	4
HDPE	1.9	0.9	7.7	8.0	62
LDPE	2.1	1.0	9.0	9.0	40

possibility that the segregation of CB particles into the amorphous regions during solidification lowered the percolation threshold. However, there was no correlation between V_c and the weight fraction crystallinity (Table II). Thus, HDPE and LDPE with relatively high crystallinities also had the highest values of V_c .

We further examined the effect of crystallization with CB-filled PP by varying the crystallization conditions. All of the crystallization conditions resulted in typical percolation behavior. The percolation threshold was about the same for all of the quenched specimens. Apparently, the crystallization rate was not strongly affected by the quench temperature. This was not surprising, as the polymers had poor thermal conductivity; hence, the cooling rate probably depended more on the CB content than on the quench temperature. However, slow cooling at about 2°C/min from the 185°C melt resulted in a lower V_c than did quenching (Table III). One can imagine that increased time in the melt, estimated to be about 30 min for slow cooling, permitted flocculation of the CB particles. In addition, slower crystal growth facilitated rejection of CB into the amorphous regions. In this case, the CB aggregates would have been less likely to be trapped in the crystalline regions where they would not be part of conductive pathways.

Effect of the MFI

The percolation threshold for the different polymer matrices from Table II is plotted as a function of matrix melt index in Figure 3. The percolation thresh-

old generally decreased with increasing MFI before increasing again with the low-viscosity HDPE matrix. The melt viscosity of the polymer matrix could impact V_c by affecting the dispersion of CB during mixing and by affecting subsequent flocculation during molding and solidification. In the dispersion process, the original CB millimeter-size macroagglomerates broke up into small aggregates of nanoparticles. The degree of dispersion depended on the mixing time and the shear force imposed by the matrix, which increased with the melt viscosity. However, even well-dispersed CB aggregates could reaggregate (flocculate) during molding. In the melt, aggregates brought together by Brownian motion agglomerated to minimize surface energy. A static surface charge on the CB aggregates accelerated the agglomeration process. Because flocculation is a diffusion process, the agglomeration of dispersed CB aggregates and the formation of a conductive network occurred faster in a lower viscosity matrix. We speculated that the decreasing trend in V_c with MFI reflected flocculation during the molding of the well-dispersed CB aggregates. However, if the viscosity of the matrix is too low (if the MFI is too high), the shear forces imposed by the matrix would not have been strong enough to effectively break up the original CB macroagglomerates. In this case, the net result was an increase in the percolation threshold

TABLE III
Effect of Thermal History on the Power Law Parameters for the Through-Thickness Resistivity of CB-Filled PP

Crystallization history	t	V_c (vol %)	Matrix crystallinity (wt %)
Quenched to -40°C	2.6	3.9	42
Quenched in water	2.0	4.0	44
Cooled in air	2.5	3.7	47
Slowly cooled	2.0	3.0	53

MFI = 3.6.

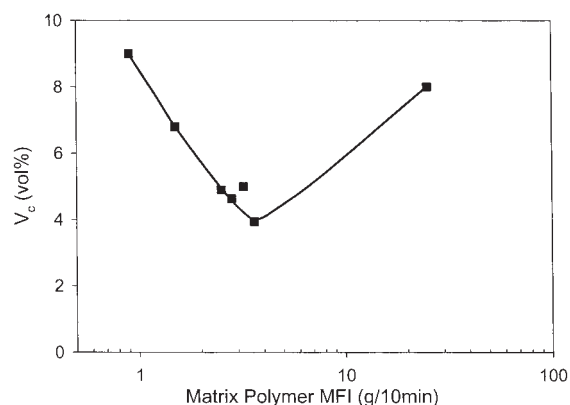


Figure 3 Relationship between the matrix polymer MFI and the percolation threshold for CB-filled polyolefins.

TABLE IV
Effect of the Matrix MFI on the Power Law Parameters for the Through-Thickness Resistivity of CB-Filled PP

Matrix MFI (g/10 min)	t	V_c (vol %)	Matrix crystallinity (wt %)
3.6	2.4	3.8	44
5.7	2.5	4.0	45
19.4	2.5	2.9	45
51.0	2.6	1.8	44
123	2.2	2.9	45

due to poor dispersion. The high V_c of CB-filled HDPE was attributed to poor CB dispersion in the low-viscosity HDPE matrix.

The effect of MFI on V_c was examined further with a series of PP matrices that differed in MFI (Table 4). As the MFI increased from 3.6 to 51.0, the percolation threshold dropped from 4.1 to 1.8 vol %. However, when the MFI increased further from 51.0 to 123, the percolation threshold increased from 1.8 to 2.9. This indicated that there was an optimum MFI for CB-filled PP (Fig. 4). The existence of a minimum in V_c reflected the two competing factors in the processing history: dispersion and flocculation. The initial decrease in V_c reflected a fast agglomeration of dispersed CB aggregates. The increase in V_c for the highest MFI polymer was attributed to poor dispersion of the macroagglomerates. This produced an optimum MFI for CB-filled PP of about 50.

