

## The effect of carbon black on the physical properties of polypropylene geotextile tapes

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**ABSTRACT:** While carbon black is often introduced into geosynthetics to improve their weatherability, little is known about its influence upon the basic physical properties of the surrounding polymer matrix. A series of polypropylene tapes containing carbon blacks with different physical properties have been produced. Carbon blacks having the lowest fundamental particle size (20 nm) and lowest aggregate structures produce minimal effects on tensile and physical structural characteristics when compared with similar unfilled polypropylene tapes. Thermal stabilities of filled tapes are comparable to those of unfilled tapes if particle size is small (16-20nm) and structure is high for carbon blacks of low volatiles content.

### 1. INTRODUCTION

The use of carbon black for enhancing light and weathering stability of polyolefins and, in particular, orientated polypropylene, such as geotextiles has been established for almost 30 years. A recent review (Mwila, Horrocks and Miraftab, 1994) collates the evidence from the scientific literature that the UV and hence weather-stabilising efficiency is inversely proportional to the carbon black particle diameter. This is a consequence of the physical nature of the stabilising activity which is associated with the opacity of the pigment; this is dependent upon the specific surface area and hence reciprocal diameter of particles. Contrary to popular belief, however, carbon black particles are not simply inert carbon particles but have distinctive physical and chemical properties which are determined by their mode of manufacture (Kuhlner and Manfred, 1993).

Carbon black particles are characterised in terms of a number of properties, the most obvious and simplest to define being their fundamental particle diameters which range typically from 20 to 60 nm. Carbon black particles do not exist separately but as aggregates which represent more accurately their effective size. The shape or structure of these aggregates is defined in terms of a surface wettability parameter or absorption of dibutyl phthalate in  $\text{cm}^3$  per 100 g carbon black (DBPA

value). Low structured blacks tend to have simple (linear or spherical) aggregated geometries, whereas highly structured blacks have complex and often branched aggregates. It is interesting to note that the fundamental carbon black particle sizes are of similar magnitude to ordered domains or crystalline regions in linear polyolefins like polypropylene and so might be expected to interact with their formation during the extrusion and stretching of tapes and filaments and hence, influence their physical and tensile behaviours. In fact, it is known that carbon black aggregates act as nucleating sites for polymer crystallisation and thus significantly enhance the rate of crystallisation during melt processing (Lin et al., 1991).

Recent work in our laboratories (Horrocks and D'Souza, 1994) suggests that the presence of carbon black in orientated polypropylene tapes can improve creep resistance and the sensitivity to thermal oxidative degradation when subjected to tensile stresses upto 10% of ultimate. However, conflicting results (Herbst, 1995) indicate that the presence of carbon black can reduce the thermal oxidative stability of polyolefins and in particular, that of polyethylene.

This paper reports the first part of an exhaustive study which has attempted to relate carbon black variables to the tensile, physical and durability properties of orientated polypropylene tapes containing them.

## 2. EXPERIMENTAL

The experimental methodology is based on the selection of a number of carbon blacks, their incorporation into polypropylene and extrusion into geotextile-grade tapes followed by characterisation for tensile and physical properties.

### 2.1 Materials and experimental design

The carbon black variables to be investigated are particle size, structure, volatiles content and concentration. A factorial experimental design was adopted and the experimental matrix in Table 1 was used to select an appropriate range of carbon blacks for the study.

The eleven carbon blacks (including two having exceptionally small particle diameters of 16 nm) selected were provided by Cabot Corporation and are listed in Table 2 with their properties and concentrations in Himont S-30-S polypropylene (MFI=1.8 g/10min, 2.16 kg) which contained a standard antioxidant. The polymer was chosen as a typical geotextile grade.

Table 1. Experimental design for carbon black selection.

Particle size, nm	Structure Low	Level Medium	High
2.5 C Black Loading			
20	X	X	X
27	X	X	X
50-60	X	X	X
5% C Black Loading			
20	X	X	X

Table 2. Properties of carbon black grades.

