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Physicochemical Surface Modification and Characterisation of Coal Fly Ash for Application in Rubber Composites

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Abstract: This study evaluated the capability of coal fly ash (untreated and physicochemically modified) when utilised as a filler in cis-1,4-polyisoprene rubber. Physicochemical modification of the ash was achieved using two techniques: (1) ammonium sulphate roasting followed by controlled aqueous dissolution and (2) sulphuric acid leaching. In addition, the effectiveness of a silane-coupling agent (Si-69) in enhancing the compatibility of untreated and physically modified ash samples with natural rubber was investigated. The ammonium sulphate roasting route increased the surface area and roughness and decreased the particle–particle agglomeration of the fly ash sample. Sulphuric acid treatment decreased the particle–particle agglomeration. However, no increase in surface roughness was observed. The untreated fly ash samples were not significantly reinforcing, and the properties they imparted were inferior to the least reinforcing carbon black. Silane treatment resulted in improved dispersion and wetting of the fly ash in the rubber matrix, leading to improved reinforcement compared to neat rubber. In situ addition of the silane during preparation of the vulcanisates led to composites with better mechanical properties than the composites containing silane-pre-treated fly ash. Composites filled with ammonium sulphate-roasted-and-leached ash performed better than the composites filled with untreated ash and sulfuric acid-leached ash. These findings suggest that modified fly ash holds promise as an effective filler for rubber materials, offering potential environmental and economic benefits by repurposing coal combustion by-products.

Keywords: coal fly ash; rubber; vulcanisates; roasting; ammonium sulphate; acid leaching

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1. Introduction

Coal fly ash (CFA) is the solid incombustible residue generated in large quantities during the direct combustion of pulverised coal in thermoelectric power stations [1]. It consists of lighter particles that ascend with flue gases during coal combustion and are captured using electrostatic precipitators or bag filter systems. Once collected, CFA is generally disposed of and managed in large ash dumps or slurry dams. CFA can pose significant environmental challenges [2]. Improperly stored ash in landfills or ponds can leach harmful substances into groundwater, posing risks to ecosystems and human health. Additionally, when airborne, the fine particulate matter contributes to air pollution, causing respiratory issues and other health problems. When South Africa's power stations were established several decades ago, abundant inexpensive land near coal mines allowed for low-cost CFA disposal with minimal public pressure to address environmental and aesthetic

impacts due to their remote locations. However, many power stations are now running out of storage space, necessitating additional ash storage facilities, which impose a long-term economic burden. South Africa generates about 35 million tons (Mt) of CFA per annum, of which only 7% is reused, primarily in the construction industry [3]. However, there is a growing body of research being conducted worldwide to develop new applications for CFA. Examples of promising applications include its use as precursors in the synthesis of mesoporous silica nanoparticles [4,5], CO_2 adsorbents such as zeolites and hydrotalcite [6], and geopolymers [7] and its use in mine water treatment [8] and as a soil ameliorant [9].

The incorporation of particulate fillers, particularly carbon black and silica, is a fundamental process in the rubber industry. This technique is so crucial that over 99% of rubber products utilise fillers, making it a central focus of research and innovation in rubber science and technology [10]. The development and optimisation of fillers have therefore become one of the most extensively studied aspects of the field. A specialised niche application for CFA is its use as an alternative reinforcement filler for rubber-based products [11,12] because of its low cost, excellent void-filling properties, and elevated thermal stability. However, its fine particle size, low specific surface area (SSA), and very smooth and inert surface [13], as well as wide variation in surface chemical composition between individual particles [14], are not conducive to good rubber–filler interaction, and negatively impact the mechanical properties of rubber composites. To address these challenges, modification of the surface of CFA particles with coupling agents has become common practice [15]. For instance, the use of silane-coupling agents [16,17] and tannic acid as a naturally occurring plant polyphenol [18] was shown to improve cure characteristics and mechanical properties. Surface modification of fly ash by corrosive microorganisms through microbial adhesion and catabolism of inorganic molecules was also found to improve the tensile strength of fluororubber compounds [19]. Fly ash modification via geopolymerisation has also been attempted to produce geopolymer fillers that were then added to the formulation of epoxidised natural rubber [20,21]. The surface of CFA has also been treated with NaOH, HCl, and NaOH/HCl solutions before being exposed to coupling agents to enhance the structure, SSA, and surface reactivity of CFA [22]. The authors reported rougher CFA surfaces and higher SSA (146 m^2/g) when treated with NaOH/HCl solutions, although little binding between surface-modified CFA and polyisoprene rubber was observed. Introducing an in situ grafting–neutralisation reaction to the process seemed to enhance surface adhesion between rubber chains and CFA particles, which in turn improved the 300% modulus and tensile strength of the resulting rubber/CFA composites without compromising their elastic properties [23,24].

Recent studies have subjected South African CFA to (1) the ammonium sulphate-roasting process coupled to aqueous leaching [25–27] and (2) direct acid leaching [3] to extract aluminium as a strategic metal. These processes not only recovered the liquid phase containing aluminium but also produced large quantities of residues. In these past studies, the solid residues were not characterised in detail. They are primarily coal fly ash particles that have mostly retained their spherical morphology but whose surfaces became rougher and often displayed deep cavities with distinct shapes. For this reason, they could represent suitable fillers in rubber composites. Their reuse in this application would ensure that aluminium can be extracted from CFA using zero solid waste processes that contribute towards a circular economy.

The primary objective of this paper is to report on the effect of the two aluminium extraction processes on CFA bulk and surface characteristics, silane coupling and rubber mechanical properties. The treatment conditions of the aluminium extraction processes were expected to change the surface and bulk properties of the fly ash particles, which in turn could improve the fly ash–polymer interaction. An outline of the processes is illustrated in Figure 1.

