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The influence of carbon black on properties of orientated polypropylene

Part I *Tensile and physical properties*

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A series of oriented polypropylene tapes each containing carbon black having defined properties and at a specified concentration were produced and tested for their tensile and physical behaviours at 20 and 130 °C. Tenacities at 20 °C decreased as carbon black concentration increased from 2.5 to 5% (w/w) and with increasing particle size. At constant particle size and concentrations, tape tenacities were also inversely dependant on carbon black structure. The observed effects were expressed in terms of occlusion of polymer within carbon black aggregates having high structures thereby increasing the pigment particles effective volumes. When tested at 130 °C, variation in tape tenacities were less, probably as a consequence of the reordering effects of annealing. DSC and IR measures of crystallinity showed that the presence of carbon black and variations in particle properties influenced the character of the crystalline regions. © *1999 Kluwer Academic Publishers*

1. Introduction

The use of carbon black for enhancing light and weathering stability of polyoelfins and, in particular, orientated polypropylene in outdoor textiles such as geotextiles has been established for almost 30 years. It is well documented [1] that improved stabilising efficiency of carbon black on pigments is inversely proportional to the particle diameter; this is a consequence of the high specific surface areas of smaller diameter black particles and hence their greater ability to absorb incident photons. The effect of carbon black in this role, therefore, is generally considered to be physical in nature.

However, in addition to its UV stabilising properties, carbon black plays a significant role in influencing thermal oxidation in polyolefins. In our earlier review [2] it has been shown that carbon black may function as an antioxidant in its own right [3–5] or influence antioxidants already present both positively [4, 6] and antagonistically [7]. Contrary to popular belief, carbon black particles are not simple, inert carbonaceous entities but have a variety of chemical and physical properties which are determined by their mode of manufacture [8]; these characteristics determine the influence that carbon black particles exercise on polyolefin physical and chemical properties.

In terms of the latter, it has been shown [3] that termination of oxidative reactions depends on presence of oxygen-containing complexes on the particle surfaces which are believed to be phenolic in character [9] . In addition, carbon black in rubber is reported to decompose peroxides [10, 11] and also act as a radical acceptor by acting as possible electron donors [12–14]. However, in rubber vulcanisates, carbon black has been shown to possess pro-oxidative activities [11, 15, 16] which are surface area-dependent, although the type of polymer and the carbon black concentration and its impurities were cited as being influential.

Using model compounds, recent work [17] reports that, while carbon black may accelerate oxidation of cyclohexane (and hence polyolefins) in the post-induction period, in the presence of phenolic antioxidants it added to the thermal antioxidant effect. Very recent research [18], however, demonstrates that carbon black can antagonise antioxidant activity in certain phenolic/hindered amine stabiliser combinations.

The chemical behaviour of carbon black within a given polymer matrix is not straight forward and it is possible that several processes occur simultaneously and for any specific formulation, the observed behaviour represents a balance of these.

The chemical activity may not be entirely divorced from any physical activity which may include surface adsorption of antioxidant and UV stabilising additives (and hence their depletion from within the polymer matrix) and the modifications of the polycrystalline structure of the polymer by nucleation effects. Neither the magnitude of adsorption and nor the effectiveness of surface-adsorbed additives is known and both will depend on the chemistries of pigment surface and sorbed species. However, the reported nucleating properties of carbon black, which not only increase the rate of polymer crystallisation [19] and change polycrystalline distribution and morphology [20], will influence the distribution and local concentration of pigment and

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additives. This is the consequence of their being located only in the non-crystalline regions and at crystalline surfaces and boundaries.

For orientated polypropylene filaments and tapes, which find applications in textiles where weathering is important and where carbon black is used for UV stabilisation (e.g. geotextiles), the possible effects of these pigments on thermal oxidative resistance and physical fine structure are of concern. In addition, the added agency of tensile stress has been shown to influence oxidative degradation of both orientated polypropylene films [21] and filaments and tapes [22, 23] more typical of geotextile products. During these latter studies, Horrocks and D'Souza documented that relative to pigment-free, orientated tapes, those containing carbon black (2% w/w) were more resistant to thermal degradation, when stressed upto 10% of respective tensile breaking loads, but were less durable at higher stresses. In addition, during air oven-ageing upto 130 °C, black-containing tapes showed less pronounced changes in tensile and thermal analytical behaviour. Creep studies at 20 °C, indicated that the presence of carbon black reduced creep elongations, thereby suggesting a physical interactive effect, although reduced rate of chain scission could be a cause if this is a major cause of creep, as recently suggested [24].

It is against this background that the current study has been undertaken with the aim of more fully quantifying the effect that carbon blacks with a range of different properties have on the physical and chemical durabilities of orientated polypropylene tapes under varying tensile loads.

This first paper describes the influence that addition of selected carbon blacks have on the tensile and physical properties of orientated polypropylene tapes prior to subsequent exposure to tensile loads under ambient and elevated temperature conditions in air.

