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Admicellar polymerization of styrene with divinyl benzene on alumina particles: the synthesis of white reinforcing fillers

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Abstract Admicellar polymerization has been used to form polymer coated white mineral particulates as alternatives to carbon black for application in rubber reinforcement. An ultra thin film of polystyrene and cross-linked with divinylbenzene was used to coat alumina particles. Optimization of reaction conditions was carried out, through investigation of factors that affect the adsorption of the surfactant, sodium dodecyl sulfate, on alumina and film formation. The surface modified particles were characterized using ultraviolet absorbance, thermogravimetry, scanning electron microscopy, and changes in hydrophobicity were determined qualitatively using a drop test. Results showed that alumina particles were successfully coated with poly(styrene-*co*-divinylbenzene), and their resistance to wetting by water was greatly enhanced after admicellar polymerization treatment.

Introduction

Particulate fillers are often used in the rubber industry to modify and improve the physical properties of elastomeric materials for commercial applications. Their addition results in increased modulus, significant improvements in abrasion and tear resistance, and greater durability and overall performance [1–5]. Although the exact mechanism of reinforcement is not fully understood, the principles of the factors that govern the stress–strain behavior of particulate filler rubber are generally agreed upon [6–10].

Carbon black (CB) is one such reinforcing filler that is widely used in the rubber industry as its incorporation offers several advantages. In addition to the significant improvements of the dimensional stability of the rubber, its incorporation offers many other properties such as ultraviolet protection, behaving as an antioxidant to prolong rubber lifetime [11]. It is however not without its limitations. For example, CB acts as a pigment resulting in black rubbers and at high filler loading, the rubber composite becomes conductive [12], which is not always desirable, such as in the production of vehicle tyres.

One of the preferred models used to explain the mechanism of reinforcing properties of CB, is the so-called "graded seal" concept [13], which results from the strong interaction of the CB with the rubber matrix. This theory proposes that the unique surface chemistry of CB allows for very strong filler–rubber interactions, resulting in the layer of rubber immediately in contact with the surface being more highly cross-linked than the matrix [9].

Much of the previous work on alternative fillers attempted to mimic CB. Surface modification of

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inorganic fillers to increase their compatibility with the rubber matrix and render them reactive in the rubber vulcanization process is one such avenue that is being vigorously pursued [1, 14–16]. A typical example is the use of silica, which is continuing to gain commercial importance as it can offer several advantages over CB. For example, the incorporation of silica in tyres can decrease rolling resistance with equal wear resistance and wet grip to CB [16]. The disadvantage of using such inorganic fillers is that they require a compatiblizing reaction, such as silane coupling to improve silica–rubber interactions, often involving expensive and toxic reagents adding significantly to the cost of production [14, 17].

Admicellar polymerization [18–20] provides an interface of controlled chemical structure and more environmentally friendly alternative to modifying the surface characteristics of inorganic fillers to mimic those of CB. It can be a useful method to produce a range of white nano-particles for rubber reinforcement. Admicellar polymerization was first reported by Wu et al. [19, 21], and it provides a means by which an ultra-thin polymer of choice can be formed on the surface of a substrate. This is achieved by polymerization of monomers that are adsolubilized in adsorbed surfactant bilayers, called admicelles. This technique offers several advantages over the existing conventional compatiblization techniques; it is relatively precise, versatile and can be adapted for different applications.

This paper is the first in a series where we investigate the use of admicellar polymerization to form surface modified white nano-particles as an alternative to CB for rubber reinforcement. To date, much of the work in admicellar polymerization has concentrated on formation of linear polymers on the surface of solid particulates with O'Haver and co-workers reporting an increase in mechanical properties of rubbers that have been reinforced by incorporation of polymer coated precipitated silica [15, 16, 22]. However, very little attention has been paid to formation of cross-linked thin films [23], and in particular those with cross-linking and residual unsaturation. A noteworthy advantage of this technique is that it should offer a convenient route to forming highly cross-linked polymer films by employing monomers with multiple functionality. In this paper we report the synthesis of a cross-linked polymer on the surface of alumina particles through admicellar polymerization of styrene (S) and divinylbenzene (DVB). It is anticipated that this would have a twofold effect; not only will it form a cross-linked network that is tightly bound to the filler, but the presence of unreacted double bonds will provide a site for chemical linking to the rubber matrix during the subsequent vulcanization process. This would result in the formation of a region around the particle which is more highly cross-linked than the rubber matrix; mimicking a graded seal. In order to establish the appropriate experimental conditions, S was initially chosen as our model as it gives rise to a relatively non-polar linear polymer that can be extracted and analyzed.