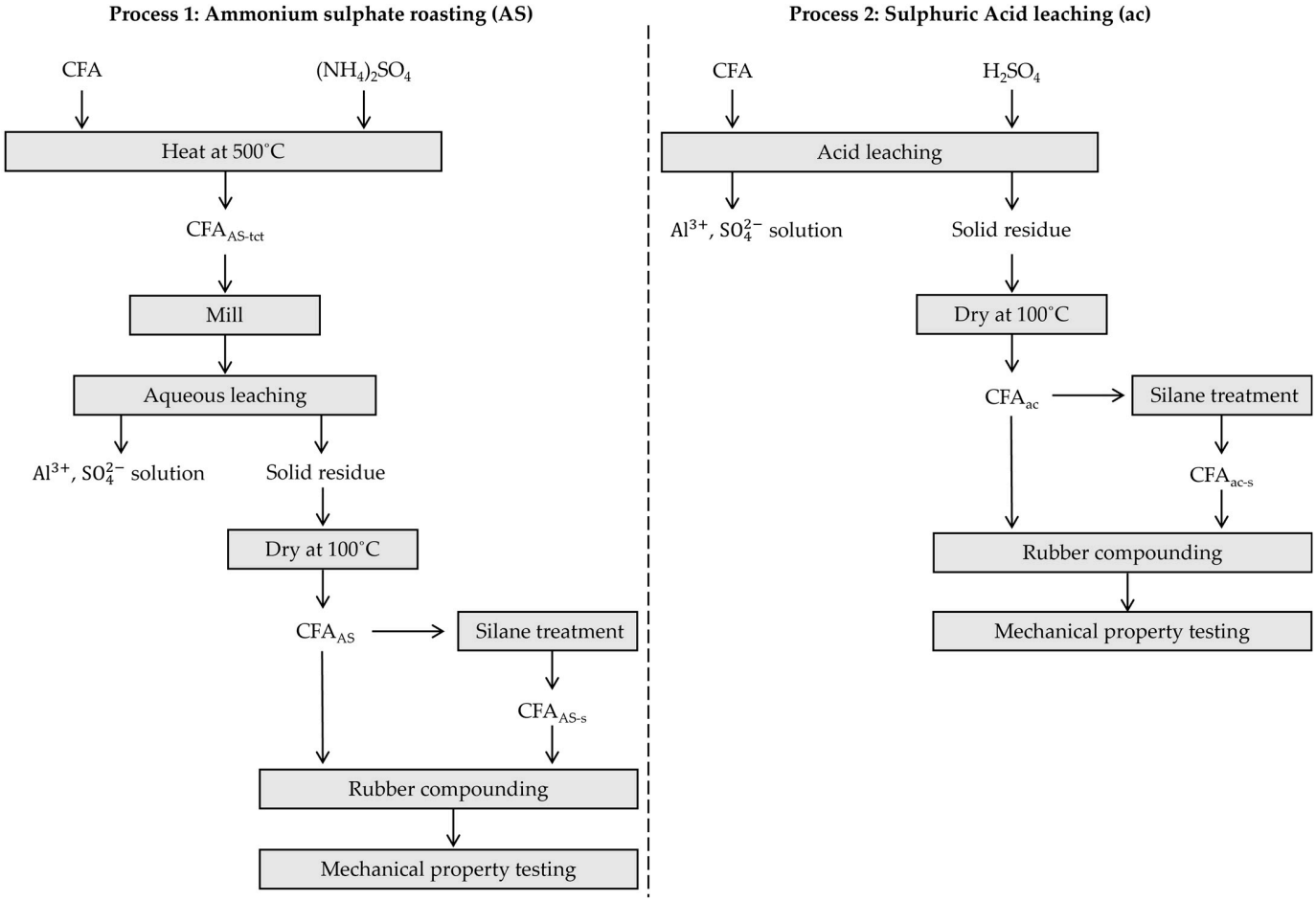

Figure 1. Process flow diagram illustrating Process 1 (ammonium sulphate-roasting treatment and water leaching) and Process 2 (H_2SO_4 leaching), followed by silane treatment.

The combination of carbon black (CB), silica, and CFA as hybrid fillers has been reported in the literature to have a synergetic effect, resulting in better mechanical performance of rubber composites compared to their use as single fillers [12,28]. Rubber composites containing untreated and modified CFA, CB, and CFA-CB hybrids were prepared, and their mechanical properties were studied to assess the viability of CFA as a filler in cis-1,4-polyisoprene rubber composites. Various grades of CB were used as references for comparison.

2. Materials and Methods

2.1. Materials

A representative sample of a classified, ultrafine siliceous CFA sample was obtained from Ash Resources (Pty) Ltd., Edenvale, South Africa. This commercial-grade CFA has a mean particle size between 3.9 and 5.0 μm and a volume distribution of more than 90% of its particles having a diameter < 11 μm. CFA was subjected to two distinct processes to prepare CFA samples with different surface properties: (1) ammonium sulphate-roasting treatment and water leaching or (2) sulphuric acid leaching.

Bis[3-(triethoxysilyl)propyl]tetrasulphide (Si-69) ($S_4[C_3H_6Si(OC_2H_5)_3]_2$; reagent grade, ≥90%), sulphuric acid (H_2SO_4; reagent grade, 95–98%), and polyethylene glycol (PEG 8000) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Ammonium sulphate $(NH_4)_2SO_4$; reagent grade, ≥99%) was supplied by Merck. The rubber compounding ingredients (i.e., stearic acid, zinc oxide, sulphur, bis[3-(triethoxysilyl)propyl]tetrasulphide (Si-69), carbon black (N330, N660, N770 and N990) and N-tert-butyl-2-benzothiazyl sulfenamide

(TBBS) were supplied by S&N Rubber (Pty) Ltd., Gqeberha, South Africa. Synthetic cis-1,4-polyisoprene rubber was supplied by Continental Tyre, Gqeberha. All suppliers were from South Africa. Distilled water was used in all experiments unless specified otherwise.

2.2. Process One: Ammonium Sulphate Roasting Treatment and Water Leaching

CFA and $(NH_4)_2SO_4$ were thoroughly mixed in a 2:3 m/m ratio in a ceramic crucible, heated in a muffle furnace at 500 °C for 24 h, and subsequently cooled to ambient temperature. This procedure was repeated 12 times. The roasted residues were combined and milled using an alumina pot and alumina milling balls in a laboratory ball mill.

A total of 1 kg of the milled roasted sample was subjected to leaching in 10 L of distilled water under continuous stirring at 1000 rpm using an overhead stirrer at ambient temperature for 48 h. The process was monitored by measuring the pH and electrical conductivity of the suspension until a plateau was reached to ensure complete dissolution of the water-soluble sulphate phases formed during the roasting step. After 12 h of settling, the supernatant was syphoned out using a vacuum pump. The final solution was filtered and stored at 4 °C until analysis by ICP-MS to determine the extraction efficiency of aluminium from CFA. The solid residue was washed three times using 1 L of distilled water, then dried in an oven at 80 °C for 24 h, and finally milled in a laboratory ball mill to ensure a homogenised particle size distribution. The milled residue is hereafter denoted CFA_{AS}.

