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Polymer encapsulation of surface-modified carbon blacks using surfactant-free emulsion polymerisation

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Abstract

Polymer encapsulations of two different grades of water-dispersible, surface-sulfonated carbon black, Sterling-4620 with an aggregate size of 260 nm and Black Pearls-800 (BP-800) with an aggregate size of 45.7 nm, were carried out using surfactant-free emulsion polymerisation of butyl acrylate, methyl methacrylate and allyl methacrylate. High levels of initiator were required because carbon black acts as an efficient radical trap. Although polymerisation in the presence of Sterling-4620 proceeded satisfactorily using ammonium persulfate (APS), the much larger specific surface area of BP-800 inhibited polymerisation with APS and the sodium salt of 4,4′-azobis(4-cyanopentanoic acid), a non-oxidising initiator, was necessary for effective polymerisation in the presence of BP-800. Several polymer-encapsulated Sterling-4620 and BP-800 products were prepared successfully using different amounts and compositions of polymer, and have been characterised using solvent extraction, pyrolysis, thermogravimetry, infrared spectroscopy, transmission electron microscopy, differential scanning calorimetry and dynamic mechanical thermal analysis.

Keywords: Carbon black; Encapsulation; Emulsion polymerisation

1. Introduction

Carbon black is an important pigment containing 90–99% of elemental carbon in which the smallest dispersible units are irregularly shaped aggregates that range from 50 to 500 nm in size. These aggregates readily form agglomerates which are held together by van der Waals' forces and are difficult to break up. Nevertheless, carbon black has many applications. It is used in thermoplastics in order to improve properties such as UV stability, electrical conductivity, blackness/jetness, opacity and modulus [1], but can also affect other properties deleteriously. For example, carbon black is used in ABS to impart UV stability and blackness, but it reduces the ultimate properties of the ABS even at levels as low as 2% [2]. This is due to the difficulty of dispersing the carbon black agglomerates in the polymer matrix. Coating and/or grafting of polymers onto/from the surface of carbon black particles may improve the dispersibility of the carbon black in organic solvents and polymers, and enhance the impact properties of carbon black filled thermoplastics.

There are several reports concerning grafting of polymers onto the surface of carbon black [3–8]. Hayashi et al. [3] and Hayashi and Tsubokawa [4] used the well-known fact that carbon black acts as strong radical trap [9] to prepare polymer-grafted carbon blacks by trapping of polymer radicals formed by the thermal decomposition of azo-containing and peroxide-containing polymers. Yoshikawa and Tsubokawa [5] studied the grafting of polymers onto carbon black by termination of living polymer cations (such as poly(isobutyl vinyl ether) cations) with nucleophilic groups (such as amino, sodium phenolate and sodium carboxylate groups) introduced onto the carbon black surface. There are also reports on growth of grafted polymer chains using free-radical [6], cationic [7] and anionic [8] polymerisation initiated from groups introduced onto the surface of carbon black. The main disadvantage of these methods is that the conversion is low, giving

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low percentages of grafting, and the reactions are carried out in organic solvents which are not environmentally friendly. The functionalisation of carbon black by surface grafting of polymers has been reviewed by Tsubokawa in 2002 [10]. Since this review, several new studies have been carried out, an example being the grafting of polymers from carbon black surfaces using atom transfer radical polymerisation [11–13].

Polymer encapsulation is an alternative method for modifying the carbon black surface. For example, a simple evaporation method [14] has been used in which pre-formed polymer is mixed with carbon black in a good solvent for the polymer using a high-shear mixer. The solvent is then evaporated in a controlled manner resulting in polymer encapsulation of the carbon black.

Emulsion polymerisation is a widely used process for the preparation of polymers and has been adapted for polymer encapsulation of a variety of inorganic particles, such as silica [15], quartz [16–18] and titanium dioxide [19]. The reaction medium in emulsion polymerisation is water and so eliminates the problems associated with the use of organic solvents. Nagai et al. [20] have investigated the polymer encapsulation of carbon black using emulsion polymerisation in the presence of carbon black dispersed in the aqueous medium using polymerisable surfactants. Zhang et al. [21] have studied the emulsion polymerisation of acrylic acid and styrene mixtures in the presence of carbon black. Miniemulsion polymerisation methods have also been used for encapsulation of carbon black in which the carbon black is dispersed in the monomer miniemulsion droplets, polymerisation of which then produces the polymer-encapsulated carbon black [22–24].

The present paper reports on polymer encapsulation of carbon black using an emulsion polymerisation method. In order to carry out emulsion polymerisation in the presence of carbon black, two different grades of water-dispersible, surface-modified carbon blacks have been used [14,25] and the effect of reaction variables on the encapsulation reaction has been studied.

2. Experimental

2.1. Materials

Sterling-4620 (specific surface area = 27.1 $m^2\,g^{-1}$, aggregate size = 260 nm) and Black Pearls-800 (BP-800) (specific surface area = 210.0 $m^2\,g^{-1}$, aggregate size = 45.7 nm) grades of carbon black were supplied by Cabot Corporation. In order to make the carbon blacks water dispersible, sodium phenylene sulfonate ($-C_6H_4SO_3Na$) groups were attached to their surfaces by Cabot Corporation using a method described elsewhere [25]. Before use, the surface-modified carbon blacks were washed thoroughly with methanol, recovered by filtration and then dried at 60 °C for 48 h.

The monomers used were butyl acrylate, methyl methacrylate and allyl methacrylate (Aldrich, $\geq$98%). The phenolic inhibitor was removed from each monomer by shaking with an equal volume of 2% (w/v) sodium hydroxide solution in a separating funnel, followed by washing several times with water, and then repeating this procedure. The inhibitor-free monomer was dried over anhydrous calcium chloride (Fisher Scientific).

The initiators used were ammonium persulfate (APS) (Aldrich, $\geq$98%) and 4,4′-azobis(4-cyanopentanoic acid) (ACPA) (Aldrich, $\geq$75%). Ammonium persulfate was used as supplied. ACPA was used both as supplied and as its sodium salt (SACPA), which was prepared by adding sufficient 0.5 wt% aqueous sodium hydroxide solution to ACPA in a beaker to give a 2:1 molar ratio of NaOH:ACPA, followed by vigorous magnetic stirring for 30 min after which all the ACPA had dissolved to give an aqueous SACPA solution that was used in the emulsion polymerisations.