Code**	Conc. %	Particle size, nm	Structure DBPA*	Bulk density, g/l
CB1	2.5	20	98	384
CB2	5	20	98	384
CB3	2.5	20	116	332
CB4	5	20	116	332
CB5	2.5	20	113	344
CB6	5	20	113	344
CB7	2.5	27	72	430
CB8	2.5	27	102	368
CB9	2.5	27	124	320
CB10	2.5	60	65	505
CB11	2.5	50	91	435
CB12	2.5	50	122	352
CB13	2.5	16	105	336
CB14	2.5	16	105	385

Notes: \*\* All are low volatiles blacks except CB14

\* Units are cm<sup>3</sup>/100g

CB13 and CB14 are presented at the bottom of Table 2 because their very low particle diameter makes them fall outside the main particle size groupings. CB14 has exactly the same physical properties to CB13 except that it has a high volatiles content as a consequence of oxidation which introduces reactive oxygenated groups to the particle surfaces. These functional groups may promote both anti- and pro-oxidant properties (Mwila, Mirafab and Horrocks, 1994).

### 2.2 Production of orientated tapes

The compounds were extruded into tapes using a Plasticisers Engineering Labline Mk I single screw laboratory extruder with subsequent drawing and relaxation to give tape tenacities of not less than 0.5 N tex<sup>-1</sup>, shrinkage of less than 5% at 130°C and dimensions, 50 µm thickness and 2.5 mm width (Horrocks and D'Souza, 1994).

### 2.3 Testing

Tensile properties: these were obtained using an Instron Model 4200 tensile tester with a cross-head speed of 200 mm min<sup>-1</sup>, sample length of 100 mm and ten test specimens per sample (expressed as an average) and tested at 20°C and 65% rh. The linear density of each tape was determined by weighing a known length and converting to the mass per 1000 m, and hence expressed as tex.

Infrared spectrophotometry: a Perkin-Elmer 881 instrument was used to determine the isotacticity/crystallinity index by averaging ten separate spectral ratios of absorbance values at 998 cm<sup>-1</sup> and 974 cm<sup>-1</sup> (Luongo, 1960) determined for each sample.

Differential scanning calorimetry: a Polymer Laboratories DSC was used to study the crystallinity, melting and oxidative behaviours of tapes before and after thermal exposure. The intensity of the fusion endotherm of each 0.8-1.5 mg sample heated under static air at 10 K min<sup>-1</sup> enabled changes in crystallinity to be studied as a consequence of introducing each carbon black into polypropylene. Integration of the endotherm yields the heat of fusion which is directly proportional to degree of crystallinity. Since it is known, however, that the thermal effects of the DSC technique itself

may influence crystallinity, the IR-determined isotacticity/crystallinity ratios were measured to enable comparison to be made in this respect.

**Thermal ageing:** unrestrained tapes were suspended in circulatory air ovens heated at 130°C to promote oxidative degradation sufficient to promote brittle failure during a period of 20 days or so according to the previously established procedure (Horrocks and D'Souza, 1994).

### 3. RESULTS AND DISCUSSION

#### 3.1 Tensile properties

Table 3 lists the tensile properties of each tape expressed as tenacity ( $\text{N tex}^{-1}$ ) and percent extension-at-break or breaking strain (%); actual linear densities, LD (from which tenacity, T values have been derived; ie.  $T=BL/LD$  where BL is the tape breaking load (N)) are included. The latter are greater for each filled tape with respect to the unfilled tape because of the presence of the more dense carbon black. They also depend on concentration (compare CB2 and CB1, for example) and structure. This latter effect may be seen by comparing respective LD values for the 27 nm particle sized blacks CB7, CB8 and CB9; CB9 has the highest linear density and the black present has the highest DBPA value (see Table 2) and hence, structure of this group. The highest linear

Table 3. Tensile properties of unfilled and carbon black-filled polypropylene tapes.

Sample code	CB conc, %	LD, tex	T, N/tex	BS, %
PP	0	93.5	0.53	14
CB1	2.5	105.6	0.51	18.1
CB2	5	120.7	0.35	24.2
CB3	2.5	114.1	0.45	18.4
CB4	5	106.8	0.43	21.1
CB5	2.5	105.1	0.45	15.2
CB6	5	110.3	0.39	15.6
CB7	2.5	108.4	0.51	13
CB8	2.5	111.2	0.45	14.6
CB9	2.5	116.9	0.43	22.2
CB10	2.5	107.2	0.52	18.6
CB11	2.5	112.7	0.49	14
CB12	2.5	110.6	0.45	15
CB13	2.5	123.9	0.37	19.3
CB14	2.5	106.4	0.42	14.8

Note: PP is the unfilled tape, LD=linear density, T=tenacity, BS=breaking strain

density is shown by the CB13 tape which has the smallest particle diameter (16 nm) and again a relatively high DBPA value.

