FACTORS AFFECTING THE PERFORMANCE OF CARBON BLACK MASTER BATCHES IN WIRE AND CABLE APPLICATIONS

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ABSTRACT

Cable jackets containing carbon black (CB) are one of the most important components in communication and power cable constructions. This jacketing provides protection for the underlying layers from physical abuse, chemical attack, and UV degradation. There are two ways to manufacture these types of cable jackets: either by fully compounding the product or by blending a combination of a resin and a black master batch (MB). In the latter approach, a main requirement is to have excellent CB dispersion in the MB. Poor dispersion in the MB results in unacceptable mechanical properties and poor UV-resistance in the finished jacket product.

This paper describes a series of single screw extrusion experiments that were carried out with let-down resins of different structures and master batches to investigate the effects of the resin structure, MB, and extrusion conditions on acceptability of the extrudates for jacketing applications. The MBs employed for this investigation are commercial products of which dispersion is acceptable based on the manufacturing QC testing. Under certain extrusion conditions with these MBs, extrudates had unacceptable surface quality and UV absorption coefficient (termed as ABS for a given range of CB content in the finished product (2.5 to 2.7 wt%). The unacceptable properties resulted from poor melt homogenization of the MB with the letdown resin at the extrusion conditions used. Good homogenization was obtained by conducting the extrusion at higher shear stress. The high shear operation can be accomplished by several methods: selection of lower MI let-down resin (within resin spec); narrow the molecular weight distribution (MWD); lower temperature profile; and higher screw speed. The employment of tighter screen packs also showed some improvement in homogenization. A possible mechanism for the good homogenization (CB dispersion) of the MB will be given.

INTRODUCTION

Polyethylene (PE) based carbon black (CB) jacketing compounds have been used for wire and cable applications for many years. Generally they offer a unique combination of processability, mechanical properties, and performance for jacket designs and applications. There are several performance criteria for black jacketing compounds. Good physical and mechanical properties are required to protect underlying layers from physical abuse and chemical attack. The jacket also needs to exhibit the capability of long-term, cost effective UV protection for stabilizing against outdoor environment and sunlight [1-4]. Previously discussed were the effects of CB type and particle size, as well as the dispersion on UV protection for jacketing applications [5-6].

There are two ways to manufacture a finished cable jacket: either by fully compounding the finished product or by blending a combination of a resin and MB. Each approach has advantages and disadvantages for producing a finished jacket product. In the latter approach, a critical factor is CB dispersion quality, particularly for highly loaded CB master batches (> 30 wt% CB). Poor dispersion of the MB content results in unacceptable mechanical properties and UV-resistance in a finished jacket product [6]. It has previously been proven that absorption coefficient (termed as ABS) values for a given CB content and type of CB are strongly related to the extent of CB dispersion in jacket compounds. In this paper, a series of single screw extrusion experiments were carried out to investigate the effects of extrusion conditions, resin structure, and type of MB on the ABS and CB dispersion of extrudates. The results of these experiments may provide a guideline in the usage of resin/MB blends for finished jacket products.

EXPERIMENTAL

Materials

The materials used for this investigation are two commercial black MBs (MB-A and MB-B) with respective loading of 35 and 40 wt% N110 type CB, a commercial jacketing grade linear low density PE(LLDPE-A) and two medium density PE(MDPE-A andd B) resins.

Test Methods

A. Basic Data

For each jacketing material we obtained the basic data of MI and density using ASTM D 2839 and D 1238. The measurements on UV absorption coefficient (ABS) were carried out using pressed thin films using ASTM D 3349.

B. Gel Permination Chromatography (GPC)

A Waters Gel Permeation Chromatography (GPC) unit measured molecular weight (Mw) and molecular weight distribution (MWD) of the resin.

C. Rheological Measurements

Dynamic complex viscosity, η^* as a function of frequency were measured by a Rheometrics ARES at 190 and 230 °C. The Viscosity up-turn was determined from the dynamic data using a Cassion plot [7]. Flow curves for steady shear viscosity vs. shear rate were obtained by a Kayness capillary rheometer at 190 and 230 °C.