2.3. Process Two: H_2SO_4 Leaching

A suspension of 100 g CFA in 400 mL of 5 M H_2SO_4 was continuously mixed on a reciprocal shaker set at 80 °C and 200 rpm for 9 h. After cooling, the solid residue (CFA_{ac}) was recovered via centrifugation at 3000 rpm for 2 min. CFA_{ac} was washed three times using 250 mL of distilled water, then dried in an oven at 80 °C for 24 h. This procedure was repeated until 4 kg of solid residue was obtained. The combined residue was finally milled in a laboratory ball mill to give CFA_{ac}.

2.4. Preparation of Silane-Treated CFA Residues

Silane grafting treatment was performed on untreated CFA, CFA_{AS}, and CFA_{ac} at ambient temperature. A 2% *v*/*v* Si-69: ethanol solution was made by adding 40 mL Si-69 and 20 mL of distilled water to 2 L of ethanol while stirring with an overhead stirrer at 100 rpm for 15 min. A total of 2 kg of CFA, CFA_{AS}, or CFA_{ac} was suspended in the ethanol solution and stirred for 1 h to achieve uniform distribution of the coupling agent. The slurries were then oven-dried at 120 °C for 12 h to ensure complete dehydration, condensation, and bond formation. The final products were milled in a laboratory ball mill to generate CFA_s, $CFA_{AS\text{-}s}$, and $CFA_{ac\text{-}s}$.

2.5. Characterisation

X-ray fluorescence analysis was used to determine the chemical composition of the fly ash samples. A Thermo Fisher ARL Perform'X Sequential fluorescence spectrometer with OXSAS software Version 2.6 was used. The samples were prepared as pressed powders. Blank and certified reference materials were analysed with each batch of samples.

X-ray diffraction (XRD) was used to determine the mineralogical composition of the samples. A PANalytical X'Pert Pro powder diffractometer with an X'Celerator detector and variable divergence with Fe filtered Co-Kα radiation was used. The phases were identified using X'Pert Highscore plus software Version 4.4a, and 20% Si (Aldrich 99% pure) was added to the samples to determine the amorphous (glass) content. The relative phase amounts were estimated by the Rietveld method (Autoquan Program).

Field emission scanning electron microscopy (FE-SEM) was used to examine the morphology of the untreated and treated fly ash samples. The samples were mounted onto an adhesive, double-sided carbon tape before coating with carbon using an Emitech K550X sputter coater (Ashford, UK). Carbon paint was applied to the edges of the samples to improve conductivity of the samples. The images were viewed under high vacuum

conditions using a Zeiss Ultra SS (Johannesburg, South Africa) Field Emission Scanning Electron Microscope operated at an acceleration voltage of 1 kV.

The particle size distribution (PSD) of the treated and untreated fly ash samples were obtained by laser diffraction using a Malvern Mastersizer 2000 fitted with a Hydro 2000 G dispersion unit (Malvern Instruments Ltd., Worcester, UK.) The samples were dispersed in water at ambient temperature, and the analysis was conducted under the following set of variables: constant obscuration between 10% and 20%, stirring speed of 650 rpm, pump speed of 1650 rpm, and ultrasonic power of 10%. The samples were run in duplicate with three runs per duplicate. The results were logged as particles per volume percent and an average obtained to produce the particle size distribution. The particle sizing analysis was performed to determine the effect of the surface modification treatments on the particle size of CFA.

Contact angle measurements were performed using a Krüss DSA25 Drop Shape Analyser, employing the double sessile drop method with water and di-iodomethane as wetting liquids. A small drop of wetting liquid was deposited on the surface of a CFA powder bed, which was pressed onto a glass slide. A profile image of the drop was captured approximately 1 s after contact with the powder surface. The reported result represents the average of two measurements.

The zeta potential of the fly ash particles was measured using a Malvern Nano ZS Zetasizer Nano particle analyser (Malvern Instrument Ltd., Worcester, UK). In total, 0.1 g of the fly ash particles were hydrolysed in 25 mL ultra-pure water for 30 min before measurement, and the initial pH was measured. Auto-titration was performed to determine the iso-electric points of the samples, during which the pH of the ash suspension was adjusted by HCl (0.25 M) or NaOH (0.10 M) to cover a pH range from 2.5 to 10 in 1.0 pH unit increments. The zeta potential was measured at each pH value in triplicate.

2.6. Preparation and Vulcanisation of Rubber Compounds

The formulations for the prepared compounds are shown in Table 1. The rubber compounds were prepared by a two-stage mixing procedure using a Banbury mixer (330 mL), with two co-rotating tangential rotors and a water-cooled two-roll mill. The optimum curing time (T90) was determined from the vulcanisation isotherms, obtained using a Moving Die Rheometer MDR 3000 Basic (MonTech Africa, Gqeberha, South Africa). Approximately 2 mm thick sheets of vulcanised rubber were obtained by heating unvulcanised rubber between heated plates at 150 °C under pressure.

Table 1. Formulations used for neat, carbon black, and fly ash filled synthetic cis-1,4-polyisoprene rubber (IR) composites.

	Material	**Parts per Hundred Rubber (phr)**
No filler (Neat rubber composite) (Fill factor = 0.75)	Cis-1,4-polyisoprene	100
	ZnO	5
	Stearic acid	2
	Sulphur	1
	TBBS	2
	Polyethylene glycol (PEG)	2
	Total	112
Fly ash filled composites (Fill factor = 0.75)	Cis-1,4-polyisoprene	100
	Fly Ash [1]	25
	ZnO	5
	Stearic acid	2
	Sulphur	1
	TBBS	2
	PEG	2
	Total	137

Table 1. *Cont.*

	Material	Parts per Hundred Rubber (phr)
Carbon black filled composites (Fill factor = 0.75)	Cis-1,4-polyisoprene	100
	Carbon Black [2]	25
	ZnO	5
	Stearic acid	2
	Sulphur	1
	TBBS	2
	PEG	2
	Total	137
Fly ash and carbon black filled composites (Fill factor = 0.75)	Cis-1,4-polyisoprene	100
	Fly Ash [1]	12.5
	Carbon Black [2]	12.5
	ZnO	5
	Stearic acid	2
	Sulphur	1
	TBBS	2
	PEG	2
	Total	137
In situ addition of Si-69 to fly ash filled composite (Fill factor = 0.85)	Cis-1,4-polyisoprene	100
	Fly Ash [3]	25
	Si-69	0.8
	ZnO	5
	Stearic acid	2
	Sulphur	1
	TBBS	2
	PEG	2
	Total	137.8

[1] CFA, CFA_{AS}, CFA_{ac}, CFA_s, $CFA_{AS\text{-}s}$ or $CFA_{ac\text{-}s}$. [2] N330, N660, N774 or N990. [3] CFA only.