2.2. Emulsion polymerisation procedure

A semi-continuous emulsion polymerisation process was used. The water and carbon black were charged to a round-bottomed flask mounted in a water bath at 70 °C. The flask was purged with nitrogen throughout the reaction. After the mixture had reached bath temperature, the initiator was added and the monomer was pumped into the flask over a period of 2 h at constant rate using either a Watson–Marlow Model 505S peristaltic pump or an Infors Predicor syringe pump. For two-stage polymerisations, the first-stage monomer was pumped-in over a period of 150 min; it was then allowed to react for a further 150 min to ensure complete reaction before pumping in the second-stage monomer over a period of 100 min. For all reactions, a final period of at least 100 min was allowed for completion of the reaction before cooling the flask to room temperature and collecting the product by filtration. The reaction products were dried at 60 °C, ground using a mechanical pestle and mortar, and sieved through a 500 μm screen to collect the particles.

2.3. Characterisation of the polymer-encapsulated carbon blacks

Emulsion polymerisation products were analysed using gas–liquid chromatography (GLC), sedimentation, solvent extraction, infrared (IR) spectroscopy, thermogravimetry (TG), pyrolysis, differential scanning calorimetry (DSC) and, for samples with a high polymer content, dynamic mechanical thermal analysis (DMTA).

GLC was used to determine the amount of unreacted monomer in the reaction and was carried out using a Perkin–Elmer Autosystem Gas Chromatograph. Solutions (1 μl) were injected at an inlet pressure of 5.0 psi into a PVMS capillary column (length 25 m, inside diameter 0.3 mm). The temperature of the oven was held at 50 °C for 5 min and then increased to 150 °C at a rate of 5 °C min^{-1}. Aliquots removed from the reactions were analysed for the presence of unreacted monomer to calculate the conversion. Methanol (BDH, AnalaR 99.9%) was added to the aliquots in order to ensure miscibility of the monomer. Quantitative analysis was carried out using butyl acetate as an internal standard.

Sedimentation experiments were carried out by dispersing small amounts (~1 g) of the carbon black material in water

(~10 g) and allowing the samples to settle under gravity. The time taken for the sample to settle provided a qualitative measure of its water dispersibility.

Extraction of the soluble polymer from the polymer-encapsulated carbon blacks was carried out by dispersing the product in a solvent (either chloroform or acetone). The dispersion was heated under reflux for 8 h. The product was then filtered to separate the soluble part from the carbon black and insoluble part. The soluble polymer was recovered through evaporation of the solvent and dried at 60 °C.

IR spectra recorded using a Perkin–Elmer 2000 FT-IR spectrometer were used to detect the presence of polymer in the emulsion polymerisation products. Typically 100 scans over the range 4000–450 $\mathrm{cm^{-1}}$ were taken from each sample with a resolution of 2 $\mathrm{cm^{-1}}$ and summed to provide the spectra. A mixture of 2 wt% carbon black in KBr was prepared and then mixed with more KBr to produce a dispersion containing 0.09 wt% carbon black from which disks were pressed. The disks were placed in the IR chamber which was then flushed with nitrogen for 1 h before the IR spectra were recorded. IR spectra of solvent-extracted material from the polymer-encapsulated carbon blacks were obtained from thin films cast from the extract solution.

TEM of the emulsion polymerisation products was carried out as follows. The carbon black product (~0.5 wt%) was added to ethanol in a sample vial and dispersed using an ultrasonic bath for 10–20 min. A drop of the dispersion was placed onto a carbon-coated copper grid (Agar Scientific, 3.05 mm, 200 mesh) situated on a filter paper and then allowed to dry. The samples were examined on a Philips 400EM transmission electron microscope employing an accelerating voltage of 80 kV.

TG was used to determine the amount of polymer present in the samples. Samples were heated under nitrogen from room temperature to 900 °C at a heating rate of 10 $\mathrm{°C\,min^{-1}}$ using a Rheometrics Scientific TG770 thermogravimetric analyser.

Pyrolysis was carried out by placing samples (~10 g) of carbon black in an aluminium dish in a furnace at 500 °C under nitrogen.

DSC was performed on reaction products that had been dried to constant weight in a vacuum oven at 60 °C. Samples were analysed under nitrogen at a heating rate of 20 $\mathrm{°C\,min^{-1}}$ on a DuPont 9000 Thermal Analyst instrument fitted with a DuPont DSC cell. The polymer glass transition temperature (T_g) was recorded as the onset of the baseline step in the DSC trace, as defined by the intercept of an extension of the baseline below the step to a tangent drawn at the point of steepest slope in the step.

For DMTA, rectangular strips were prepared from polymer-encapsulated carbon blacks by compression moulding of the emulsion polymerisation products at 170 °C for 2 min and subsequent cooling to room temperature. A sinusoidal displacement was applied at a frequency of 1 Hz whilst the specimen was heated at 2 $\mathrm{°C\,min^{-1}}$ from −100 to 150 °C in a Rheometrics RMS800 instrument. The experimental data were converted to values of storage modulus, G', loss modulus, G'', and loss tangent, tan δ, for each temperature; T_g was taken as the temperature location of the peak in tan δ.

3. Results and discussion

The objective of the research reported here was to develop an emulsion polymerisation method for polymer encapsulation of carbon black particles dispersed in water. The principle of the emulsion polymerisation polymer encapsulation method is shown schematically in Fig. 1 and described here. Key to this method is the use of carbon black particles which readily disperse in water to form a stable colloidal dispersion. The emulsion polymerisation simply involves the aqueous dispersion of carbon black, a water-soluble initiator and the monomer, i.e. no surfactant is used. During the early stages of the polymerisation, oligomeric free radicals are formed in the aqueous phase, where they grow by homogeneous aqueous phase polymerisation until they reach a critical chain length at which they become water insoluble and precipitate [26]. In the presence of colloidal carbon black particles and the absence of surfactant, precipitated oligomers should be trapped by the carbon black particles provided that a sufficiently large number of carbon black particles are available to ensure that the oligomeric radicals coagulate onto the carbon black particle surfaces rather than forming independent polymer particle nuclei by coagulating with themselves. The locus of polymerisation then is transferred to the surface of carbon black at which the oligomeric chains can continue to grow to form a layer of polymer.

