Investigation into the Adsorption of a Commercial Coupling Agent for Polymers onto Pretreated Fly Ash Filler Particles

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ABSTRACT: Fly ash can be used as a filler in polymer composite materials. Two fly ash samples (one from the UK, UKFA, and another one from South Africa, SAFA) were washed with water and HCl and compared to investigate their interaction with a commercial coupling agent employed to enhance their incorporation into the polymer matrix. The removal of certain ions from the filler surface resulted in a decrease in the heat of adsorption values due to the reduced number of linkage points for the coupling agent. The coupling agent-filler interaction was possible for some of the metals of the second group (calcium, magnesium, and sodium) and some of the "p" group (aluminum, sulfur, and phosphorous) on the surface of fly ash. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3985–3992, 2013

INTRODUCTION

Fly ash is a residue that consists of fine spherical particles that are formed as a result of the combustion of coal in power stations. During coal combustion CO_2 (gas) and fly ash (solid waste) are produced.[1] CO_2 is responsible for many environmental problems (e.g., global warming), but not much information has been reported about fly ash's consequences.

The boom in the production of fly ash occurred after the industrial revolution in the second half of the 18th century, when there was a huge increase in the use of coal, especially in the United Kingdom. Years later, and due to its low cost, availability and ease of transport, our dependence on this material (coal) was so high that the 60% of global electricity was produced in coal-fired power stations, resulting in great amounts of fly ash residue.[1] One of the most serious hazards associated with fly ash are leachable heavy metals and toxic metals (Pb, Cd, Zn, and Cu). Apart from being environmentally unfriendly, several epidemiological studies have associated the exposure to these metals with lung cancer, heart disease, or asthma.[2,3]

Since landfill is increasingly becoming a less attractive choice for disposal of waste due to increasing amounts of tax imposed,[4] one of the options is using it as filler in polymeric systems.[5,6] Among other applications, fly ash can be used as a replacement of clay in bricks,[7] in road pavements,[8] or in waste management.[9]

Fillers can affect the stability, crystallinity, and other properties of many polymers and polyolefin blends. To ensure a good polymer-filler adhesion and to obtain a usable composite material, the use of additives (i.e., coupling agents) is normally required. Silanes/organosilane type coupling agents have been demonstrated to behave effectively in polymeric materials, but their high cost and their general unsuitability for use with calcium carbonate filler have led to the exploration of alternative coupling compounds for interfacial modifiers. Liauw et al.[10] studied the development of a novel reactive unsaturated interfacial modifier named OUCA (Oligomeric Unsaturated Carboxylic Acid) and compared it with 1,3-phenylene dimaleimide (1,3-PDM). While 1,3-PDM gave a pink-brown color to the composites, OUCA countered those disadvantages by giving similar mechanical properties at a lower price and with arguably less toxicity than 1,3-PDM. Iraola et al.[11] also examined the application of different fillers for surface treatments of fly ash at 50% wt levels in polypropylene based composites in order to find the most suitable coupling agent for the system. Lubrizol Solplus® C800 coupling agent was found to give the best strength-toughness balance.

While adsorption of metal ions and organic compounds onto fly ash in water treatment applications have been reported widely,[12–20] no evidence could be found in the literature of a similar type of study involving the adsorption of a coupling

agent onto fly ash, particularly not for enhancing its application as a filler material in polymer composites. In the present study the adsorption of a coupling agent, abbreviated as C800, on to UK and South Africa sourced fly ash particles, will be investigated after different pretreatments of the fly ashes, such as water and HCl washing. Contrary to the typical adsorption studies in aqueous solution, flow micro-calorimetry (FMC), mass loss measurements, and infrared spectroscopy measurements will be employed in this investigation. The purpose of this work is to better understand the interaction between C800 coupling agent and the fly ash surface in order to identify the most suitable filler treatment for future composite making.

EXPERIMENTAL SECTION

Materials

Two different types of fly ash were used for the study.

- Mintron 7 fly ash, supplied by Rocktron Limited, Bristol, UK (coded UKFA, with an average particle diameter of 3.1 μm and an aqueous slurry pH of 9.3).
- Superfine SuperPozz (ultrafine fly ash), supplied by Ash Resources, South Africa (coded SAFA, with an average particle diameter of 3.2 μm and an aqueous slurry pH of 10.4).

The N_2 BET surface areas however, are significantly different, i.e., 1.9 and 5.1 $m^2 g^{-1}$ for SAFA and UKFA, respectively. This indicates that UKFA probably has a porous surface. One can therefore expect a difference in their adsorption capacity and behavior. The smallest particles showed some aggregation.