TABLE I Experimental design for sample production from a single polymer grade

	Structure level		
Particle size (nm)	Low	Medium	High
	At 2.5% CB loading, low volatile content		
20	X^a	X	X
27	X	X	X
50	X	X	X
	At 5.0% CB loading, low volatile content		
20	X	X	X
	At 2.5% CB loading, medium structure level		
20	X	—	X

[a] X = Polymer composite for subsequent extrusion and ageing.

2. Experimental

The objective of this study is to investigate the influence of carbon black physical parameters on the properties of derived polypropylene, PP tapes at low concentration of carbon black. The parameters of carbon black investigated include

(i) particle size
(ii) structure level
(iii) surface chemistry or so-called volatile content, and
(iv) concentration.

Factorial experimental design was adopted for sample preparation and subsequent data analysis. The following matrix (Table I) was designed to include all the above variables.

Materials

Polymer	Polypropylene (Himont S-30-S, MFI 1.8 g/10 min, 230 °C, 2.16 kg)
Stabiliser System	0.5% w/w Irganox B215 (blend of Irgafos 168 and Irganox1010, Ciba Geigy)
Carbon Blacks	11 different grades supplied by Cabot Corporation (see Table II)
Control Compound	PP + stabiliser system without carbon black (Code No. CB15)

Table II lists nominal carbon black grade properties determined in the laboratories of Cabot corporation. Surface area values have been derived from nitrogen adsorption measurements, particle size values originates from transmission electron microscopy data, dibutyl phthalate sorption measurements are indicative of the geometric aggregation or "structure" of particle

TABLE II Nominal properties of carbon black grades used

Code	Grade	Surface area	P-size[a] (nm)	DBPA[b] ($cm^3/100$ g)	Volatiles (%)	D[c] (g/l)
CB1, 2	Elftex TP	130	20	98	1.5	384
CB3, 4	Vulcan P	140	20	116	1.5	332
CB5, 6	Elftex 670	140	20	113	1.5	344
CB7	Elftex 430	80	27	72	1.0	430
CB8	Elftex 460	84	27	102	1.0	368
CB9	Elftex 490	87	27	124	1.0	320
CB10	United 120	30	60	65	1.0	505
CB11	Elftex 160	35	50	91	1.0	435
CB12	Elftex 180	37	50	122	1.0	352
CB13	Black Pearls 880	220	16	105	1.5	336
CB14	Black Pearls 1000	343	16	105	9.5	385

[a] P-size = particle diameter.
[b] DBPA = dibutyl phthalate absorbtion.
[c] D = bulk density of pellets.

aggregates and volatiles represent the loss in mass through loss of surface functional groups after heating under nitrogen at 950 °C. DBPA measurements also indicate measures of the voidage between fundamental carbon particles in aggregates.

2.1. Production of C-black masterbatches

Masterbatches containing 40% (w/w) C-black and 10% (w/w) antioxidant were produced using a ZK twin screw extruder in the laboratories of Cabot Plastics Ltd., Dukinfield, UK. These were then each diluted down to 2.5% (w/w) C-black content (except for CB1 & 2 and, CB3 & 4 and CB5 & 6 which were diluted to 2.5 and 5% (w/w), see Table IV), and 0.5% (w/w) antioxidant content using a single screw extruder followed by pelletization before extrusion into tape. The compounds were characterised for dispersion, actual content of carbon black and concentration of antioxidant using screen count, thermogravimetric analysis (TGA) and high performance liquid chromatography (HPLC) respectively in the laboratories of Cabot Plastics Ltd., Dukinfield, UK.

2.2. Production of oriented tapes

The compounds were extruded into tapes on a Plasticiser MK1 Single Screw Extruder which has a screw L/D ratio of 21 and film die of dimensions 63.5×0.38 mm. Extrusion conditions were pre-determined in trials performed on virgin polymer to obtain oriented tapes with properties similar to those of a commercial tape for geotextile applications , i.e. tenacity of not less than 0.5 N/Tex, shrinkage of less than 5%, thickness of 50 ± 5 μm and width of 2.5 ± 0.25 mm [26]. Optimum conditions used are detailed in Table III.

TABLE III Extrusion conditions for tape production from himont S30S

Extrusion temperatures (°C)	220, 240, 260, 265
Draw temperature (°C)	70/90
Nominal draw ratio	8 : 1 followed by 2 : 1 (two stages)
Relaxation temperature (°C)	180

Nominal draw ratio is defined by the ratio of the draw and feed roll surface velocities. The actual draw ratios listed in Table IV were determined from the ratio of the tape linear densities at the draw and feed rolls respectively.

2.3. Characterisation of tapes

2.3.1. Shrinkage

Tapes were tested for shrinkage using a Testrite yarn shrinkage instrument at 130 °C for 30 s. The results reported were an average of at least 3 tests.

2.3.2. Linear density

Tape linear density was measured by weighing a known length of tape and calculating the weight of 1000 m of tape from the result. An average of at least 5 readings was taken for each tape sample (see Table IV).

