Triboelectric charging of carbon-black-impregnated suspension-polymerized copolymers

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Carbon-black/copolymer-based toner particles have been made by fragmentation of suspension-copolymerized styrene–n-butyl methacrylate copolymer leads. The latter were impregnated with carbon black during their formation from the liquid comonomers. This procedure eliminates the costly technology associated with conventional melt-mix processes. Triboelectric coefficients of such toners are generally lower than conventionally formed species, as a result of the different nature of the carbon-black dispersion achieved. Coefficients pass through a maximum value as the carbon-black content is increased, and good correlation with conventionally produced species can be achieved in copolymerizations that are made highly alkaline. This results in simultaneous hydrolysis of some of the butyl methacrylate groups, yielding sodium methacrylate residues. The latter have a very significant effect on the nature of the carbon-black dispersion achieved, which appears to correspond much more closely to that achieved by melt mixing.

(Keywords: triboelectrification; pigmented polymer particles; suspension polymerization; carbon black; dispersion of carbon black)

INTRODUCTION

Polymer particles of $\sim 10\,\mu m$ in diameter impregnated with carbon black and other pigments are widely used in reprographic applications[1,2]. Such materials are referred to as toners and the facility to manipulate and transfer these physically depends on their ability to generate and trap static charge during contact electrification. Conventionally the dispersion of carbon black in a polymer matrix is achieved by melt mixing using essentially rubber processing technology. The so-formed heterogeneous composite is then micronized and air-classified to produce the required toner particles. We have recently described a novel process in which carbon black is intimately mixed with liquid comonomers and the whole polymerized in suspension to form black copolymer beads[3]. The latter can function as a convenient source for toner production, and this paper describes our efforts to achieve this.

A number of factors can influence the triboelectrification of carbon-black-impregnated polymer systems. The type of carbon black itself is important[4], and in particular its characteristic properties such as surface chemical functionality, surface area and porosity[5]. The nature of the dispersion achieved in the polymer matrix seems to play a vital role[5,6], and the level of carbon black located in the toner surface itself also seems important[7]. In addition the microstructure of the polymer matrix has a strong influence[8].

We have already reported some results on melt-mixed toners and have pointed out some differences between these and toners produced by *in situ* suspension polymerization[9]. In this paper we explore further the latter systems.

EXPERIMENTAL

Materials

The monomers, initiators and stabilizers used in the suspension polymerizations were obtained from sources already reported[3]. The carbon blacks used, namely Regal 300, Regal 400, Vulcan 9, Vulcan XC-72, Black Pearls L and Raven 5250, were from Cabot, and the manufacturer's specifications are summarized in *Table 1*.

Preparation of carbon-black-impregnated suspension copolymer beads

Typically preparation of these was carried out in a one-litre glass baffled reactor using a paddle-type impeller rotating at 900 r.p.m. The carbon black (usually 10 g) was dispersed in the monomer mixture (styrene, 58 ml; n-butyl methacrylate, 42 ml) by shearing it at high speed for 30 s using a small nozzle-type homogenizer (Ultra-Turrax, Janke and Kunkel). The initiator, azobisiso-

Table 1 Properties of carbon blacks

Carbon black	Particle size (nm)	pH	Surface area ($m^2\ g^{-1}$)
Regal 300	27	7.5	80
Vulcan 9	19	7.0	140
Vulcan XC-72	30	5.5	254
Regal 400	25	4.0	96
Black Pearls L	24	3.0	138
Raven 5250	25	2.0	575

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butyronitrile (AIBN), weights as shown in the tables, was added, and the whole mixture poured into the reactor already containing the aqueous phase. The latter consisted of a 1% solution (720 ml) of poly(vinyl alcohol) (99–100% hydrolysed, $MW \sim 115\,000$). The whole reaction mixture was flushed with gaseous N_2 and then heated at 85°C for 5 h. The resulting suspension was diluted with about twice the volume of water and the beaded product (50–1500 μm) collected by suction filtration, and washed copiously with water, before being dried at 50°C for 6 h in a fluidized-bed drier. Further details of the preparative procedure are presented in ref. 3.