Experimental

Materials

Styrene (99% purity) and divinylbenzene (80% purity) were purchased from Aldrich Chemical Company. Monomers were purified prior to use via filtration through a column of activated basic alumina to remove any inhibitor. Careful precautions were taken when handling S and DVB due to their inherent toxicity and carcinogenicity. Sodium dodecyl sulfate (SDS) (99% purity) was purchased from Aldrich and used without further purification. Sodium chloride was purchased from BDH chemicals and alumina (Al_2O_3) powder (surface area, 155 m^2/g, neutral, activated) from Merck, were both used without further purification. All organic solvents including methanol (HPLC purity), ethanol, tetrahydrofuran (THF) and diethyl ether were of analytical reagent grade unless stated otherwise and obtained from Ajax Finechem Ltd. Azobisisobutyronitrile (AIBN) initiator was purchased from Scheving Industrial Chemicals, UK and purified by recrystallization from diethyl ether. Milli-Q purified water was obtained by passing distilled water through a Milli-Q system until the conductivity fell below 0.1 $\mu S\ cm^{-1}$.

Methods

Determination of critical micelle concentration (cmc)

The critical micelle concentration of SDS surfactant solutions were measured in Milli-Q water and determined from a plot of conductivity versus concentration. The pH of the surfactant solutions was adjusted using 10 mol/m^3 HCl solution. Conductivity and pH were measured using a WP-81 pH-Cond-Salinity TPS meter that was calibrated via standard procedures.

Determination of concentration of SDS, S and DVB

Concentrations of SDS, S and DVB were determined by high-pressure liquid chromatography (HPLC) (Waters

600E) purchased from Waters, using an Aqua reverse phase C18, (5 μm Phenomenex) column. The mobile phase used consisted of 75% methanol and 25% deionized water. SDS was detected using an Alltech 550 conductivity detector and at a flow rate of 1 cm^3/min the retention time was 6.5 min. S and DVB were detected using a Waters 486 Tunable UV Absorbance Detector (λ_{max}, 247 nm), with a retention time of 8.30 min and 13.20 min at a flow rate of 1×10^{-6} m^3/min for S and DVB, respectively.

Determination of the amount of SDS adsorbed onto alumina

The amount of SDS adsorbed onto alumina powder was studied in the presence and absence of monomer, and the concentration of SDS determined after adsorption using high-performance liquid chromatography (HPLC). A solution of SDS of the desired concentration, salt and ethanol content was first prepared and pH was adjusted to 4.0–4.5 using 10 mol/m^3 HCl solution. Aliquots of this solution were pipetted into 50-cm^3 round bottom flasks containing a pre-weighed amount of alumina powder, equipped with magnetic stirrers. To overcome the difficulties in controlling styrene evaporation, flasks were capped with suba seals prior to the injection of monomer. The desired amount of S was added to the flasks using a micro syringe and left to equilibrate for a set period. After equilibration an aliquot of the supernatant was removed, filtered through a 0.45 μm syringe filter and concentration was determined using HPLC.

Determination of the SDS adsorption onto alumina

The adsorption of SDS on alumina were obtained by exposing 1.0 g of alumina to 30 cm^3 of a 6,000 mmol/m^3 solution of SDS, which was determined to be below the cmc. The admicelles were prepared as described above. The reaction mixture was equilibrated at room temperature and at regular time intervals, an aliquot of the supernatant was obtained and the final concentration of surfactant was determined. The amount of SDS adsorbed onto the alumina particles was calculated where

$$[\mathrm{SDS}]_{\mathrm{adsorbed}} = [\mathrm{SDS}]_{\mathrm{initial}} - [\mathrm{SDS}]_{\mathrm{final}} \qquad (1)$$

The adsorption was obtained by plotting $[\mathrm{SDS}]_{\mathrm{adsorbed}}$ versus time. In the case where the adsorption of SDS was obtained in the presence of monomer, the desired amount of S was added using a micro syringe.

Determination of styrene adsolubilized into the admicelle

The amount of S adsolubilized into the admicelle was determined as the difference between the initial and final monomer concentration. Experiments were carried out by exposing 1.0 g of alumina to 30 cm^3 of a 6,000 mmol/m^3 SDS solution in a 50-cm^3 round bottom flask. An amount of styrene was injected to give a concentration of 4,370 mmol/m^3. After equilibration was complete, the final concentration of S in the supernatant was determined by HPLC, and the amount adsorbed calculated.

