

## THE IMPACT OF CARBON BLACK MORPHOLOGY AND DISPERSION ON THE WEATHERABILITY OF POLYETHYLENE

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### ABSTRACT

Carbon black is one of the most widely used and most effective ultraviolet (UV) light stabilizers for plastics applications. Several important segments of the plastics industry rely on carbon black for UV stabilization of weather-resistant products, including telecommunications and power cable jacketing, plastic pipes, geosynthetic membranes and agricultural films. Recent research at Cabot Corporation confirms that the quality of the dispersion of the carbon black in a plastic medium (i.e. polyethylene) is an important component of both the UV-resistance and mechanical properties of the finished plastic article. There is a significant body of research into the linkage between carbon black morphology, including particle size, and UV performance. There is also anecdotal evidence demonstrating the linkage between dispersion quality and overall weatherability. In this study, Cabot will demonstrate that incremental improvements of carbon black dispersion can positively influence the expected life of plastic articles. With industry standard carbon blacks as a reference point, Cabot documents the morphological considerations of UV energy absorption and presents laboratory data demonstrating the link between dispersion and weatherability as well as between morphology and weatherability.

### INTRODUCTION

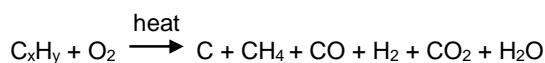
Carbon black (CB) is more than a colorant. In addition to its tinting power, electrical or filler action, it provides plastics with a long-term and low cost UV protection, stabilising polyolefins and other polymers against sunlight [1-4]. The UV protection property of CB is dependent on its morphology, loading and surface chemistry. However if the CB is poorly dispersed or diluted, its full benefit will not be realized.

These effects will be highlighted by comparative weathering results and UV absorption data obtained for low density polyethylene films.

### 1) Basic Information on Carbon Black

#### • Production

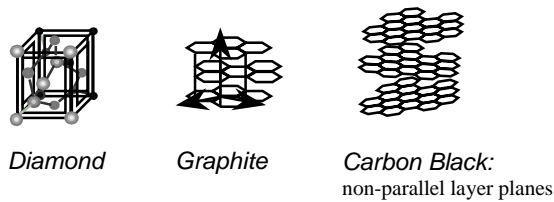
CB results from incomplete combustion or thermal cracking of a hydrocarbon raw material (**figure 1**). Nowadays almost all carbon black is manufactured by the *oil furnace process*: a highly aromatic feedstock is partially burned by atomization into a hot flame made of natural gas and preheated air, the reactor temperature reaching more than 1500°C. At the process end, *powder* ("fluffy") or *pelletized* carbon black is collected. The oil furnace process permits efficient control of end product physical and chemical properties.



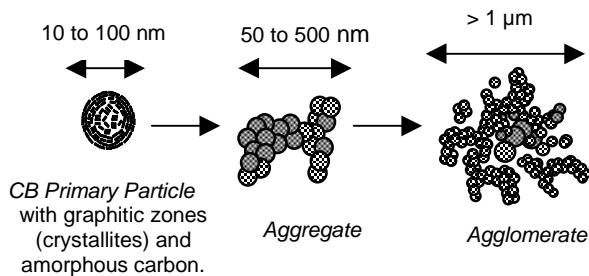
**Figure 1:** partial oxidation of aromatic hydrocarbons.

#### • Form

Carbon black is a particulate form of industrial carbon which exhibits a "*quasi-graphitic*" microstructure (**figure 2**). The manufacturing process leaves various forms of oxygenated groups on carbon black layer planes: mainly phenolic, quinolic and carboxyl chemisorbed complexes [5]. During the nucleation process (**figure 3**), three to four layers form *crystallites*, which combine to form *primary particles* which continue to grow into *aggregates*. *Agglomerates* are a dense collection of aggregates formed due to the small distances between them and the strong van der Waals forces present. CB dispersion into a polymer matrix will require the breaking of these links. An *aggregate* is *indivisible* and represents the carbon black "*base unit*", although a carbon black is often characterized by its *primary particle size*, as we will do further on.