Functionalisation of carbon black surfaces with hydrophilic groups is a way of introducing water dispersibility to carbon blacks that has been used in this work. Both Sterling-4620 and BP-800 carbon blacks provided by Cabot Corporation had been functionalised with sodium phenylene sulfonate groups for this purpose using the diazonium reaction shown in Scheme 1. Fig. 2 shows TEM micrographs of these surface-modified carbon blacks which reveal that the blacks are aggregates of much smaller primary particles of carbon black,

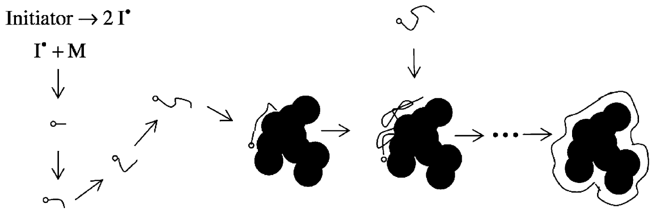
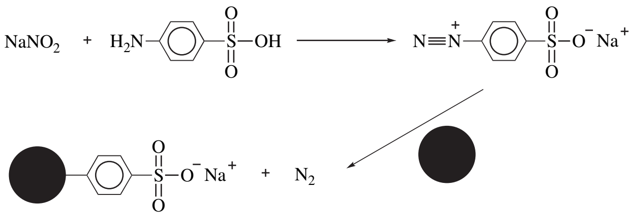


Fig. 1. Schematic representation of polymer encapsulation of a carbon black particle using surfactant-free emulsion polymerisation (I• represents an initiator radical and M represents monomer).



Scheme 1. Diazonium reaction for functionalising the surface of carbon blacks [25]. The solid circles represent carbon black particles.

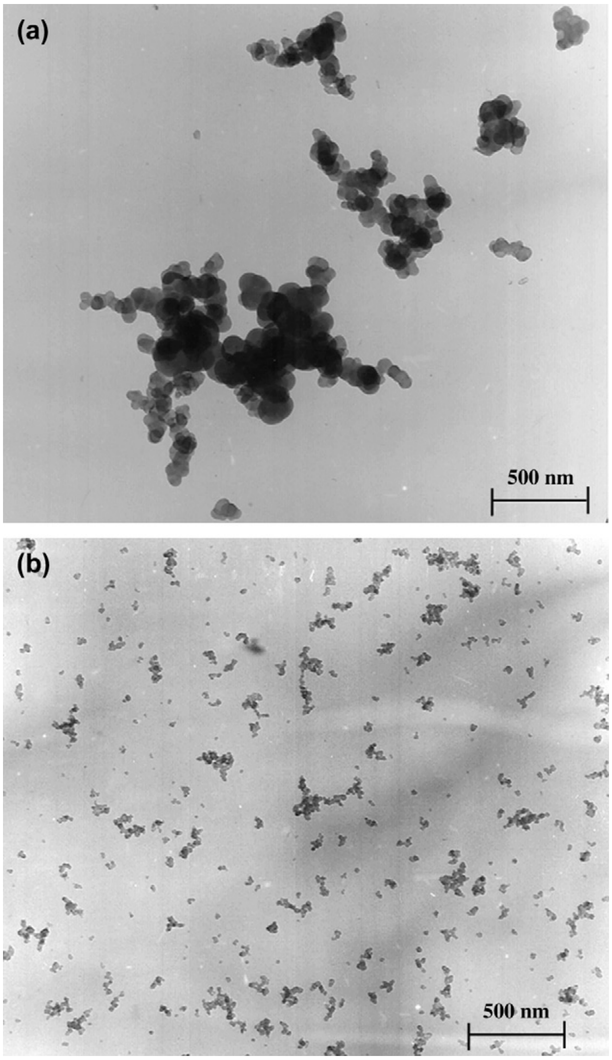


Fig. 2. Transmission electron micrographs of surface-sulfonated (a) Sterling-4620 and (b) BP-800.

as is normal for carbon black. These aggregate particles as supplied will, however, be referred to as the carbon black ‘particles’ within this paper.

3.1. Effect of carbon black and initiator on the polymerisations

Table 1
Formulations for the emulsion polymerisations carried out in order to determine the optimum conditions for encapsulating Sterling-4620 and BP-800 carbon blacks

Reaction code[a]	Component/g					Conversion/%
	Carbon black	Water	BA	Initiator		
				Type	Amount	
S10-B13-IP21	10	30	1.49	APS	0.32	33
S10-B11-IP36	10	30	1.26	APS	0.45	43
S10-B12-IP50	10	30	1.3	APS	0.65	100
S60-B12-IP52	60	180	7.92	APS	4.08	100
S50-B31-IP26	50	250	21.95	APS	5.61[b]	51
S50-B31-IP42	50	250	21.95	APS	9.12[b]	100
BP50-B31-IP42	50	250	21.95	APS	9.12[b]	–
BP50-B31-IP83	50	250	21.95	APS	18.24[b]	–
BP50-B31-IA14	50	250	21.95	ACPA	3.00	100
BP50-B31-IS16	50	250	21.95	SACPA	3.47	100

[a] Reaction codes beginning with “S” and “BP” indicate reactions carried out using Sterling-4620 and BP-800, respectively, with the following numbers giving the weight (g) of carbon black used in the reaction. The next letter indicates the monomer composition (B indicating BA) and the next number is the targeted percentage polymer in the encapsulated product. “IP”, “IA” and “IS” indicate use of APS, ACPA and SACPA as initiators, respectively, with the number following the initiator type giving 100× the weight ratio of initiator to monomer.

