



**RHEOLOGY OF
SEMICONDUCTIVE BLACK COMPOUNDS
WITH LOW CARBON BLACK**



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RHEOLOGY OF SEMICONDUCTIVE BLACK COMPOUNDS WITH LOW CARBON BLACK

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ABSTRACT

In certain wire and cable applications, semiconductivity or low surface/volume resistivity is required. This is accomplished primarily through the addition of high structural carbon black to a natural resin. Typically, to produce a compound with acceptable resistivity, the carbon black (CB) content will range from 20 to 40wt%. This amount of CB loading can result in two difficulties: 1) high melt viscosity; and 2) poor CB dispersion.

This paper describes rheological methods which can be used to characterize and to design semiconductive compounds with reduced CB loading (<15%) while retaining good resistivity, viscosity and CB dispersion.

It was found from dynamic rheology that semiconductive compounds show viscosity up-turns at low frequencies (< 0.5 rad/sec). This "up-turn" is believed to be a CB particle-particle network structure, which is critical to CB dispersion as well as conductivity. Rheological methods are presented to characterize the up-turn and a model is proposed supporting the correlation between "up-turn", dispersion, and conductivity.

INTRODUCTION

In certain wire and cable applications, semi-conductivity or low surface/volume resistivity is required. This is accomplished primarily through the addition of high structural carbon black to a natural resin. Typically, to produce a compound with acceptable resistivity, the carbon black (CB) content will range from 20 to 40 wtpercent [1-4]. This high amount of CB loading can result in two difficulties: 1) high melt viscosity and 2) poor CB dispersion.

Since rheology can be used to help understand polymeric structures and flow properties [5-9], it can also be a useful tool to investigate carbon black filled compounds. For example, it has been noted in the literature [10] that the addition of carbon black into polymer matrix results in unusual rheological behavior, i.e. viscosity up-turn at low frequencies. However, little information has been published on the correlation between the noted "up-turn" and the issues faced in designing semi-conductive compounds.

This paper describes the rheological characterizations of semi-conductive compounds and supports the correlations between low and high frequency viscosity to dispersion, conductivity and processability. In addition, a morphological model of semi-conductive compounds is proposed.

EXPERIMENTAL

I. MATERIALS

Table I describes the types of carbon black (CB) fillers (A through D), with their particle sizes, and filler loading. Small amounts of additive (0.5 wt% calcium stearate) and antioxidant (500 PPM of Irganox 1010) were added to the compounds. The carrier resins used were conventional 6 MI, Low Density PE (LDPE I through III) resins produced by different polymerization processes.

2. COMPOUND PREPARATION

A Farrel OOC Banbury mixer (2400 CC) was used to produce the semiconductive compounds for this investigation. At the initial mixing stage, the mixture of carbon black, resin, antioxidant, and calcium stearate was loaded into the mixing chamber maintained at 95°F. Ram pressure was applied to the chamber at 40 psi. Flux was achieved after approximately 40 seconds, the ram raised and the throat was cleaned for 15 seconds. The pressure was reapplied to the chamber and mixing was continued for at least 3 minutes to reach 340°F. The Banbury drop was pelletized through a 25-mm single screw extruder to produce the final compound.

3. COMPOUND CHARACTERIZATION

A. Rheological Measurements

Steady state shear viscosity measurements were carried out on an Instron Capillary Rheometer equipped with an 8-mm die and a L/D of 20 at 210°C. Bagley and Rabinowitsh corrections [11,12] were not made.