D. CB Dispersion Test

A pressure rise test (PRT) for the CB dispersion of the MBs was used in this investigation. The PRT is analogous to a screen pack-plugging test, which is used to determine the quality of MBs. The PRT test uses a Haake 90 single screw extruder (L/D= 24, D= 19 mm). The heated die has a breaker plate followed by the following screen pack arrangement in mesh: 60-60-325-60. The extruder screw was run at 150 RPM. The MB was let down to a final 5.2 wt% CB content using the let down resin (LDPE, 2 MI, 0.920 density). The pressure rise (PR) in psi is obtained by subtracting the pressure at the first 5 minutes reading from the 35 minutes reading. PR is inversely proportional to the quality of dispersion, meaning a higher PR would indicate poorer dispersion due to quicker screen pack plugging.

E. Extrusion Test

A lab scale Haake single screw extruder (L/D= 24, D= 19 mm, compression ratio = 3:1) with standard screw geometry (no mixing section) extruder at two temperature, 190 °C and 230 °C was used for the preliminary investigation of resin/MB blends at a 2.6 wt% CB loading. The extrudates were collected for a visual inspection of surface quality, qualitative CB dispersion (with optical microscopy on thin pressed film), and UV absorption. The extrudate obtained at 190 °C and 230 °C was pelletized for testing the physical and mechanical properties.

Two different types of Killion screws were employed (D= 38 mm, L/D=24, compression ratio=3:1): (a) standard configuration with no mixing, (b) Barrier with Maddock mixing section. These screws were selected to investigate the effects of different type of screw configuration with extrusion conditions such as screw speed and temperature on ABS.

RESULTS AND DISCUSSION

1. Structural Data of the Let Down Resin

Table 1 shows basic data and structure for the letdown resins. Beside density difference between LLDPE-A and MDPEs, some differences were observed in MI and M_w between LLDPE-A and MDPE-A. MDPE-A had lower MI and higher M_w when compared to LLDPE-A. Also observed was a difference in molecular weight distribution (MWD) between MDPE-A and MDPE-B in which MDPE-B had a narrower MWD when compared to MDPE-A. These structural differences would reflect rheological behavior differences such that LLDPE-A would show less viscous material in the molten state with similar rheological MWD (RMWD) when compared to MDPE-A and MDPE-A would show a broader RMWD with lower high shear viscosity when compared to MDPE-B. All resins show similar melt elasticity (Er). This means that the structural difference leads to viscous effect (rather than elastic) for CB dispersion mechanism. The effect of such structural differences among the resins on ABS and CB dispersion will be investigated.

2. Black Master Batches Characterization

Figure 1 shows the complex viscosity as a function of frequency for the MB-A (35 wt% CB loading) and MB-B (40 wt%). Compared to LLDPE-A (in Fig. 1), MB-A and MB-B show much higher viscosity and unusual rheological behavior seen as an up-turn in viscosity at the low frequency region. The higher viscosity for MB-A and MB-B is a result of the higher CB addition. MB-B also shows a higher up-turn when compared to MB-A. Compared to MB-A, the higher up-turn seen in MB-B may result from better CB dispersion in addition to 5 wt% more CB loading. A correlation between the up-turn and CB dispersion has been published previously [8]. Interestingly,MB-A with lower CB loading shows higher viscosity at high frequency region than MB-B. We also confirmed such a higher viscosity for MB-A in the shear viscosity data as shown in figure 2. This discrepancy may be related to the difference in formulation as well as compounding conditions.

Table 2 illustrates the quantified up-turn with G^*_o and CB dispersion obtained from the PRT test. Compared to MB-A, MB-B shows not only much lower pressure rise data, which indicates better CB dispersion, but also higher viscosity up-turn, which indicates more CB network structure. It has been discussed that the presence of such network structure is very common in highly filled system with small particle sizes [8-9]. Also, the network structure is predominately physical in nature, which means very fragile with shearing [9].

3. Extrusion trials

Figure 3 shows the ABS of extudates with 2.6wt% CB content as a function of extrusion speeds, 30 and 60 RPM at 190 °C and 230 °C produced by dry blending pellets of LLDPE-A with MB-A (extrudate-A), MDPE-B with MB-A (extrudate-B), and LLDPE-A with MB-B(extrudate-C). At 30 RPM, extrudate-A shows very low ABS (<400) value. Extrudate-A also shows poor surface quality with detectable lumps and pimples, indicating poor mixing (poorly homogenized) between LLDPE-A and MB-A with high temperature and lower screw speed. In general, poor CB dispersion with the presence of agglomerates shows lower ABS value, based on the fact that in the presence of agglomerates, UV light is more likely to be scattered than absorbed. Using the optical microscopy, we confirmed a poor CB dispersion from the extrudate-A produced at 30 RPM and 230°C. The increased screw speed from 30 to 60 RPM shows dramatic improvement in the ABS, as well as surface quality of all extrudates. The improvement with increased screw speed results from better homogenization associated with higher shear stress between resin and MB.