2.3.3. Tensile properties

Tensile properties of the tapes at ambient temperature (20 °C) were obtained using an Instron Model 4200 machine with a crosshead speed of 200 mm/min and a sample length of 100 mm at ambient exposure. Elevated temperature (130 °C) tensile properties were carried out using the Insron environmental chamber accessory at a crosshead speed of 100 mm and reduced sample gauge

TABLE IV Tensile properties of C-black-filled PP tapes at 20 °C

Sample code	Concentration (%)	Actual DR^a	LD^b (Tex)	BL^c (N)	BS^d (%)	T^e (N/Tex)	SH^f (%)	Modulus (N/Tex)	Iso^g-index	H^{fh} (J/g)	T_m^i/°C
CB1	2.5	10.3	105.6	53.7	18.1	0.51	3.9	3.9	0.615	81.5	161.2
CB2	5.0	10.1	120.7	42.7	24.2	0.35	3.5	3.1	0.504	79.4	164.2
CB3	2.5	10.1	114.1	51.7	18.4	0.45	4.0	3.9	0.636	84.2	163.8
CB4	5.0	11.2	106.8	45.8	21.1	0.43	3.6	3.7	0.580	79.6	167.3
CB5	2.5	12.0	105.1	48.4	15.2	0.45	4.1	4.2	0.607	79.4	163.2
CB6	5.0	11.3	110.3	42.6	15.6	0.39	3.6	3.5	0.495	74.3	166.7
CB7	2.5	11.3	108.4	56.1	13.0	0.51	3.0	5.5	0.587	78.6	165.0
CB8	2.5	11.3	111.2	50.4	14.6	0.45	3.8	3.8	0.617	78.8	162.3
CB9	2.5	10.2	116.9	50.4	22.18	0.43	3.9	3.1	0.601	74.8	164.1
CB10	2.5	11.3	107.2	56.3	18.6	0.52	2.6	3.6	0.616	76.1	164.7
CB11	2.5	11.3	112.7	55.2	14.0	0.49	4.5	4.6	0.623	74.8	161.8
CB12	2.5	10.8	110.6	47.1	15.0	0.45	3.5	4.8	0.681	80.1	165.0
CB13	2.5	10.6	123.9	45.8	19.25	0.37	4.9	2.7	0.581	75.6	172.3
CB14	2.5	12.6	106.4	44.5	14.76	0.42	2.8	4.2	0.579	59.5	167.5
No CB	0.0	12.3	93.5	49.8	14.0	0.53	3.8	5.1	0.769	24.03	161.0

[a] Draw ratio.

[b] Linear density.

[c] Breaking load.

[d] Breaking strain.

[e] Tenacity ($= BL/LD$).

[f] Shrinkage.

[g] IR-derived isotacticity/crystallinity index.

[h] DSC heat of fusion.

[i] DSC fusion maximum.

length of 50 mm. Each reported tensile value is the average of at least 10 specimens.

2.3.4. Infrared

The Perkin-Elmer 881 Infrared spectrophotometer was used to determine the isotacticity/crystallinity index of the tapes. Each sample was scanned 10 times and the average calculated. The isotacticity/crystallinity index was calculated by taking the ratio of the peak intensities at 998 cm^{-1} to that at 974 cm^{-1} according to Luongo [25].

2.3.5. Differential scanning calorimetry

A polymer laboratories DSC was used for this study. The sample (0.8–1.5 mg) was loaded in an aluminum pan and heated at a heating rate of 10°/min from ambient to 200 °C in flowing air at 10 ml/min. From the melting endotherm, the degree of crystallinity is considered to be proportional to the heat of fusion which was measured by calculating the area under the melting endotherm. The temperature at the peak of the endotherm was taken as the melting temperature of the sample.

3. Results and discussion

Table IV is a summary of the mechanical and morphological properties of the C-black tapes.

The results show that for all C-black-filled samples the linear densities are higher than in unfilled polypropylene (see Fig. 1). This follows the laws of simple mixtures since the density of C-black is higher (1.8 g cm^{-3}) than that of polypropylene (0.91 g cm^{-3}). This increase is dependent on both concentration (compare CB2, CB4 and CB6) and structure of the black. Linear density rises as concentration increases and is directly proportional to the structure (measured as DBPA sorption) of the black. It is notable that the highest linear density was obtained in CB9 which has the highest DBPA value (see Table II).

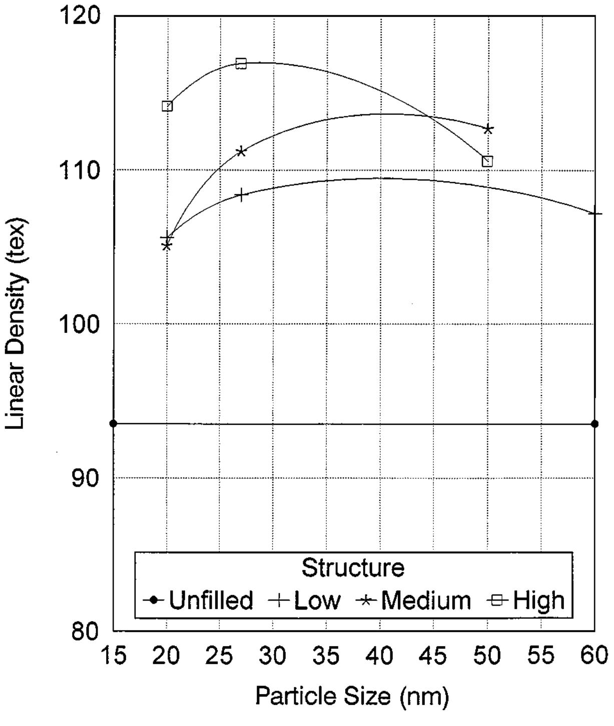

Figure 1 Effect of C-black variables on linear density.