[b] Sixty percent of the initiator was added at the beginning of the reaction. After the addition of monomer was completed, an aqueous solution of the remaining initiator was fed to the reaction continuously over 2 h using a peristaltic pump.

Table 1 shows the formulations and the conversions of the emulsion polymerisations carried out using the two grades of carbon black in order to establish the optimum conditions for encapsulation. APS was chosen as the initiator because it is one of the most widely used initiators in emulsion polymerisation [27]. As can be seen from Table 1, the amount of APS required for polymerisation of butyl acrylate (BA) to proceed in the presence of carbon black is much higher than that normally used for emulsion polymerisation of BA. This is not unexpected, as the surface of carbon black contains chemisorbed oxygen-containing species [1], some of which (e.g., quinonic groups) are known inhibitors of free-radical polymerisation [28]. The capacity of a particular grade of carbon black for trapping free radicals depends on its specific surface area and properties. Although having similar surface functionality to Sterling-4620, BP-800 has a specific surface area seven times larger. Therefore, the level of initiator that resulted in complete conversion of BA to polymer in the presence of Sterling-4620 did not give rise to polymerisation in the presence of BP-800 (reaction BP50-B31-IP42). Even at higher levels of APS, polymerisation of BA in the presence of BP-800 did not proceed (reaction BP50-B31-IP83). APS is an oxidising agent and carbon black has a tendency to extend its surface layer of chemisorbed oxygen-containing species in the presence of oxidising agents [1,29]. Hence, a non-oxidising initiator, ACPA, was investigated for polymer encapsulation of BP-800 and resulted in 100% conversion of monomer to polymer (reaction BP50-B31-IA14). However, since ACPA has a higher solubility in monomer, the polymerisation occurred mainly within the monomer emulsion droplets and instead of polymer-encapsulated carbon black particles, polymer beads 2–3 mm in diameter were obtained. In order to prevent this, the sodium salt of ACPA (SACPA) was used since it has a much higher water solubility; this resulted in successful encapsulation of BP-800 (reaction BP50-B31-IS16).

Fig. 3 shows IR spectra of poly(butyl acrylate) and the material extracted from the product of the S10-B12-IP50 reaction. The peak at 1750 cm^{-1}, due to C=O stretching, provides clear evidence of the presence of poly(butyl acrylate) in the S10-B12-IP50 product. Fig. 4 shows the TG curves for Sterling-4620 as-supplied and the product from the S10-B12-IP50 reaction. Although Sterling-4620 does not show any significant weight loss up to around 400 °C, the S10-B12-IP50 reaction product shows a weight loss of 10.3 wt%

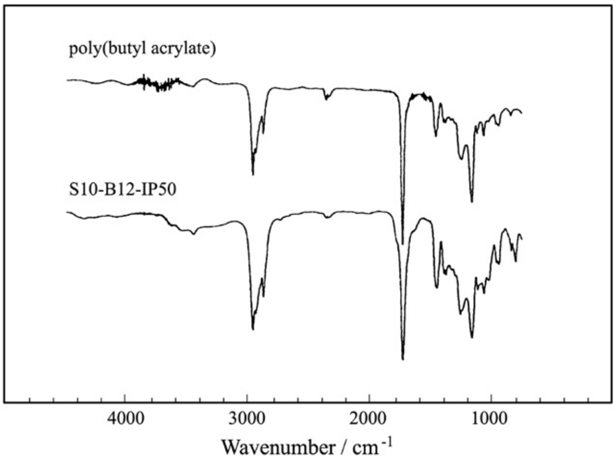


Fig. 3. IR spectra of poly(butyl acrylate) and the product extracted from S10-B12-IP50.

between 200 and 400 °C due to degradation of the polymer present in the material. This value is similar to the expected polymer content (11.5 wt%) based on the reaction formulation and the monomer conversion measured by GLC.

Sedimentation of the emulsion polymerisation products was used as another indication of successful encapsulation of the carbon blacks. The as-supplied surface-modified carbon blacks form stable dispersions in water that do not separate even when centrifuged. However, when monomer was successfully polymerised in the presence of the carbon black, the resulting product settled with time. This suggests that the polymer formed on the carbon black surface masks at least some of the surface charges that stabilised the original carbon black dispersion.

3.2. Effect of crosslinking on the encapsulation of Sterling-4620

The effect of crosslinking on the encapsulation of Sterling-4620 was investigated using BA, and mixtures of BA with allyl methacrylate (ALMA) as a crosslinking monomer, using different BA to ALMA ratios in the encapsulation reactions. Table 2 presents the formulations for these reactions, the weight loss from each reaction product after extraction by chloroform and after pyrolysis, and the theoretical weight percentage of polymer for comparison. The amount of polymer extracted by the solvent is much less than the total polymer detected by pyrolysis because only the non-crosslinked polymer can dissolve in the solvent. Hence, the difference between the extraction and pyrolysis values should give the amount of crosslinked polymer present. Clearly, the product from reaction S60-B13-IP50, in which ALMA was not used, also has a significant proportion of crosslinked polymer. This is due to the known crosslinking of poly(butyl acrylate) during polymerisation, which results from coupling of propagating long-chain branches arising from intermolecular chain transfer to polymer [30]. The effect of introducing ALMA and increasing its concentration is to increase the amount of crosslinked polymer, thus reducing the amount of extracted polymer. As for the S10-B12-IP50 reaction product, the polymer contents obtained by pyrolysis again were lower than the theoretical polymer contents. Since unreacted monomer could not be detected at the end of the emulsion polymerisations, this observation could be explained in terms of the evaporation of small amounts of monomer from the reaction vessel during polymerisation (which can be significant when working at these relatively small scales) and/or incomplete degradation of the polymer because pyrolysis was carried out under a nitrogen atmosphere.