On the other hand, the extrudate-B showed improvement in ABS (Figure 3) as well as surface quality, compared to extrudate-A. The improved surface quality definitely indicates improved CB dispersion, leading to higher ABS. The improvement in ABS and CB dispersion results from the use of narrow MWD resin with lower MI. The narrower MWD resin resulting from higher viscosity at extrusion shear (see Table 1) can be attributed to improving homogenization between resin and MB during extrusion from the extrudate of MDPE-A, compared to that of MDPE-A. This observation demonstrates the effect of resin structure on ABS and CB dispersion.

The result of extrudate-C is an example for the effect of different MB on ABS as compared to that of extrudate-A. Switching over to MB-B from MB-A at 30 RPM and 230 °C shows improved ABS and surface quality. This observation is critical because it shows the importance of selecting an acceptable MB for a given letdown resin to produce an extrudate with acceptable ABS and surface quality. The extrudate-A produced at 190 °C and 30 RPM showed smooth surface quality and better CB dispersion than that at 230 °C. We observed similar improvement in surface quality and CB dispersion for extrudates-B and extrudate-C with the extrusion of lower temperature. The use of MB-A provides a much wider processing window for acceptable finished product than that of MB-A. The usage of tighter screen pack showed some improvement in dispersion. From this preliminary extrusion trial, we learned the effects of resin structure, characteristic feature of MB, and extrusion conditions such as screw speed, usage of screen pack, and temperature on improving ABS and CB dispersion

In order to investigate the effect of screw type with given extrusion conditions on ABS, a lab scale extrusion trial was performed with a standard metering screw and the DFM type barrier screw [10] attached with the Maddock mixing section. Table 3 shows the results of the extrusion trials, indicating improved ABS with lower temperature and with the use of Barrier screw. From this test, the extrusion with lower temperature and with Barrier screw demonstrates improvement in ABS.

4. **CB dispersion mechanism in the use of MB**
   It has widely accepted that the better dispersion of minor phase in two-phase system can be accomplished by closer viscosity ratio in the extrusion/compounding shear rate [11]. Figure 4 shows the viscosity ratio at two temperatures, 190 °C and 230 °C as a function of shear rates for individual component. The higher ratio means more temperature sensitivity in viscosity difference. Compared to LLDPE-A, MBs show much variation in viscosity with temperature. It is clear that viscosity ratio decreases with increases in shear rate between LLDPE-A and MB. As a result, the viscosity ratio between LLDPE-A and MB reduces with increased shear rate. This observation helps explain the improvement in ABS and CB dispersion with increased screw speed (Fig.3).

   The use of MB-B with LLDPE-A showed better ABS value and CB dispersion than that of MB-A at the extrusion temperature of 190 °C. The better CB dispersion seen when using MB-B, compared to that of MB-A can not be explained by the conventional concept of viscosity ratio (as shown in Fig. 4) where MB-B shows a much higher viscosity ratio than LLDPE-A. This unusual behavior when using MB-B can be explained by the presence of a fragile and physical network structure. Extruding at lower temperatures can break the network structure more easily. The agglomerates being responsible for poor dispersion may not be fragile (hard to break) therefore, the resin blend with MB-A (containing more agglomerates) shows worse CB dispersion. Schematics for the MB breaking mechanism are shown in Figure 5.

CONCLUSIONS

It was found that the acceptability of jacket performance based on CB dispersion and ABS depends on the structure of the base resin, extrusion conditions, and the nature of the MB. The MB with better dispersion and more network structure provides a wider fabrication window than that with poorer dispersion and less network structure. The ABS and CB dispersion of a jacket compound produced by a single screw extrusion can be improved by using an appropriate combination of extrusion conditions, resin selection and MB. The following are the options for the improvements:

1. For a given MB and extrusion conditions, use of lower MI resin, or narrow MWD with higher high shear (> 100 sec^{-1}) viscosity
2. For a given MB and resin, use a lower temperature extrusion profile
3. For a given resin and extrusion conditions, use a MB with better dispersion and more network structure
4. For a given resin and MB, use extrusion conditions that generate higher shear operation
5. For a given resin and MB, use a higher shear mixing screw and tighter screen pack

We also propose a mechanism for the dispersion of the MB in the jacket production of a resin and MB combination.

