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Polypropylene / Fly Ash Composites: Effect of Coupling Agents on Mechanical Properties and Matrix Crystallinity

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Summary: Polypropylene homopolymer/fly ash (50 %wt) composites have been prepared from two samples of fly ash. One of the samples has a greater soluble group I and II metal content. A screening study indicated that Lubrizol Solplus® C800 (an unsaturated carboxylic acid coupling agent), initiated with dicumyl peroxide (DCP), conferred the best strength–toughness balance to composites produced by small scale batch mixing followed by compression moulding, i.e. long residence time in the melt. In the latter case, however the good mechanical properties were related to detachment of the interfacial region due to possible extraction of PP-C800 adduct-group I and II ion reaction products. Interfacial adhesion was arguably too high in the case of the fly ash sample bearing a lower level of group I and II ions. These deductions were also supported by DSC data. However, higher shear - low residence time processing, i.e. by twin screw extrusion and injection moulding, led to better mechanical properties being obtained from C800-DCP modification when the fly ash contained a reduced level of soluble group I and II ions.

Keywords: fly ash; polypropylene; composite; coupling agent; β-polypropylene.

Introduction

Fly ash is a waste product from thermal power plants that has very good mechanical properties due it being composed mainly of strong materials such as silica and alumina. Within the EU alone, fly as is produced at a rate of more than 60 kT p.a. [1]. In recent years the use of fly ash as a filler for polymers has been explored and is attracting a lot of interest [2-4]. Due to the dissimilarity in surface chemistry (i.e. polyolefins are generally hydrophobic and fillers are generally hydrophilic), filled thermoplastics are often weaker than the unfilled matrix. In order to overcome this problem, coupling agents, that strengthen the adhesion between filler and matrix, are often used.

In this study a variety of such additives are examined on two fly ash samples, blended into a polypropylene homopolymer matrix. One of the fly ash samples is produced at Fiddler's Ferry power station in the UK (RockTron MinTron™ 7, coded UKFA) and the other is produced at the Lethabo power station in South Africa (Ash Resources Super-Pozz® coded SAFA). The latter was found to be the most suitable after screening several other samples from South Africa [5].

The coupling agents investigated in the study include Lubrizol Solplus C800 which is an unsaturated carboxylic acid type coupling agent and 1,3-phenylene dimaleimide. We have carried out a lot of previous work on the latter particularly [6,7] and have reviewed the evolution of free radical activated coupling agents including dimaleimides and unsaturated carboxylic acids elsewhere [8]. We have also included industry standard controls here too which include a methacrylate functional silane and maleic anhydride grafted polypropylene (mPP).

Experimental

The two fly ash samples (Mintron 7, Rocktron, UK (coded UKFA) and Superozz, Ash Resources, South Africa (coded SAFA)) were analysed using energy dispersive X-ray analysis (Jeol JSM 5600LV SEM fitted with Oxford Instruments INCA EDX system, accelerating voltage 10 kV). The water and acid (69 % nitric acid) soluble ions leached from UKFA and SAFA were identified using inductive coupled plasma optical emission spectroscopy (ICP-OES). A Varian Vista AX ICP-OES instrument was used with glass nebuliser and spray chamber. Manufacturers figures for average particle size (D_{50}) are 5 μm and 7 μm for SAFA and UKFA, respectively.

Composites containing fly ash (50 %wt.) in a polypropylene (PP) homopolymer matrix (Borealis HD120MO (MFR 8 dg min^{-1} (230 °C / 2.16 kg)) were prepared via batch melt mixing using a Thermo Haake Rheomix 600 mixing bowl fitted with roller rotors and driven by a Thermo Haake Polydrive. The set bowl temperature was 170 °C, rotor speed was 60 rpm and mixing time was 10 minutes. The chunks of melt from the mixing bowl and rotors were then pressed into a ca. 6 mm thick patty using a hand press. The latter acted as a pre-form for the compression moulding of test plaques (102 mm x 102 mm x 3 mm) which were formed using a frame mould at 190 °C in a 50 tonne press. The patty was allowed to pre-heat for 2 minutes with the platens in contact, before full pressure was applied for a further 2 minutes. The mould was then transferred to a cold press with platens maintained at 15 °C and pressed at full pressure for 5 minutes. The moulding was then removed from the mould and cut up into test pieces for flexural and impact testing using a band saw. Composites produced using the Haake then compression moulding route will from henceforth, be described as being produced by the Haake-CM route. Selected composites were also produced by twin screw extrusion using a Thermo Prism HC24 co-rotating twin screw extruder fitted with a relatively harsh 28:1 L:D screw profile and three-hole die. The set temperature profile ranged from 195 °C at the feed hopper and 180 °C at the die. Screw speed was 300 rpm and the output rate was 4.8 kg hr^{-1}. Tensile and impact test pieces were injection moulding using a Battenfeld BA230 reciprocating screw machine at a set barrel temperature of 200 °C and mould temperature of 40 °C. Samples produced in this manner will from henceforth be referred to as TSE-IM samples.