2.7. Measurement of Mechanical Properties

The neat synthetic cis-1,4-polyisoprene rubber (IR), fly ash- and carbon black filled rubber composites were tested for their mechanical properties.

A Hildebrand Durometer Operating Stand Model OS-2 was used to determine the Shore-A hardness in accordance with the ASTM D2240 standard [29]. The hardness was determined at three different positions and the indicated mean value.

Tensile strength measurements were performed using ASTM D412 [30]. An Instron 3360 tensile test machine with a knurled, self-tightening grip, crosshead speed of 500 mm min^{-1}, and 1 kN load cell was used to determine the tensile properties. The sheets from which the dumbbells were cut were left overnight to condition before being subjected to tensile testing. Since a die C (ASTM D412) dumbbell cutter was not available, a special cutter was used to produce smaller non-standard dumbbell shaped specimens. The sample dimensions were 25 mm by 4 mm instead of 33 mm by 6 mm in die C. The specimens were symmetrically placed in the grips of the testing machine to achieve uniform tension distribution over the cross section.

3. Results and Discussion

3.1. Characterisation of Untreated and Treated CFA

3.1.1. Chemical and Mineralogical Compositions

The chemical and mineralogical compositions of CFA, CFA_{AS}, CFA_{ac}, and the respective silane (Si-69)-treated fly ash samples (CFA_s, $CFA_{AS\text{-}s}$ and $CFA_{ac\text{-}s}$) are shown in Tables 2 and 3, respectively.

Table 2. Chemical compositions of CFA, CFA_{AS}, CFA_{ac}, and the silane treated CFA_s, CFA_{AS-s}, and CFA_{ac-s}.

		Concentration (wt. %) [1]									
		SiO_2	Al_2O_3	CaO	Fe_2O_3	TiO_2	MgO	K_2O	P_2O_5	SO_3	Total
	CFA	52.6	37.1	4.3	2.9	1.8	1.1	0.9	0.7	0.2	102.7
	CFA_{AS}	61.8	20.0	4.6	3.3	2.2	0.8	0.5	0.6	3.1	96.3
	CFA_{ac}	55.3	28.8	4.0	2.0	1.4	0.5	0.9	0.1	4.4	97.1
Silane treated	CFA_s	53.6	33.0	4.2	3.2	1.7	1.2	0.7	0.7	1.5	102.7
	CFA_{AS-s}	63.9	18.8	3.5	2.9	1.9	0.9	0.3	0.8	4.7	96.4
	CFA_{ac-s}	58.4	28.0	3.4	1.9	1.4	0.5	0.6	0.1	4.3	96.8

[1] Other elements present in small amounts (<0.1%): ZrO_2, MnO, V_2O_5, Cr_2O_3, NiO, Na_2O, CuO.

Table 3. Mineralogical compositions of CFA, CFA_{AS-tct}, CFA_{AS}, CFA_{ac}, and silane treated CFA_s, CFA_{AS-s}, and CFA_{ac-s}.

Mineral Phase (wt. %)		CFA	CFA_{AS-tct}	CFA_{AS}	CFA_{ac}	CFA_s	CFA_{AS-s}	CFA_{ac-s}
Amorphous		69.1	39.5	86.6	57.1	67.1	87.5	58.4
Mullite	$Al_6Si_2O_{13}$	29.1	1.6	3.5	29.6	25.3	3.6	28.4
Quartz	SiO_2	5.8	3.8	6.9	7.0	7.0	6.3	6.8
Gypsum	$CaSO_4.2H_2O$	-	-	3.0	-	-	2.7	-
Anhydrite	$CaSO_4$	-	3.8	-	6.4	-	-	6.2
Hematite	Fe_2O_3	0.7	-	-	-	0.7	-	-
Alunogen	$Al_2(SO_4)_3.17H_2O$	-	16.0	-	-	-	-	-
Godovikovite	$NH_4Al(SO_4)_2$	-	9.8	-	-	-	-	-
Millosevichite	$Al_2(SO_4)_3$	-	25.6	-	-	-	-	-

The major constituents of CFA were SiO_2 (52.6%), Al_2O_3 (37.1%), CaO (4.3%), Fe_2O_3 (2.9%), MgO (1.4%), and TiO_2 (1.6%). ZrO_2, MnO, V_2O_5, Cr_2O_3, NiO, Na_2O, and CuO were <0.1%. The combined Al_2O_3 and SiO_2 content was more than 85%, and the average SiO_2/Al_2O_3 ratio was 1.4. A low lime ash containing more than 70% Al_2O_3 + SiO_2 + Fe_2O_3 is classified as siliceous (ASTM International, 2012). The total alkaline earth metals (CaO + MgO) content was about 6%, while the total alkaline (Na_2O + K_2O) concentration was less than 1%. These findings are consistent with results obtained from a similar study [13].

Upon application of processes 1 and 2, the Al_2O_3 content decreased from 33.8% wt. % in CFA to 20.0 wt. % in CFA_{AS} to 28.8 wt. % in CFA_{ac}. This agreed with aluminium extraction efficiencies of 39.0% and 17.9% during processes 1 and 2, respectively. No change in the Al_2O_3 content was observed in CFA_{AS-s} and CFA_{ac-s} following silane treatment. The change in CaO content after silane treatment was also negligible in all three samples. Sulphur analysis showed that the SO_3 content increased from 0.2 wt. % in CFA to 3.1 wt. % in CFA_{AS} and 4.4 wt. % in CFA_{ac}. No change in SO_3 content was observed in the silane-treated samples or in the content of the oxides of other elements (e.g., Fe, Ti, K and P) in all the samples.

CFA consisted of an amorphous aluminosilicate glass phase (69.1 wt. %) and two crystalline phases: mullite (29.1 wt. %) and quartz (5.8 wt. %). These results are consistent with data obtained by van der Merwe et al. [14] for a similar CFA sample. CFA_{AS} contained a higher amorphous content (86.6 wt. %) and significantly less mullite (3.5 wt. %). The data on CFA_{AS-tct} showed that the ammonium sulphate-roasting process induced the formation of several metal sulphate minerals (anhydrite, alunogen, godovikovite, and millosevichite), which dissolved during leaching, except for anhydrite, which hydrated to form gypsum (CFA_{AS}). The amorphous content of CFA_{ac} was lower (57.1 wt. %), probably due to the formation of anhydrite (6.4 wt. %). Silanisation had no effect on the mineralogical composition of the samples.