**Figure 2:** carbon black “quasi-graphitic” microstructure compared to the two regular crystalline forms of carbon (diamond and graphite).



**Figure 3:** CB primary particles fuse together in the reactor and form aggregates and agglomerates.

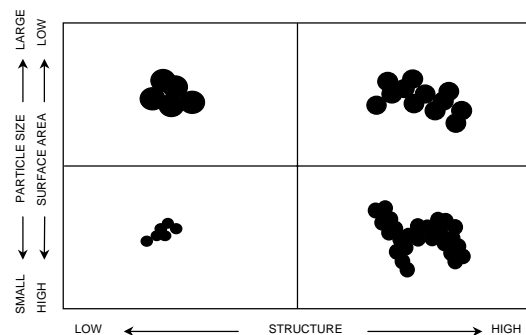
## 2) Some Carbon Black Fundamental Characteristics (figure 4)

- **Particle size** (nm): arithmetic mean of diameters of a sufficient number of primary particles of a carbon black grade. Diameters are determined by TEM (Transmission Electron Microscopy) measurements using ASTM D-3849.
- **Surface area** (m<sup>2</sup>/g): specific surface area is determined by nitrogen adsorption capacity using the BET (Brunauer-Emmet-Teller) procedure. Small particles will confer a large surface area per unit weight.
- **Structure** or DBP oil absorption (ml/100 g): the amount of DBP (di-butyl-phthalate) absorbed by 100g of carbon black at a fixed torque value, according to ASTM D-2414. Structure or the DBP adsorbed is function of the aggregates void volumes and describes the degree to which the CB particles have fused together to form aggregates: a low structure black (low DBP) is made of few primary particles compactly fused together while a high structure black (high DBP) is made of many primary particles with considerable branching and chaining.

## 3) Polyethylene Degradation

Finished materials designed for external applications may degrade in use, with time. They are said to “weather” when their structure changes due to *light, heat, moisture* and *oxygen* contact. Materials like plastics absorb sunlight

radiations and undergo photo-chemical reactions. Oxidation occurs leading to an alteration of their colour, texture or composition resulting in impact loss, embrittlement, chalking or surface cracking. Out of the whole solar emission spectrum (range defined by CIE [6]), only the smallest part, the 290-400 nm UV region, is responsible for most of the polymer damage [7]. Photo-oxidation of polyethylene proceeds by a free radical chain mechanism in presence of oxygen: the ultraviolet light absorbed by the polyethylene provides sufficient energy to break key molecular bonds and generate free radicals that propagate to give *hydroperoxides*, compounds containing *hydroxyl, carbonyl and vinyl groups*, which also absorb UV radiation and undergo further degradative processes (i.e. Norrish type I and II reactions of the carbonyl group). As a result, succession of chain scissions and chain recombinations (cross-linking), including more fragile units, induces drastic physical degradations [1].



**Figure 4:** visualisation of carbon black *particle size / surface area* and *structure*.

## EXPERIMENT

Polyethylene protection from UV degradation can be achieved by adding appropriate additives such as antioxidants, typical UV stabilisers (i.e. HALS) or carbon black. Parallel to its colorant function, carbon black is known to act as a UV absorber and antioxidant [8, 9]: it offers the best UV protection for many materials, by absorbing / screening out damaging wavelengths, and by inhibiting photo-oxidation via its surface chemical properties. The following experimental data highlight morphology, dispersion and dilution influence on carbon black UV stabiliser role.

### 1) Influence of carbon black morphology, emphasis on particle size [experiment 1]

Several black pigmented LLDPE (linear low density polyethylene) films were submitted to an accelerated weathering test.

Material lifetimes versus particle sizes and loadings are shown. CB morphology influence on weathering performance is discussed.