In experiments using varying initial levels of Black Pearls L the product was dry-screened into fractions using standard test sieves (Endecotts Ltd).

Production of toner particles

Each sample of carbon-black-pigmented copolymer beads was ground in a planatory ball mill (Fitsch) for a period of 60 min. Typically the bead sample (40–90 g) was added to the stainless-steel mill with 15 steel ball-bearings of 20 mm diameter. The resultant material was then classified using a sieve shaker. The sieves (Endecotts Ltd) were of 5–50 μm steel mesh. To assist classification, it was found useful to place a few small ball-bearings in each sieve to aid agitation of the powder. The toner fraction used in these studies was that retained by the 5 μm sieve and corresponded to 10% of the feed material.

The particle size was measured using a Coulter TA instrument operating in the 2–500 μm range. The mean sizes (not recorded here) were used to normalize the triboelectric coefficient data (see later) to a value of 12 μm.

Triboelectrification measurements

The contact charging of the toner particles was achieved using a procedure in which the toner was first rolled with a metal carrier and then removed by an air jet blow-off experiment. The method was essentially as described by Duke and Fabish[10]. The toner was initially rolled with carrier in a glass bottle for a period of approximately 10 min. The carrier and toner were then transferred to a cylinder the ends of which were constructed from fine mesh. The cylinder was then subjected to an air jet, alternatively from one end and then the other. This procedure removes the toner and the residual charge on the carrier was then measured using an electrometer. Values obtained from a standard commercial toner material were in agreement with those supplied by the manufacturer (Rank Xerox Ltd). Since these measurements are highly sensitive to the ambient laboratory conditions, the following precautions were always taken. Each toner was preconditioned by storage in a humidity cabinet at 45–55% humidity and 298 K for a period of 24 h prior to measurement. In order to correct for possible drifts in the calibration of the apparatus, the standard toner material was measured at the beginning and the end of each day. Data were either scaled or rejected on the basis of the magnitude of the drift observed in the calibration data. In order to avoid the possible effects of variation in the mean surface area as a consequence of the variation in the toner particles, the values quoted in *Tables 2–5* have been scaled to a nominal size of 12 μm, corresponding to the size of the commercial toner sample.

The data were normalized to a particle size of 12 μm to allow for the possible effects of small variations in the surface area associated with changes in the particle size distribution. In practice, this correction was smaller than the variation between individual measurements.

Molecular weight, molecular-weight distribution and glass transition temperature of toner copolymers

The former two parameters were determined by gel permeation chromatography using polystyrene standards. To protect the columns it was necessary to remove the carbon-black component prior to analysis. The procedure has been described before[3].

Glass transition temperatures, T_g, were determined using a differential scanning calorimeter (Du Pont 910). In this instance samples were analysed without removal of their carbon-black component. The glass transition is often marked by a change in the conductivity of the polymer matrix. Measurements of the T_g of individual samples were carried out so that any possible contribution from a variation of the value of T_g could be monitored.

Characterization of the content and degree of dispersion of carbon black in toner samples

The carbon content of each sample was determined from its C and H elemental microanalysis and that of the relevant carbon black and the corresponding unpigmented copolymer of the same comonomer

Table 2 Properties of toner particles[a] prepared using different types of carbon black

Carbon black[b]	AIBN (g) used in polymerization	Derived toner		
		T_g (°C)	M_w (M_n)	Triboelectric coeff.[c] (μC g^{-1})
Regal 300	1.8	52	61 500 (32 000)	9.9[d]
Regal 400	1.8	47	35 100 (6 000)	8.8
	2.5	52	62 800 (8 700)	8.8
	25+1 (2 h)	50	59 800	9.5
Vulcan 9	1.8	52	69 800 (26 200)	8.9
	1.8	50	62 700 (17 900)	7.8
Vulcan XC-72	1.8	50	71 300 (18 700)	8.1
	1.8	50	–	7.5
Black Pearls L	2.5	44	74 500 (10 700)	11.0
	3.0	48	62 400 (12 200)	11.0
	2.0+1 (1 h) +1 (2 h)	50	56 800 (9 400)	11.9
Raven 5250	2.0+1 (1 h)	38	–	12.0[e]