3.1.2. Physical Properties

The lognormal particle size distribution of this sample was bimodal with peaks at ca. 1 µm and 5–6 µm, respectively (Figure 2). The mean particle size (D50) was 5.2 µm, with 90% of the volume distribution of the sample having particle sizes smaller than 16.0 µm. The data obtained for the particle size distribution of the CFA sample were consistent with the results obtained for a similar sample by van der Merwe et al. [14]. Processes 1 and 2 did not affect the D50 value substantially (Table 4) or the particle size distribution, which indicated little effect of these two treatments on particle size. In contrast, the effectiveness of the silane grafting treatment was indicated, to some extent, by the ability of the silane-treated ash particles to disperse in water. For instance, particles of the CFA_s sample floated on the water's surface and were not dispersed by the pumping action during particle size analysis, indicating that the surface of CFA particles became hydrophobic. This meant that PSD of CFA_s particles could not be measured using laser diffraction. On the other hand, CFA samples that had been subjected to processes 1 or 2 prior to silane grafting (i.e., $CFA_{AS\text{-}s}$ and $CFA_{ac\text{-}s}$) could be analysed, indicating that the two samples contained particles that had not been coated, at least fully, by the silane-coupling agent and therefore had hydrophilic properties that allowed them to disperse in water.

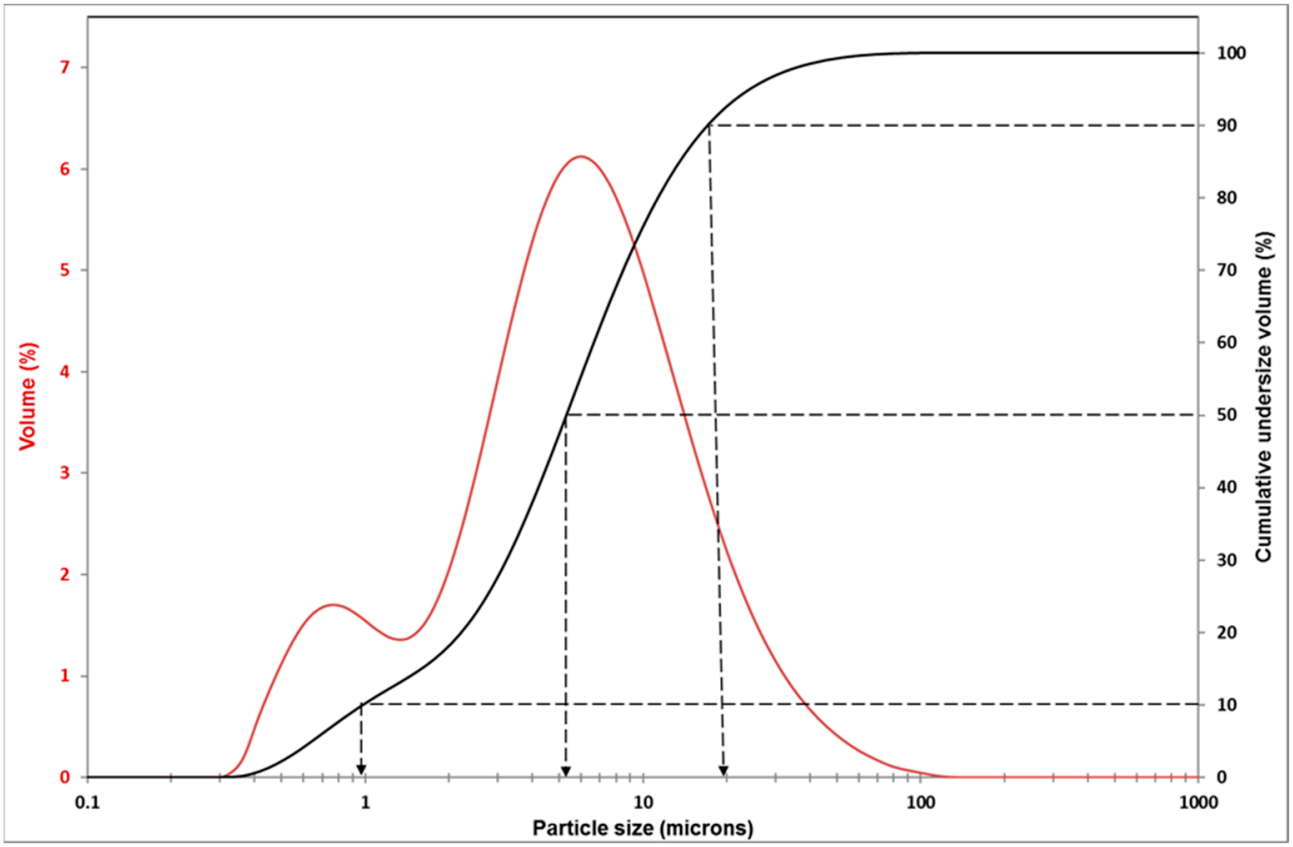

Figure 2. Particle size distribution of untreated coal fly ash (CFA).

Table 4. Particle size distribution (D50) and BET surface area of CFA, $CFA_{AS\text{-}tct}$, CFA_{AS}, CFA_{ac}, CFA_s, $CFA_{AS\text{-}s}$, and $CFA_{ac\text{-}s}$.

Sample	CFA	CFA_{AS}	CFA_{ac}	CFA_s	$CFA_{AS\text{-}s}$	$CFA_{ac\text{-}s}$
D50 (µm)	5.2	6.5	5.4	-	6.2	5.8
Surface Area (m^2/g)	0.99	7.97	11.02	0.62	9.37	10.26

The BET specific surface area (SSA) was a better indicator of the usefulness of processes 1 and 2 in altering the surface of CFA (Table 4). The SSA of CFA was low (0.99 m^2/g). There was a substantial increase in the SSA after the treatment of CFA through processes 1 (7.97 m^2/g; CFA_{AS}) and 2 (11.02 m^2/g; CFA_{ac}). Silanisation had little, if any, effect on the SSA.

The contact angles of CFA and CFA_s were measured using water and diodomethane as wetting liquids (Figure 3). The contact angle of diodomethane on the surface of CFA ranged between 39° and 46°, indicating high wettability of the CFA sample. The contact angle of pure water on CFA could not be determined because the drop was absorbed too quickly. For CFA_s, the contact angles of diodomethane and water were 147° and 145°, respectively. The increased contact angle of CFA_s indicates low wettability and high hydrophobicity of the silane-treated CFA sample. Contact angle images for $CFA_{AS\text{-}s}$ and $CFA_{ac\text{-}s}$ could not be obtained because the water and diodomethane drops were absorbed too quickly by these samples. The contact angle results were essential in demonstrating the success of silane grafting treatment and coupling of Si-69 on the CFA surface but not on that of $CFA_{AS\text{-}s}$ and $CFA_{ac\text{-}s}$.