Of particular importance to technical filaments and tapes containing filler particles, is their maintenance of tensile strength. Figure 1 shows a plot of tenacity for the 2.5 % concentration tapes versus carbon black structure (as DBPA value) for the different particle sizes 20, 27 and 50 nm. There is clear evidence that tensile strength depends on both particle size and structure at constant concentration. Closer inspection of the results in Figure 1, suggest that although low particle sizes yield the highest strength tapes, there is a significantly greater apparent dependence between strength and structure.

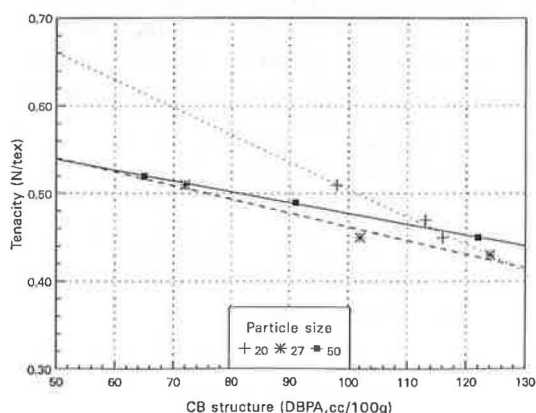


Figure 1. Effect of carbon black structure and particle size on the tenacity of polypropylene tapes.

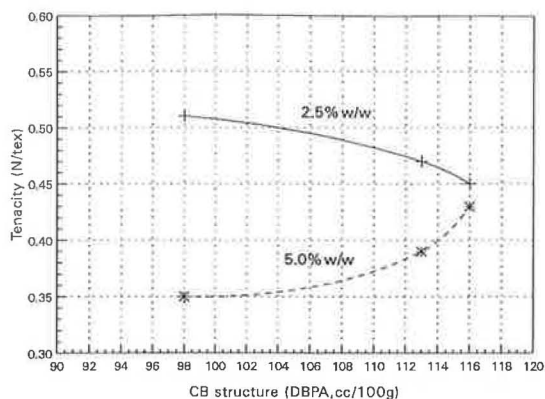


Figure 2. Effect of carbon black concentration on tape tenacity for 20nm diameter carbon black particles.

Figure 2 shows the effect of carbon black concentration on tape tenacity for particle diameters of 20 nm. Note that increased concentration reduces tenacity and that this reduction is less for more highly structured pigments.

With regard to the tape tenacity results, and as mentioned above, the low-structured carbon blacks gave the highest values (see Table 3 and Figure 1). This effect has been noted by Medalia (Medalia, 1970) in rubbers and he explained it in terms of the proportion of polymer removed from the general polymer matrix by being occluded in the internal voids of the carbon black aggregates. Clearly, polymer chains are too large to be occluded within the voids of individual particles, but they may become trapped within the larger voids present in structured aggregates. Such trapped or occluded chains could be considered to be those which first "wetted" the surfaces of aggregates. These polymer fractions are therefore effectively "removed" from the main polypropylene matrix and so are unable to take part in the macrodeformation of the polymer when subjected to a tensile stress. The occluded polymer, therefore, behaves more like filler and so the effective volume of the polymer is reduced. Conversely, the effective concentration of the carbon black increases and does so with its level of structure; thus highly structured blacks at a given concentration yield lower tape tenacities.

Medalia (Medalia, 1970), based on his studies of rubber, related the effective volume fraction,  $v_{eff}$  of a carbon black to its actual concentration fraction,  $v_{cb}$  and structure as DBPA value by the following equation:

$$v_{eff} = v_{cb} (1 + 0.02139 \text{ DBPA}) / 1.46 \dots (1)$$

In order to calculate  $v_{cb}$ , the density,  $\rho$  must be found using the equation (Janzen, 1982) from the respective bulk density,  $D$  (see Table 2) of each black:

$$\rho = (610/D - \text{DBPA})^{-1} \dots (2)$$

Using this last equation, the density of each carbon black was determined and, from equation (1), the respective value of  $v_{cb}$  and hence  $v_{eff}$  calculated. Since tenacity is a direct measure of the intrinsic strength of a tape, assuming that each tape containing 2.5% carbon black has the same density, then each volume fraction is plotted as a function of tape tenacity in Figure 3 for the

samples CB1-CB12 at 2.5% concentration.