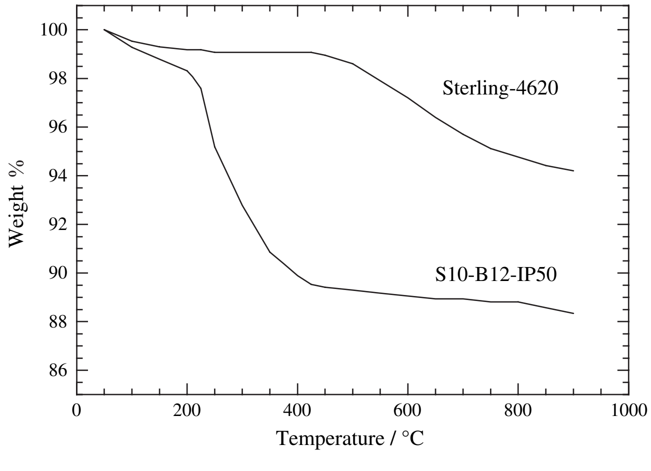


Fig. 4. TG traces of surface-sulfonated Sterling-4620 and the S10-B12-IP50 product.

3.3. Effect of polymer content on the encapsulation of Sterling-4620

The effect of varying the polymer content was investigated using a fixed monomer composition (98 mol% BA, 2 mol% ALMA). Table 3 shows the data for representative polymerisations, including a polymerisation carried out in the absence of carbon black to produce just the crosslinked poly(butyl acrylate), XPBA1. Monomer conversion in the S10-XB21-IP24 polymerisation was 86%; hence, higher levels of initiator were used when the monomer content was above 22%.

DSC was performed on the reaction products in order to detect the polymer. Representative DSC traces of the as-supplied Sterling-4620, XPBA1, and the reaction products are shown in Fig. 5. XPBA1 shows a clear transition indicated by a step-change in the heat flow (ΔQ) at approximately −40 °C, which is due to the glass transition of the polymer, whereas, as expected, Sterling-4620 did not show a transition at this temperature. The reaction products show the same transition as XBPA1, but the change in heat flow becomes smaller as the polymer content decreases. The measured values of T_g and ΔQ are given in Table 4 together with theoretical values of the change in heat flow (ΔQ_{theor}) for each reaction, which was calculated using the value of ΔQ at T_g for XPBA1 and the weight fraction of polymer (w_p) in the product assuming complete monomer conversion. As can be seen, the measured

Table 2
Effect of crosslinking on encapsulation of Sterling-4620 carbon black (CB)

Reaction code[a]	Component/g					Weight loss/%				
	Water	CB	BA	ALMA	APS	Extraction[b]		Pyrolysis[b]		Theoretical wt% polymer content[e]
						Overall loss[c]	Polymer loss[d]	Overall loss[c]	Polymer loss[d]	
S60-B13-IP50	300	60	7.83	–	3.92	6.6	4.1	22.6	8.7	11.5
S60-XB11-IP50-1	300	60	7.42	0.11	3.83	4.7	2.2	22.5	8.5	11.1
S60-XB11-IP51-2	300	60	7.49	0.19	3.95	3.1	0.6	22.3	8.4	11.3

[a] Reaction codes are defined in Table 1. "XB" represents crosslinked encapsulating polymer, and the final numbers 1 and 2 indicate the mol% level of crosslinking agent (ALMA) in the monomer mixture.

[b] The weight loss of Sterling-4620 before encapsulation was 2.8% in extraction and 15.7% in pyrolysis.

[c] $$\text{Overall loss }(\%) = \frac{\text{Initial weight (g)} - \text{final weight (g)}}{\text{Initial weight (g)}} \times 100.$$

[d] $$\text{Polymer loss }(\%) = \text{Overall loss }(\%) - \{\text{weight fraction of CB} \times \text{weight loss of CB }(\%)\}.$$

[e] $$\text{Theoretical polymer content }(\%) = \frac{\text{mass BA} + \text{mass ALMA}}{\text{mass CB} + \text{mass BA} + \text{mass ALMA}} \times 100$$

{Note that the APS was excluded from this calculation because only a small proportion of the initial APS was expected to become attached to the carbon black particles as end groups on polymer chains; the majority of the residues from APS will arise from oxidation of the carbon black surface and should reside in the aqueous phase separate from the particles, as will any unreacted APS.}

Table 3
Effect of polymer content on encapsulation of Sterling-4620 carbon black

Code[a]	Component/g			Weight loss/%				
	BA	ALMA	APS	Extraction[b]		Pyrolysis[b]		Theoretical wt% polymer content[e]
				Overall loss[c]	Polymer loss[d]	Overall loss[c]	Polymer loss[d]	
S10-XB12-IP53	1.32	0.03	0.72	3.2	0.7	22.2	8.4	11.9
S10-XB17-IP33	1.94	0.04	0.65	4.6	2.3	22.2	9.1	16.5
S10-XB21-IP24	2.66	0.06	0.65	4.7	2.4	24.1	11.3	18.4
S10-XB22-IP40	2.69	0.06	1.09[f]	5.1	2.9	29.5	17.2	21.6
S10-XB30-IP26	4.31	0.09	1.13[f]	7.3	5.4	33.0	22.1	30.5
S10-XB36-IP20	5.44	0.13	1.13[f]	8.0	6.2	41.3	31.2	35.8
S10-XB55-IP09	11.86	0.26	1.12[f]	9.3	8.0	59.5	52.4	54.8
XPBA1	2.67	0.06	0.66	–	–	–	–	–

[a] All reactions employed 50 g of water and 10 g of Sterling-4620, except the XPBA1 reaction in which the Sterling-4620 was omitted.

[b–e] See the corresponding footnotes in Table 2.

[f] APS (0.41 g) was added 3 h after the start of the reaction.

and calculated values are similar, indicating that the polymer has coated the Sterling-4620 as intended.

Sedimentation experiments showed differences between the products with different polymer contents. The surface-modified Sterling-4620 was readily dispersible in water and no sedimentation was observed. The S10-XB12-IP53 and S10-XB17-IP33 products were easily dispersible in water but settled after a few hours. The S10-XB21-IP24, S10-XB22-IP40 and S10-XB30-IP26 products were dispersible in water, but began to settle after a few minutes. The S10-XB36-IP20 and S10-XB55-IP09 products were not dispersible in water and settled rapidly. Thus the water dispersibility of the encapsulation products decreased with increasing polymer content, consistent with the presence of a polymer layer of increasing coverage/thickness on the carbon black surface which masks surface sulfonate groups and reduces water dispersibility.