Admicellar polymerization

Polymerization of styrene on alumina was carried out by contacting an aliquot of a 6,000 mmol/m^3 SDS: 500 mol/m^3 ethanol solution (with a measured pH 5.2–5.4), and the addition of monomer(s) to the alumina powder in a desired alumina to SDS to monomer weight ratio and AIBN initiator at 0.2% of total monomer. The reaction mixture was left to equilibrate at room temperature for 24 h while stirring. After equilibration, the reaction was heated to 60–70 °C for times ranging between 60 min and 240 min in a temperature controlled oil bath to initiate polymerization. After polymerization, the reaction was immediately quenched by immersing the flasks in an ice bath. After quenching the supernatant was removed by filtration and the alumina washed with a 500 mol/m^3 ethanol solution to remove any residual monomer and surfactant. The alumina powder was collected, air dried and placed in a vacuum oven at 60 °C for 4 h to remove any excess water and monomer.

Determination of polymer film formation

PS was removed from the surface of alumina by extraction with THF. This was achieved by transferring the coated alumina particles in a screw capped vial with THF and stirring the suspension over several days, to ensure good solvent–alumina contact. The THF extract was then analyzed by UV–visible spectroscopy (Agilent 8453 UV–visible spectrophotometer), using THF as the reference solution. Whenever there was visual evidence that the contact solution exhibited suspended alumina particles, the extracted solution was centrifuged (Eppendorf 5702 centrifuge, 4.4 rpm, 18 min). The presence of PS was ascertained by comparison to a PS standard, of MW 2,630 g/mol, obtained from Tosho Corporation, MANATO-KU Tokyo, Japan.

Hydrophobicity testing

The hydrophobicity of the coated alumina was determined by adapting a literature procedure used by Pongprayoon et al. [20]. A drop of water was placed on the alumina surface using a standard laboratory glass pipette dropper with an internal diameter of 1 mm. The time taken for the water droplet to disappear was determined. Each drop test was performed in triplicate and variance was found to be within ±10 min. The alumina was judged hydrophobic when the time taken for the droplet to disappear was greater than 30 min.

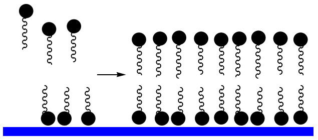
Characterization of the coated alumina powders

Thermogravimetry (TGA) was performed on the particles using a Perkin-Elmer TGA7. Scanning electron microscopy (SEM) was employed for surface visualization using a Philips Model XL30 scanning electron microscope. Specimens for SEM, were mounted and gold splutter coated according to standard procedures using a Dynavac Mini Coater prior to the imaging.

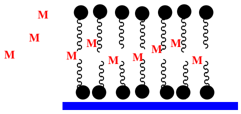
Results and discussion

The governing principle behind admicellar polymerization is the tendency of surfactant molecules to self-assemble into ordered structures in aqueous solutions onto a solid surface. More specifically, this technique exploits their ability to form bilayers or admicelles at a solid-aqueous interface. It is within this hydrophobic region of the admicelle that monomers such as S and DVB are adsolubilized, and in the presence of an initiator polymerized as illustrated in Fig. 1.

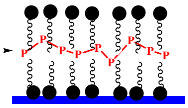
An inherent feature of admicellar polymerization that is encountered and noted by many researchers in this field; is the small amounts of polymer that are actually formed [18]. As a result, difficulty arises when trying to characterize the polymer formed. It is evident in the existing literature that the optimum reaction conditions for any given system can vary significantly often causing uncertainty as to how to achieve a good surface coverage. In any case the coverage of polymer is expected to be influenced, in part by the surface coverage of the admicelle on the substrate hence the optimization of reaction conditions, such as surfactant and monomer concentrations, temperature, addition of additives, equilibration and polymerization times all need to be considered [24]. Therefore the first part of this work was to determine appropriate conditions for admicelle formation on the alumina particle surface and the polymerization conditions suitable for this system.



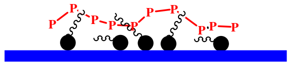
Stage 1. Adsorption of surfactant onto solid substrate, formation of admicelles.



Stage 2. Adsolubilization of monomer into the admicelles.



Stage 3. Polymerization of monomer.



Stage 4. Surfactant removal.

Fig. 1 A schematic illustration of the admicellar polymerization process

Determination of optimum reaction conditions for adsorption of SDS onto alumina

Determination of cmc of SDS

In typical admicellar polymerization, it is important that the bulk surfactant concentration is maintained below the critical micelle concentration. This is to ensure that micelles do not form in order to avoid further complications such as emulsion polymerization [18,19,24]. Therefore it is important to investigate the factors that influence the cmc, in order to determine an appropriate initial feed concentration of surfactant.