Lubrizol Solplus® C800 coupling agent was used in this investigation. Its structure is shown in Figure 1 (please note that because the structure is proprietary, only a schematic structure, showing the key parts of the molecule, is provided).

Solplus® C800 is an unsaturated carboxylic acid liquid type coupling agent manufactured by Lubrizol Advanced Materials, UK. It was supported 50% wt on silica to give a more easily manageable powder. This form is named Solplus® C825 and its effectiveness lies in the formation of a carboxylate linkage with
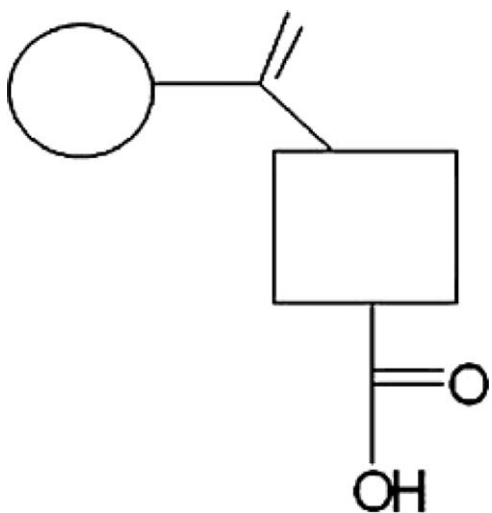
Figure 1. Schematic molecular structure of Solplus® C800 coupling agent.

basic filler surfaces together with its active double bond, which can interact with matrix macro-radicals.

Removal of Ions from the Surface of Fly Ash Particles

Fly ash (300.0 g) was added to deionized water (1.0 L) or HCl (2.0M, 0.5 L) depending on the ion removal treatment. The suspension/slurry was stirred for 30 min using a magnetic stirrer. The fly ash was then isolated using Buchner filtration. The filter cake was washed with deionized water (5 × 0.2 L) before drying in an oven at 110°C for 3 h. The fly ash filter cake was micronized twice using a Waring blender fitted with a stainless steel chamber.

pH Measurement of an Aqueous Slurry of Fly Ash Particles

Fly ash (15.00 g) was added to deionized water (45.0 mL) and after 30 min of continuous stirring using a magnetic stirrer, the pH of the slurry was measured with a HANNA pH 209 Microprocessor pH meter. The latter was calibrated using two standard calibration buffer solutions of pH 4.0 and 7.0 (obtained from Fisher Scientific).

### Determination of Leachable Metal Content by Inductive Coupled Plasma Spectroscopy (ICP)

ICP spectroscopy was used to determine the presence of different metals (alkaline, transition metals, etc.) in the fly ash samples. Aqueous samples were taken from Buchner filtrated solutions after H_2O or HCl washing of the fly ash. The equipment used was an ICP-AES Spectrophotometer (VISTA AX, Varian) fitted with a CCD (Charged Coupled Device) detector technology. The plasma source was an axially mounted One Piece Quartz glass and the sample Introduction System used was a Glass Nebulizer and Spray chamber.

Adsorption Study of C800 Coupling Agent on to Fly Ash Surface

The adsorption of C800 onto washed and unwashed fly ash types (UKFA and SAFA) was studied at ambient temperature in heptane. The adsorption was verified by DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) using a Thermo-Nicolet NEXUS FTIR spectrometer fitted with a Spectra-Tech DRIFTS cell. Before the analysis, all fly ash samples were diluted to 5% wt with finely ground KBr. The KBr was preground using an agate pestle and mortar. All spectra (from 500 cm^{-1} to 4000 cm^{-1}) were recorded from 164 scans with resolution set to 4 cm^{-1}.

The level of adsorption of C800 onto each fly ash sample was determined by mass-loss on ignition. Fly ash (5 g) was dispersed in heptane (50 mL) and the adsorbant (10% fly ash mass, 0.5 g C800) was added to the mixture. After filtering the solution through a Buchner funnel and washing the remaining unreacted coupling agent with heptane, the C800 content in fly ash was determined as follows:

– Crucibles were heated at 800°C for an hour [to remove any organic residues and to ensure complete dryness. Crucibles were then placed in a dessicator (the dessicant was silica gel)].
– Masses of the crucibles were then determined.
– Samples of fly ash with C800 adsorbant were heated at 80°C overnight (to remove absorbed water).
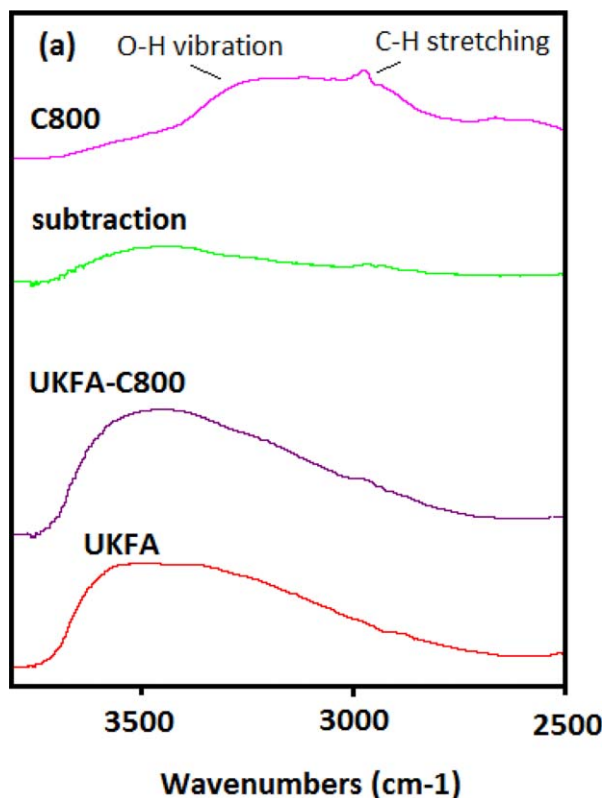
Figure 2. DRIFTS spectra of C800, modified and unmodified unwashed UKFA and subtraction spectra at 3800–2500 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

– Samples were the weighted again.
– The fly ash with C800 adsorbant was heated at 800°C for 3 h (removal of C800 and any structural water from the fly ash).
– A final mass measurement was obtained of the remaining sample.

C800 levels in fly ash were determined by mass difference calculations with a 95% confidence level.

Flow Microcalorimetry (FMC)

FMC is probably the most notable technique associated with the absorption or desorption of a compound onto a solid surface as a change in enthalpy (exotherm in adsorption and endotherm in desorption) occurs during the process. In this type of analysis, the enthalpy change is measured as the adsorbant changes from a first to a second equilibrium (i.e., from pure solvent to a solution of an adsorbate in solvent), defining the initial and final states and, therefore, relating the enthalpy to the appropriate adsorption or desorption process.[21]

The instrument for FMC contains four highly sensitive thermistors placed behind PTFE membranes and their signals are amplified. The sample is charged to the calorimeter cell, where a previous heating treatment under vacuum or equilibration with pure solvent is done. In this case a Microscal flow calorimeter was used with heptane as the solvent. The pure solvent was heptane and its signal at equilibrium was compared with that of a dilute solution of the relevant fly ash in heptane as a second fluid in the system at equilibrium. As each fluid is adsorbed

onto the surface of the sample, the heat of adsorption will cause an increase in temperature, which will be detected by the thermistors and recorded for producing the final graphical representation. The desorption of the probe species will result in a decrease in temperature.

Once the adsorption/desorption process is finished, a calibration stage is normally required to normalize the obtained response, as depicted in Figure 2.

The exothermic character of adsorption can be easily detected. Desorption shows more endothermic behavior. The heat of reaction can be experimentally quantified according to eq. (1).

$$\Delta H_{reaction} = \frac{A_1}{A_2} \times P \times t \qquad (1)$$

where A_1 is the area of the reaction peak, A_2 is the average value of the calibration peak, P refers to the applied power, and t is defined as the calibration time. Depending on the process, the heat of reaction will be positive (desorption) or negative (adsorption).

RESULTS AND DISCUSSION

Effect of Fly Ash Particle Washing

The water or acid washing of fly ash particles will result in the removal of several ions from the filler surface. These ions may vary or appear in different concentrations due to the different geological composition of each fly ash type (see Table I).

More ions were removed as a result of the HCl washing than H$_2$O washing. This fact is directly related to the fact that most ions tend to form stable chloride-compounds, which are soluble in aqueous solutions. Some ions removed in the H$_2$O washing process belong to the first and the second groups of the periodic table (i.e., Ca), although some p elements concentrations have also been detected (S, Si, etc.). These elements appear as an aluminosilicate glass matrix (Si$_x$Al$_y$O$_z$), recrystallized quartz (SiO$_2$), mullite (Al$_{4+2x}$Si$_{2-2x}$O$_{10-x}$), or lime (CaO) in fly ash particles.[1] The mullite and quartz feature surface hydroxyl groups that will, together with the free lime, result in a basic pH. This basicity can facilitate the interaction with several classes of filler surface modifiers (i.e., coupling agents).