A scale-up of the S10-XB30-IP26 reaction was carried out (coded S50-XB30-IP42) in which the amounts of water, carbon black and monomers were five times that of the original reaction. Fig. 6 shows TEM micrographs of the product as obtained from the reaction and after recovery through filtration and drying. The presence of encapsulating polymer is evident in the micrographs and has the appearance of being particulate suggesting that colloidally-unstable polymer particles were formed, which then coagulated onto the surface of the colloidally-stable carbon black particles. Careful inspection of TEM micrographs of the as-produced material (e.g., Fig. 6a) also reveals the presence of independent polymer particles, which are not present in TEM micrographs of the product after filtration and drying (e.g., Fig. 6b), suggesting that the independent polymer particles were removed through filtration and/or had coalesced with the encapsulated carbon black particles during the work-up. These observations most probably arise because the number of carbon black particles per unit volume of the reaction dispersion is insufficient for capturing all the oligomeric radicals before they form polymer particle nuclei. Given that the density of carbon black is $1.8\ \text{g cm}^{-3}$ [31] and the average diameter of Sterling-4620 particles is 260 nm, the number of carbon black particles per unit volume in this polymerisation is $1.2 \times 10^{13}\ \text{cm}^{-3}$ (treating the particles as solid

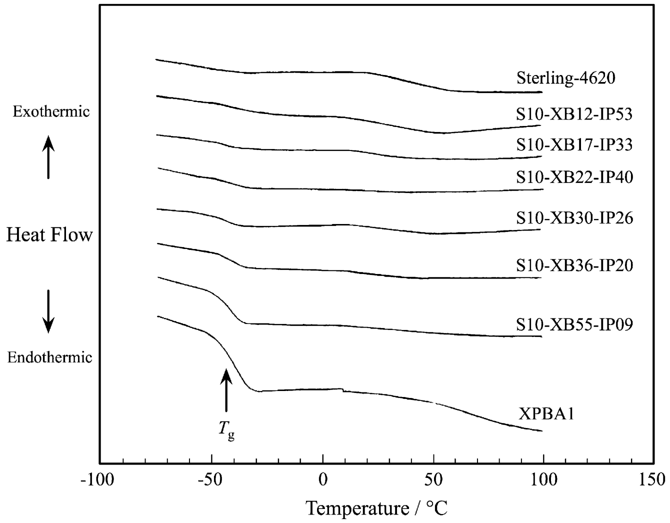


Fig. 5. Effect of polymer content on DSC traces of encapsulated surface-sulfonated Sterling-4620.

spheres). This particle concentration is slightly lower than the minimum value reported by Hergeth et al. [32,33] (2×10^{13} cm^{-3}) to stop the secondary nucleation of polymer particles. Nevertheless, the TEM micrographs confirm that polymer-encapsulated Sterling-4620 had been produced and recovered through the work-up procedure.

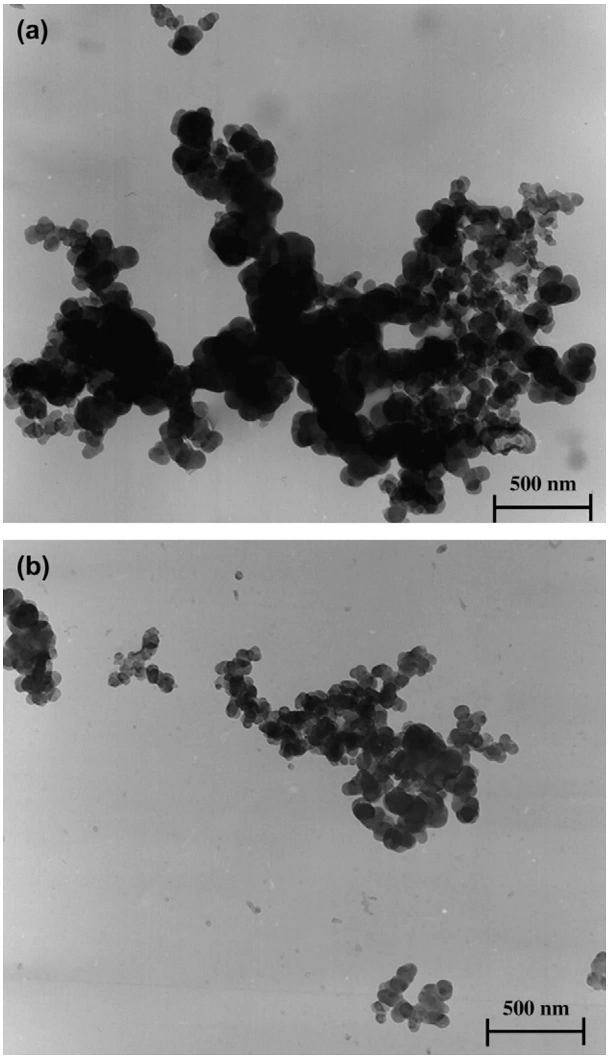


Fig. 6. Transmission electron micrographs of the S50-B31-IP42 product (a) as obtained directly from the reaction and (b) after filtration and drying at 60 °C.