Flocculation in the quiescent melt

We examined flocculation in the quiescent melt by holding CB-filled PP specimens in the compression molder at 185°C for various periods of time before quenching. Figure 5 shows the effect of time in the melt on ρ of compositions close to the percolation threshold. Typical percolation-like behavior was observed for compositions with 2 and 3 vol % CB. Spec-

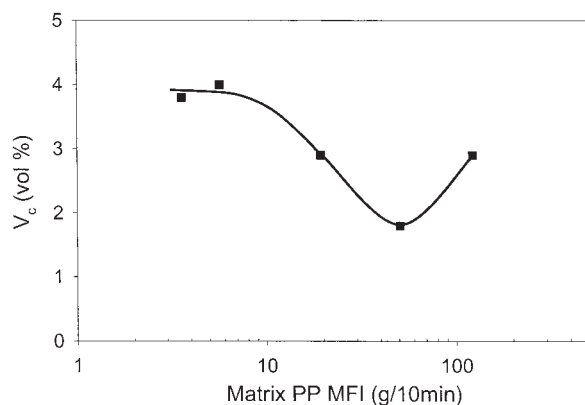


Figure 4 Effect of matrix MFI on ρ of CB-filled PP.

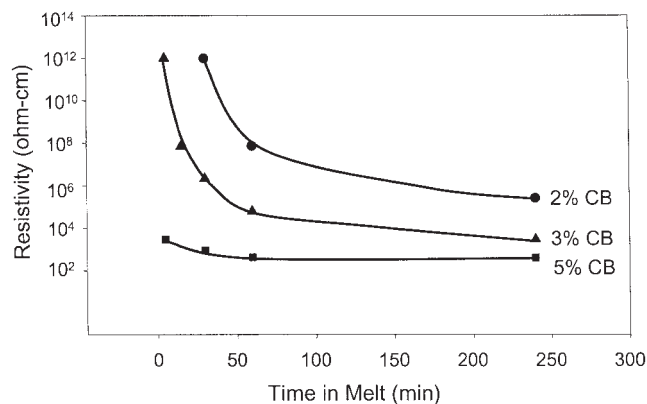


Figure 5 Effect of time in the melt on ρ of CB-filled PP (MFI = 3.6).

imens were initially insulative; however, as time in the melt increased, ρ gradually decreased into the 10^3 – 10^6 Ω cm range as flocculation produced conductive pathways. An increase in CB content reduced the melt time required to reach percolation and increased the number of conductive pathways as indicated by lower ρ values above the percolation threshold.

The agglomeration of CB was probed directly with atomic force microscopy. The images in Figure 6 illustrate the effect of time in the melt on the morphology of PP with 3 vol % CB. The image in Figure 6(a) shows that after 5 min under compression at 185°C, the original CB millimeter-size macroagglomerates were broken up and dispersed as 0.3–1.5- μ m aggregates of nanoparticles. Although there were some small clusters of aggregates, there was no indication of a continuous CB network. Images of specimens held for 15 min and 60 min in the melt showed the gradual appearance of larger clusters and some extended arrays of aggregates [Fig. 6(b,c)]. After 4 h, the aggregates had agglomerated into a well-defined network with relatively large regions of unfilled matrix [Fig. 6(d)].

The flocculation of PP with 3 vol % CB in the quiescent melt was examined at various temperatures between 185 and 240°C. At all temperatures, percolation-like behavior was observed with an initial rapid decrease in ρ and a much slower decrease in ρ at longer times. Linear fits were made to the data in the two regions, and a characteristic flocculation time (t_c) was defined by their intersection. The Arrhenius plot of the characteristic t_c is shown in Figure 7. An activation energy of 43 kJ/mol was obtained for PP filled with 3 vol % CB. This value was very close to the dynamic percolation activation energy of 40 kJ/mol, which was obtained by measurement of the time-dependent ρ in the melt of PP filled with a lower structure CB.¹⁷ Similarity in the activation energy from the two approaches indicated that quenching froze the CB dispersion in the melt state and, thereby, preserved the dynamics of the flocculation process.