Table I. ICP-AES Data for Water and HCl Extracts of the Fly Ash Samples

| | Element concentration (ppm) | | | |
| | Aqueous leaching | | HCl leaching | |
Element	UKFA	SAFA	UKFA	SAFA
Al	–	–	441.1	737.9
Ca	106.3	191.0	302.7	404.0
Fe	–	–	231.2	182.8
P	–	–	143.3	405.4
S	301.9	662.0	106.9	249.4
Si	1.2	2.5	67.5	64.7
≤0.5 ppm				

Table II. pH Values of the Fly Ash Slurries

Sample treatment	pH UKFA	pH SAFA
Unwashed	9.27	10.41
H$_2$O wash	8.94	9.87
HCl wash	4.27	5.06

However, during the HCl washing process a greater quantity of ions was removed, basically *p*-type elements, most of them due to their chloride—compound forming ability.

From Table II it appears that washing the two fly ashes with water slightly decreased the pH of the respective aqueous slurries and washing with 1*M* HCl led to substantial reductions in slurry pH. This effect is probably consistent with removal of calcium oxide and aluminum, which may have existed as aluminosilicate or mullite and free lime. These forms are responsible for promoting basicity on the fly ash surface. HCl would have removed more of the CaO and aluminum compounds than the water, leaving behind silanol groups, which can be slightly acidic.

This change in the basicity of the media will affect the interaction of the filler with the coupling agent as different mechanisms can operate depending on the pH value (see Scheme 1).

FMC Study Adsorption of C800 on to Fly Ash
Table III shows the recorded heats of reaction for the different fly ash samples during the FMC analysis.

Table III. Heats of Reaction for Washed and Unwashed UKFA and SAFA Samples

	ΔHreaction (mJ m^{-2})			
	UKFA		SAFA	
	Adsorption	Desorption	Adsorption	Desorption
Unwashed	−159.8	26.9	−28.7	8.3
H$_2$O washed	−125.3	0.3	−76.0	0.7
HCl washed	−32.6	2.2	−22.3	0.6