[a] *In situ* impregnated suspension copolymer; styrene–n-butyl methacrylate (58/42 v/v); 1% aq. PVA stabilizer (99–100% hydrolysed, $MW \sim 115\,000$). Beaded product 50–1500 μm fragmented to toner particles, ~12 μm. (See 'Experimental' for further details)
[b] 10% by weight of total monomers
[c] Corrected daily to a known standard and normalized to a particle size of 12 μm
[d] Approx. 18 μC g^{-1} for toner produced by melt mixing
[e] Approx. 25 μC g^{-1} for toner produced by melt mixing

Table 3 Properties of toner particles prepared using different feed levels of Black Pearls L[a]

BPL in feed (wt%)	AIBN used[b]	Product: Bead fraction[c]	Product: Carbon-black content found (%)	Derived toner: T_g (°C)	Derived toner: M_w	Derived toner: $\frac{M_w}{M_n}$	Derived toner: Triboelectric coeff.[d] ($\mu C\ g^{-1}$)
10.0	2.5+	NF	9.8	51	50400	6.5	8.0
	0.5 (2 h)	A	22.1	47	28500	5.1	10.5
		D	13.9	50	35900	4.3	9.0
		G	8.3	49	48400	4.4	8.6
12.5	3.2+	NF	11.0	49	–	–	9.0
	1.0 (2 h)	A	19.6	47	–	–	9.1
		D	23.5	48	–	–	10.1
		G	8.2	49	–	–	9.4
15.0	4.0+	NF	17.6	46	–	–	11.1
	1.5 (2 h)	A	19.6	44	–	–	12.2
		D	16.1	48	–	–	13.6
		G	10.1	49	–	–	13.8
18.0	5.0+	NF	16.7	46	–	–	10.4
	1.0 (2 h)	A	23.8	43	–	–	12.4
		D	19.7	45	–	–	12.3
		G	12.9	48	–	–	12.4
25.0	8.0+	NF	23.6	33	18500	6.7	9.5
	2.0 (2 h)	A	30.3	28	14800	6.0	8.0
		D	19.2	37	17100	6.3	12.5
		G	12.9	40	24900	7.0	11.1

[a] See *Table 2*
[b] Sequential additions of AIBN at times shown to overcome inhibition displayed by BPL
[c] NF = non-fractionated; bead fractions, A > 1204 μm; 355 > D > 150 μm; G < 63 μm
[d] See *Table 2* footnote *c*

Table 4 Preparation of beaded copolymers containing Black Pearls L: effect of sodium hydroxide on polymerization and properties of derived toner[a]

BPL in feed[b] (wt%)	AIBN (g) used	NaOH aqueous phase (g)	Product: Yield of beads (%)	Product: Carbon-black content found (%)	Derived toner: T_g (°C)	Derived toner: Triboelectric coeff.[c] ($\mu C\ g^{-1}$)
10	2.8	–	90	9.8	51	8.0
10	3.2	1.0	60	10.0	50	13.4
10	3.2	2.5	50	15.0	48	13.7
10	3.2	5.0	40	21.5	51	14.9
10	2.6	10.0	40	30.5	49	10.3
10	2.8	10.0	40	24.8	54	17.9
10	3.3	10.0	35	23.2	50	14.4
10	2.8	15.0	35	30.4	49	15.0
25	9.0	10.0	55	37.6	48	9.8
10[d]	1.8	10.0	35	24.7	52	9.0

[a] See *Table 2* footnote *a* and 'Experimental' for details
[b] Based on initial weight of comonomers
[c] See *Table 2* footnote *c*
[d] Regal 300

composition. Again, details of the procedure have been reported already[3].