The following coupling agents, that feature at least one reactive double bond per molecule, were evaluated at constant molar level of 41.51 μmol of reactive double bond per gram of fly ash: Lubrizol Solplus® C800 (an unsaturated carboxylic acid), N,N'-(1,3-phenylene) dimaleimide (BMI) and γ-Methacryloxypropyltrimethoxy silane (γ-MPS). Dicumyl peroxide (DCP) was used as an initiator for C800, γ-MPS and BMI. The optimised level of DCP was found to be 0.06 parts per hundred filler by mass (phf) [5]. The DCP was dissolved in the γ-MPS and the mixture was added to the filler before melt mixing; a Waring blender was used to ensure uniform coverage. As BMI is a solid it was combined with the DCP and added to the filler prior to melt mixing. The C800 was supplied pre-adsorbed at 50 %wt on a high surface area inorganic carrier (this supported form of C800 is actually known as Solplus® C825), DCP was added and the mixture added to the filler prior to melt mixing. Maleic anhydride grafted PP (mPP) (Arkema Orevac® CA100, containing ca. 1 %wt maleic anhydride) was included as a non-reactive coupling agent for comparison. The m-PP level used was 6 phf. Use of a molar equivalent level of maleic anhydride grafts on mPP to the monomeric coupling agent dosage, would give an mPP level of ca. 41 phf. Such a level would be impractical as the matrix properties would be modified due to the high MFR (150 – 200 dg min^{-1} (230 °C / 2.16 kg)) of the mPP.

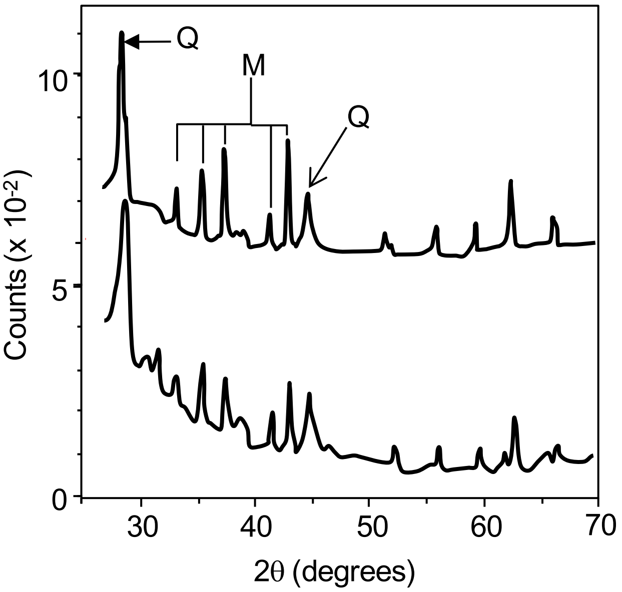

Figure 1. WAX data for (a) SAFA and (b) UKFA showing increased levels of quartz (Q) and Mullite (M) in the latter.

The flexural (48 mm span, 10 mm min^{-1} crosshead speed), and impact properties (un-notched and notched (0.5 mm tip radius 45 "v", 2 mm deep) Charpy (span was 40 mm)) were determined at 22 °C (± 1 °C) using ca. 10 mm x 3 mm cross section test pieces. The melting and crystallisation characteristics of the matrix were studied using differential scanning calorimetry (DSC). A Perkin-Elmer DSC-7 power compensation type instrument programmed with a heat (20 °C to 220 °C at 20 °C min^{-1}) – hold (for 5 min at 220 C) - cool (220 °C to 20 °C at 20 °C min^{-1}) – heat cycle (20 °C to 220 °C at 20 °C min^{-1}) was used. Samples (ca. 5 mg) were contained in crimped close aluminium pans.