It is evident that that there is a significant difference in the C800 adsorption behavior of these fly ash samples. The UKFA fly ash adsorption is much more energetic than that of the SAFA. This is probably due to the larger surface area of UKFA as compared to SAFA, which can be described to a more porous surface of the UKFA particles. Treatment of the fly ash with water and hydrochloric acid also brought some changes in the adsorption behavior. Treatment with water had little effect on the adsorption activity of UKFA but almost tripled the activity of the SAFA. However, treatment with HCl had little effect on the adsorption activity of SAFA but reduced the adsorption activity of UKFA by a factor of almost five. In all cases the heat of desorption is substantially less than the heat of adsorption, indicating that the C800 is strongly retained on the fly ash surfaces.
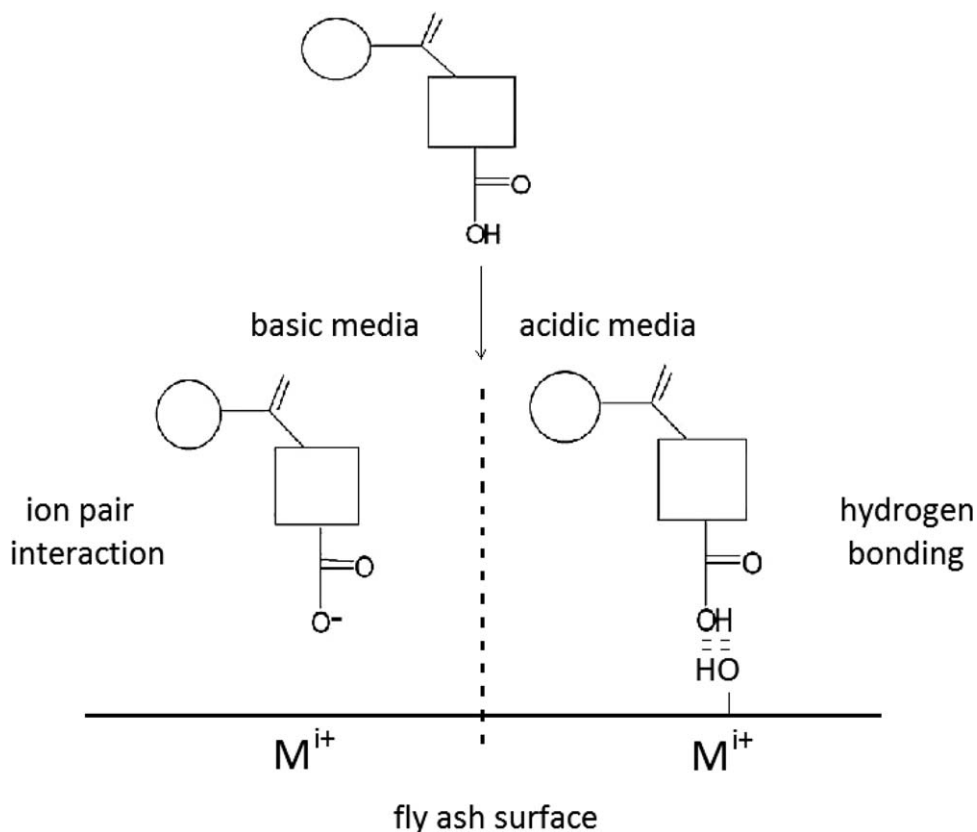
Scheme 1. C800—fly ash reaction diagram.
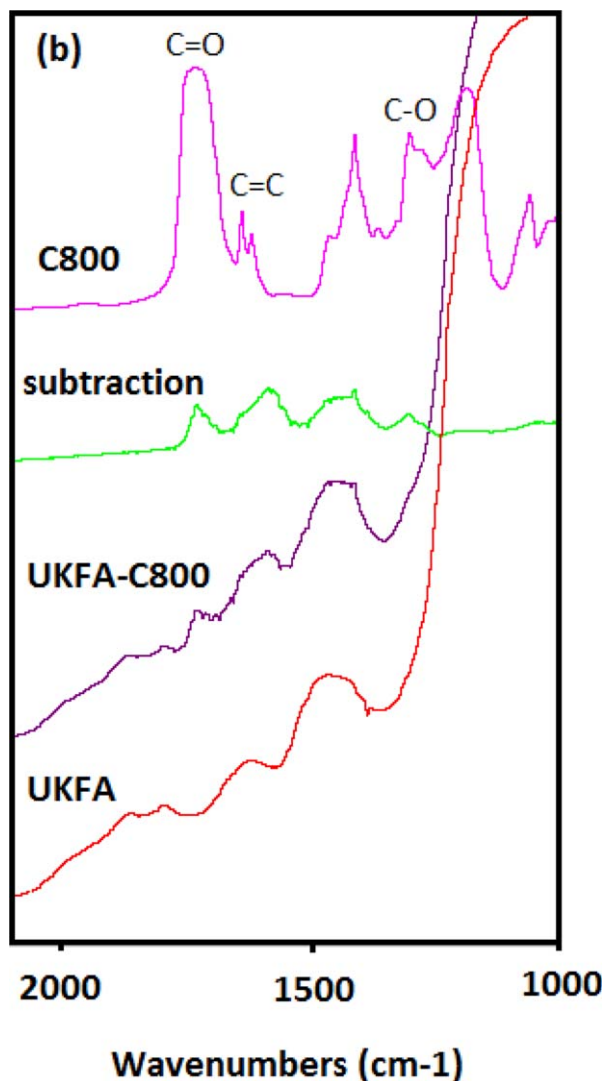
Figure 3. DRIFTS spectra of C800, modified and unmodified unwashed UKFA and subtraction spectra at 2100–1000 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Treatment of the fly ash with water and particularly HCl removes certain ions from the surface. These treatments will generally reduce the surface concentration of adsorption sites and therefore reduce adsorption activity. For this reason, there is a logical decrease in the heat of adsorption values recorded for the different UKFA samples. As expected, the greatest reduction occurred in the case of the HCl washed sample.

However, SAFA shows a different behavior. The highest adsorption value was obtained for the H$_2$O washed sample instead of for the unwashed one. This may mean that the SAFA has some strongly acidic sites on its surface, which were dissolved by water but not by HCl. Apart from that, the temperature used during the analysis may have an effect on the adsorption of C800 coupling agent on to the filler.

DRIFTS Analysis

Focusing on the chemical interaction between fly ash and C800, it can be deduced that such reaction occurs via ion pair interac-

tion due to the terminal carboxylic acid group of the C800, which can be easily deactivated as pH increases[22] (Scheme 1).

This linkage will directly affect the DRIFTS profile of both UKFA sample and C800 adsorbent as shown in Figures 3 and 4.