The dynamic rheological measurements were conducted on a Rheometrics RDA-II equipped with parallel plates. The measurements were conducted at 190, 210, and 240°C using a frequency sweep from 100 to 0.0398 rad/sec with a strain of 5%. All compounds reported in this paper had unusual rheological behavior with viscosity up-turn at low frequencies. The up-turns were quantified by a G^* parameter (zero frequency dynamic modulus) which can be derived from G' and G'' values. The parameter G^* was obtained by plotting $(\omega)^{0.5}$ versus $(G^*)^{0.5}$ data, where G^* is defined as $((G')^2 + (G'')^2)^{0.5}$. The extrapolation of this to $\omega = 0$ yields $(G^*)^{0.5}$. As an example, Figure 1 shows the dynamic data of polypropylene impact copolymers with different degrees of viscosity up-turns at low frequencies [13]. Copolymer A shows a normal rheological behavior: with gradual viscosity increases with decreased frequencies, whereas copolymers B, C, & D show the usual viscosity up-turns at low frequencies. Plots for an intercept values of $(G^*)^{0.5}$ vs. $(\omega)^{0.5}$ from dynamic data (figure 2) indicate that the higher up-turn leads to higher G^* . This method is analogous to the Casson [14] plot, which is used to determine the yield stress from steady state data.

B. Dispersion Quality Measurement

The pressure rise test (PRT), which is analogous to the screen pack plugging method, was used to evaluate the dispersion quality of the compounds. A Haake Rheomix 90 single screw extruder (25 -mm diameter) was used. The heated die had a breaker plate containing a 60-60-325-60-mesh screen pack arrangement. Zones 1 through 3 were heated to 235°C and the die was heated to 305°C. The extruder screw was run at 150 RPM. The pressure rise (PR) in psi was determined by subtracting the first 5 minutes reading from the final 20 minutes reading.

C. Surface/Volume Resistivity Measurements

Surface resistivity (inverse relation to surface conductivity) was determined following ASTM D 991. Film samples were produced by a 120-mm slot die under the same conditions using a Haake single screw extruder. The die gap was set at 0.76 mm at 485°F, and a molten web was stretched to approximately 0.025-mm thickness using Haake film take-up equipment. Also, compression molded plaques were prepared following ASTM D 991 using slow and rapid cooling processes for volume resistivity measurements.

RESULTS AND DISCUSSION

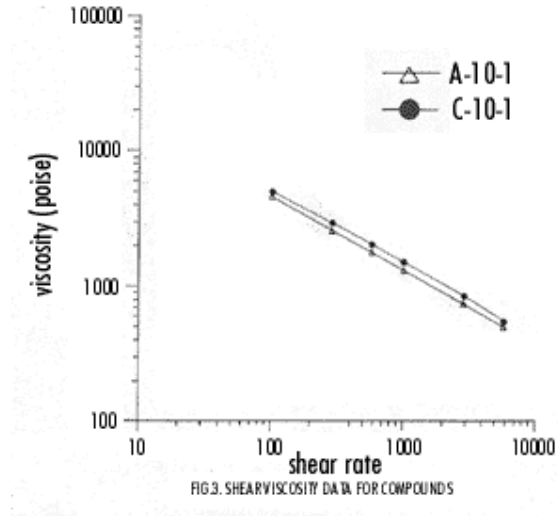


Figure 3 shows the steady-state shear viscosity for compounds A-10-1 and C-10-1. Each were made from the same carrier resin and loaded with 10 % CB, but with different CB types. The observed viscosity difference between these two compounds results from the different CB types used. Also note that each compound shows similar shear thinning behavior (decreased shear viscosity with increased shear rates).