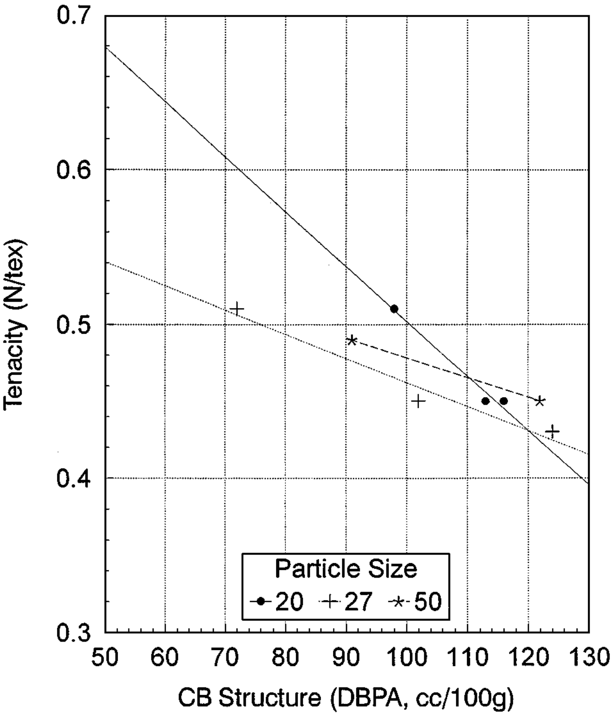

Figure 2 Effect of C-black properties on tenacity of polypropylene tapes (2.5% C-black concentration).

3.1. Tensile properties of carbon black-filled PP tape

From Fig. 2, there is clear dependence of strength of tapes on both the particle size and structure of C-black aggregates at 2.5% loading. Closer investigation of this result shows that although low particle sized blacks give the highest strength, there is a stronger dependence on structure than on particle size. Higher structured blacks yield lower strength tapes than lower structured ones at any given particle size.

Fig. 3 shows the effect of changing the concentration of the black on tenacity. At constant particle size, there is a significant drop in tenacity at the higher concentration of 5% (w/w). This drop in tenacity is less when higher structured blacks are used.

When tensile tested at 130 °C, oriented tapes show a general reduction in strength in comparison with respective 20 °C values as expected (compare Fig. 4 and Table IV). The three dimensional plot of tenacity verses tape shrinkage verses carbon black bulk density show two well-defined trends. Firstly tenacity values increase with increased shrinkage experienced by the tapes and secondly during thermal exposure a decrease with increased bulk density as shown in Fig. 4.

These results indicate that carbon black has a significant influence on the physical properties of polypropylene tapes when tested at 20 and 130 °C. Of the three key C-black parameters of particle size, structure and concentration, concentration has the greatest effect on physical properties. On average, the breaking load

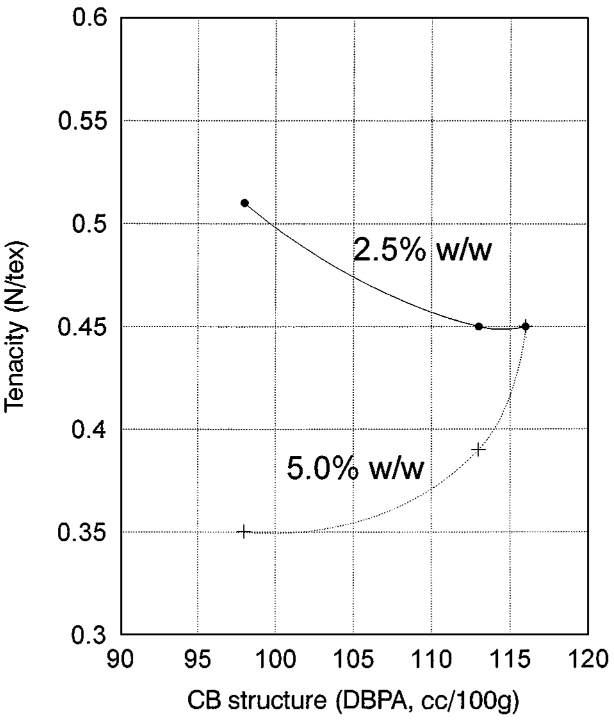

Figure 3 Effect of C-black loading on tenacity of polypropylene tapes (at constant particle size of 20 nm).

decreases by 15% when concentration is increased from 2.5 to 5%. This is possibly due to a reduction in the average inter-aggregate distances of the carbon black and re-agglomeration of carbon black aggregates into larger clusters [8]. These clusters could behave as flaws which lead to crack formation causing catastrophic failure in the sample when stressed.