The occluded volume of polypropylene within the aggregate voids equals the difference between the effective and actual volume fractions and these values are included in Figure 3 for the same tapes. Although the straight lines in Figure 3 do not have very high correlation coefficients, they do indicate significant trends. Clearly, tape tenacity is unaffected by  $v_{cb}$ , which is constant for each carbon black, but a smooth decrease occurs as the effective volume fraction increases. The trend is wholly ascribed to the occluded volume fraction component which supports the above argument that high carbon black structure will effectively remove polymer from the stress-bearing macromolecular structural elements.

### 3.2 Morphological properties

Measures of the crystallinity of each tape and hence the influence of crystallinity upon it were assessed using both the DSC and IR methods outlined above. Neither method was used to provide absolute values, however, and both were used to improve the level of confidence that possible changes in crystallinity might be related to carbon black properties. The IR method gives an indication of the fraction of isotactic polypropylene monomeric repeats which are in ordered domains in each tape; DSC, however, via the heat of fusion, yields a measure of the polycrystalline population which melt the expected temperature range, 160-175°C. Both measures of crystalline order should

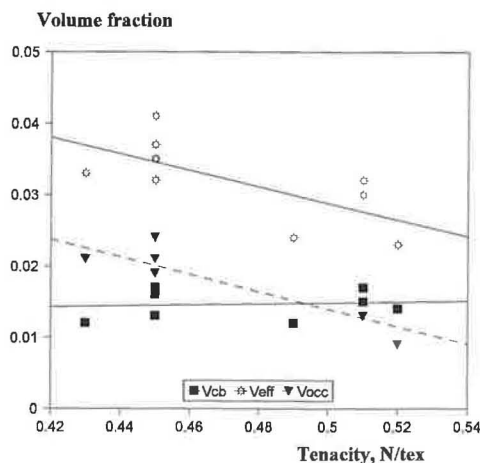


Figure 3. The effect of volume fractions on tenacity for tapes containing 2.5% carbon black

respond similarly if the presence of carbon black and its variation in properties causes the overall degree to change while not unduly influencing the type of crystalline structure or the distribution of polycrystallinity.

Typical DSC responses are shown in Figure 4 for unfilled and 2.5%(CB1) and 5%(CB2) filled tapes from which the onset and maximum temperatures of fusion and the areas within the fusion endotherms, which equal the heats of fusion,  $H_f$  are derived.

Table 4 lists the IR-derived crystallinity indices and the corresponding heats of fusion and fusion endotherm, minimum temperatures for all tapes. From this table, it is seen that the IR-index of all carbon black-containing tapes are less than respective values for the unfilled tapes suggesting that they have lower degrees of order. The same is true for the relative changes for heats of fusion. The role of added carbon black is clearly not simple, however, and recent studies (Lin et al., 1991) have suggested that, although the total order may be less, the particles nucleate additional crystallisation sites resulting in smaller crystalline domains with a narrower size distribution. However, by comparing all the results for filled tapes, various trends may be observed. The effect of increasing concentration from 2.5 to 5% shows a reduction in both IR index and heat of fusion values which indicates that higher black concentrations reduce overall order. This is reflected in the lower tenacities of CB2, CB4 and CB6 with respect to their lower (2.5%) concentration analogues CB1, CB3 and CB5.

The effect of carbon black aggregate structure is shown in Figure 5 where both IR index and  $H_f$  are plotted against respective DBPA values for the 2.5% filled tapes.

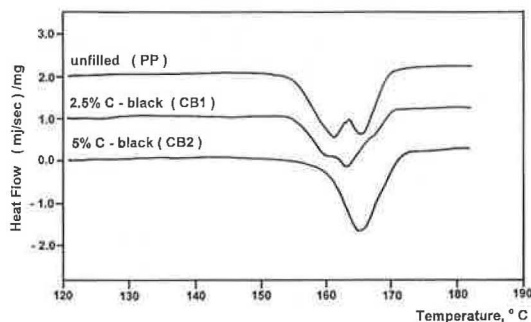


Figure 4. Typical DSC response in air at  $10 \text{ K min}^{-1}$  for a filled or unfilled polypropylene.

Both crystallinity parameters show similarly increasing trends with increase in structure, although the slope is less for the heat of fusion. This is possibly a consequence of the DSC thermal history which will further anneal samples and reduce differences in order generated during tape production. Particle size, however, seems to have little influence on the crystallinity as shown in Figure 6 below.