• **Sample preparation**

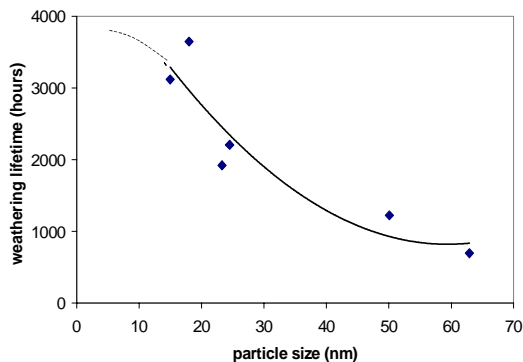
Cast films of 75 μm thickness were made from LLDPE Mi0.5 with 1.5, 2.5 and 3.5% CB of particle size ranging from 15 to 60 nm. Masterbatches were first produced at 35% loading on a 30 mm twin-screw extruder, then diluted to the above % in a second extrusion step. CB main characteristics are detailed in **Table 1**. The films were exposed in a QUV accelerated weathering machine at 60°C using UVA-340 nm (\*) fluorescent lamps (ASTM G53-95) with no condensation cycle and irradiance level of 1.25 W/m<sup>2</sup>@340 nm. (\*) Sunlight simulation in the region of 295 to 400 nm with max. at 340 nm.

• **Weathering results**

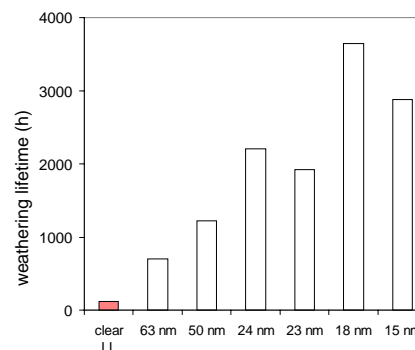
Tensile properties were measured on an Instron 4204 per ASTM D882-9. Failure time was determined when % elongation at break reached 50% of the original value. Material lifetime is expressed as a function of CB particle size, at the same CB loading (**figure 5**) and for various CB loadings (**figure 7**). Clear LLDPE film was also tested (**figure 6**).

**Table 1.** CB characteristics. [Experiment 1]

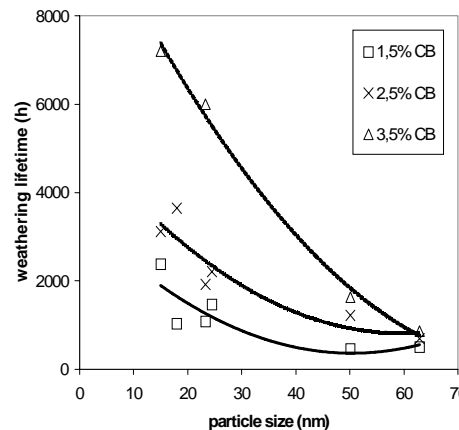
particle size ASTM D-3849 (nm)	surface area BET / N <sub>2</sub> ads. (m <sup>2</sup> /g)	structure DBP abs. ASTM D-2414 (ml/100g)
63	30	72
50	41	125
24	78	72
23	79	102
18	120	114
15	252	68



**Figure 5.** Influence of CB particle size - at same loading - on UV stability. (75 μm LLDPE films, 2.5% CB). [Experiment 1]



**Figure 6.** Weathering lifetime of clear LLDPE versus black LLDPE (75 μm, 2.5% CB). [Experiment 1].



**Figure 7.** Influence of CB particle size - at different loadings - on UV stability. (75 μm LLDPE films, 1.5, 2.5% and 3.5% CB). [Experiment 1].

• **Results discussion**

Virgin LLDPE exhibits very poor weathering stability. CB addition strongly improves weathering performance (**figures 5 and 6**): LLDPE lifetimes is 6 to 30 times higher when 2.5% CB is added. Maximum performance was achieved with CB with particle size <20 nm and high structure.