It has been noted above that low structured carbon blacks give the best tensile properties (see Fig. 2) and this observation agrees with similar results in rubbers where Medalia [28] explained his observation in terms of polymer fractions filling the internal voids of carbon black aggregates. These fractions are "occluded" from the rest of the matrix and are unable to fully participate in the macrodeformation of the major polymeric phase during application of stress. The occluded polymer, therefore, behaves more like a filler than a polymer and hence the effective volume fraction of the polymer will be reduced. This occluded fraction increases the effective volume of the carbon black and is equivalent to increasing the loading of the carbon black. Therefore, the higher structured blacks will generally give lower tensile strength.

The occlusion of polymer, as proposed by Medalia and his coworkers, seems to be particularly relevant in explaining most of the results obtained in this study. This volume depends on the volume and accessibility of voids between particles in the carbon black aggregates or structure level as determined by DBPA measurements. Medalia [28] proposed that the effective volume fraction of the C-black is governed by the following empirical formula:

$$V_{\text{eff}} = V_{\text{cb}}\left(\frac{1 + 0.02139\text{DBPA}}{1.46}\right) \qquad (1)$$

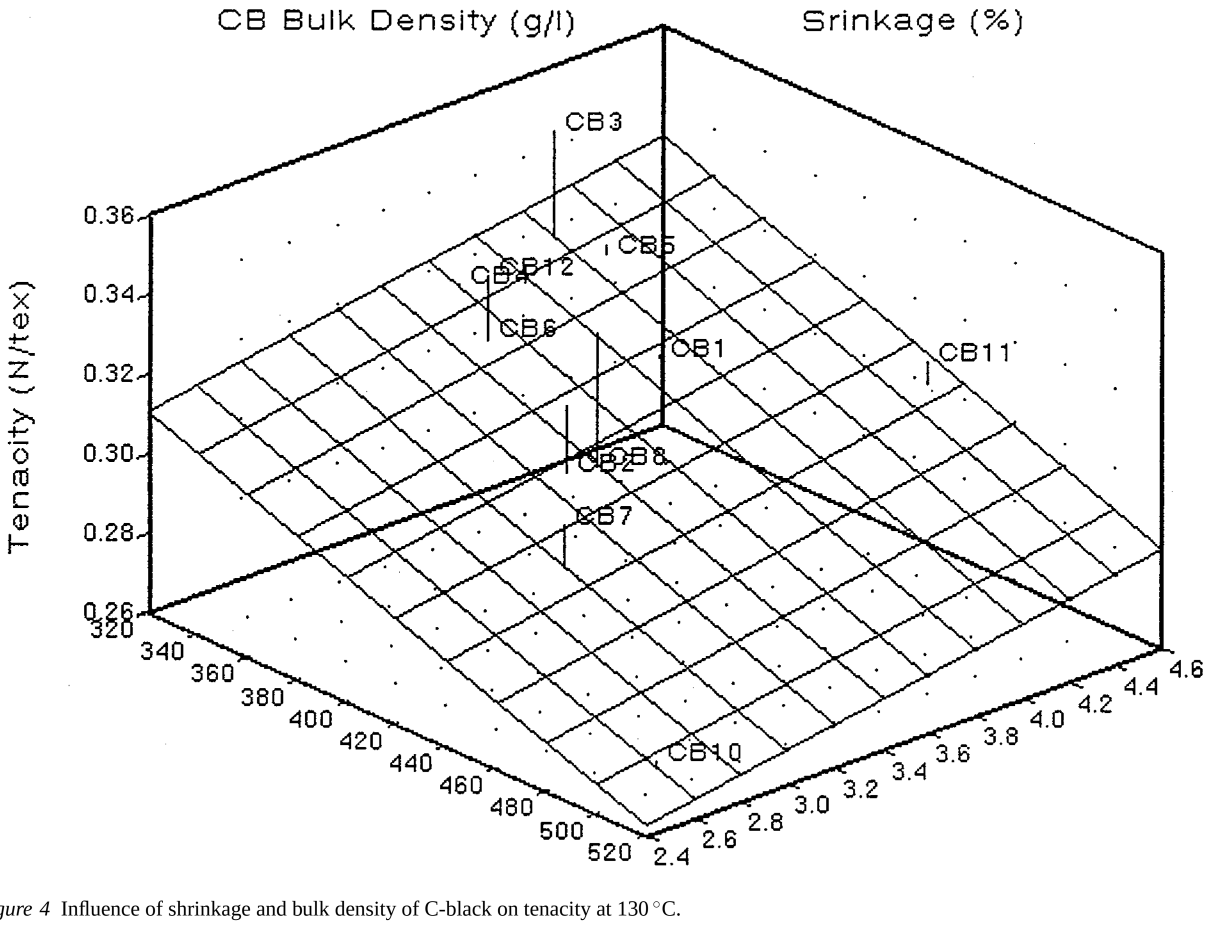

Figure 4 Influence of shrinkage and bulk density of C-black on tenacity at 130 °C.