The effect of the carbon black on the shape of the fusion endotherm and its minimum value is not obvious, suffice it to say that the drop in crystallinity at higher carbon black loadings is accompanied by a sharpening of the endotherm

Table 4. IR crystallinity indices and DSC-derived heats of fusion and melting temperatures.

Sample code	IR Index	H <sub>f</sub> , J/g	T <sub>m</sub> , deg C
PP	0.769	100.8	161
CB1	0.615	81.5	161.2
CB2	0.504	79.4	164.2
CB3	0.636	84.2	163.8
CB4	0.58	79.6	167.3
CB5	0.607	79.4	163.2
CB6	0.495	74.3	166.7
CB7	0.587	78.6	165
CB8	0.617	78.8	162.3
CB9	0.601	74.8	164.1
CB10	0.616	76.1	164.7
CB11	0.623	74.8	161.8
CB12	0.681	80.1	165
CB13	0.581	75.6	172.3
CB14	0.579	59.5	167.5

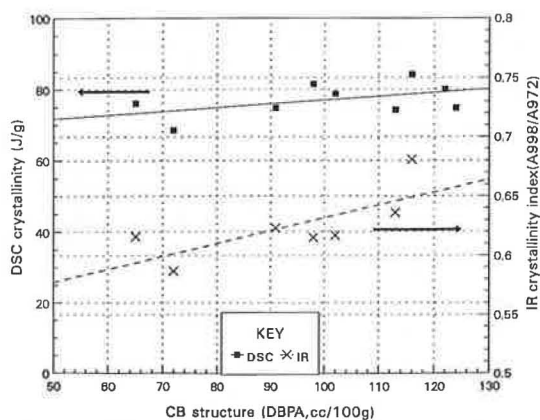


Figure 5. Effect of carbon black structure on polypropylene tape crystallinity.

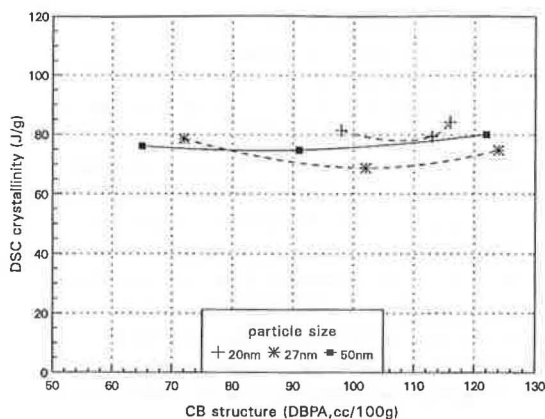


Figure 6. DSC heats of fusion plotted against structure and resolved into different particle sizes.

and a shift of the minimum to higher values (see Figure 4). These observations agree with the previously suggested reduction in crystallite size distribution caused by carbon black (Lin et al., 1991).

### 3.3 Effect of oven exposure at 130°C in air

Oven ageing was undertaken with the selected tapes PP, CB1, CB2, CB3, CB4, CB10, CB12 and CB14. In this way, the variables of small and large particle size, low and high structure, low and high volatiles content and concentration could still be investigated (see Tables 1 and 2), but with a reduced, more efficient experimental matrix. For each sample, several sets of 10 specimens were freely suspended and sets were removed for periodic tensile testing. Figures 7 and 8 present the effect oven ageing on the percentage retained breaking load for the sample sets PP, CB1, CB2, CB3, CB4 and PP, CB10, CB12, CB14 respectively.

Figure 7 shows that both unfilled and filled tapes show a gradual loss in tensile strength. It should be noted that, typically with polypropylene tapes and filaments, embrittlement occurred suddenly. With PP, CB2 and CB3 this took place after 20 days whereas with CB1 and CB4, embrittlement was evident after only 15 days. There was thus no obvious affect of carbon black concentration although the relative rates of loss of tensile strength suggest that the higher concentration tapes are slightly more stable.