*The UV stability effectiveness of a carbon black increases with decreasing particle size (as already reported in [10]) with some comments:*

- close particle size blacks (e.g. 23 and 24 nm) may be differentiated by their structure. Lower structure tends to provide slightly better UV protection [11] provided the CB's are equally well dispersed.
- very small particle size blacks (e.g. 15 nm) see their protection benefit tempered by the difficulty to disperse them completely.

*The higher the CB loading, the better the UV protection. (figure 7)*

- CB loading may be limited by physical properties of the compound or other considerations.

In a paper to be published by J.R. Wilson [12], a theoretical model is proposed which shows the 2-dimensional projected surface area of the CB aggregate is directly correlated with its ability to absorb light. Hence, *both particle size and structure* (to a lesser extent) are important parameters affecting UV protection. However both of these parameters also affect dispersion characteristics, so in practice the actual performance of the carbon black in the compound is dependent on a number of factors.

## 2) Influence of Carbon Black Dispersion

Choosing small particle size blacks is a must to reach good weathering performances. However, to get that total benefit, care must be taken to disperse them correctly in the polymer matrix. Dispersion quality impacts the final carbon black agglomerate size in the polymer:

- an optimal dispersion is one that evenly distributes carbon black throughout a polymer down to the smallest carbon black units, the aggregates,
- a poorer dispersion results in larger agglomerates (**figure 3**).

In the presence of agglomerates, UV light is more likely to be rather scattered than absorbed, and polymer UV degradation may start as CB screening protective effect is reduced. *Accelerated weathering tests* [**experiments 2 and 3**], transmitted *light measurements* [**experiment 2**] and COA (375 nm UV absorption coefficient) [**experiment 4**] have been carried out on well and deliberately badly (or less well) dispersed carbon blacks in low density polyethylene films. All other parameters were kept constant.

### a) **Effect of dispersion on weathering** [Experiment 2]

#### • **Film preparation**

- Three different CB, of various particle sizes, were analysed: 60, 25 and 20 nm.
- 30 to 40% CB masterbatches were prepared on a Banbury BR 1.5 mixer: the different CB were incorporated into LDPE Mi7 with a slight and constant amount of lubricant (0.1% lubricant per 10% CB).
- 2.5% CB compounds were obtained by diluting the above masterbatches in LDPE Mi4 and extrusion in a Betol BK32 machine (L/D=30; single screw extruder with additional CTM mixing unit).
- 55 µm cast films were made on a semi-industrial Collin extruder (L/D=27; compression ratio 3:1; 210°C).

The deliberately under-dispersed (UD) samples

were obtained by reducing the Banbury mixing time and shear. **Table 2** summarises CB dispersion quality and films involved.

#### • **Dispersion quality assessment**

Via *Screen 100 mesh (#)* and *film* tests:

- The *screen 100 mesh* test consists of extruding 40 g of MB, slightly diluted in LDPE Mi2, through a Betol extruder ended with a 100 mesh screen. The number of particles trapped in the screen is then counted. Results are in "particle number".
- The *film* test consists of making a 50 µm blown LDPE Mi0.3 film containing 1% of CB. The film is then sufficiently translucent for analysis by transmission on a light cabinet. Spots are detected by touch and visually counted. Results are in "speks per gram".

#### • **Accelerated weathering test**

- Films were placed in an *ATLAS xenon arc machine* and exposed to the standard accelerated weathering norm for films ISO 4892-2, with conditions: ATLAS Ci65A machine, 6500 W xenon lamp, borosilicate-s / borosilicate-s filters (\*), irradiance = 0.35 W/m<sup>2</sup>@340 nm, cycles = 102 minutes light followed by 18 minutes light + specimen spray, light cycle temperature = 65°C (BST), light cycle relative humidity = 65%. (\*) Simulation of total solar emission spectrum, starting from 290 nm.
- Five rectangular 10 mm wide strips were submitted after exposure to a traction test using an Instron 4466 machine complying with ISO 527-3 norm. The percentage of elongation at break (% E at B) in function of weathering exposure time was recorded to trace material degradation.