3.4. Effect of polymer composition on the encapsulation of BP-800

3.4.1. One-stage encapsulations

Encapsulation of BP-800 was carried out using BA, methyl methacrylate (MMA) and ALMA as the monomers. Table 5 shows the formulations of the two encapsulation reactions together with the formulations used for the preparation of the corresponding BA/ALMA (XPBA2) and MMA/ALMA (XPMMA) copolymers. Fig. 7 shows the TEM micrographs of the products from the encapsulation reactions. Unlike the S50-B31-IP42 reaction product, independent polymer particles were not observed in the products from BP-800 encapsulation (compare Fig. 6a with Fig. 7a and b). This may be explained by the much higher number concentration of carbon black particles in the reaction medium as a result of the smaller size of the BP-800 particles compared with the Sterling-4620 particles. The number of BP-800 particles per unit volume in the BP50-XB33-IS14 and BP50-XMM33-IS14 polymerisations was 2.2×10^{15} cm^{-3}, which is much higher than the minimum number of particles [32,33] required to avoid nucleation of polymer particles. The sizes of the encapsulated particles, however, are larger than expected for encapsulation of individual BP-800 particles and the products had broad particle size distributions. Some large agglomerates of BP-800 and polymer with particle sizes up to 1 μm were

Table 4
T_g and heat flow data from DSC for polymer-encapsulated Sterling-4620 and XPBA1

Sample	w_p	T_g/°C	ΔQ^a/W g^{-1}	$\Delta Q_{theor}{}^b$/W g^{-1}
S10-XB12-IP53	0.119	−42	0.027	0.018
S10-XB17-IP33	0.165	−43	0.027	0.025
S10-XB22-IP40	0.216	−41	0.043	0.032
S10-XB30-IP26	0.305	−43	0.052	0.046
S10-XB36-IP20	0.358	−41	0.053	0.054
S10-XB55-IP09	0.548	−41	0.080	0.082
XPBA1	1	−40	0.150	0.150

See Table 3 for further details on these materials.

[a] Change in heat flow at the glass transition of the PBA in the polymer-encapsulated Sterling-4620.

[b] $\Delta Q_{theor} = w_p \times \Delta Q_{XPBA1}$.

Table 5
Formulations for the one-stage encapsulations of BP-800

Reaction code	Component/g					
	BP-800	Water	SACPA	BA	MMA	ALMA
XPBA2	–	300	0.24	24.51	–	0.49
BP50-XB33-IS14	50	300	3.47	24.51	–	0.49
XPMMA	–	300	0.24	–	24.46	0.55
BP50-XMM33-IS14	50	300	3.47	–	24.46	0.55

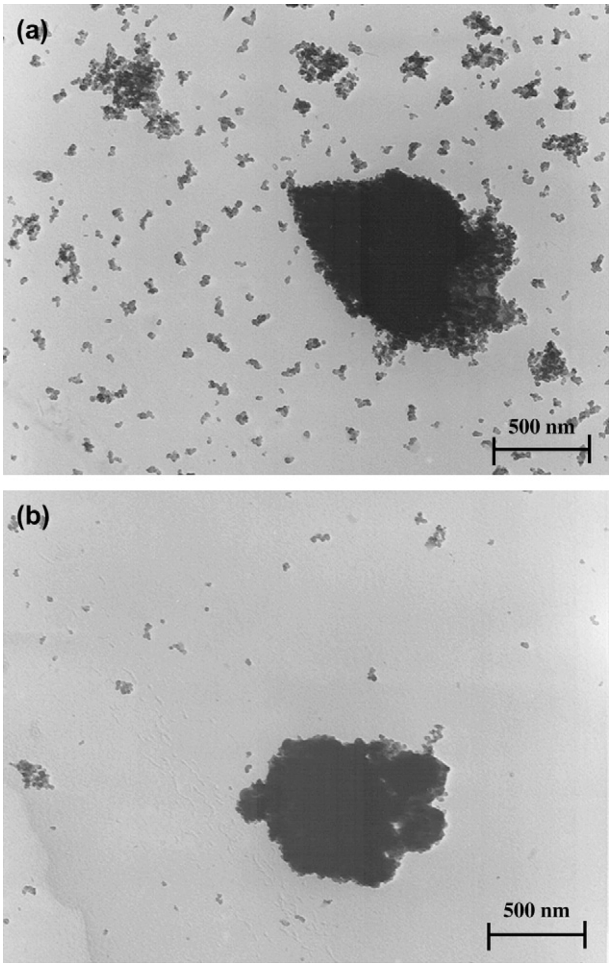


Fig. 7. Transmission electron micrographs of (a) the BP50-XB33-IS16 and (b) BP50-XMM33-IS16 products.

observed in the products. The combined effects of the much higher number concentration of carbon black particles, the masking of surface charges by the polymer coating and the absence of ionic and/or steric colloid stabilisers in these polymerisations would be expected to lead to limited coagulation of polymer-coated BP-800 particles during polymerisation, thereby explaining the presence of larger agglomerates and the broad particle size distribution of the encapsulated products.

3.4.2. Two-stage encapsulation

Sequential two-stage encapsulation of BP-800 was carried out to produce crosslinked PBA in the first stage and poly(methyl methacrylate) (PMMA) in the second stage. ALMA was used to crosslink the rubbery PBA layer and to provide residual allylic groups for grafting of the PMMA onto the crosslinked PBA [34]. Three two-stage encapsulations were carried out, each with the same overall polymer content but with different proportions of the rubbery and glassy polymers. The formulations for these polymerisations are shown in Table 6. The conversion–time plots for the encapsulation reactions are shown in Fig. 8, from which the emulsion polymerisations can be seen to have proceeded in a controlled way under the monomer-starved conditions that are necessary for sequential growth of successive layers [30].

Table 6
Formulations for the two-stage encapsulations of BP-800

Component	Mass of component/g		
	BP-(XB71/MM29)[a]	BP-(XB55/MM45)[a]	BP-(XB41/MM59)[a]
BP-800	100	100	100
Water	1000	1000	1000
SACPA	11.57	11.57	11.57
BA	147.05	113.72	84.30
ALMA	2.95	2.28	1.70
MMA[b]	59.62	95.1	127.61

[a] XB indicates crosslinked PBA and MM grafted PMMA; the numbers indicate the percentage of the total monomer used in forming each phase.

[b] MMA addition started 1 h after the reaction of BA/ALMA was completed.

Acetone extraction of the products from the two-stage encapsulation reactions was carried out in an attempt to measure the amount of non-grafted polymer. However, although BP-800 was not dispersible in acetone, the BP-(XB71/MM29), BP-(XB55/MM45) and BP-(XB41/MM59) products gave stable dispersions in acetone from which the encapsulated carbon blacks could not be separated by filtration. Hence, the sol fractions could not be measured. However, the increased dispersibility of the products in acetone suggests that the carbon black particles are sterically stabilised in acetone by a grafted encapsulating polymer layer.