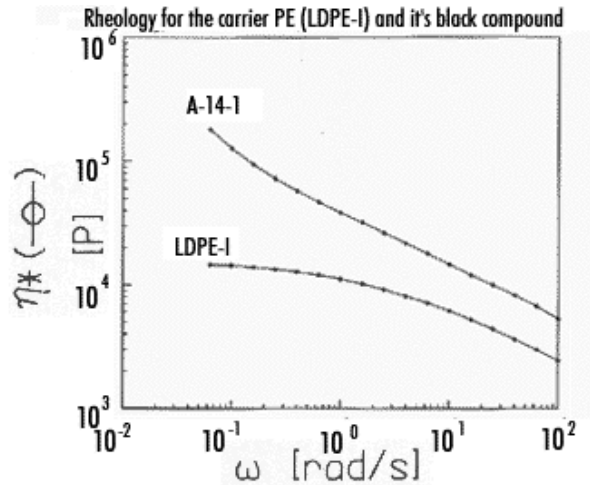


Figure 4

Figure 4 shows the dynamic data for the carrier LDPE and its corresponding CB compound, A-14-1. As expected, the addition of CB results in two observations: a) increased viscosity with similar shear thinning behavior at high frequencies (> 10 rad/sec); and b) low frequency (< 0.1 rad/sec) viscosity up-turn. This viscosity up-turn is a result of the formation of a network structure due to filler/filler interaction within PE matrix [15,16,17].

As noted in the literature [16], the conductivity of CB filled materials results from the presence of CB network structure. Interestingly, rapid cooled (with a cooling rate of approximately 200°C/minute) compression molded specimens showed almost no conductivity ($> 15 \log\Omega m$) on both compounds A-10-I and A-10-III (Table 2). Literature states [18] that the difference in conductivity between slowly and rapid cooled specimens is the result of different crystalline morphologies produced in the carrier resin. A-10-I also had higher PRT (610 psi) than compound A-10-III (490 psi) indicating poor filler dispersion (Table 2). The poor dispersion of CB in compound A-10-I (compared to A-10-III) appears to correlate with the lower degree of CB network structure present (as indicated by lower up-turn). Also, as expected, increasing the CB loading to 14% (A-14-I) resulted in even poor dispersion as indicated by PRT. In summary, Table 2 supports the correlation between higher "up-turn" (as indicated by G''_o) and improved dispersion of CB filled materials.

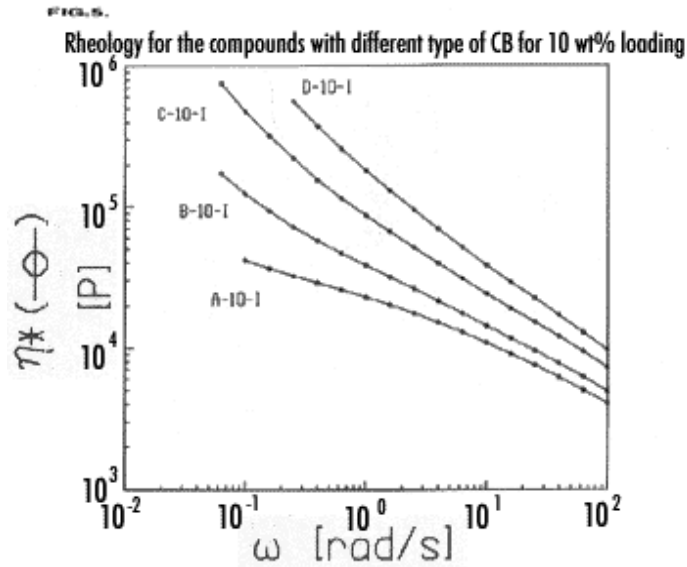


Figure 5

Figure 5 shows the dynamic data of the compounds, A-10-I, B-10-I, C-10-I, and D-10-I. Each was made from the same carrier resin, LDPE-I and 10% CB loading, but with different types of CB. The viscosity at high frequencies and the degree of viscosity up-turn at low frequencies varies depending on the type of CB. For an example, type D carbon black in compound D-10-I shows the highest viscosity and up-turn. D-10-I also has the best dispersion and conductivity, as indicated in Table 2, G''_o . This data supports that the higher the relative "up-turn", the better the dispersion and conductivity. It should also be noted that due to the high viscosity of compound D-10-I, it could not be drawdown into a thin (0.025-mm) film and consequently, was not further evaluated. These observations indicate that the type of CB, at similar loading, has a significant impact on dynamic viscosity.