### Retained BL, %

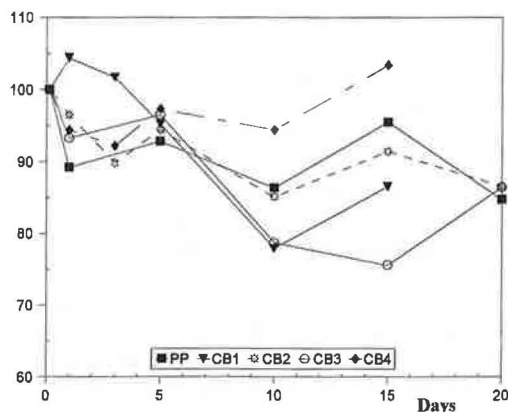


Figure 7. Effect of oven-ageing at 130°C on retained breaking load for CB1, CB2, CB3 and CB4 tapes.

### Retained BL, %

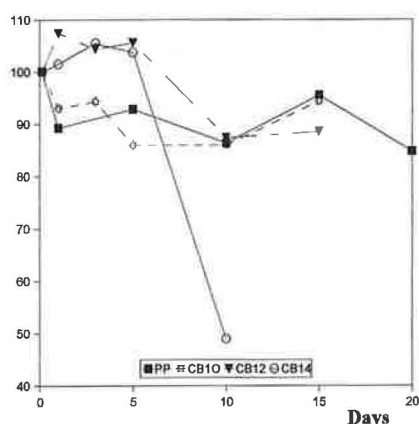


Figure 8. Effect of oven-ageing at 130°C on retained breaking load of PP, CB10, CB12 and CB14 tapes.

Again, in Figure 8, the last point shown on each curve represents the highest pre-embrittlement time for that tape. CB10 and CB12 show similar trends to the filled tapes in Figure 7 as well as the unfilled tape. The loss in strength of the high volatiles-content, carbon black-containing CB14 is dramatic, coupled with the halving of its maximum pre-embrittlement time to 10 days. Therefore, while all of the carbon blacks at 2.5% concentration and with low volatiles content, and hence low concentrations of oxidised species on their particle surfaces, show thermal stabilities which are comparable to unfilled polypropylene (except, perhaps, for CB1), presence of high

## B Strain, %

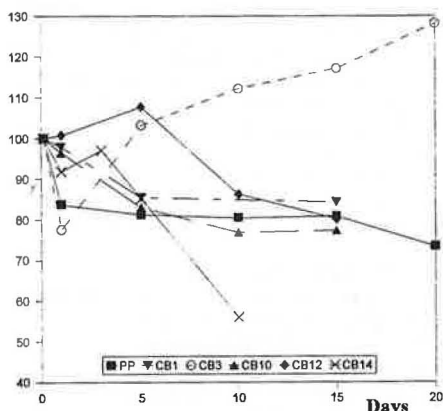


Figure 9. Effect of oven-aging at 130°C on retained breaking strain for 2.5% carbon black-filled tapes.

volatiles-content, carbon black obviously sensitises thermal oxidative degradation.

A more sensitive means of comparing the relative thermal stabilities would be to compare the relative rates of loss of tape breaking load during oven-aging. The scatter present and relative low number of data points for each tape exposure experiment does not allow confident line fitting and hence slope determination to occur. Both linear and power law regressions give correlation coefficients below 0.80. This is not the case, however, if the relative changes in breaking strains for each tape during exposure are compared. Figure 9 presents the changes in retained breaking strain for tapes containing 2.5% carbon black during oven exposure at 130°C.

In our previous studies (Horrocks and D'Souza, 1994), evidence was provided which suggested that during exposure of a series of tapes produced from polypropylenes of different MFI and aged under varying levels of applied stress, the changes in breaking strain with time were a more sensitive indicator of their relative thermal stabilities. Linear regression of each of the trends in Figure 9 enables best-fit lines to be constructed with correlation coefficients of 0.77 or better. Table 5 shows the predicted intercepts and slopes for each of the trends in Figure 9.

Ideally, each intercept should equal 100% breaking strain retention and the variations from this value are a consequence of the relatively low number of data points per ageing experiment, coupled with the consequences of known annealing effects that occur during the first day's

Table 5. Linear regressional analyses of retained breaking strain trends in Figure 9.