Conductivity measurements yielded a cmc of between 8,100 mmol/m^3 and 7,600 mmol/m^3 (average 7,850 mmol/m^3) for SDS at 20–21 °C in the absence of any additives. The pH of these solutions was not adjusted and was between 5.2 and 5.3. This cmc value compares favorably to that obtained by Wu et al. [19] of 8,400 mmol/m^3 for similar conditions. In the presence of an organic solvent such as ethanol, at a concentration of 500 mol/m^3 that is typical for these systems, the cmc of SDS decreased to 6,500 mmol/m^3, but remained within the same order of magnitude. It is not fully understood how ethanol acts to lower the cmc

[25] but its addition is important as it partly solubilizes the S and DVB in the aqueous reaction medium.

A typical additive to admicellar polymerizations is salt, typically sodium chloride; however there is some confusion in the literature as to whether it is required. The rationale for the addition of salt was described by Skahalkar and Hirt [24], who postulated that it acts to stabilize the bilayer structure. It does this by reducing the repulsive electrostatic forces between the charged polar head groups of the admicellar surfactant molecules through counterion binding. In an earlier patent filed by Harwell et al. [26], the addition of salt was deemed unnecessary. The addition of salt to our system resulted in a substantially lower cmc, and even at low salt concentrations of 10 mol/m^3 and 30 mol/m^3, the cmc is reduced to 5,000 mmol/m^3 and 3,500 mmol/m^3, respectively. This trend is consistent with previously reported data [27]. At salt concentrations above 30 mol/m^3, the ionic strength of the solution was too high to measure the cmc with any certainty using our method.

The pH of the solution, as expected was found to influence the cmc of SDS solutions. A slight decrease in cmc from 7,850 mmol/m^3 to 7,500 mmol/m^3 was observed for pH from 5.2 to 4.1. Accurate measurement of cmc at low pH became increasingly difficult using our method. As the inherent pH of the resulting SDS solution was 5.2–5.3, which is below the point of zero charge of alumina [21], it was decided that pH would not be adjusted further for subsequent experiments.

The SDS adsorption onto alumina

The adsorption of SDS onto the surface of alumina under varying conditions was investigated. It is apparent from the literature that the time required for the adsorption equilibria to be reached is unclear and can vary quite significantly from system to system, with literature reports of equilibration times of up to 4 days [15, 19, 24, 26, 28]. In the current system, the adsorption of SDS in the presence of 500 mol/m^3 ethanol was shown to be essentially complete after 20 h as shown by Fig. 2. The majority of the adsorption occurs within the first 5 h, approximately 90 μmol/g of alumina, and then it continues to increase at a much slower rate up to approximately 20 h where it diminishes to a constant value of between 110 μmol/g and 120 μmol/g.

In the absence of ethanol (Fig. 3), the observation was similar, with the majority of adsorption occurring within the first 5–10 h, but in contrast to the previous trend, the maximum adsorption appeared to be reached after 10 h. The overall amount of SDS adsorbed under the current conditions was not significantly altered, remaining at 110–120 μmol/g. These results were somewhat unexpected, since much of the existing literature using similar conditions simply assumes the equilibria to be reached after 4 days [24].

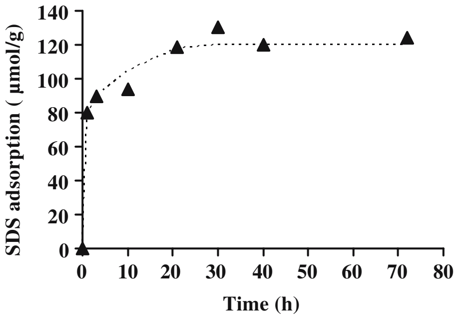


Fig. 2 Adsorption of SDS onto alumina over time ([SDS]$_{\text{initial}}$ = 6,000 mmol/m^3; [ethanol] = 500 mol/m^3; temperature = 18–20 °C)

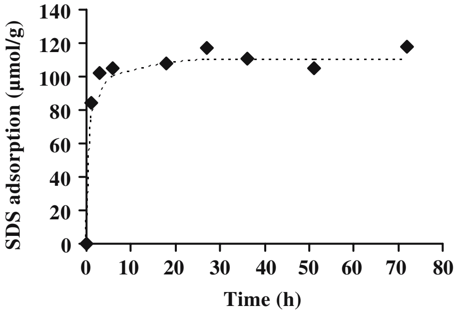


Fig. 3 Adsorption of SDS onto alumina over time ([SDS]$_{\text{initial}}$ = 6,000 mmol/m^3; [ethanol] = 0.0 mol/m^3; temperature = 18–20 °C)