Some idea of the nature of the carbon-black dispersion was obtained by transmission electron microscopy (TEM). Toner particles were embedded in epoxy resin and then suitably thin sections obtained using an ultramicrotome. The specimens were then either partially oxidized or coated with gold to increase their conductivity.

RESULTS AND DISCUSSION

Toner production and properties

We have previously reported our success in producing carbon-black-impregnated copolymer beads by suspension polymerization and this work demonstrates quite clearly that such materials can be used successfully to produce toner particles. The yield of the particle size fraction ($\sim 12\ \mu m$) useful for toner application is low

Table 5 Properties of toner particles: Black Pearls L in different suspension copolymer matrices[a]

Comonomer composition[b]	AIBN (g)	Yield of polymer beads (%)	Derived toner T_g (°C)	Derived toner Triboelectric coeff.[c] ($\mu C\ g^{-1}$)
58 St; 34 BMA; 8 AA	2.5	65	52	12.9
46 St; 42 BMA; 12 AA	2.8	30	52	6.2
58 St; 34 BMA; 8 MAA	3.2	70	50	11.8
58 St; 34 BMA; 8 MAA[d]	3.2	70	50	15.7
46 St; 42 BMA; 12 pCSt	2.8	–	50	9.5
52 St; 42 BMA; 9 MAN	8.0[e]	75	46	10.7
46 St; 42 BMA; 12 MAN	8.0	70	48	9.1
46 St; 42 BMA; 12 MAN[f]	8.0	65	45	8.0
46 St; 42 BMA; 20 Vpy	2.5	80	50	2.0
46 St; 42 BMA; 20 Vpy[f]	2.8	85	45	−14.3
46 St; 42 BMA; 20 Vpy[g]	2.5	85	47	−12.3
46 St; 42 BMA; 20 Vpy[h]	2.5	80	51	−0.2

[a] 10% by weight of total monomers
[b] St = styrene; BMA = n-butyl methacrylate; AA = acrylic acid: MAA = methacrylic acid; pCSt = *p*-chlorostyrene; MAN = methacrylonitrile; Vpy = 4-vinylpyridine
[c] See *Table 2* footnote *c*
[d] 2 g NaOH in aqueous phase
[e] Polymerization temperature reduced to 75°C, hence AIBN increased
[f] Regal 300 replaced BPL
[g] 2.5 g nickel acetate added to monomer, product washed with dilute mineral acid
[h] 2.5 g copper acetate added to monomer, product washed with dilute mineral acid

(~10%), but this is controlled by the relatively crude fragmentation technology available to our small-scale operation in the laboratory. Undoubtedly this could be improved to a suitable level for industrial production, when carried out on a large scale using appropriate micronizer technology. The direct production of pigmented copolymer beads in the size range 50–1500 μm automatically eliminates much of the heavy engineering procedures required in conventional melt-mix toner production.

The results summarized in *Table 2* show that the suspension polymerization process is suitable for a broad spectrum of carbon blacks of both high and low pH, and high and low surface area (*Table 1*). The influence of these factors on the polymerization process has been discussed before[3]. Somewhat surprisingly the values obtained for the triboelectric coefficient of toners derived from this range of carbon blacks fall within a relatively narrow band. Indeed, the values are reduced relative to those for toners produced by melt mixing: 10% Regal 300, ~18 $\mu C\ g^{-1}$; 10% Raven 5250, ~25 $\mu C\ g^{-1}$. A number of factors may cause this:

(i) In the present procedure, each system is saturated with water.

(ii) The presence of carbon black during polymerization inhibits the free-radical process and the molecular weights of copolymer are generally reduced and their distributions broadened. As a consequence, the glass transition, T_g, is also reduced.

(iii) Since the polymeric composite is not melted and sheared as in the conventional process, the nature and degree of dispersion of the carbon black might be substantially different.