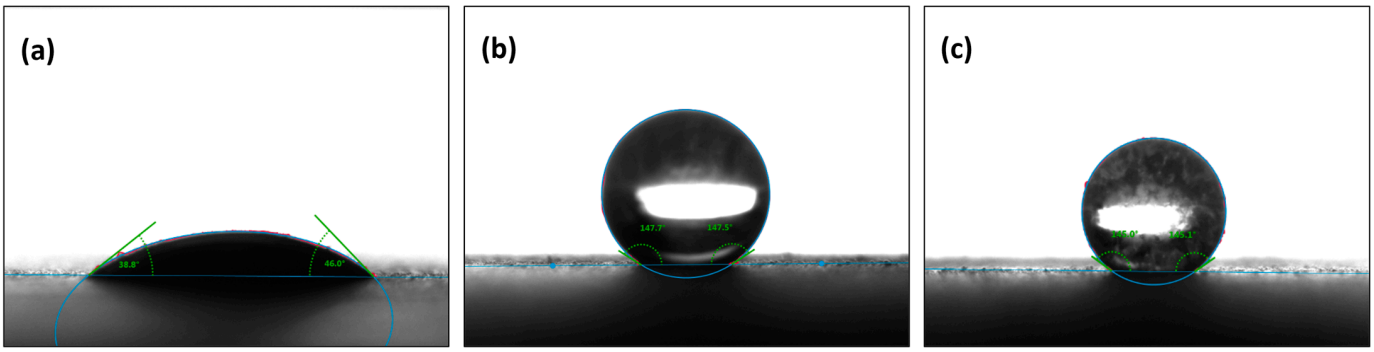

Figure 3. Sessile drops of (**a**) diodomethane on CFA, (**b**) diodomethane on CFA_s, and (**c**) pure water on CFA_s to illustrate integrity of silane coating on CFA.

FE-SEM was used to compare the morphology and surface characteristics of ash particles before and after treatment (Figure 4). The particle shape and distribution of CFA was spherical or "ball-bearing", with some of the particles seen to be tightly attached to each other, forming agglomerates of varying sizes (Figure 4a). Their relatively smooth surface was clearly visible at higher magnification (Figure 4b). CFA particles retained their spherical shape upon treatment. However, surface roughness increased following ammonium sulphate roasting coupled to leaching, as shown by the numerous particles featuring square and/or rectangular cavities formed from the formation, growth, and subsequent dissolution of $Al_2(SO_4)_3$ crystals at the surface of CFA (Figure 4c,d), as observed previously [27]. This explains the increase in SSA observed in the BET analysis. This increased surface roughness makes the fly ash surface more accommodating to adhesion with polymer chains and is important in the development of adhesive forces between the fly ash filler and the rubber matrix [31]. Figure 4e,f show that the surface roughness of the fly ash particles did not change after acid treatment, meaning the increase in the SSA recorded by BET may have been due to an increase in porosity in the fly ash particles. Figure 4c,e showed the presence of elongated crystals, possibly anhydrite, identified by XRD; however, they occurred in very small numbers and were unlikely to have contributed substantially to the SSA.

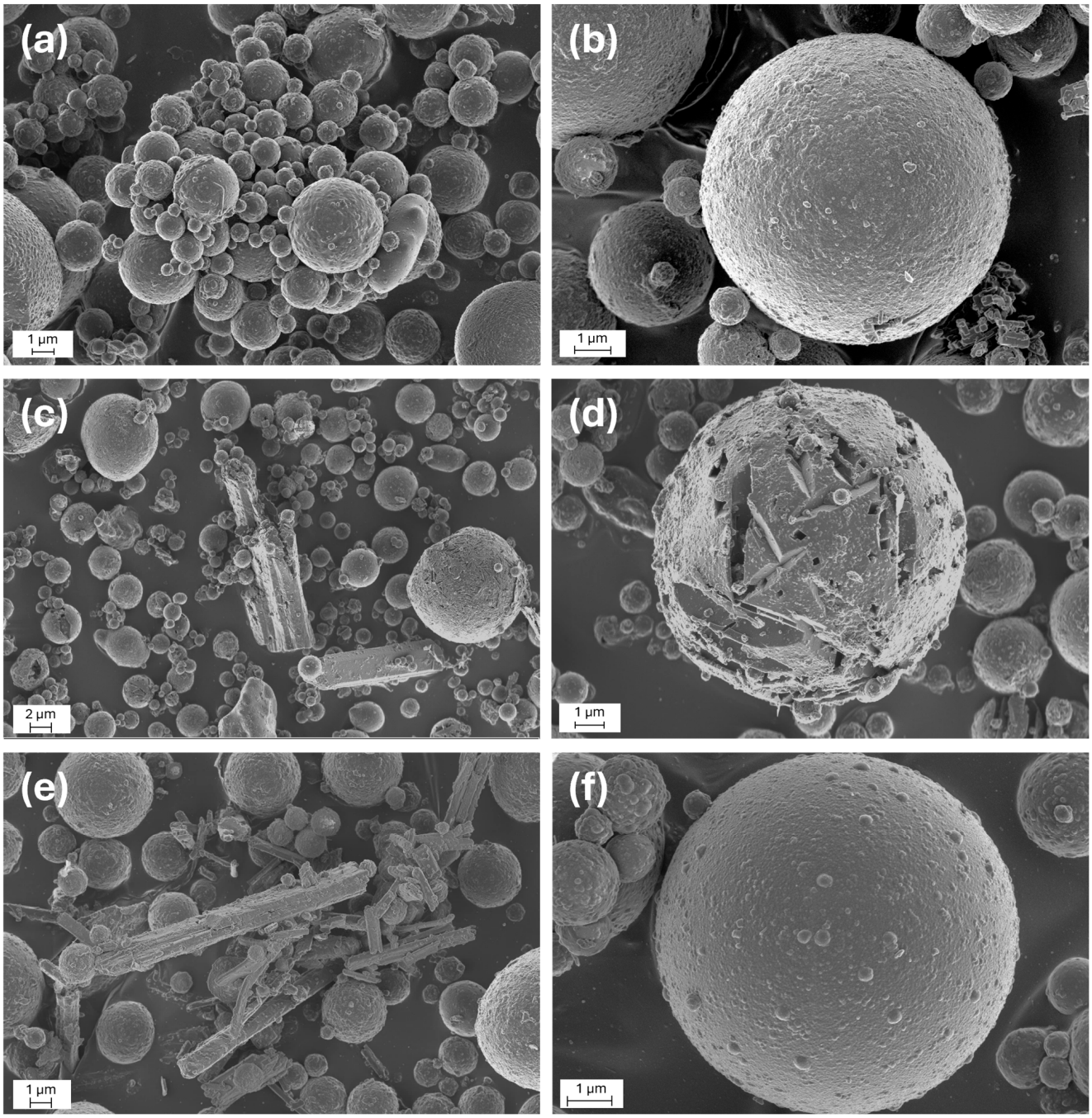

Figure 4. FE-SEM images of untreated CFA (**a**,**b**), CFA_{AS} (**c**,**d**) and CFA_{ac} (**e**,**f**).