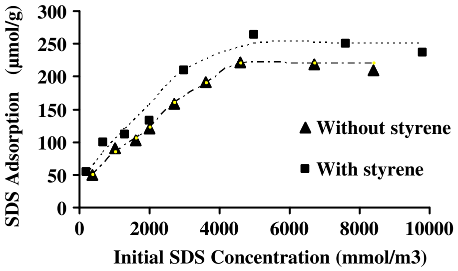


Fig. 4 SDS adsorption in the presence of styrene ([SDS]$_{\text{initial}}$ = 6,000 mmol/m^3; [styrene]$_{\text{initial}}$ = 4,370 mmol/m^3; [ethanol] = 500 mol/m^3; temperature = 21–22 °C)

In the presence of monomer, the adsorption of SDS was enhanced when the initial SDS concentration is above 3,000 mmol/m^3 as illustrated in Fig. 4, whilst the amount of S and alumina in the system are fixed at 4,370 mmol/m^3 and 1 g, respectively. When S is present, the maximum adsorption reached was around 250 μmol/g.

Interestingly, the adsolubilization of styrene into the surfactant layer approached a constant ratio of 2.5–2.9:1 of SDS to S, respectively. This final SDS to S ratio was achieved irrespective of the initial starting SDS to S ratios (Table 1). Similar trends were also observed both when the amount of alumina in the system was altered and the initial ratios were maintained, or when both the amount of alumina and the initial ratios were altered. The observed trend is consistent with results reported by Wu et al. [19] and is supportive of the hypothetical 'sandwich,' or bilayer structure.

In order to ensure that we were not observing any homo polymerization in the supernatant layer during the polymerization process and that the polymer recovered was from the surface of the alumina, an initial monomer concentration of 4,370 mmol/m^3 was used in the subsequent polymerizations. This condition was chosen, as it was found that after equilibration (24 h), there was no detectible S in the supernatant by HPLC. Therefore, under the chosen conditions the assumption was made that the majority of monomer initially present in the system migrated to the surface of the alumina. It was established that there was no significant loss of monomer through the suba seals used to seal the reaction flasks.

As a consequence of the above study, and the requirement that ethanol be present to partially solubilize S and DVB, an initial surfactant solution of 6,000 mmol/m^3 was chosen and kept constant for all future experiments. Salt was omitted and pH not adjusted.

Admicellar polymerization of styrene onto alumina

In order to establish the conditions appropriate for polymer formation, S was initially used as it was anticipated that the linear PS, being relatively nonpolar, would be able to be extracted for analysis. The polymerization was initiated using AIBN at 60–70 °C. The admicellar treated particles were collected and the surface polymer was extracted with THF. Spectroscopic evidence that polymerization had been achieved was provided by comparing the UV absorbance of the THF extractant to a solution of a PS standard as shown in Fig. 5. The spectrum of the THF extract as compared with a PS standard (0.1 mg/cm^3) is similar showing a maximum absorbance at 260 nm. This demonstrates that polymerization has indeed occurred. Direct observation of PS on the surface of the alumina particles using attenuated total reflectance (ATR) and diffuse reflectance infrared Fourier transform (DRIFT) techniques were inconclusive, which may be due to the sensitivity of the method.

Table 1 Adsorption of SDS and adsolubilization of S monomer onto alumina

Al_2O_3 (g)	Initial SDS/S ratio	μmol SDS adsorbed/Al_2O_3 (g)	μmol S adsorbed/Al_2O_3 (g)	Adsorbed SDS/S ratio
0.13	10.3/1	3015	1025	2.9/1
0.25	5.2/1	1392	556	2.5/1
0.25	10.3/1	672	276	2.4/1

In all cases the initial feed consisted of 30 cm^3: $[SDS]_{initial}$ = 6,000 mmol/m^3; and [ethanol] = 500 mol/m^3; temperature = 20–21 °C

It was noted that extraction of the polymer was difficult, and only small amounts could be obtained. It was also noted that even after the extraction process the treated alumina still possessed a distinct hydrophobic character, resistant to wetting by water in drop test, indicating that not all of the polymer was removed. In addition to THF, other solvents including chloroform, dichloromethane and cyclohexane were also tried, in addition to hot extraction methods. Therefore it was not clear how much of the polymer was actually removed. A possible explanation for the difficulty in recovering the polymer coating is that it may be either grafted onto the substrate or physically entangled. Attempts to dissolve the alumina particles were inconclusive.

Very little comment had been made in the literature about the difficulty of achieving full extraction. It has been discussed by O'Haver et al. [18] as one of the reasons why little is known about the admicellar process, since true characterization of the polymer formed is made difficult. It was also suggested that this becomes particularly important for porous substrates, such as alumina. This has important implications when a cross-linked polymer film is formed and DVB is added to the system.