#### • **Results and discussion**

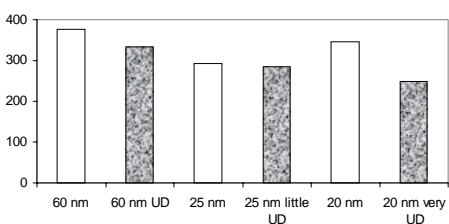
- *Impact of dispersion on initial properties.*

Initial physical properties of a material are dependent on the sample preparation or sample "history" (resin type, loading, processing conditions, thickness...). Care was taken to work comparatively, to only link CB type and dispersion degree to weathering performance, all other parameters were similar.

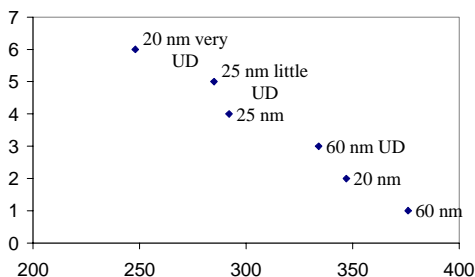
Unaged materials' initial elongation at break (**figures 8 & 9**) appears to be directly dependent on dispersion quality or "global dispersion ranking" (**table 2**): the better the CB dispersion quality, the better the initial physical properties; the poorer the dispersion or the higher the UD gap within same CB particle size, the higher that physical property difference (**table 2, figure 10**).

**Table 2.** Dispersion results and ranking (UD= under-dispersed). Description of films involved in **experiment 2**.

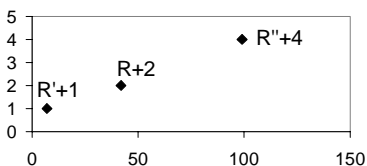
CB Type	Screen Test 100#	Film Test	Global Dispersion Ranking	Dispersion Comparison by CB Type	Films Submitted To Weathering - identification -
<i>particle size</i>	<i>particle number</i>	<i>speks per gram</i>	<i>from best (1) to worst (6) - arbitrary scale -</i>	<i>UD gap compared to reference</i>	<i>LDPE 55µm 2.5% CB</i>
60nm	4	0.7	<b>1</b>	Reference = R	<b>60nm</b>
60nm "UD"	9	0.8	<b>3</b>	(3-1) → = R +2	<b>60nm "UD"</b>
25nm	6	7.2	<b>4</b>	Reference = R'	<b>25nm</b>
25nm "UD"	10	11	<b>5</b>	(5-4) → = R' +1	<b>25nm little "UD"</b>
20nm	5	0.5	<b>2</b>	Reference = R''	<b>20nm</b>
20nm "UD"	10	>20	<b>6</b>	(6-2) → = R'' +4	<b>20nm very "UD"</b>



**Figure 8.** Initial % E at B of 55 µm LDPE films (2.5% CB). [Experiment 2].



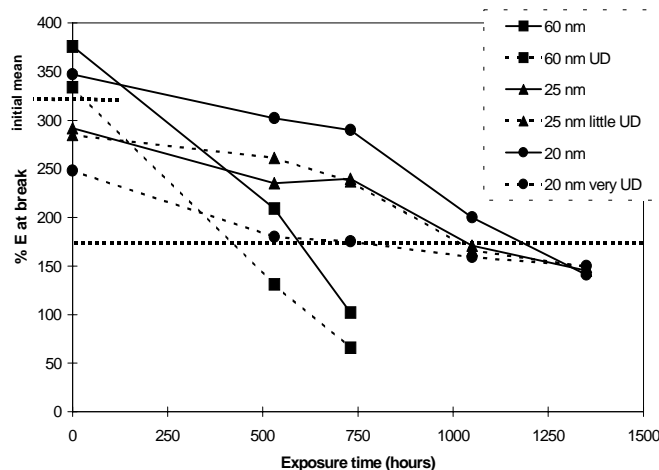
**Figure 9.** Dispersion quality ranking (1 = best dispersion, 6 = worst dispersion) in function of initial % E at B of films. [Experiment 2].