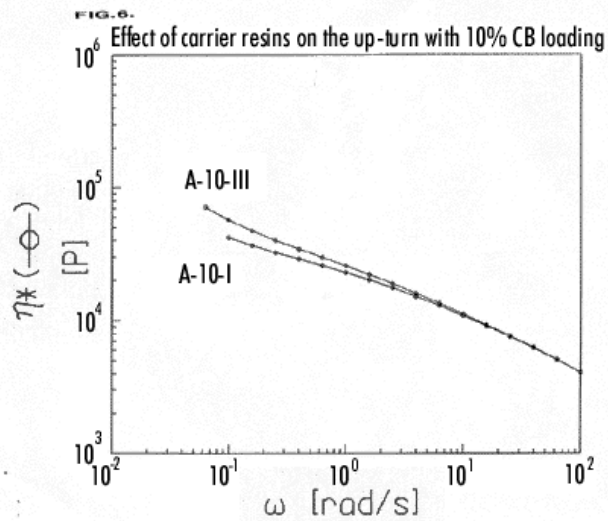


Figure 6

Figure 6 shows the dynamic data of compounds A-10-I and A-10-III. Both compounds were produced with type A carbon black, but with different carrier resins: LDPE-I for A-10-I and LDPE-III for A-10-III. Both compounds have identical complex viscosity at high frequencies above 50 rad/sec. However, at low frequencies, below 0.1 rad/sec, compound A-10-III shows the higher up-turn ($G^*_{\omega} = 560$) than A-10-I ($G^*_{\omega} = 510$). It is believed that this higher up-turn results from the increased degree of network structure associated with this particular LDPE type. It is also believed that the increased degree of network structure in A-10-III, resulted in higher surface conductivity (9 logohm for A-10-III compared to 12 logohm for A-10-I).

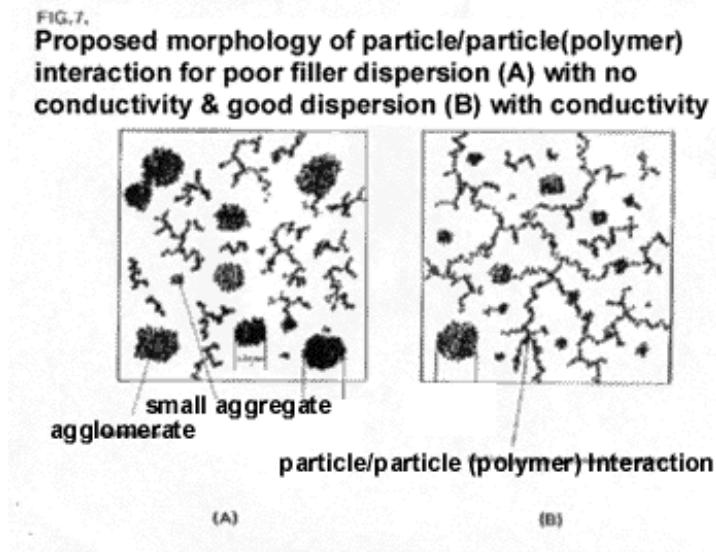


Figure 7

A model morphology is presented in Figure 7 to help understand the correlation between rheological parameters (mainly up-turn) to dispersion and conductivity. In this model, (A) depicts poor conductivity (less network structure) and poor CB filler dispersion (more agglomerates). (B) depicts improved conductivity (more network structure) with good dispersion (fewer agglomerates). It is proposed that these model structures can be detected by the rheological methods discussed.