Results from the zeta potential experiments are shown in Table 5. The aqueous suspension of untreated CFA was alkaline (pH 8.78). In contrast, suspensions containing CFA_{AS} or CFA_{ac} were acidic (4.00–4.27) (Table 5). This change in pH was probably caused by the SO_3 content of treated CFA (3.1–4.4 wt. %), which was not present in untreated CFA (0.2 wt. %) (Table 2). The zeta potential at the initial pH was −27.6 mV for CFA, +16.3 mV for CFA_{AS}, and −0.5 mV for CFA_{ac}. The pH at the isoelectric point was 3.72 for CFA, between 7.75 and 8.4 for CFA_{AS}, and 4.27 for CFA_{ac}.

Table 5. Initial pH, zeta potential, and isoelectric points of aqueous suspensions of CFA, CFA_{AS}, and CFA_{ac}.

Sample	CFA	CFA_{AS}	CFA_{ac}
Initial pH	8.78	4.00	4.27
Zeta potential at initial pH (mV)	−27.6	+16.3	−0.5
pH at isoelectric point	3.72	7.75–8.4	4.27

3.2. Cure Characteristics and Mechanical Properties of Rubber Composites

The CB-filled vulcanisates (Table 6) exhibited the shortest cure time (T90), ranging between 3.8 and 6.5 min, likely due to the higher SSA of CB, which enhances the interaction of the filler with curatives and rubber. In contrast, the vulcanisates filled with hybrid CFA-CB fillers showed a notable increase in cure time, although no consistent trend was observed. Complete replacement of CB with CFA resulted in even longer cure times, indicating that the filler retarded the curing process. This behaviour, compared to CB, can be attributed to the lower SSA, larger average particle size, and reduced interaction between CFA and rubber, as noted in previous studies [12,18]. CFA_{AS} and CFA_{ac} demonstrated improved cure characteristics relative to CFA, likely due to the increased SSA after treatment (Table 4). However, the cure characteristics of CFA_{ac}-filled vulcanisates remained inferior to those of neat rubber, while CFA_{AS} had no significant impact, neither improving nor worsening the cure characteristics of the rubber. There was no indication that silanisation had any influence on the cure characteristics of the vulcanisates.

Table 6. Cure characteristics and mechanical properties of neat, carbon black-, and fly ash-filled cis-1,4-polyisoprene rubber vulcanisates.

	Sample	Cure Rate (dNm)	T90 (min)	$M_{300\%}$ (MPa)	$M_{600\%}$ (MPa)	UTS (MPa)	Hardness (Shore-A)
	Neat	7.0	9.5	1.2	4.7	19.0	35.7
CB	**N660**	10.7	5.9	3.2	22.1	25.5	43.3
	N774	9.7	5.2	3.0	20.4	30.4	44.0
	N990	8.4	6.5	2.2	12.4	28.5	41.7
CFA	**CFA**	8.0	11.2	1.5	6.1	18.5	38.7
	CFA-N330	9.6	7.0	2.6	17.0 *	19.9	42.7
	CFA-N660	9.2	6.6	2.2	14.4 *	24.9	43.0
	CFA-N774	9.7	7.1	2.1	14.0 *	22.2	41.3
	CFA-N990	8.9	12.1	1.8	10.5	24.9	39.7
	CFA_s	9.0	11.2	1.8	9.3	22.5	40.7
	CFA-Si69 in situ	9.8	13.4	2.0	11.2	16.3	
CFA_{AS}	**CFA_{AS}**	8.3	9.4	1.7	8.2	19.6	40.7
	CFA_{AS}-N330	9.9	9.1	2.7	19.5 *	22.1	43.0
	CFA_{AS}-N660	10.2	8.7	2.7	19.4 *	27.6	43.7
	CFA_{AS}-N774	10.7	9.3	2.5	18.2 *	29.3	42.3
	CFA_{AS}-N990	8.5	8.5	1.8	10.2	24.8	41.3
	CFA_{AS-s}	7.7	11.7	1.6	7.5	18.1	39.3
	CFA_{AS}-Si69 in situ	9.9	11.5	1.9	9.5	14.9	
CFA_{ac}	**CFA_{ac}**	8.3	10.6	1.4	6.4	21.7	39.1
	CFA_{ac}-N330	10.1	8.4	2.5	17.0 *	25.5	42.7
	CFA_{ac}-N660	9.0	9.3	2.4	16.3 *	27.5	42.0
	CFA_{ac}-N774	9.2	9.5	2.3	16.1 *	25.8	41.3
	CFA_{ac}-N990	9.5	10.7	1.8	10.8	21.5	40.7
	CFA_{ac-s}	8.2	11.4	1.8	9.0	23.1	40.0
	CFA_{ac}-Si69 in situ	9.4	13.2	2.0	11.5	12.2	

* The asterisks indicate samples with a modulus at 600% elongation that matched or were better than the lowest reinforcing carbon black (N990).

As expected, neat rubber exhibited the lowest M600% value (4.7 MPa), while vulcanisates containing 25 phr N660 CB exhibited the highest M600% (22.1 MPa), followed by N770- and N990-filled vulcanisates (20.4 MPa and 12.4 MPa, respectively). Similar observations were made for M300%. This can be explained by the differences in the surface area of the carbon blacks. N660 and N770 CB's have SSA values of 35 m^2/g and 30 m^2/g, respectively, and are described as medium reinforcement and modulus fillers. N990 has a low SSA (9 m^2/g) and exhibits low reinforcement and low modulus in vulcanisates [32].