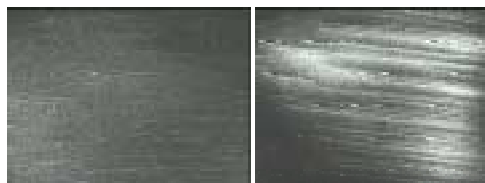
**Figure 10.** UD gap (within same CB particle size) in function of initial % E at B difference. [Experiment 2]

- Impact of dispersion on properties retention. (figure 11) To make things objectively comparable, the initial *mean* % elongation at break has been indicated and a bold dotted line

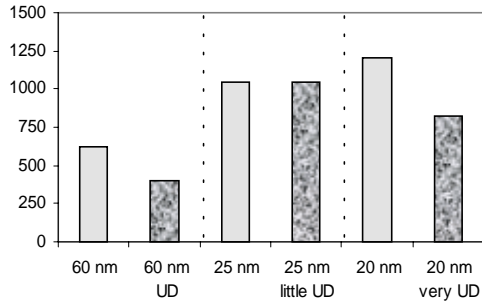
has been drawn at half that value: the test end limit is set at 175% E at B (in accordance with CEN for agricultural films recommendation + safety margin). Weathering lifetimes: see figure 13. Magnification of weathered films: see figure 12. UD gap versus lifetime loss: see figure 14. Shorter weathering lifetimes are obtained with under-dispersed samples except for "25 nm" where UD gap is the smallest. The highest UD gap induces the highest lifetime difference.



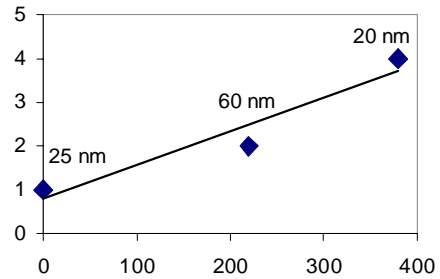
**Figure 11.** Dispersion influence on weathering stability - 55 µm LDPE films, 2.5% CB: Atlas xenon arc (ISO 4892-2 / ISO 527-3), % E at B in function of exposure time. [Experiment 2].



**Figure 12.** Magnification (15x) of weathered films - 800 hours ageing: left= 60 nm: right= 60 nm UD. [Experiment 2].



**Figure 13.** Film weathering lifetimes (hours) [Experiment 2].



**Figure 14.** UD gap in function of lifetime loss (hours). [Experiment 2].

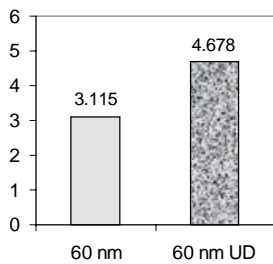
*- Transmitted light study*

Films have been placed between a powerful 100,000 lux light source and a luxmeter with detection in the visible range. The number of lux transmitted through the film is expressed in figures 15a, b. Light transmission effectiveness is correlated to weathering performances (figures 16a, b). These figures, as well as figure 11, spot the 2 different groups: the 60 nm and the 25, 20 nm. First group transmits more light, second group is more effective to trap it. Additionally, *the UD films transmit more light or absorb less, inducing worse UV stability, except the "25 nm" where UD gap is very low.* Initial visible light

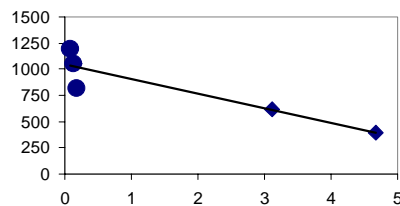
transmission data are linked with UV stability data.