The effect of water is not likely to be a major one. Copolymer beads are thoroughly dried in a fluid-bed drier, each bead is then fragmented to produce toner particles, and the latter are then conditioned in a humidity cabinet. It is unlikely therefore that the water contents will differ very significantly from those of toner from a melt-mix process. In contrast, the molecular weight and, in particular, the T_g of pigmented suspension copolymers are lower than the corresponding melt-mix composite (T_g ~ 56°C). However, the data in *Table 2* suggest that there is no significant correlation between the triboelectric coefficient and T_g, and this must therefore be regarded as a secondary and less important effect, if indeed it contributes at all. This leaves the nature of the carbon-black dispersion and distribution as the most likely factor causing the reduction in the triboelectric coefficients (see later).

Carbon-black contents of toner particles

In designing toner materials, the carbon-black content would be anticipated to influence the value of the triboelectric coefficient observed. This is undoubtedly the case with the present method of toner production. *Table 3* shows the data for materials derived from pigmented copolymer beads where the feed level of Black Pearls L was varied from 10–25 wt% of the comonomers. Again the range of values for the triboelectric coefficient is rather small, but the toners made from random bead samples from each batch (i.e. the non-size fractionated, NF, samples) do show a dependence on the carbon-black feed: 8.0 (10%), 9.0 (12.5%), 11.1 (15.0%), 10.4 (18.0%), 9.5 (25.0%), with a maximum around 15% Black Pearls L. In fact, the situation is very much more complex than this, because the actual content of carbon black (i.e. percentage found by analysis) varies with the copolymer bead size fraction as shown in *Table 3*. Within a given suspension polymerization, the largest bead fraction (> 1200 μm) yields a carbon-black content as much as a factor 2 below the feed value; while the smallest bead fraction (< 60 μm) yields a carbon-black content as much as a factor 2 above the feed value. Thus to correlate the triboelectric coefficient more realistically with carbon-black content, all bead fractions must be examined separately. *Figure 1* shows the appropriate data plotted out. Clearly there is a big spread here, but nevertheless a general pattern emerges which confirms the composite data shown above. The triboelectric coefficient moves through a maximum of ~14 $\mu C\ g^{-1}$ at a content of Black Pearls L of ~18–19 wt%. This can be rationalized when

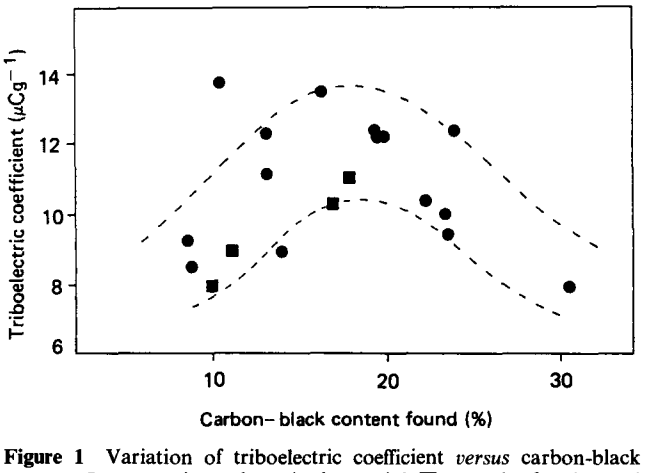

Figure 1 Variation of triboelectric coefficient *versus* carbon-black content: ●, suspension polymerized material; ■, non-size-fractionated samples