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KEW WORDS

Jacketing
Carbon Black
Absorption Coefficient
Single screw
Dispersion

Table 1. Basic data for the resins

Resin	LLDPE-A	MDPE-A	MDPE-B
MI	0.77	0.67	0.65
Density	0.918	0.935	0.936
M_w x e3	110.9	121.9	123.5
M_w/M_n(MWD)	9.0	9.2	8.5
$Eta,_1$ x e5	4.29	4.92	4.57
$Eta,_2$ x e3	7.11	7.94	8.73
$Eta,_1/Eta,_2$	60	62	52
Er	3.9	4.2	3.9

Eta, 1 and Eta, 2 are the complex viscosities at 0.0251 rand 251 rad/sec.

Table 2. Dispersion and viscosity up-turn data for MB-A and MB-B

	MB-A	MB-B
Carbon black content, wt%	35	40
Delta P,psi	670	110
Go* x E5 (dyne/cm^2)	3.0	3.8

Table 3. Effect of type of screws on ABS with extrusion conditions for LLDPE-A and MB-A blend

Screw Type	Temperature, °C	Screw Speed, RPM	ABS	CB Content, %
Standard	190	25	430	2.63
		100	441	2.60
	230	25	382	2.55
		100	406	2.58
Barrier	230	25	440	2.70
		100	435	2.50