**• Results Discussion**

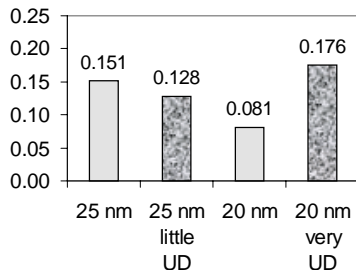
Weathering and opacity results are in line: the lower the transmission (higher the opacity), the better the UV stability. Both are function of CB type and %, film thickness, and on a microscopic scale, seem a function of dispersion. Poor dispersion induces lower opacity and poorer weathering performances. From what we may deduce dispersion and UV stability are directly dependent, with however a major impact of dispersion on initial physical properties.



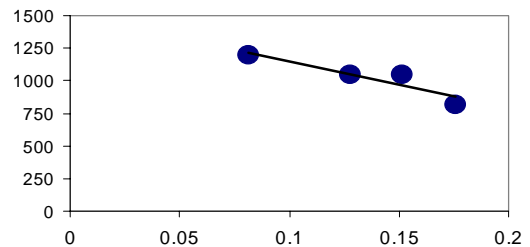
**Figure 15a.** Transmitted light (Lux). [Experiment 2].



**Figure 16a.** Lifetime (hours) in function of transmitted light (Lux). [Experiment 2].



**Figure 15b.** Transmitted light (Lux). [Experiment 2].



**Figure 16b.** Lifetime (hours) in function of transmitted light (Lux). (= Zoom of a 16a region). [Experiment 2].

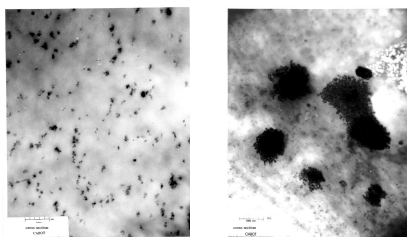
**b) Effect of dispersion on weathering [Experiment 3]**

**• Weathering results and discussion**

**Table 3. Experiment 3 results. \* bad dispersion**

CB Particle size nm	Failure Time days to reach 50% retention
None	5
60	21
19	43
15	99
15	39*

Above film samples (1.5% CB) were prepared and tested as in **experiment 1**. The 15 nm CB sample which exhibited shorter than expected failure time was examined for dispersion quality. Thin sections (100 nm) were prepared using an RTE ultra-cryomicrotome then viewed at 50,000X magnification by Transmission Electron Microscope. Numerous agglomerates of CB were detected, as illustrated in **Figure 17**. The other film samples, examined in a similar manner, showed no such defects. *These results also clearly show the impact of bad dispersion on weathering performance of the LLDPE.*



**Figure 17.** TEM images: *left*= 15 nm CB sample “good dispersion”; *right*= 15 nm CB sample “bad dispersion”.

**c) Effect of dispersion on COA [Experiment 4]**

**• Sample preparation**

Three CB with different primary particle sizes were compounded into LLDPE Mi20 resin on a laboratory size Kobelco internal batch mixer at three different loadings (**table 4**). Masterbatches (except 2.5%) were then letdown (i.e. diluted) in LLDPE Mi0.7 using the Kobelco mixer to 2.5% CB loading.

**Table 4. Experiment 4 samples**

CB particle size nm	CB masterbatch loading %
19	35, 20, 2.5
25	40, 20, 2.5
60	50, 20, 2.5

**• Coefficient Of Absorption**

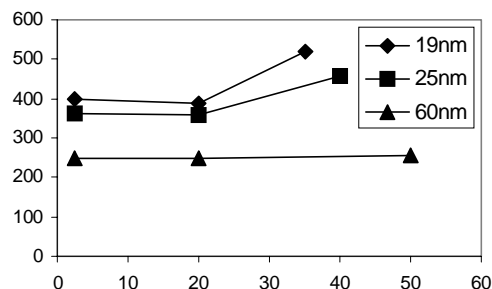
COA was measured per ASTM D-3349\*. This test measures the amount of light transmitted through a black pigmented film (typically less than 5% CB). Conversely, the amount of light *not* transmitted is absorbed, forming the basis for the calculation of the COA parameter (Beer’s Law).