The subtraction of both modified and unmodified UKFA spectra gives important information about the new bonds created after the adsorption of C800 onto the filler surface.
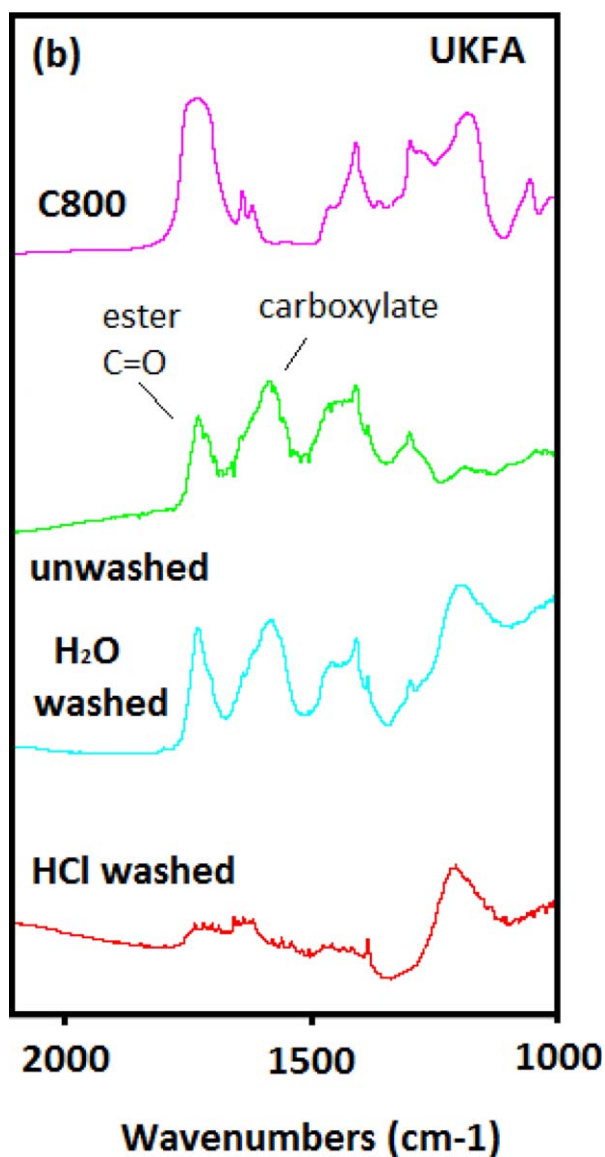
The oxides present on the fly ash surface give bands in the range of 1300–2000 cm^{-1}. These oxides belong to metallic ions (i.e., Al$_2$O$_3$), giving an Al—O stretching band at about 1650 cm^{-1}.[23] The O—H stretching absorptions appear at 2900–3600 cm^{-1} region because of the presence of the mullite and quartz feature surface hydroxyl groups.

The spectra of C800 cannot be fully interpreted and understood as the exact molecular structure is proprietary. However, the main and most important groups can be deduced as follows[24]:

- The terminal carboxylic acid group can be recognized from three different peaks. The O—H vibration shows a wide band in the 3000–3500 cm^{-1} region, while the two different C—O
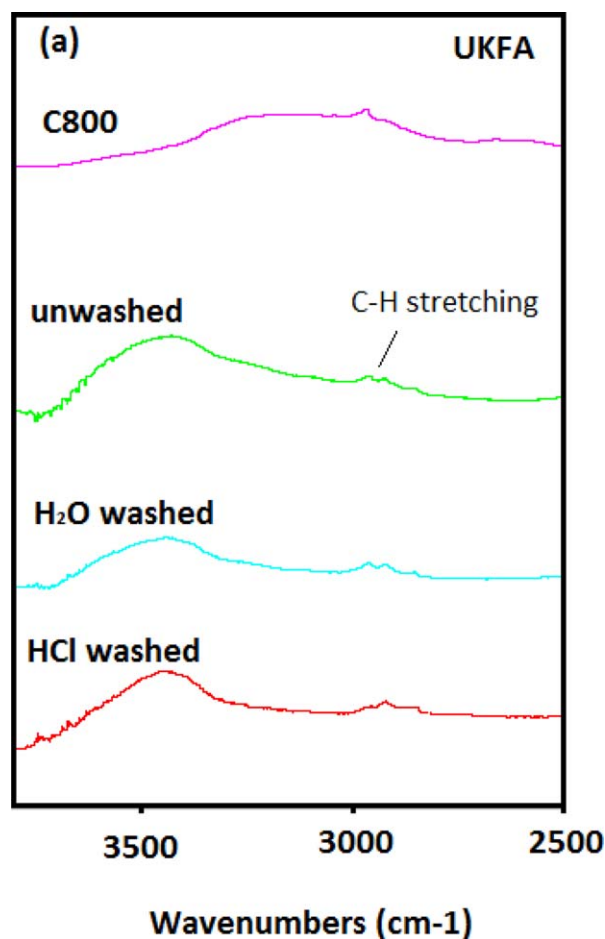
Figure 4. Subtraction spectra of washed and unwashed UKFA compared with C800 at 3800–2500 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