Table 1. Chemical composition of the fly ash (wt %) by EDX

Sample	C	O	Al	Si	Ca	Mg	K	Fe
SAFA	18.8-20.7	58.7-61.0	9.6-13.5	10.8-14.1	0.8-0.9	-	-	-
UKFA	20.4-28.4	55.0-56.8	6.0-7.7	8.3-11.6	0.7-0.8	0.6	0.4-0.8	1.5-0

Results and Discussion

The EDX data and the ion leaching data for UKFA and SAFA are shown in Tables 1 and 2, respectively. It is evident that the EDX data confirms the major constituents of fly ash, namely quartz (SiO_2) with some Mullite ($3Al_2O_3.2SiO_2$) type material; interestingly SAFA appears to be somewhat richer in these components, a finding which was confirmed by WAXS. The level of carbon is higher in UKFA and the elements magnesium, potassium and iron are also present in measurable quantities; the carbon and iron in particular may explain the darker colour of UKFA. Table 2 shows the ion leaching data (which was obtained by both aqueous and nitric acid leaching) for the two fly ash samples. The most striking feature of the data is that the SAFA features a greater proportion of group 2 metal ions, some of which are removal via aqueous leaching. This observation has important implications in terms of how the coupling agents may interact with the fly ash surface; interaction with an extractable ion may result in detachment of the coupling agent. WAXS data for the two fly ash samples is shown in Figure 1 where it was evident that SAFA features Mullite and quartz related reflections of greater intensity than those of UKFA.

The mechanical properties of the Haake – CM produced composites modified with the coupling agents described above, and based on UKFA and SAFA, are compared in Figure 2. Considering the flexural modulus data, the UKFA and SAFA gave broadly similar values. Addition of the coupling agents increased stiffness relative to the unmodified composite with C800-DCP and BMI-DCP giving the largest increases. Comparison of the flexural strength data reveals all the coupling agents usefully boosted strength to varying degrees;

Table 2. ICP data obtained for UKFA and SA4 under different leaching conditions (some transition elements have been omitted for brevity)

Element	Element concentration (ppm)			
	Aqueous leaching (soluble "surface" ions)		Nitric acid leaching (ions from within wall of particle)	
	SAFA	UKFA	SAFA	UKFA
Al	-	-	91.8	58.9
B	1.6	-	3.5	0.5
Ba	-	-	6.7	9.7
Ca	17.0	10.3	73.2	59.7
Fe	-	-	25.4	50.1
K	-	-	0.7	2.3
Mg	2.8	1.8	21.0	22.4
Na	4.5	5.3	18.2	23
Si	2.8	1.5	56.6	43.8
Sr	-	-	2.8	0.9
Ti	-	-	5.4	1.9
Zn	-	-	0.9	1.5

A dash indicates a level less than 0.5 ppm.