The treated alumina particles became significantly more hydrophobic as shown by their resistance to wetting by water. In the case of untreated alumina the water droplet disappeared immediately, whereas for

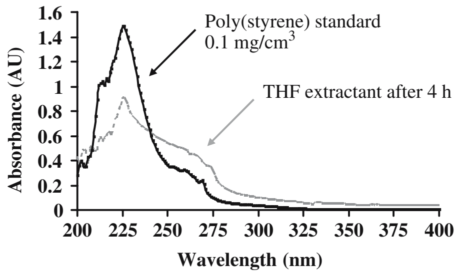


Fig. 5 UV spectrum of THF extractant and PS standard

the PS treated alumina it formed a near spherical droplet that stayed on the surface for longer than 30 min. Alumina treated with SDS only resisted wetting for up to 20 min (±10 min). These results clearly demonstrate that the fundamental nature of the surface of the alumina particles was altered, becoming more hydrophobic, which is consistent with the presence of a PS coating. It was also found that the SDS:S ratio affected the water droplet disappearance time (Table 2). The trend observed was that at a given polymerization time, an increase in the amount of S in the system corresponded to an increase in wetting resistance. Even when 10% of the S is replaced with DVB the time taken for the water droplet to disappear also increased.

Polymerization time

The general trend observed was that with longer polymerization times, the droplet disappearance time also increased (Fig. 6). The water droplet disappearance time, increased up to a polymerization time of about 4 h, where it began to approach a value of 90 min.

Admicellar polymerization of S and DVB onto alumina particles

Polymerization of S and DVB on alumina was carried out using the conditions established earlier. The initial feed concentration of SDS and ethanol were maintained at 6,000 mmol/m^3 and 500 mol/m^3, respectively. AIBN was also used as the initiator at a weight fraction of 0.2% of monomer and polymerization time was set to 4 h at 60–70 °C. The total monomer concentration was maintained at 4,370 mmol/m^3, and increasing amounts of S were substituted for DVB on a molar basis, therefore taking into account the difference of molecular weight of each monomer. The amount of DVB used ranged from 10% to 100% replacement. Under these conditions, no S or DVB was detectable using HPLC after the 24 h equilibration period, therefore limiting the formation of homopolymer in the supernatant during the polymerization process.

Table 2 Water droplet disappearance times

SDS/S ratio	Water droplet disappearance time (min)
1/0.9	35 ± 10 min
1/2	60 ± 10 min
1/0.9[a]	70 ± 10 min

In all cases the initial feed consisted of 30 cm^3: [SDS]$_{\text{initial}}$ = 6,000 mmol/m^3; and [ethanol] = 500 mol/m^3; alumina = 1 g; AIBN = 0.2 mol%; polymerization time 3 h at 60–70 °C

[a] 10% replacement of S with DVB

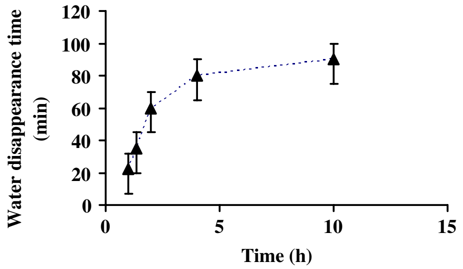


Fig. 6 Graph of water droplet disappearance time of treated alumina at different polymerization times ([SDS]$_{\text{initial}}$ = 6,000 mmol/m^3; [ethanol] = 500 mol/m^3; [S]$_{\text{initial}}$ = 4,370 mmol/m^3; AIBN = 0.2 mol%; polymerized at 60–70 °C)

Characterization of PS-co-DVB cross-linked film

As noted earlier, the extraction of PS was difficult, and with the addition of DVB to the system in amount ranging from 10% to 40% no polymer was extracted as detected by UV–visible spectroscopy. This observation was expected, as it would be anticipated that the cross-linked PS-*co*-DVB polymer formed would be even more tightly bound to the particle surface and thus impossible to be extracted.

SEM was used to visualize the surface of the alumina particles, and clearly shows that the alumina surface was modified as a result of treatment (Fig. 7). Comparison of the SEM micrographs of untreated alumina (a), with that of 10% DVB (b), and alumina coated with PS only (c), shows that there is a significant difference in topography. However using this technique it was not possible to distinguish between the different coatings; that is when alumina is coated with SDS only (d), PS coated alumina (c) and PS-*co*-DVB coated alumina (b). In contrast, the hydrophobicity nature of alumina coated with 10% DVB polymer increased to 70 min from 20 min as compared with when only SDS was present.