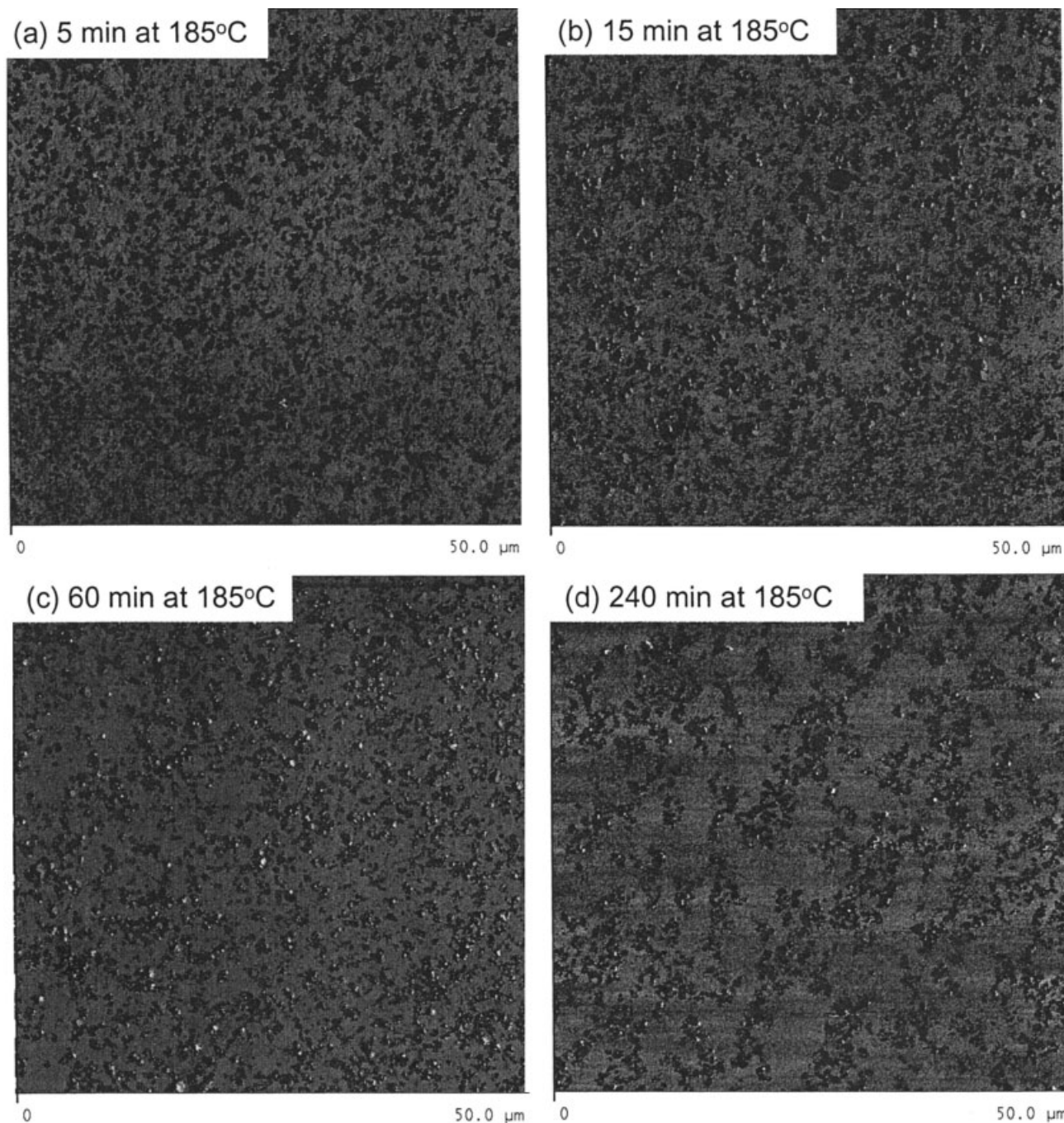


Figure 6 Effect of melt time at 185°C on the morphology of PP (MFI = 3.6) filled with 3 vol % CB: (a) 5, (b) 15, (c) 60, and (d) 240 min.

CONCLUSIONS

Shear forces during blending broke up the porous CB macroagglomerates into the small CB aggregates seen by atomic force microscopy. In all of the materials studied, increasing CB content led to a percolation threshold where the concentration was high enough for the CB aggregates to form conductivity pathways. The percolation threshold depended on how well the CB was dispersed during blending and the extent to

which it flocculated during subsequent compression molding. The matrix viscosity affected both dispersion and flocculation. A higher MFI favored the flocculation of well-dispersed CB aggregates during molding, which facilitated the formation of conductivity pathways. This reduced the percolation threshold. However, if the MFI was too high, the shear forces generated during blending were not high enough to produce good dispersion. This had the effect of increasing

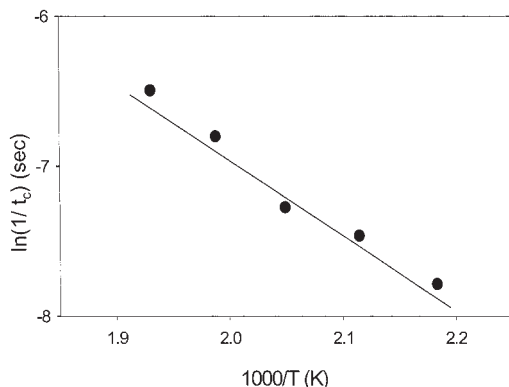


Figure 7 Arrhenius plot of the characteristic t_c for PP (MFI = 3.6) filled with 3 vol % CB.

the percolation threshold. The competing effects resulted in an optimum matrix polymer MFI. This phenomenon was demonstrated in this study with polyethylenes of various branch types and contents that also differed in MFI and was confirmed with PPs with different MFIs.

Increasing the molding temperature or the time in the quiescent melt facilitated the formation of conductivity pathways by enhancing the flocculation process. The temperature dependence of the percolation time was described by an Arrhenius relationship. We considered the possibility that the polymer matrix crystallization also affected the formation of conductive pathways, for example, by concentrating the CB aggregates in the noncrystalline interlamellar or inter-

spherulitic regions. Indeed, the slow crystallization of CB-filled PP resulted in a lower percolation threshold than did quenching.

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