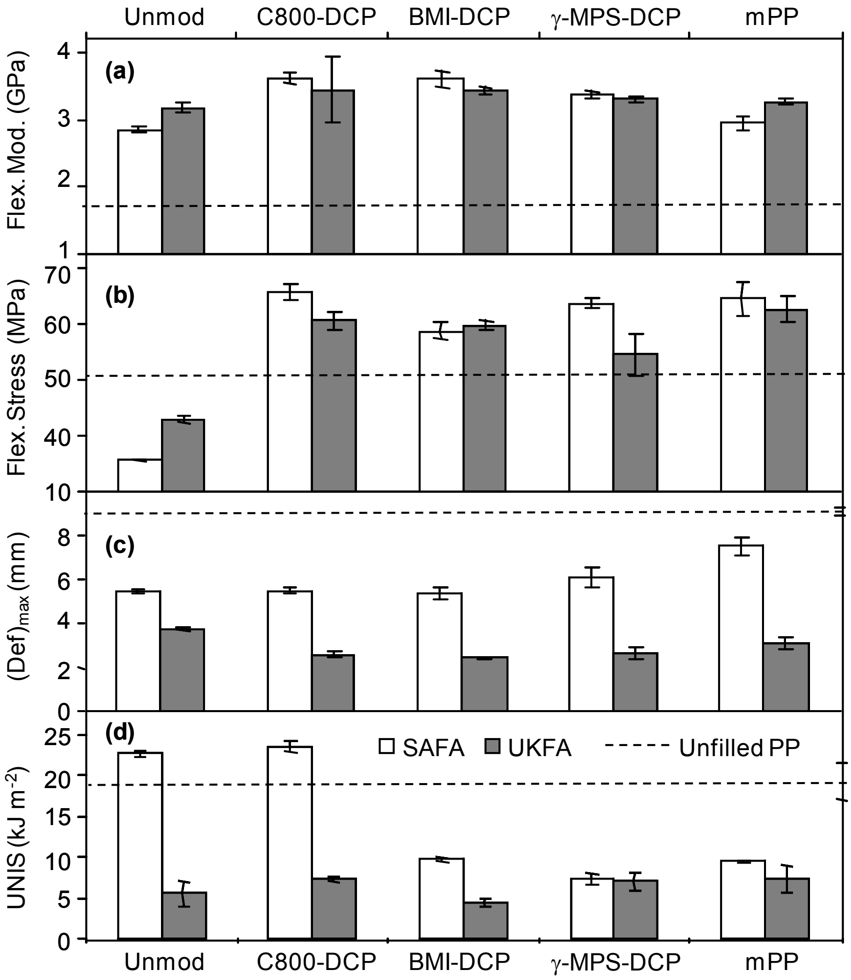

Figure 2. Effect of fly ash source and surface modification on flexural and impact properties (a) Flexural modulus, (b) Flexural stress at maximum (or breakpoint) (c) Deformation at maximum stress (or breakpoint) ($(\mathrm{Def})_{\mathrm{max}}$) and (d) Un-notched impact strength (UNIS).

C800-DCP and m-PP were arguably the best and most consistent performers, with similar levels of improvement being realised in both fly ash samples, though in both cases SAFA gave slightly better performance. BMI-DCP also gave notably consistent performance in both fly ash samples, but the level of performance was somewhat lower than with the latter two modifications. The silane γ-MPS gave poorer performance in the UKFA based composite and a similar performance to C800-DCP and m-PP in the SAFA based composite. In the unmodified composite the performance of UKFA was notably superior. In all composites the SAFA gave a substantially higher deflection at maximum stress ($(\mathrm{Def})_{\mathrm{max}}$) than UKFA, this may be due to differing particle size distributions and interfacial properties. SAFA also gave composites with generally higher impact strength, this was strikingly true of the unmodified and C800-DCP modified composite. In the latter composites, impact strength exceeded that of the unfilled matrix. This observation together with SEM imaging of the fracture surfaces [5] (not shown here), indicated that the enhancement in toughness was due to a debonding related toughening mechanism. The interfacial adhesion in the case of the other coupling agents was too strong to be advantageous at the filler level investigated. The latter was also true of the C800-DCP modified UKFA based composite. This observation hinted at significant differences in surface composition between UKFA and SAFA. As the C800 – DCP modification gave the best strength – toughness balance (notably in SAFA based composites) at the 50 wt.-% fly ash loading. This is the system to be taken forward for the TSE-IM study.

The effect of C800-DCP on composites based on the two fly ash samples, but this time produced via the TSE-IM route, are compared in Table 3. The unmodified composite samples had similar flexural modulus values, probably due to the crystallisation being controlled by the filler more than the cooling rate. The latter was less true for the unfilled matrix; the slower cooling associated with CM resulted in a slightly higher flexural modulus. Interestingly the flexural modulus of the TSE-IM produced composites was not affected by C800-DCP modification, an effect that may be related to the interfacial region not extending into the bulk matrix. The minimal shear conditions associated with CM are more conducive to growth of thicker interfacial regions. The flexural strength data reveals clear superiority of the UKFA under these processing conditions, though the relative improvements made on C800-DCP modification appear similar. The flexural strength of the equivalent composites produced using the Haake-CM route is noticeably higher.

Table 3. Effect of fly ash type and surface modification on flexural and impact properties of composites produced via the TSE–IM route.

Sample	Flexural modulus (GPa)	Flexural strength (MPa)	Def$_{max}$. (mm)	Notched Impact strength (kJ m^{-2})	Unnotched impact strength (kJ m^{-2})
Unfilled PP	1.44 (0.02)	44.0 (0.4)*	9.0 (0.1)	5.4 (0.3)	81.7 (1.5)
SAFA	3.19 (0.02)	37.8 (0.1)	6.3 (0.5)	5.3 (0.4)	15.3 (0.4)
UKFA	3.20 (0.02)	41.3 (0.1)	5.7 (0.2)	6.0 (0.5)	12.6 (0.2)
SAFA-C800/DCP	3.22 (0.02)	43.7 (0.1)	5.0 (0.1)	5.1 (0.3)	12.9 (0.3)
UKFA-C800/DCP	3.18 (0.02)	51.7 (0.1)	5.8 (0.1)	6.4 (0.7)	14.8 (0.1)