As it was not possible to extract any polymer from the alumina surface when DVB was added to the system and SEM did not show significant differences between PS and PS-*co*-DVB coated particles, TGA was used and provided strong evidence for the formation of PS-*co*-DVB coatings. Figure 8 shows TGA curves for four materials—pure SDS (a), pure PS (b), 40% replacement of S with DVB (c) and 100% DVB coated alumina (d). Pure SDS shows a distinctive decomposition temperature of 235 °C and PS decomposes at approximately

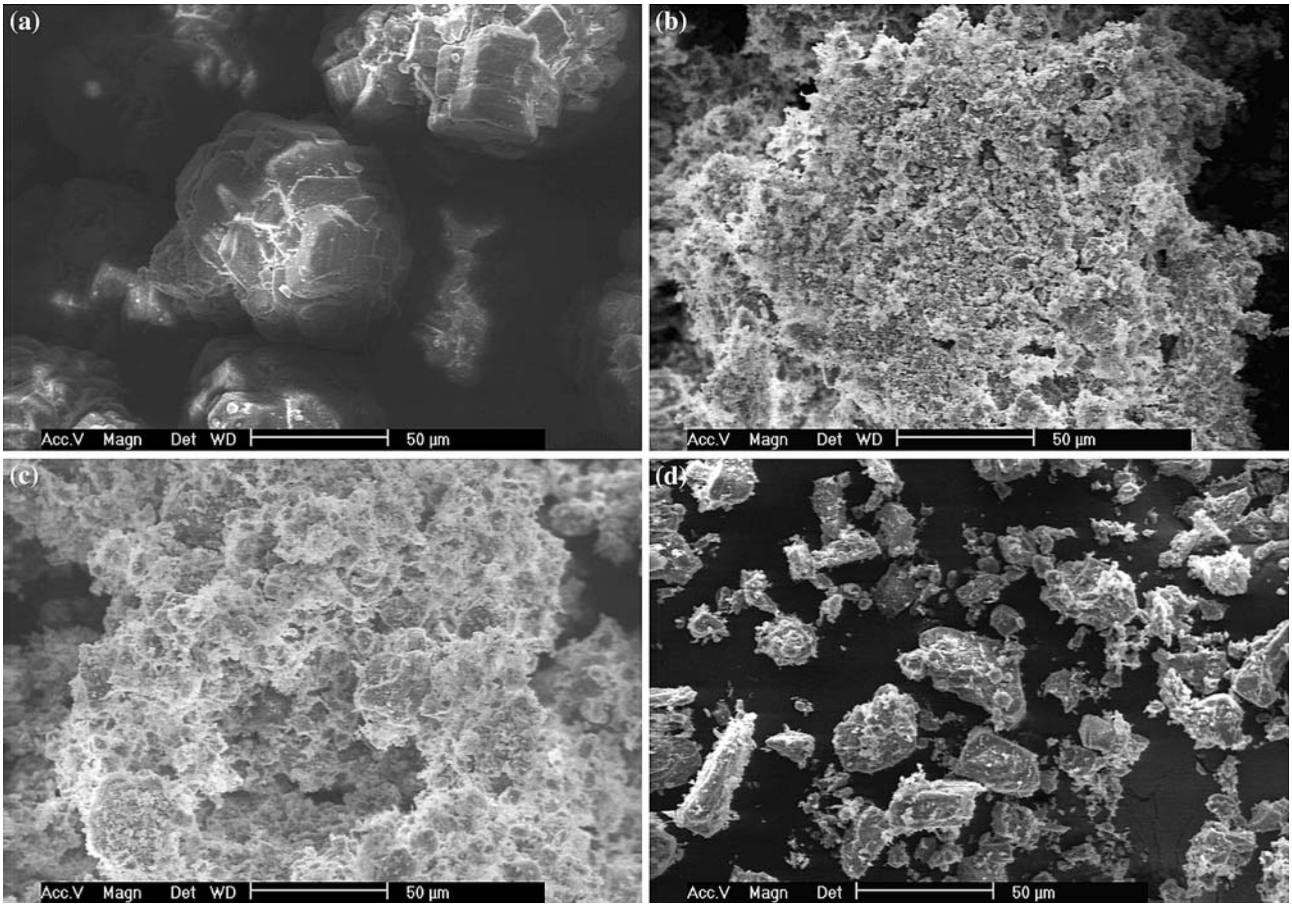


Fig. 7 SEM micrographs of (magnification 1,000×): (a) untreated alumina, (b) admicellar treatment alumina with 10% replacement of S with DVB, (c) polystyrene coated alumina, and (d) SDS treated alumina. The scale bar on micrographs is equal to 50 µm

450 °C. The TGA curves of 40% and 100% replacement of S with DVB, both show a mass loss at approximately 250 °C, which has been attributed to the presence of residual SDS. One explanation for the slight shift to higher temperature may be due to entanglement of the residual SDS that becomes entrapped with the surface polymer. Figure 8(c) consisting of 40% DVB, gives two distinctive decomposition temperatures at 460–560 °C and 610 °C and are both attributed to the PS-*co*-DVB cross-linked polymer. The lower derivative peak is mainly due to the linear PS component and the higher peak due to the cross-linked network. In the case where there is 100% DVB, only the peak at 600 °C was observed resulting from the decomposition of the network. The peak at about 700 °C is due to combustion of carbon residue when the purge gas was changed from nitrogen to air.