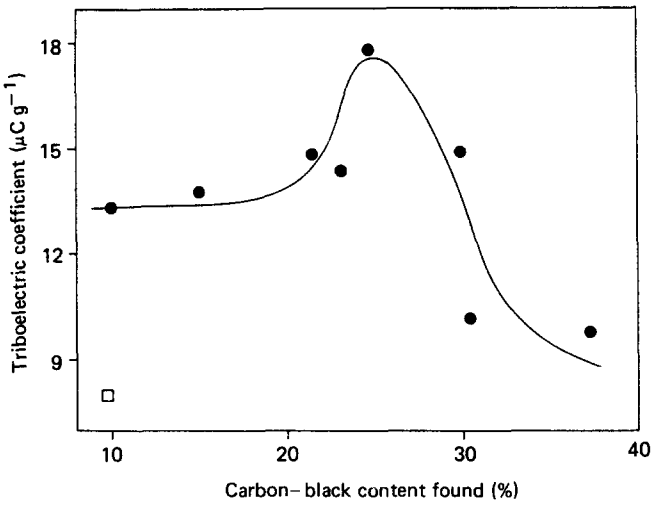

Figure 2 Variation of triboelectric coefficient *versus* carbon-black content for various toners: ●, prepared with NaOH; □, without NaOH

it is appreciated that carbon-black particles not only provide suitable trap sites in which charge might reside, but also can provide a conducting pathway along which charge might be dissipated. Clearly, therefore, in this case these factors reach their optimum balance when the Black Pearls L content is 18–19%.

Nature of the carbon-black dispersion

As pointed out earlier the most characteristic feature of the triboelectric data for all types of carbon black is their reduced values relative to species made by melt mixing. In the case of Regal 300 the surface area and surface chemical functionality are both low, as indicated by the observed high pH (*Table 1*). Many attempts (not recorded here) were made to increase the functionality of this carbon black by the use of additives, e.g. aromatic carboxylic acids and their salts. Such additives were impregnated into the carbon black prior to mixing with the comonomers and were also added to polymerization mixtures. In no case was a significant shift in the value of the triboelectric coefficient achieved. Similarly, amine bases and metallic salts had little effect. In order to try to achieve some control over the degree of dispersion of carbon black within the comonomer/copolymer, various dispersion agents were also examined. Species known to be useful for dispersing solids in liquid phases were chosen specifically, but again no significant shift in the triboelectric data was achieved.

Bearing this in mind, the modification to the triboelectric coefficient achieved by making the suspension polymerization aqueous phase alkaline came as a complete surprise. This effect was studied in detail with Black Pearls L (*Table 4*). The data for the triboelectric coefficient of derived toner particles show first a marked increase of $\sim 5.5\,\mu C\,g^{-1}$ when 1 g of sodium hydroxide is added to the standard polymerization reaction for 10 wt% Black Pearls L. Furthermore, subsequent increases in the weight of sodium hydroxide used produces a series of toners whose triboelectric coefficient seems to pass through a maximum.

In practice, elemental microanalysis of these tones, all derived from 10 wt% Black Pearls L, shows the actual carbon-black content to rise progressively (*Table 4*). Simultaneously the yield of beads from each reaction (i.e. weight of copolymer and carbon black expressed as a percentage of comonomers and carbon black) decreases. Furthermore the characteristic odour of n-butyl alcohol from reaction mixtures confirmed that significant hydrolysis of butyl ester groups (in the monomer and/or copolymer) occurs simultaneously with polymerization. Indeed, it seems logical to ascribe the increasing low yields and increasing actual carbon-black content to loss of copolymer solubilized as the sodium carboxylate salt in the aqueous phase. *Figure 2* shows how the derived toner triboelectric coefficients change with the actual Black Pearls L content. Clearly all the values are enhanced relative to the normal one (obtained in the absence of sodium hydroxide) and there is good evidence for a maximum in the curve. The number of data points is small (compared to those in *Figure 1*) and so the position of the maximum can be placed only tentatively at ~25 wt% carbon black. This is a shift of ~6% from the position of the maximum found without alkaline hydrolysis, and suggests strongly that a significant change in the carbon-black dispersion/distribution within toner particles is achieved with this modified process. It is also important to remember that the actual carbon-black content for a 10 wt% Black Pearls L feed in the absence of sodium hydroxide is 9.8%; with only 1 g of hydroxide the actual content shifts only to 10.0% yet the triboelectric coefficient of derived toners jumps $\sim 5.5\,\mu C\,g^{-1}$. Again this suggests that a major change in the carbon-black dispersion/distribution is involved.