*Yield value

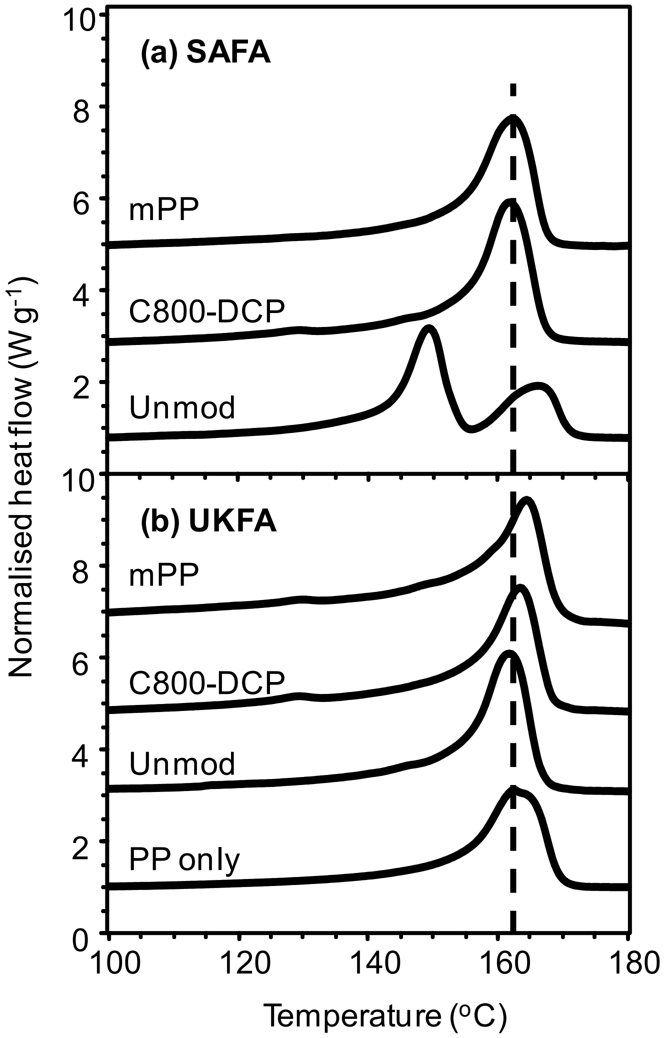

Figure 3. DSC data from first heat segment obtained for (a) SAFA and (b) UKFA based composites produced via the Haake-CM route. Composites are modified as indicated above each heat flow versus temperature plot. Crystalline content (X_c) is written to the right of the peaks.

The $(Def)_{max}$ data shows similar values for all composites (if error bars are considered) apart from C800-DCP modified PP/SAFA which is the poorest performer. Arguably UKFA is the best performer as it gives the highest strength when modified with C800-DCP. Furthermore, the $(Def)_{max}$ of the UKFA based composite was not affected by C800-DCP modification. The notched Charpy impact strength data follows the same trend as $(Def)_{max}$. Addition of UKFA (unmodified and most particularly C800-DCP modified) led to an improvement in impact strength beyond that of the unfilled matrix. SAFA based composites performed worse on C800-DCP modification and those based on UKFA improved. The latter again gave the best result. Un-notched impact strength data followed the same trend.