It was clear from the TGA study that cross-linked PS-*co*-DVB was formed on the surface of the alumina particles. They gave two decomposition temperatures, one was due to the linear component of the polymer at about 500 °C and the other at around 600 °C is due to the decomposition of the cross-linked component of the network.

Conclusion

This study has shown that admicellar polymerization of styrene and divinylbenzene to form a cross-linked polymer coating on alumina particles can be achieved. Optimization of reaction conditions resulted in equilibration times of between 20 h and 24 h and reaction times of at least 4 h. Evidence for formation of a polymer coating on the surface was demonstrated from the fundamental change in the surface character, with a greater water repellence, resisting wetting by water for up to 90 min, as compared with untreated alumina that showed no resistance time. Admicellar treated alumina was analyzed using TGA and SEM, which provided further evidence of a coated polymer layer. TGA showed decomposition temperatures at 460–560 °C and

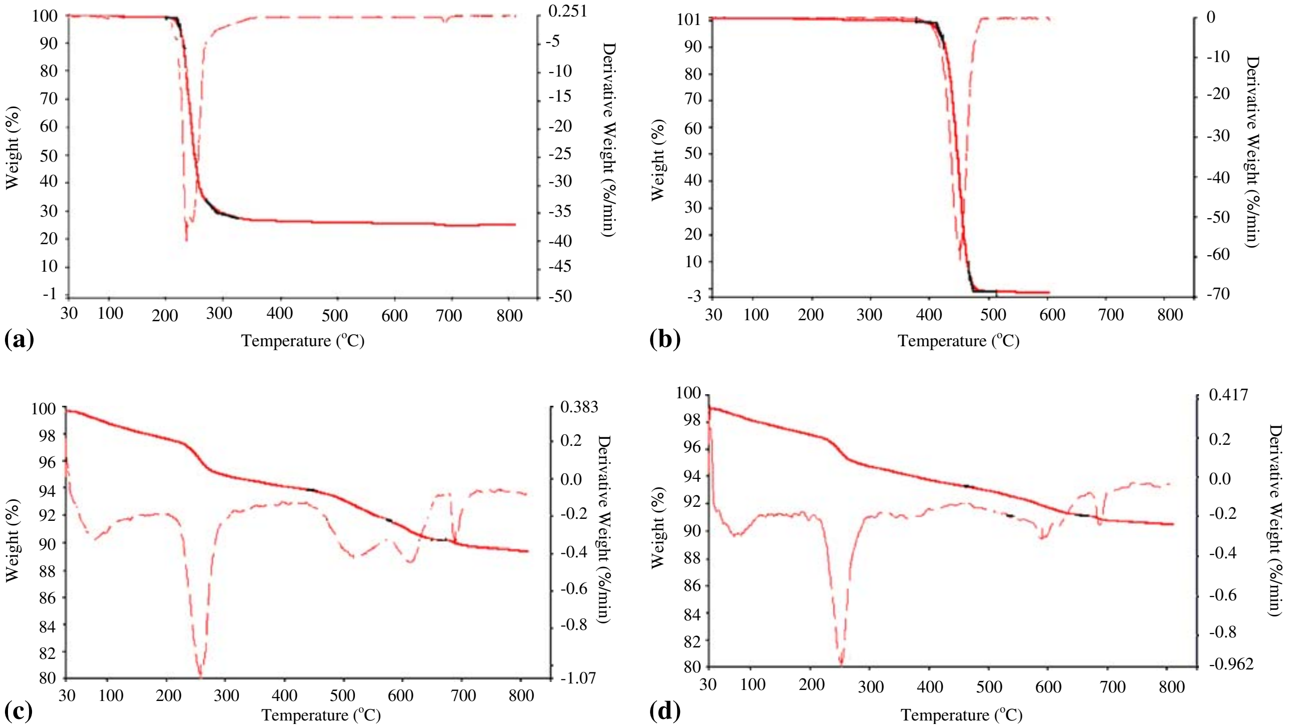


Fig. 8 TGA curves of: (a) SDS Standard, (b) PS standard, (c) 40% replacement of S with DVB, and (d) 100% DVB

610 °C which were characteristic of a PS-*co*-DVB polymer coating. In the case where only the monomer S was used, partial extraction of PS using THF was achieved; but with the addition of DVB no polymer was extractable from the surface.

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