Figure 3 shows a series of TEMs of toners derived from copolymers, all made with 10 wt% Black Pearls L, but with increasing levels of sodium hydroxide in the aqueous phase. Though it is difficult to draw detailed conclusions, these do confirm the increase in the actual carbon-black content as the amount of sodium hydroxide used is increased. In addition, however, there is also a suggestion that a larger percentage of the incorporated carbon black is dispersed within the interior of toner particles rather than near the surface. The electron micrographs presented indicate the type of variation of the distribution of carbon black in the samples. It is, however, very difficult with a single picture to give a true representation of the dispersions present. From examination of a large number of pictures it was possible to observe the differences in these distributions and also the extent to which segregation of the carbon black was occurring at the particle surface. We have previous argued[9] that the conventional suspension copolymerization technique tends to produce beads with an excess of carbon black in the surface. In addition toner produced from these is therefore likely to contain a component with low carbon-black content (originating from bead interiors) and a component with high surface carbon-black content (originating from bead surfaces). Indeed this seems to explain the dielectric behaviour of these materials[9]. The TEMs in *Figure 3* therefore seem to confirm that hydrolysis of butyl ester groups and the generation of sodium carboxylate anionic charge in the toner copolymer aids the dispersion of Black Pearls L within the bulk of the latter.

There does remain, however, a limiting level of carbon black beyond which the triboelectric coefficient falls again, presumably as argued earlier because of the ease of charge dissipation via conducting pathways. This is