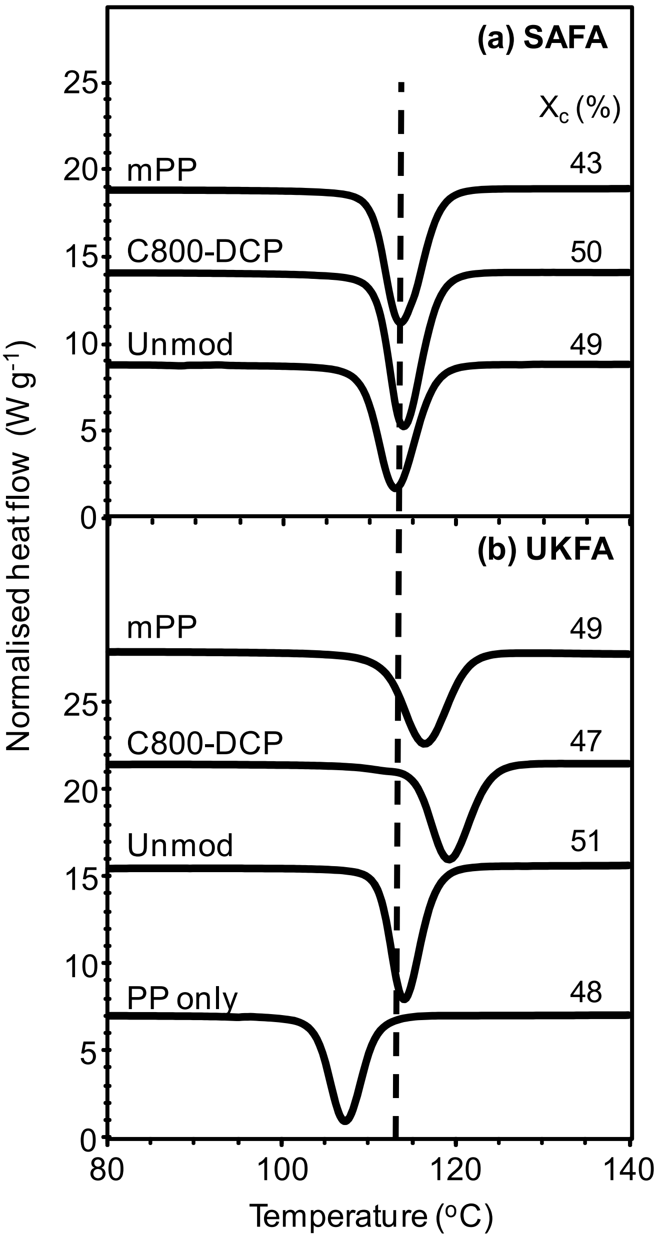

Figure 4. DSC data from the cooling segment obtained for (a) SAFA and (b) UKFA based composites produced via the Haake-CM route. Composites are modified as indicated above each heat flow versus temperature plot. Crystalline content (X_c) is written to the right of the peaks.

The switch in superiority to UKFA observed on changing to the TSE-IM processing route is interesting and shows that Haake–CM data is not always a good predictor of performance when scaling up to TSE–IM processing. In this study the poor performance of SAFA may be related to a weak boundary layer that can be stripped off as a result of the higher shear environment of the TSE-IM processing. The melting and crystallisation characteristics of the matrix, discussed in the following paragraphs, provide further insight in to this aspect.

Figure 3 compares a selection of the DSC data from the first heat segment of the heat-hold-cool-heat cycle for the SAFA and UKFA based composites formed using the Haake–CM route. The selection of the data was made on the basis of most significant observations and representation of the unmodified composite, modification with monomeric and polymeric coupling agents (i.e. C800-DCP and MA-g-PP, respectively) The unmodified SAFA based composite shows a melting endotherm peak (at 150 ºC) due to the presence of β-^{i}PP. The latter is absent, and α-^{i}PP is the dominant polymorph, in all the composites containing surface modified SAFA. Therefore it appears that the pristine surface of SAFA is able to nucleate β-^{i}PP to a sufficient level for it to be observed in DSC measurements. The unusually good impact strength observed with the unmodified SAFA based composite may be related to the β-^{i}PP content in the matrix [9]. Other researchers have found that fly ash can be a β-^{i}PP nucleating agent for PP [10]. It has also been argued that β-^{i}PP can lead to improved impact strength, an effect that may be related to the radial spherulitic structure of this polymorph [11]. The cross-hatched structure of α-^{i}PP spherulites in the composites may not be so effective at absorbing deformation energy. The crystalline content (X_c) of the matrix is also given in Figure 3; it is evident that this parameter did not vary to a significant degree though both composites modified with C800-DCP had a slightly higher crystalline content. This may be due to chain scission caused by the DCP.

In DSC data (Figure 4) obtained on cooling from the melt after the 5 minute hold period at 220 ºC, the unmodified composites based on SAFA and UKFA gave similar levels of elevation of the crystallisation peak temperature (ca. 114 °C) relative to the unfilled matrix (ca. 107 °C). In the case of the composites based on SAFA, interfacial modification had an insignificant effect on the nucleation activity. In contrast, however the UKFA based composites showed enhanced nucleation activity when interfacial modification was used, this was particularly true in the case of C800-DCP which elevated the crystallisation peak temperature to 119 °C. A lack of removable ions in UKFA may have increased the strength of adhesion to the matrix via the coupling agents, such strong tethering of the matrix chains to the filler surface my have led to enhanced nucleation relative to the unmodified UKFA surface. The matrix crystalline content formed during crystallisation is also shown on Figure 4 and shows no significant variation.