It was observed that the hybrid CFA-CB filler samples had lower moduli than their respective CB-filled samples; therefore, they were less reinforcing. However, the vulcanisates containing the CFA-CB hybrid fillers were stiffer than the neat sample. This suggests that none of the fly ash samples tested improved the mechanical properties of CB-filled composites. The observation may be ascribed to the fundamental properties of CFA that are associated with the interaction between filler and rubber, such as surface reactivity, shape, particle size, degree of dispersion, and structure [33]. Easy slippage of the polymer matrix over the smooth surface of the spherical fly ash particles reduces the mechanical strength of the composites [34]. Despite the decrease in moduli, the order of increasing tensile moduli amongst the CFA-CB composites remained the same, with CFA-N330 hybrid vulcanisate exhibiting the highest M600% (17.0 MPa), followed by CFA-N660 (14.4 MPa), CFA-N774 (14.0 MPa), and, lastly, CFA-N990 (10.5 MPa). Comparable results were obtained for M300%.

When the CFA loading was increased to 25 phr with no CB added, the M600% of the rubber vulcanisates decreased, as previously observed by Sombatsompop et al. [35], Kanking et al. [36], and Ismail et al. [37]. Kanking, et al. [36] explained the results using SEM micrographs, which revealed poor dispersion of bagasse fibre ash in the rubber matrix due to particle aggregation. According to Ismail et al. [37], the decrease in strength may be a result of agglomeration of ash particles due to hydrophilic particle–particle interactions. These undispersed agglomerates serve as failure-initiating flaws and result in poor mechanical properties. Sombatsompop et al. [35] observed that the interaction between fly ash and the rubber matrix was poor, noted by voids present between the rubber phase and the fly ash particles. The untreated CFA filled vulcanisate had the lowest M600% (6.1 MPa) amongst the CFA samples. The M600% amongst the CFA-filled vulcanisates increased in the order CFA < CFA_s < CFA-Si69 in situ. These three samples showed an improvement in reinforcement when compared to the neat rubber (4.7 MPa). However, this was still lower than the least reinforcing carbon black (N990). Silane treatment resulted in improved dispersion and wetting of CFA in the rubber matrix, and therefore, the increase in M600% was anticipated [36]. According to Thongsang et al. [16] and Ansarifar et al. [38], the reaction of Si-69 ethoxy groups and silanol groups on the surface of fly ash reduces the number of silanol groups, thus weakening the filler–filler interactions and preventing formation of aggregates. These changes help improve the mechanical properties of the vulcanisates. Following silane treatment, the M600% of the CFA_s-filled sample increased, with the in situ CFA-Si69-filled vulcanisates exhibiting a higher modulus (11.2 MPa) than the pre-treated CFA_s vulcanisates (9.3 MPa). The tensile moduli were, however, still less than that of the N990-filled vulcanisate.

CFA_{AS}-filled vulcanisates exhibited improved M600%. The order of increasing M600% amongst these vulcanisates was $CFA_{AS\text{-}s}$ < CFA_{AS} < CFA_{AS}-Si69 in situ. Unlike with the CFA-filled samples, the silane-treated $CFA_{AS\text{-}s}$ resulted in the vulcanisate with lowest M600% amongst the CFA_{AS} samples. Silane grafting onto CFA_{AS} was unsuccessful, as evident in the contact angle measurements, and this, therefore, explains why $CFA_{AS\text{-}s}$ did not show an improved M600%. Hybrid fillers of CFA_{AS} and CB yielded the same trend as that of CFA samples, CFA_{AS}-N990 < CFA_{AS}-N774 < CFA_{AS}-N660 < CFA_{AS}-N330. All the M600% values for CFA_{AS} samples were higher than for the corresponding CFA samples. This is attributed to the higher surface area of the CFA_{AS} sample (7.97 m^2/g) compared to the CFA sample (0.99 m^2/g).

CFA_{ac}-filled samples exhibited similar trends and M600% values as the CFA-filled samples with the 25 phr samples increasing in the order CFA_{ac} < $CFA_{ac\text{-}s}$ < CFA_{ac}-Si69 in situ and the hybrid filler vulcanisates having the order CFA_{ac}-N990 < CFA_{ac}-N774 < CFA_{ac}-N660 < CFA_{ac}-N330. The CFA_{ac} sample had the highest surface area (11.02 m^2/g) and was expected to exhibit the highest M600%; however, the sample exhibited inferior properties in the compounds. The CFA_{ac} vulcanisates did not cure evenly. Some parts of the pressed rubber were observed to be under-cured. This could be explained by the acidity of the CFA_{ac} sample, which might have been responsible for retarding the curing of the rubber. Acidic components are traditionally applied as retarders in curing systems and interfere with the activity of basic accelerators, causing a delay in the vulcanisation reaction. Acids slow down the curing rate, retard the scorch time, and reduce the ultimate state of cure [39].

The trends observed for hardness corresponded with that of the M600% for similar reasons. However, the ultimate tensile strength (UTS) of the hybrid CB-CFA-filled vulcanisates showed unexpected results. CFA-N990 vulcanisates exhibited better UTS, followed by FA-N660, FA-N774, and FA-N330, respectively. Investigation of filler dispersion in these compounds may be necessary to explain this observation. It may also simply be due to cis-1,4-polyisoprene strain crystallising, in which case this region is where the cis-1,4-polyisoprene may have taken over, and the observation may just be noise.

4. Conclusions

This study evaluated the properties of untreated and chemically treated CFA and their performance as fillers in cis-1,4-polyisoprene rubber composites. Untreated CFA was characterised by an amorphous aluminosilicate phase, low surface area, agglomeration, and alkaline pH. Chemical treatments significantly altered the physicochemical properties of CFA:

1. Ammonium sulphate treatment (CFA_{AS}) increased surface area and roughness, reduced agglomeration, and enriched silicon content while producing an acidic pH and positive zeta potential.
2. Sulphuric acid treatment (CFA_{ac}) reduced agglomeration, slightly increased specific surface area due to porosity, and enriched the quartz phase but did not alter morphology or size distribution.
3. Silane treatment enhanced mechanical properties only when applied to untreated CFA.

CFA, CFA_{AS}, and CFA_{ac} were evaluated as fillers in cis-1,4-polyisoprene rubber composites, alongside carbon black as a reference filler. Incorporation of fly ash in cis-1,4-polyisoprene vulcanisates resulted in marginal improvement in the cure and mechanical properties compared to neat rubber. However, the fly ash samples were weakly reinforcing, and the properties they imparted were inferior to the least-reinforcing carbon black. Silane treatment enhanced mechanical performance, with CFA_{AS}-filled vulcanisates outperforming CFA- and CFA_{ac}-filled counterparts. Using CFA-CB blends confirmed literature reports that hybrid fillers, combining CB, silica, and CFA, have a synergistic effect, resulting in better mechanical performance than single fillers. These hybrid fillers may be well-suited for non-tyre rubber applications.

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