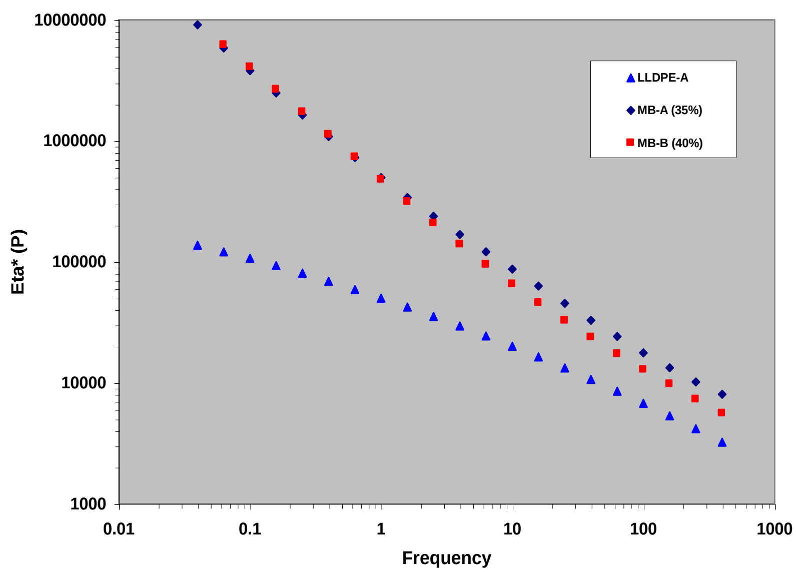


Figure 1. Complex viscosity vs. frequency for LLDPE-A, MB-A, and MB-B at 230°C

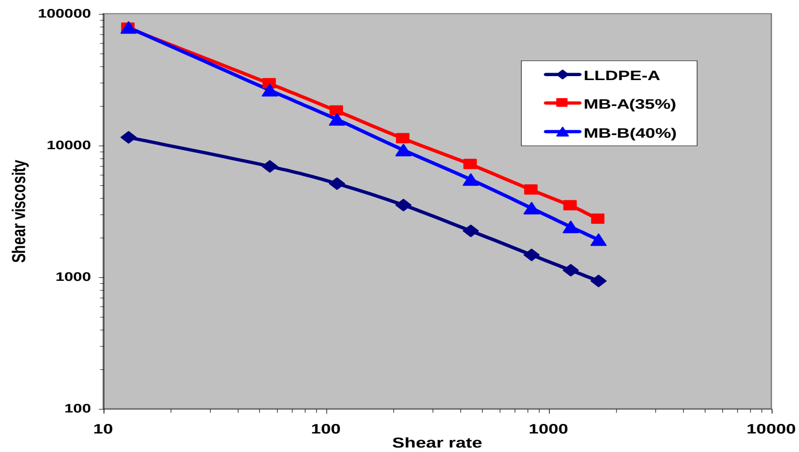


Figure 2. Flow curves at 230 C for LLDPE-A, MB-A, and MB-B

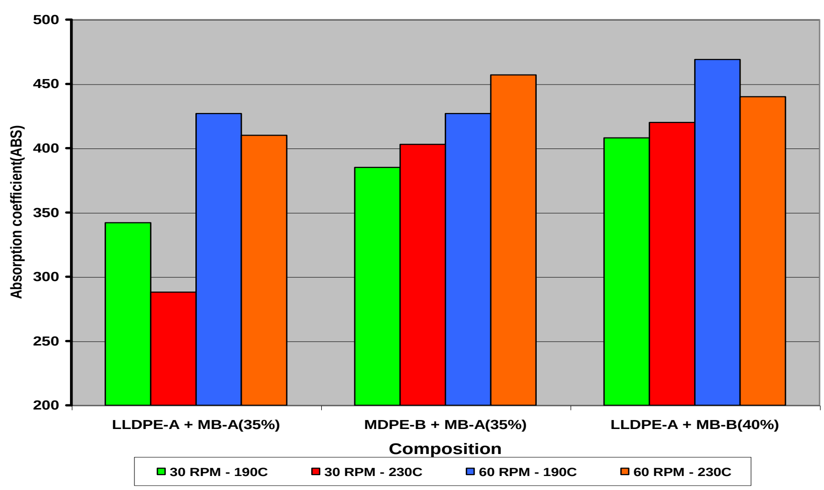
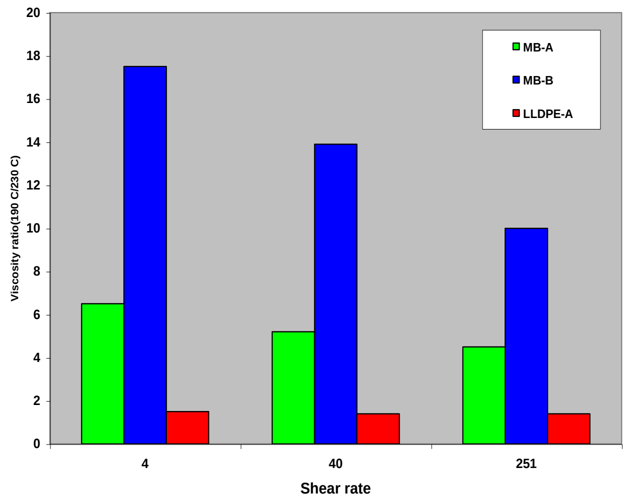


Figure 3. ABS vs. screw speed for the jacket blends extruded at 190 °C and 230 °C



4. Shear dependent viscosity ratio at 190 and 230 °C for LLDPE-A, MB-A, & MB-B

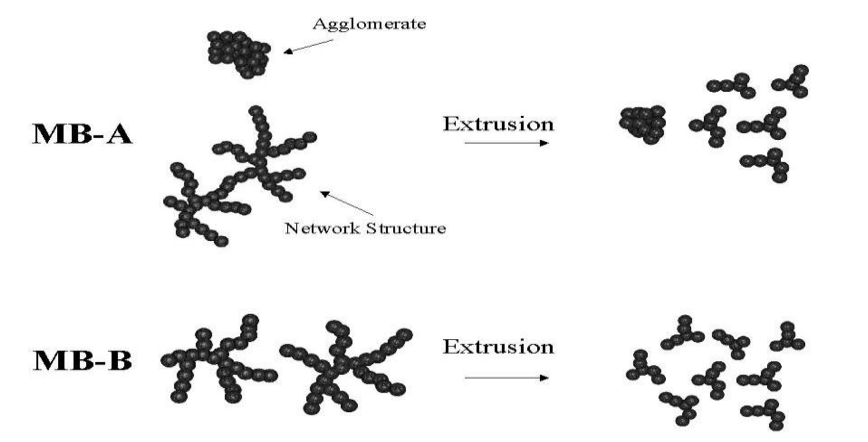


Figure 5. A proposed CB dispersing mechanism with MB-A (35%) and MB-B (40%)

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