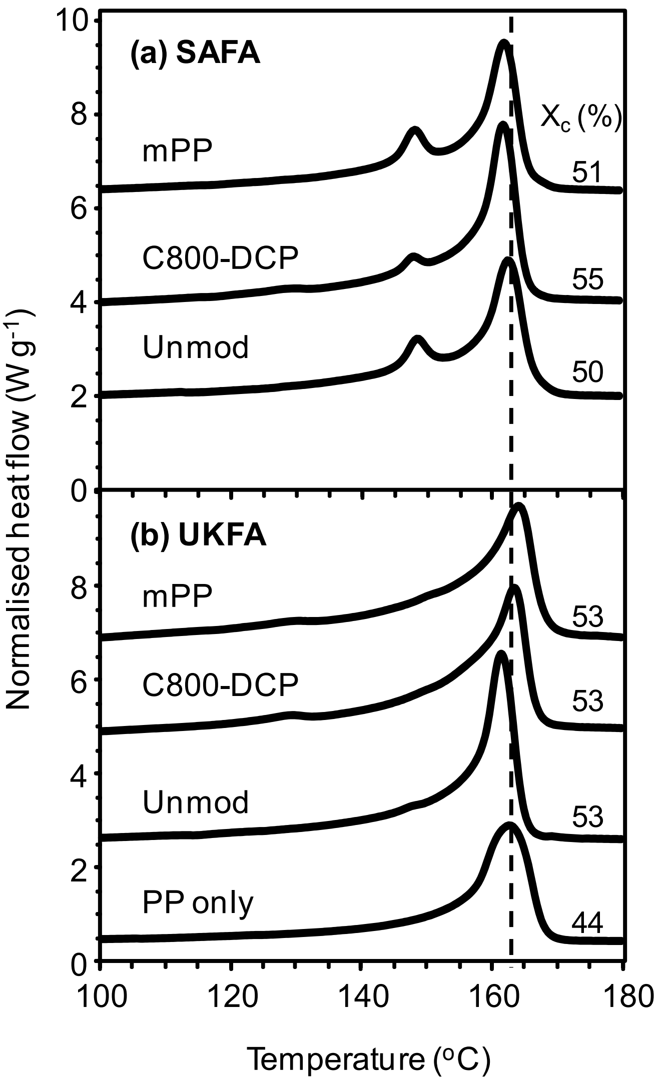

Figure 5. DSC data from the second heat segment obtained for (a) SAFA and (b) UKFA based composites produced via the Haake-CM route. Composites are modified as indicated above each heat flow versus temperature plot. Crystalline content (X_c) is written to the right of the peaks.

The structures formed during the controlled crystallisation (second heat, Figure 5) are likely to be free of effects related to shear induced orientation of the PP chains. In the Haake-CM produced composites, the presence of β-^{i}PP in second heat data for all the SAFA based composites (with the exception of the composite modified with BMI/DCP (not shown)) indicates that there is an inherent β-^{i}PP nucleation capacity. The level of β-^{i}PP was similar regardless of the surface modification, an observation that may be indicative of desorption of the surface modifiers together with the weakly attached metal ions, leaving a pristine β-^{i}PP nucleating surface. The lack of β-^{i}PP formation in the case of the BMI-DCP modified composite may be due to the high crosslink density associated with homopolymerised BMI and BMI-PP adducts in the interfacial region. Such an effect may prevent desorption and the resultant β-^{i}PP nucleation effect. The melting peak temperature of the dominant α-^{i}PP component was 162 °C in all cases and represented predominantly cross-hatched lamellae [12]. Interestingly β-^{i}PP was absent in all the UKFA based composites, though small increases in the melting peak temperature were apparent in the modified composites which may be a result of the enhanced nucleation observed.

SAFA based composites produced via the TSE-IM route did not show DSC resolvable levels of β-^{i}PP in the first heat data. This is in contrast to the behaviour observed for the Haake-CM produced composites and is likely to be due to both the higher shear experienced by the polymer during TSE-IM processing and the considerably faster cooling rate associated with injection moulding. Incorporation of SAFA led to a reduction in the "as moulded" X_c from ca. 55 % in the unfilled matrix down to an average of ca. 44 % for the unmodified and C800-DCP modified composite. It should be noted that the X_c of the unfilled matrix was more affected by the different processing route than the composites; the Haake-CM processed unfilled matrix had an X_c of 45 %. On cooling from the melt SAFA led to increased nucleation activity with the crystallisation exotherm peak being elevated by 9 °C, relative to the unfilled matrix. Modification of the SAFA based composite with C800-DCP, however, had no effect on the nucleation characteristics. The crystallisation exotherm peaks mirrored the first heat melting endotherm peaks in terms of extent of crystallisation. Observation of melting behaviour after the controlled crystallisation revealed some β-^{i}PP in the unmodified SAFA based composite, an observation that indicates that the β-^{i}PP nucleation characteristics of SAFA become apparent at lower cooling rates (as with compression moulding). C800-DCP modification reduced formation of β-^{i}PP during controlled crystallisation to non-resolvable levels. The crystalline content of the unfilled matrix after controlled crystallisation remained the same as for the first heat, whilst matrix X_c in the SAFA based composites increased to 47 % for both the unmodified and C800-DCP modified varieties.