COA test procedure\*:

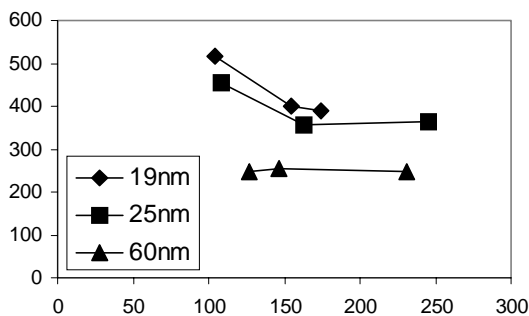
1. Thin films are pressed to approximately 0.01mm.
2. Samples are exposed to UV light at 375 nm wavelength using a Beckman Model B spectrophotometer.
3. COA is calculated based on the absorbance value and sample thickness.
4. COA units are (1000 absorbance unit / meter).
5. ASTM D-3349 Least Significant Difference (within lab): Sr = 24.

**• Dispersion evaluation**

Dispersion was evaluated using image analysis. Six small pieces of each sample were pressed on a glass slide at 215°C for 5 minutes. The pressings were examined at 100X magnification. Agglomerates were sized and counted using Kontron Image Analysis software. Results are shown in **figures 18 and 19**.



**Figure 18.** COA versus initial masterbatch loading (% CB) - for different CB particle sizes, at 2.5% CB in final letdowns. [**Experiment 4**]



**Figure 19.** COA versus total agglomerates (# of pips), for different CB particle sizes at 2.5%. [**Experiment 4**]

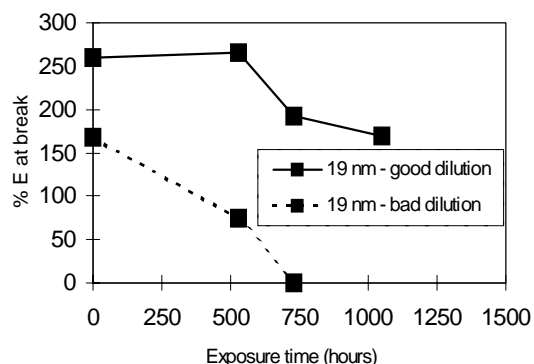
## Results discussion

COA shows a significant improvement at higher masterbatch loadings for the 19 nm and 25 nm CBs, presumably from better dispersion resulting from increased shear stress at higher masterbatch viscosity. The COA for the more easily dispersible 60 nm CB was flat over the range of loading studied. For the 19 nm and 25 nm CB the COA was highest for samples which had the fewest total agglomerates, an indicator of dispersion quality.

### 3) Influence of Carbon Black Dilution

#### • Experimental results

In **experiment 2** dispersion study, films were made via the masterbatch *and* compound route: the cast film extrusion line used did not mix and homogenize material sufficiently well to work directly with masterbatches. Without that last compounding step, films would have been very poorly diluted and full of fragile, less concentrated zones. We included however in the same study an additional film (19 nm CB) based on direct dilution. **Figure 20** shows comparative weathering evolution for “good” and “poor” dilution quality.



**Figure 20.** dilution influence on weathering stability - 55 µm LDPE films, 2.5% CB: Atlas xenon arc (ISO 4892-2 / ISO 527-3); % E at B in function of exposure time. [Experiment 2+].

#### • Discussion

A bad dilution can adversely affect polymer performance and weathering stability. The way to incorporate CB in a polymer matrix must be in total harmony with the equipment design and requirements or vice versa.

## CONCLUSION

Black polymer UV resistance prediction is always a combination of several parameters, especially CB morphology, loading and dispersion quality. This study has demonstrated the very positive

influence of small particle size CBs on polyethylene weatherability as well as the importance of good dispersion and dilution quality to maintain that benefit. Although dispersion quality is mainly affecting the initial physical properties of the films, retention of those properties with ageing time has been shown: physical property drop appears to be directly dependent on the dispersion degree. These results were consolidated with light transmission data which show an increased transmission with poorly dispersed samples.

## ACKNOWLEDGEMENTS

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