TABLE V Calculation of effective volume fraction and fraction of occluded polymer in polypropylene tapes

Code	Bulk density, D (g/l)	DBPA (cm^3/100 g)	V_{cb}	V_{eff}	V_{occ}
CB1	384	98	0.015	0.032	0.017
CB2	384	98	0.030	0.064	0.034
CB3	332	116	0.017	0.041	0.024
CB4	332	116	0.034	0.081	0.047
CB5	344	113	0.016	0.037	0.021
CB6	344	113	0.034	0.080	0.046
CB7	430	72	0.017	0.030	0.013
CB8	368	102	0.016	0.035	0.019
CB9	320	124	0.012	0.033	0.021
CB10	505	65	0.014	0.023	0.009
CB11	435	91	0.012	0.024	0.012
CB12	352	122	0.013	0.032	0.019

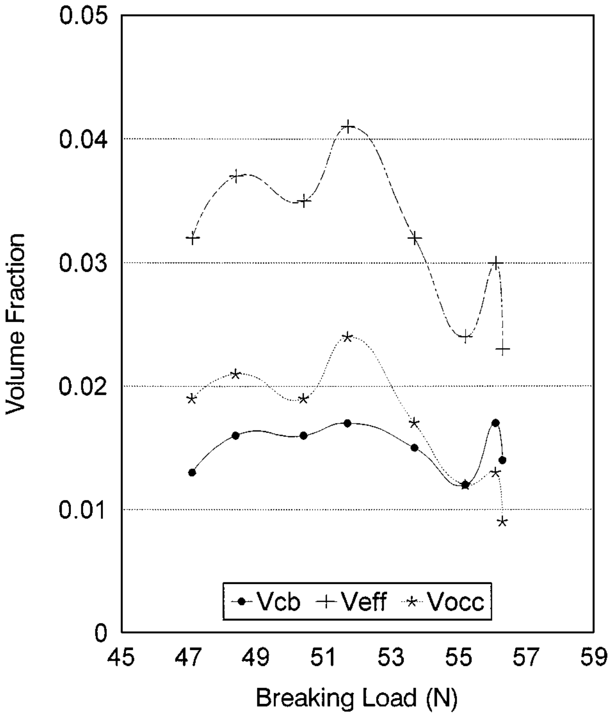

Figure 5 Dependence of breaking load on volume fraction.

where V_{eff} = effective volume fraction of C-black including that of occluded polymer and V_{cb} = volume fraction of C-black.

In order to calculate the actual density of each C-black, the following empirical formula according to Janzen [29] was used:

$$\rho = \left(\frac{610}{D} - \text{DBPA}\right)^{-1} \tag{2}$$

where ρ = C-black density and D = Bulk density.

Using Equation 2, the density for each carbon black grade was calculated and from Equation 1 the respective V_{eff} value was determined. Table V shows the results obtained which show that the volume of occluded polymer is directly related to the level of structure of the C-black used. Fig. 5 relates tape breaking load to the occluded volume (V_{occ}), C-black actual volume fraction (V_{cb}) and the effective volume fraction (V_{eff}), which is the sum of the two former values. The result shows a slightly stronger apparent negative correlation between the breaking load and both V_{eff} and V_{occ} than with V_{cb}. This provides support for the suggestion that the contribution of the occluded polymer to the tensile properties of the tapes is significant.

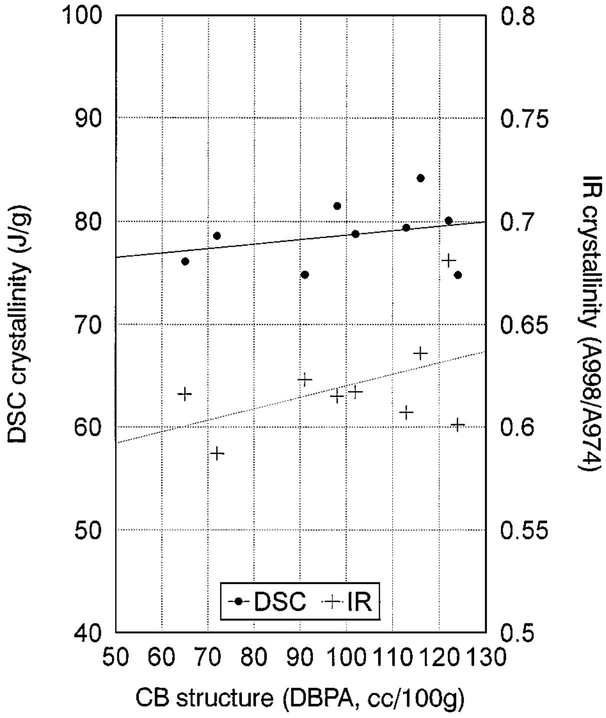

Figure 6 Effect of C-black structure on crystallinity of polypropylene tapes.