The UKFA based composites showed no β-^{i}PP in the first heat data, though matrix X_c was reduced to 46 % and 41 % for the unmodified and C800-DCP modified composites, respectively. The latter reduction is probably significant and may be due to enhanced nucleation associated with more effective tethering of matrix chains to the C800-DCP modified UKFA surface. However, the crystallisation data indicates that like SAFA, UKFA led to a 9 °C elevation of the crystallisation exotherm peak temperature (T_{cp}). Modification of the UKFA based composite with C800-DCP led to further elevation of the T_{cp} to 121 °C, 18 °C higher than T_{cp} of the unfilled matrix. This difference in behaviour is consistent with that observed in the cases of the Haake-CM processed composites. Under controlled crystallisation conditions the matrix X_c measured from the exotherm peaks were 47 % in both composites. The second heat data for the UKFA based composites revealed no β-^{i}PP though X_c was lower than that for the unfilled matrix; with values of 44 and 49% being obtained for the unmodified and C800-DCP modified composites respectively.

EDX studies and ICP-OES of aqueous and acid leachate samples from the two fly ash samples revealed that SAFA had a higher level Group I and Group II metal ions. Full reaction of the latter ions with surface modifier molecules is likely to result in extraction from the filler surface. Such effects have been observed in studies of other fillers by Gilbert and Liauw [13, 14]. The pristine surface resulting from such desorption may nucleate β-^{i}PP. Such an occurrence is certainly consistent with the relatively poor interfacial adhesion observed in these composites. The unmodified UKFA based composite prepared by TSE-IM did not contain any β-^{i}PP. Bearing in mind the superior mechanical properties and improved interfacial adhesion observed with the C800/DCP modified UKFA based composites, it is likely that C800 adsorbed on the surface of UKFA was not so easily pulled off.

Conclusions

Both fly ash samples were relatively easy to melt blend into PP via either the batch mixing–compression moulding (Haake-CM) or the twin screw extrusion–injection moulding (TSE-IM) routes. The Haake-CM route was successfully used to select the best performing coupling agent which, at 50 %wt fly ash, was Lubrizol Solplus® C800 initiated with dicumyl peroxide (DCP). The latter certainly gave the best strength-toughness balance of all the Haake-CM samples in composites based on the South African fly ash (SAFA). The superiority of the latter was thought to be due to an intermediate level of filler-matrix adhesion which was associated with possible detachment of (PP-C800 adduct)$_2$M^{2+} and (PP-C800 adduct)M^{+} species. SAFA has a higher level of M^{+} and M^{2+} ions (i.e., sodium, calcium and magnesium ions) than UKFA. Due to their ability to selfcross link, γ-MPS, BMI and m-PP promoted excessive filler-matrix adhesion, resulting in brittle failure occurring though the bulk matrix. SAFA, in its pristine state, was found to be a moderate β-^{i}PP nucleating agent under the Haake-CM processing conditions. Surface modification of the SAFA blocked the surface adsorption sites and greatly reduced β-^{i}PP nucleation activity. Due to the shorter residence time and higher shear associated with TSE-IM processing, the C800-DCP modified UKFA based composite performed better in terms of mechanical properties than the equivalent TSE-IM processed composite based on SAFA. Under TSE-IM conditions stronger retention of PP-C800 adducts to the fly ash surface was clearly an advantage. In SAFA based composites produced by TSE-IM, β-^{i}PP was not present in the first heat data, but was evident in the second heat data for the unmodified composite, indicating that the shear regime and thermal profile associated with injection moulding is not conducive to β-^{i}PP formation. The increased nucleation activity in the TSE-IM processed C800-DCP modified UKFA based composite, together with increased mechanical properties supports improved adhesion of PP-C800 adducts to UKFA.

This study shows that the composition of fly ash (particularly soluble ion content) has an important influence on filler-matrix adhesion in PP based composites modified with carboxylic acid functional coupling agents. This aspect must be carefully considered if the commercial viability of fly ash as a filler is to be increased.

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