The presence of rubbery and glassy phases in the double-layer coated particles was detected by DMTA, the results from which are shown in Fig. 9 and summarised in Table 7. As can be seen, two glass transitions were observed for each sample, indicating the presence of separate PBA and PMMA phases. The room temperature storage modulus of the compression moulded specimens produced from the encapsulated

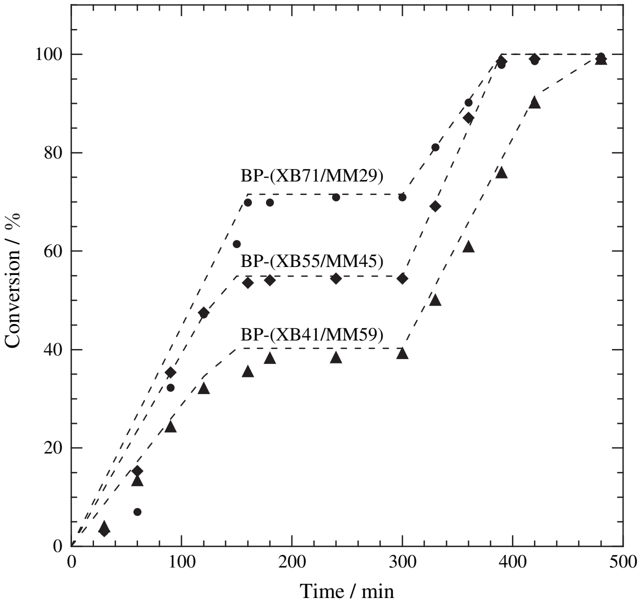


Fig. 8. Conversion–time plots for the two-stage polymer encapsulation reactions carried out using BP-800. The dashed lines are the monomer feed profiles and the symbols show the respective measured overall monomer conversions.

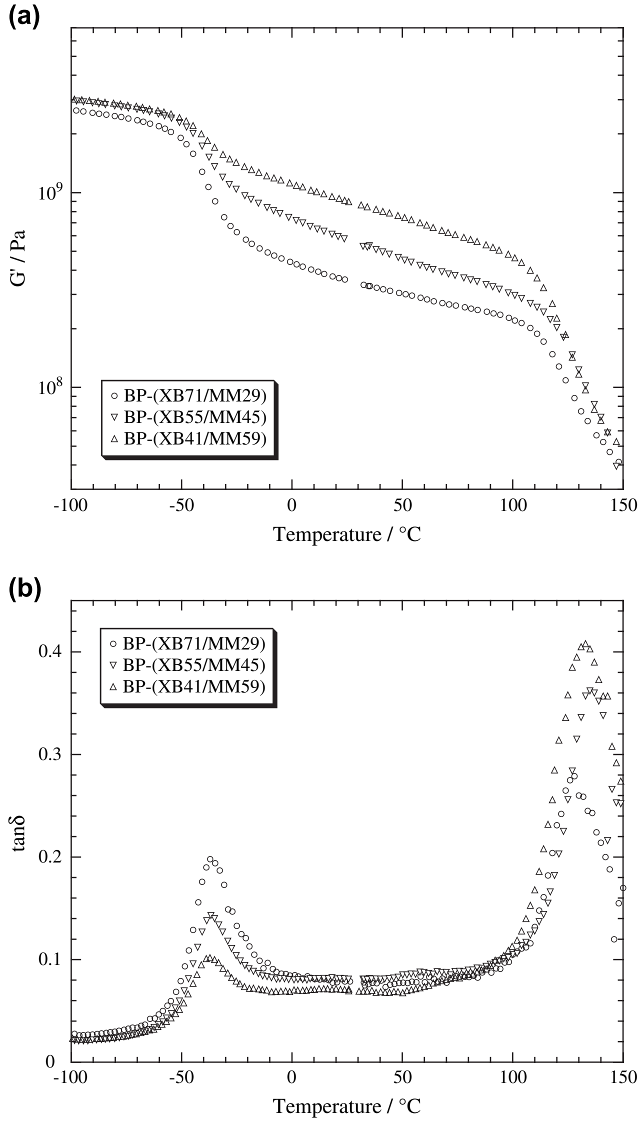


Fig. 9. (a) Storage modulus, G', and (b) loss tangent, tan δ, data for the two-stage polymer-encapsulated BP-800 products.

Table 7
DMTA data for two-stage encapsulated BP-800

Material	T_{g1}[a]/°C	T_{g2}[a]/°C	G'/Pa at 25 °C
BP-(XB71/MM29)	−37	130	3.55×10^8
BP-(XB55/MM45)	−36	134	5.74×10^8
BP-(XB41/MM59)	−37	132	9.06×10^8

[a] T_g determined from the location of the peak in tan δ.

products increased as the proportion of PMMA increased, as would be expected. The area under the peak in tan δ for each polymer phase in the samples (see Fig. 9b) correlated directly with the proportion of the polymer in the product.

4. Conclusions

The amount of initiator required for encapsulation of surface-sulfonated Sterling-4620 and BP-800 carbon blacks by surfactant-free emulsion polymerisation was higher than that normally used in emulsion polymerisation due to the ability of the carbon blacks to trap radicals. Encapsulation of the Sterling-4620 progressed readily using APS, whereas a larger amount of the non-oxidising initiator, SACPA, was required for encapsulation of BP-800 because of its much higher specific surface area. The encapsulated products were characterised using various techniques which provided firm evidence for encapsulation of the carbon blacks by polymer. For Sterling-4620 particles, the number concentration of carbon black particles in the reaction was less than that required to prevent nucleation of independent polymer particles, most of which, however, coagulated onto the carbon black particles. For the much smaller BP-800 particles, however, the number concentration exceeded that required to prevent nucleation of separate polymer particles and all the polymers formed around the carbon black particles. A number of polymer-encapsulated carbon black products with different amounts and compositions of polymer have been prepared successfully using this surfactant-free emulsion polymerisation method, including sequential coating of BP-800 by crosslinked PBA and then grafted PMMA.

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