depending on the most stabilized canonic form of the equilibrium. For this reason, an asymmetric peak will appear in the 1680 cm^{-1} area (shifted slightly to the right after interaction with C800) influenced by both canonic forms. The reduced frequency of this band is due to the different interacting ions.

The now present alkene in the modified UKFA is responsible for the alkenic C—H stretching band at about 3040 cm^{-1} and alkenic C—H deformation vibration at 1600 cm^{-1}. The appearance of a new peak at about 1590 cm^{-1} is related to the carboxylate linkage with the metal from the filler surface, which again verifies the adsorption of C800 onto fly ash. However, the carbonyl group is also present in the newly formed ester group, which results in a peak at 1730 cm^{-1}. These explanations may not appear too clear in the spectra as the oxides present on the fly ash surface also give bands in the range of 1300–2000 cm^{-1} that may superimpose on those described above.

The subtraction of the spectra gave valuable information about filler-C800 bonding. In all cases the fly ash spectrum was subtracted from the fly ash sample with the adsorbed C800 coupling agent. The washed and unwashed UKFA and SAFA subtraction spectra are shown in Figures 5–7.

Figure 5. Subtraction spectra of washed and unwashed UKFA compared with C800 at 2100–1000 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vibrations (carboxylic C=O and C—O ether) appear at 1710 and 1300 cm^{-1}, respectively.
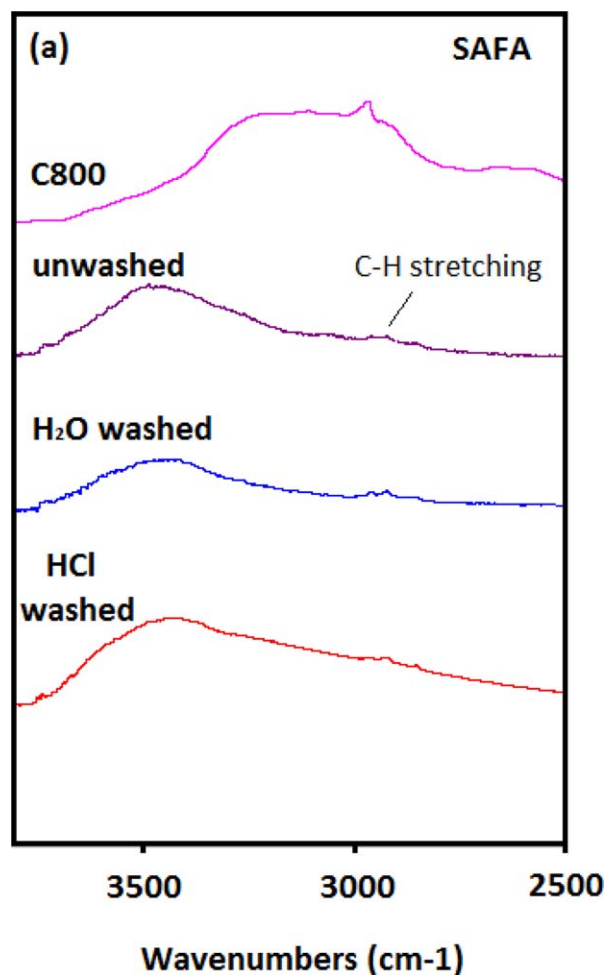
- The alkenic double bond shows a vibration peak around 1600 cm^{-1}.
- The band at 3040 cm^{-1} is due to some alkenic C—H stretching vibrations.