Code	Intercept	Slope	Correlation coefficient
PP	90.6	-0.86	0.77
CB1	97.2	-1	0.83
CB3	89.9	1.94	0.88
CB10	96.5	-1.57	0.91
CB12	104.4	-1.52	0.84
CB14	102.3	-4.27	0.95

exposure (Horrocks and D'Souza, 1991, 1994). The slopes, however, should be independent of any such shift and so these may be more directly compared. If the increase in negativity of slope is a measure of thermal stability, then the tapes may be ordered in terms of their increasing sensitivity to thermal oxidation as follows:

$$CB3 < PP < CB1 < CB10 = CB12 \ll CB14$$

This order is close to that for reducing values of maximum pre-embrittlement time of:

$$PP = CB3 < CB10 = CB12 < CB14$$

as discussed above. This ordering suggests that not only do high volatiles-content, carbon black particles sensitise thermal oxidation of polypropylene, but that the combination of small particle size, high structure and low volatiles content (typified by CB3) has minimal effect. Increasing particle diameter, reducing structure or both may lead to an increase in the thermal oxidative behaviour of polypropylene in which such carbon blacks are present. This combination of properties could be the cause of reports in the literature that carbon black sensitises thermal degradation of polyolefins (Herbst, 1995).

## 4. SUMMARY AND CONCLUSIONS

The above results and discussion suggest that the following conclusions may be drawn:

- (i) Addition of 2.5% carbon black to polypropylene produces increases in breaking loads of derived, orientated tapes (of typical geotextile quality) although this converts to a reduced tenacity when values are divided by respective linear densities. Increases in concentration to 5% cause further reductions in tenacity.



(ii) Tape tenacities are greatest for carbon blacks having the lowest particle sizes and structure (as DBPA value). The latter effect is explained in terms of the ability of highly structured blacks to occlude higher fractions of polymer and thus remove it from the stress-bearing polymer matrix.

(iii) Crystalline character is modified in terms of both degree of order and polycrystalline structure in the presence of carbon black. Both IR and DSC-derived measures of crystallinity increase with the level of carbon black structure.

(iv) Thermal oxidative stabilities of carbon black-filled tapes may be adversely affected if the pigment has a high volatiles content or, if of low volatiles content, it has a high particle diameter and/or high structure. A combination of low particle diameter and high structure has minimal effect on the thermal stability of the polymer.

The above research, which describes the first part of a more comprehensive study, provides clear evidence for the first time that the presence of carbon black and its structural characteristics have significant effects on the tensile and structural properties and thermal stabilities (and hence durabilities) of filled polypropylene tapes. The later parts of this study will corroborate earlier results (Horrocks and D'Souza, 1990, 1994) which showed that carbon black may influence the stress sensitivity of polypropylene to thermal oxidation and hence its durability.

On a final note, it may be stated that carbon blacks should be carefully selected for use in polypropylene geotextiles if maximum durabilities are to be achieved in end-use while maintaining acceptable tensile properties. Thus while small particle sizes favour both maintenance of polypropylene tape tensile properties and thermal stability, low structure favours the former and high structure, the latter.

## 5. ACKNOWLEDGEMENTS

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## REFERENCES

Herbst, H 1995. Stabilisation allows higher added value to post-used plastics. In A.Barrage & X.Edelman (eds), *R'95 Recovery, recycling, re-integration*, 2: 83-92, Geneva: EMPA.

Horrocks, A.R. & J.A.D'Souza 1990. Physicochemical changes in laboratory-aged oriented polypropylene tapes. In G.den Hoedt (ed), *Geotextiles, geomembranes and related products*, 2: 709-714, Rotterdam: Balkema.

Horrocks, A.R. & J.A.D'Souza 1991. Physicochemical changes in stabilised, oriented polypropylene films during the initial stages of thermal oxidation. *J. Appl. Polym. Sci.* 42: 243-261.

Horrocks, A.R. & J.A.D'Souza 1994. The effects of stress, environment and polymer variables on the durabilities of oriented polypropylene tapes. *Polym. Deg. Stab.* 46: 181-194.

Janzen, J 1982. *Rubber Chem. Technol.* 55: 669.

Kulner, G. & V.Manfred 1993. In J.D.Donnet, R.C.Bansal & M.J.Wang (eds), *Carbon black science and technology* :1.New York: Marcel Dekker.

Lin, Y., J. Zou & J.E.Spruiell 1991. *Antec*: 1950

Luongo, J.P 1960. Infrared study of polypropylene. *J. Appl. Polym. Sci.* 3: 302.

Medalia, A.I 1970. *Colloid Interf. Sci.* 32: 115.

Mwila, J., M.Mirafteb & A.R.Horrocks 1994. The effect of carbon black on the oxidation of polyolefins - a review. *Polym. Deg. Stab.* 44: 351-356.