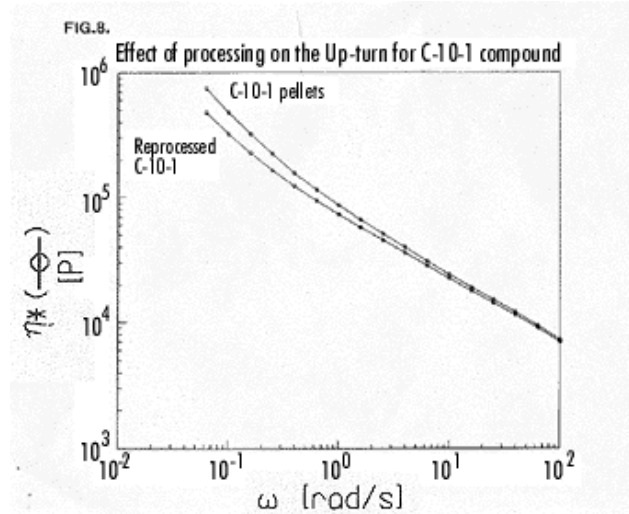


Figure 8

It is also interesting to note that these network structures appear to be predominately a physical phenomenon. What is meant by this statement is that the degree of up-turn is reduced in samples that have been re-extruded C-10-1 (figure 8), indicating the network structure is fragile but reversible in nature [19].

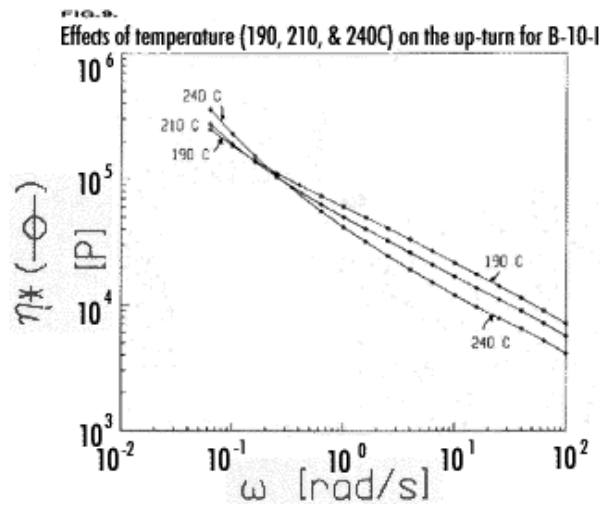


Figure 9

Last, the network structure formed in these semi-conductive compounds was effected by temperature (Figure 9 for compound B-10-1). As expected, viscosity at high frequencies decreased with increased temperature. However, unexpectedly, viscosity up-turn increased with increased temperature. This unusual behavior observation may be a result of increased mobility of the CB particles at higher temperature leading to increased network structure.

CONCLUSIONS

Dynamic rheological measurement can be used to observe low frequency viscosity up-turns of semi-conductive compounds at low levels (~10%) of carbon black loading, whereas no unusual behavior was observed in steady-state capillary shear viscosity. There was observed a direct correlation between the degree of low frequency viscosity up-turn to conductivity and dispersion. This low frequency up-turn is a result of a CB network structure and appears to be a useful tool to predict compound conductivity as well dispersion quality.

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Table 1. Composition for the compounds investigated for this paper.

COMPOUND	CB TYPE	PARTICLE SIZE [nm]	CB CONTENT [wt%]	CARRIER RESIN
A-10-I	A	18	10	LDPE-I
A-10-II	A	18	10	LDPE-II
A-10-III	A	18	10	LDPE-III
A-14-I	A	18	14	LDPE-I
B-10-I	B	20	10	LDPE-I
C-10-I	C	23	10	LDPE-I
D-10-I	D	35	10	LDPE-I

Table 2. Rheological, dispersion, and resistivity data for the compounds.

COMPOUND	G* [dyne/cm ²]	$\eta^* 100 \times 10^{-3}$ [Poise]	Dispersion [psi]	Surface Resistivity [log-ohm]	Volume Resistivity [log-ohm]
A-10-I	510	4.05	610	>15	—
A-10-II	400	4.10	940	>15	—
A-10-III	560	4.00	490	>15	—
A-14-I	9,400	5.51	880	>15	>15
B-10-I	13,400	5.73	360	9.5	>15
C-10-I	22,800	6.60	160	6.1	-1.24
D-10-I	38,000	9.51	120	*)	0.92



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