The comparison of C800 and subtraction spectra is important in terms of resolution of new bonds. As explained, the carboxylic group of C800 will interact with the different metal ions of the fly ash surface, which will significantly modify the vibration of the different bonds present in the new linkage.[25] A carbonic group can occur in two different forms, with the carboxylic form (C=O) being the most stable. However, when introducing an external group or atom to the system, the vibration frequency will increase or decrease as a result of that interaction,
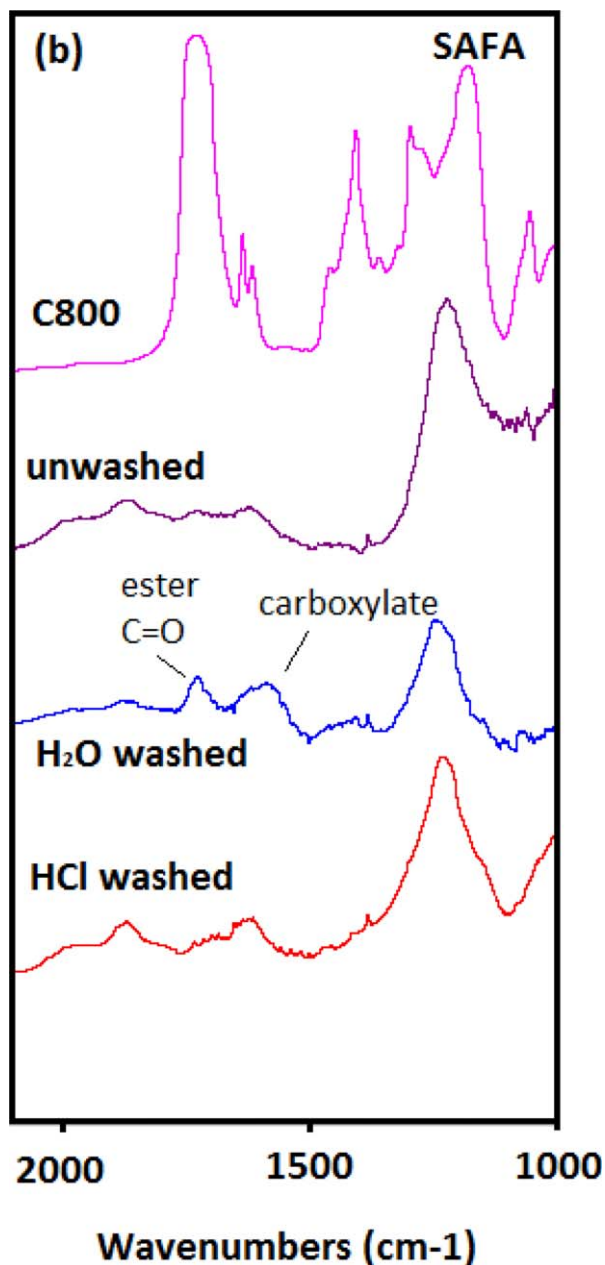

Figure 6. Subtraction spectra of washed and unwashed SAFA compared with C800 at 3800–2500 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. Subtraction spectra of washed and unwashed SAFA compared with C800 at 2100–1000 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As the pH of the washing decreases, the intensity of the bands also diminishes in the case of UKFA. Logically this reduction in intensity appears to occur in the same magnitude as the adsorption value does (see Table III), showing little adsorption changes in the case of the HCl washed sample. Following the same reasoning, H_2O washed SAFA showed more intense bands.

Table IV. Adsorbed C800 Proportions in Unwashed and HCl Washed UKFA Samples

	Unwashed UKFA	HCl washed UKFA
mg C800/g FA	15.72	0.12

Mass-Loss on Ignition

From a quantitative point of view, the adsorbed C800 amount was calculated by mass-loss on ignition for unwashed and HCl washed fly ash due to their huge difference in the heat of adsorption. After considering the volatile and internal water removal of the UKFA samples during the ignition process, the following C800 proportions were calculated for both unwashed and HCl washed UKFA samples (Table IV).

Unwashed UKFA shows a 100 times greater proportion of adsorbed amount of C800 in comparison with the HCl washed sample, which supports the results exhibited in Table III. In terms of quantity, the removal of ions from the fly ash surface by acid washing significantly affects the number of adsorbent molecules interacting with the particles, resulting in an important reduction that will affect the subsequent properties of the filled polymer system and final composite material.

CONCLUSIONS

The washing of certain ions from the filler surface reduced the linkage points for C800, resulting in a decrease in the heat of adsorption values as the pH of the media decreased. However, H_2O washed SAFA seems to experience different adsorption, possibly depending on the processing temperature used. Quantitatively, the unwashed UKFA powder allows 100 greater mass of adsorbent molecules in comparison with the HCl washed sample. The ICP data confirmed the interaction between the C800 coupling agent, which probably occurs with some of the metals of the second group (i.e., calcium) and some of "*p*" group (aluminum, sulfur, and phosphorous) on the surface of fly ash.

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