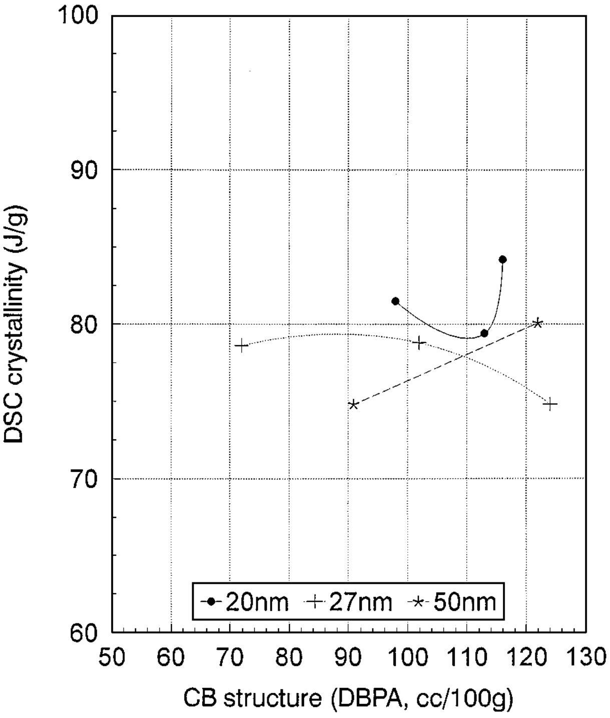

Figure 7 Effect of C-black properties on crystallinity of polypropylene tapes.

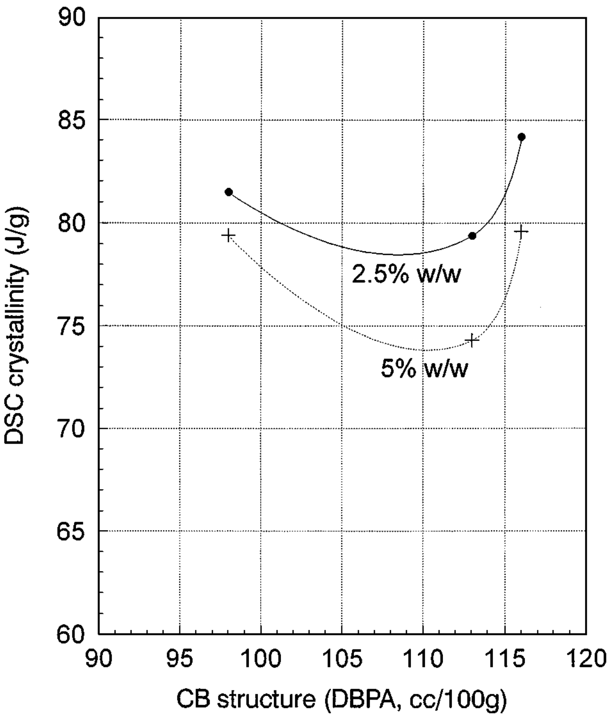

Figure 8 Effect of C-black loading on DSC crystallinity of polypropylene tapes (at 20 nm particle size).

3.2. Morphological properties

Fig. 6 shows the effect of carbon black properties on both the DSC measure of crystallinity (as heat of fusion) and the isotacticity index of tapes. Results suggest that crystallinity increases with increase in the structure of the black. Changes in isotacticity index with structure are more marked than those in heats of fusion, suggesting that the presence of carbon black affects the reordering of polypropylene molecules during the DSC temperature cycle itself. DSC indications of crystallinity are highest for small particle sized blacks and show a tendency to increase with structure (see Fig. 7).

At higher concentration (5% w/w), Fig. 8 shows that there is a marked drop in heats of fusion of the tapes for which all the other pigment properties are the same (see Table II). Furthermore, the drop in the degree of crystallinity is more severe for high structured blacks than low structured ones. This drop in crystallinity at the higher loadings was accompanied by a sharpening of the respective melting peak and shift in melting temperature to higher values as illustrated in Fig. 9. Previous studies have shown [20] that while carbon black promotes nucleation of additional crystallisation sites resulting in smaller spherulites with a narrower size distribution at higher loadings, since this is a consequence of increased sets of crystallisation, the total population may in fact be less. Clearly, further morphological studies would be necessary to clarify these findings.

4. Conclusions

From the foregoing results and discussion, the following conclusions can be drawn:

(i) Addition of 2.5% w/w to polypropylene results in an increase in breaking load of tapes compared to unfilled ones; increasing concentration to 5% (w/w) results in a decrease in the breaking load by 15% on average. This decrease in strength at the higher concentration is attributed to a possible reduction in the inter-aggregate distance leading to reagglomeration into larger clusters which lower the strength of the tapes.