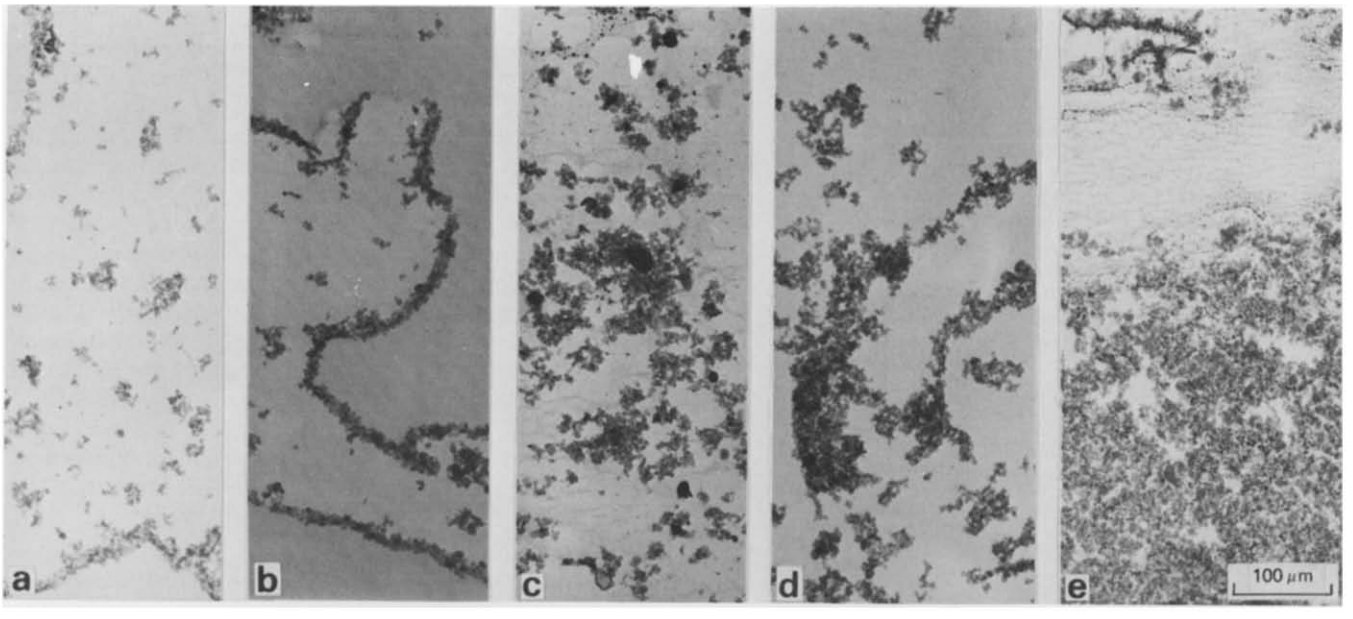

Figure 3 TEM pictures of materials produced with NaOH in polymerization mixture: (a) 1 g NaOH, (b) 2.5 g NaOH, (c) 5.0 g NaOH, (d) 10 g NaOH, (e) 15 g NaOH; all toners contain 10% carbon black

apparent in *Figure 2* where an actual carbon-black content of ~30 wt% causes the coefficient to fall to a value only marginally above the normal. The TEM corresponding to this species (*Figure 3e*) shows this dense carbon-black concentration. This situation is further confirmed by a toner material where the carbon-black feed value was 25%, yielding an actual content of ~40% as a result of hydrolysis during polymerization. The corresponding triboelectric coefficient of the derived toner was only 9.8 $\mu C\,g^{-1}$ (*Table 4*).

In principle, of course, if the above model is true it should be possible to produce very similar changes in carbon-black distribution and triboelectric coefficients by using methacrylic and acrylic acids directly as comonomers, as a partial replacement for the n-butyl methacrylate component. A few attempts were made to do this and the results are shown in *Table 5*. Acrylic acid copolymers were unsatisfactory. The yields of beads were low, probably due to the inherently high aqueous solubility of this monomer. The results with methacrylic acid were more satisfactory. This was particularly so in the presence of added sodium hydroxide to generate the salt form of the carboxylic species. In this case a toner was derived with a triboelectric coefficient of ~16.0 $\mu C\,g^{-1}$ (10% Black Pearls L, carbon-black feed). This approach was not pursued further, but clearly it seems to be an alternative possibility for achieving optimum triboelectric effects.

Effect of polymer microstructure

It might be argued that introducing additional comonomers such as methacrylic acid actually changes the nature of the copolymer microstructure, and this is undoubtedly true. Such changes are also known to influence triboelectric behaviour[8]. In crude terms other electron-withdrawing copolymer segments should behave similarly to methacrylate residues, whereas electron-donating segments might give rise to other major changes. Though this has not been investigated in great detail in this work, some remarkable changes have indeed been demonstrated. Methacrylonitrile would be expected to introduce the strongly electron-withdrawing nitrile group, and indeed copolymer beads prepared with this monomer yield toner particles that behave essentially as the styrene–n-butyl methacrylate based system does (*Table 5*). Both Regal 300 and Black Pearls L were examined. 4-Vinylpyridine, however, would be expected to introduce strongly electron-donating segments. Indeed copolymer beads prepared from a mixture containing 20 wt% of this monomer yield toner particles that charge with completely the opposite sign to the previous toners against the same metal carrier (triboelectric coefficient, ~ −12–14 $\mu C\,g^{-1}$) in the case of both Regal 300 and Black Pearls L carbon blacks. When such toners are treated with protonic acid to form pyridinium ion containing segments, the electron-donating character is destroyed and in this case the triboelectric coefficient falls to ~0 $\mu C\,g^{-1}$. Clearly considerable scope exists here for manipulating the triboelectric behaviour of these composite particles.

CONCLUSIONS

Carbon-black/copolymer-based toners can be readily made by fragmentation of suspension-copolymerized copolymer leads, impregnated with carbon black during polymerization. Good correlation with the triboelectric behaviour of conventionally prepared melt-mix toner can be achieved by arranging for simultaneous hydrolysis of n-butyl methacrylate residues during polymerization. The nature of the carbon-black dispersion appears to control the triboelectric properties and the latter procedure seems to produce dispersions similar to those achieved with melt mixing.

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