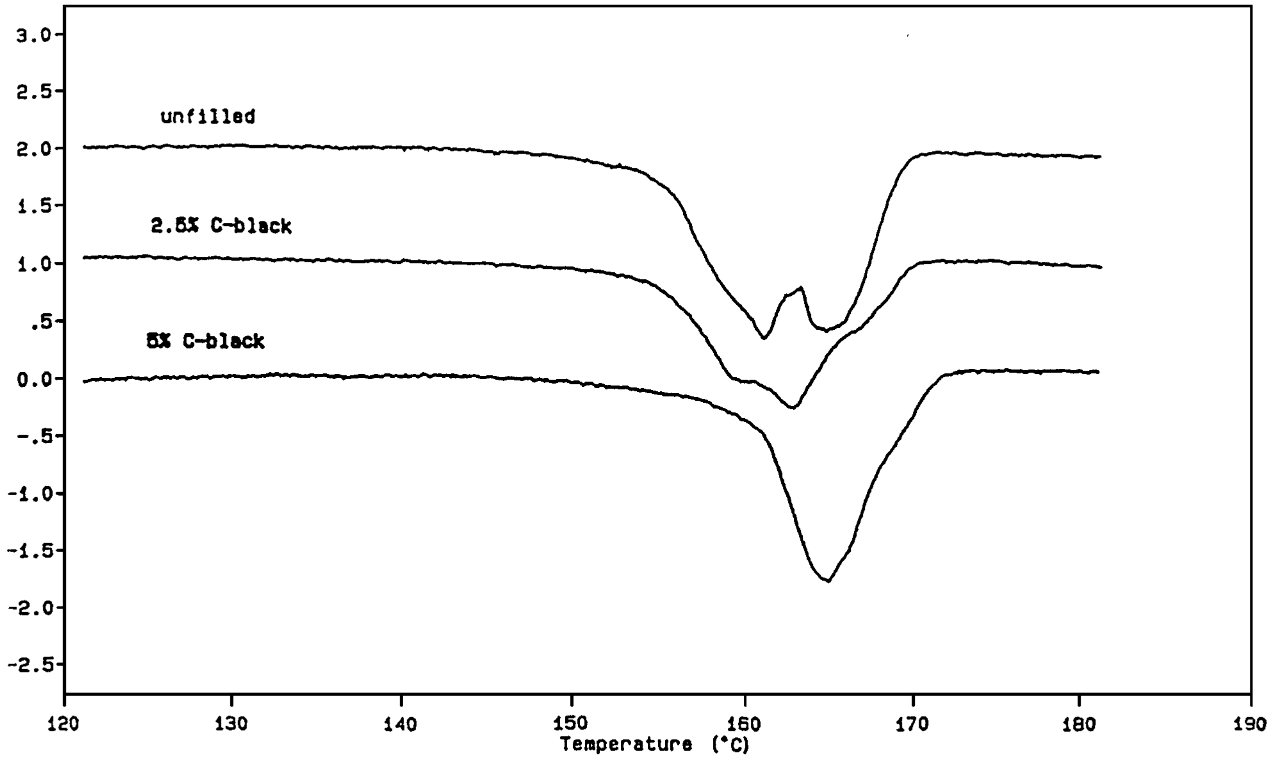

Figure 9 Influence of C-black concentration on DSC fusion endotherm of polypropylene tapes.

(ii) Because linear densities of filled tapes increase, tenacities of filled tapes are less than those of the unfilled analogues. Tenacities of filled tapes show a dependency on both the particle size and structure of the carbon black present. At 2.5% (w/w) of carbon black tenacity reduction relative to unfilled tapes is inversely proportional to particle size and at any given particle size, tapes filled with higher structure blacks exhibit lower strength, than those containing lower structured ones.

(iii) At 130 °C, tenacity values for all samples fall within a relatively smaller range of variations i.e. 0.35–0.53 N/Tex at 20 °C compared to 0.27–0.35 N/Tex at 130 °C suggesting that annealing effects at 130 °C smooth out larger carbon black-dependent changes observed at ambient temperature. Furthermore, tenacity values at 130 °C increase with increased shrinkage present in the tapes and decreased bulk density of carbon black. The former is probably a consequence of polymer reordering which occurs during the elevated temperature studies.

(iv) The occluded polymer principle as proposed by Medalia [28] has been used to explain the dependence of breaking load of the tapes on both structure and concentration of the carbon black present. The results indicate a slightly stronger negative correlation between breaking load with effective volume fraction V_{eff} than with actual volume fraction V_{cb} of the C-black present suggesting that the contribution of the occluded polymer to the macrodeformational properties of the tapes is significant.

(v) Both DSC-derived measures of crystallinity and IR crystallinity index values of filled tapes increase with increase in the structure of the black at 2.5% (w/w) concentration. At 5% (w/w) concentration, crystallinity measures decrease in all filled tapes and this is accompanied by both a sharpening of the melting peak and a shift to higher melting temperature of the DSC fusion endotherm. These are probably a consequence of nucleation which results in a population of overall lower degree of crystallisation comprising smaller spherulites having narrower size distributions at higher loadings of carbon black [20].

In summary, it can be concluded that the presence of carbon black significantly affects the properties of orientated polypropylene tapes. To optimize properties, careful selection of carbon black pigment grade is important. In general, the results in this study suggest that filled polypropylene tapes containing a low particle size, high structured carbon black at 2.5% concentration exhibit properties which are similar to or better than commercial analogues containing no pigment.

The thermal degradation behaviours of these tapes during thermal ageing under varying levels of tensile stress will be reported in detail in subsequent parts of this series of papers.

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