J Mater Sci (2007) 42:10219–10227
DOI 10.1007/s10853-007-1732-5

Effect of coupling agents on the crystallinity and viscoelastic properties of composites of rice hull ash-filled polypropylene

Roya Khalil · Andrew George Chryss · Margaret Jollands · Satinath Bhattacharya

Received: 11 January 2007 / Accepted: 26 March 2007 / Published online: 22 September 2007

Abstract This paper focuses on the application of silica rich, rice hull ash (RHA) from the rice industry as filler in polypropylene (PP). The dynamic rheological behaviour and the crystallinity of its composites with semi-amorphous polypropylene were used as performance indicators. The effect of coupling agents on RHA/PP compatibility was also investigated. Addition of RHA increased storage modulus (G′), and the onset (T_{co}) and peak (T_c) crystallinity temperatures, and decreased the degree of crystallinity of the system. Two coupling agents, maleated polypropylene (MAPP) and an amino functional silane, were used to improve the interfacial adhesion of RHA and PP. Addition of MAPP increased G′, T_c and T_{co} and the crystalline phase of the system. Addition of silane had mixed effects. It increased the rheological properties at higher concentrations, it increased T_c and T_{co} at all the concentrations and increased crystallinity at lower concentrations and decreased it at higher concentrations. Results from a thermogravimetric analyser were useful in revealing the mechanism by which silane bond to RHA and its effect on the rheology and crystallisation behaviour of the composites.

Introduction

The annual worldwide output of rice hulls is approximately 80 million tons. The rice hull contains "opaline" silica in combination with a large amount of a phenyl propanoid structural polymer called lignin [1]. Silica concentrations in the dry hull can be as high as 21.5 wt% which corresponds to 3.2 million tons of silica per annum [2]. Such a high percentage of silica and the intimate blend of silica and lignin make the rice hull resistant to water penetration and fungal decomposition and so rice hulls are very hard to dispose of by biodegradation.

Burning rice hull as a fuel to generate energy may be a partial more environmentally friendly alternative than landfill. Rice hull ash (RHA) is the by-product from this process. RHA is about 97–99% silica and the remainder is carbon and other impurities. RHA is mainly amorphous and hence is called 'opaline' silica ash [3].

Because of growing environmental concern and the need to conserve energy and resources, efforts have been made to burn the husks under controlled conditions and to utilize the resultant ash in alternative environmentally friendly applications such as filler in the cement, geopolymers and polymer industries.

This research explored the use of silica from RHA as filler in thermoplastic polypropylene (PP). The main problem of preparation of RHA-thermoplastics composites is the incompatibility of hydrophilic RHA and hydrophobic PP, which yields composites with poor properties. This paper focuses on a study of effect of filler and coupling agents on the dynamic rheological properties and the crystallinity of the system. The interfacial adhesion between filler and matrix, and the efficiency of the coupling agents, and the filler dispersion are considered. Dynamic shear rheology was used to study the effect of filler on the viscosity and the elasticity of the matrix. The extent of surface treatment of filler by silane coupling agents was investigated using thermo-gravimetric analysis (TGA) and dynamic rheological methods. The effect of addition of polymer based coupling agent, maleic

---

R. Khalil (✉) · A. G. Chryss · M. Jollands · S. Bhattacharya
Rheology and Materials Processing Centre, School of Civil and Chemical Engineering, RMIT University, 124 La trobe Street, Melbourne, VIC 3000, Australia
e-mail: roya.khalil@rmit.edu.au

anhydride polypropylene (MAPP) on the compatibility of RHA and PP was studied using differential scanning calorimetry (DSC) and dynamic rheological methods.

Theory

Polymers are mixed with fillers to improve bulk properties such as shear modulus. Coupling agents are often used to enhance these improvements. Fillers and coupling agents also affect the composite's rheological behaviour and morphology. The selection of the best coupling agents for a system depends on understanding the effect of the filler on the processability and morphology of the composites.

Introduction of any type and shape of filler in a polymer increases the viscosity and the elastic response of the system, with some shapes having more impact than others do. The increase in complex viscosity, η^* (a measure of the material's overall resistance to flow as a function of shear rate, which can be obtained from the vector sum of the elastic (η') and viscous (η'') dynamic viscosities ($\eta^* = \eta' + i\eta''$) of the system is due to the resistance of solid filler particles to deformation and the increase in G′ (measure of the elasticity of the system: energy stored and recovered per cycle, when different systems are compared at the same strain amplitude, defined as the stress in phase in the strain in a sinusoidal shear deformation divided by the strain measure of the $\left(G'(\omega) = \frac{\tau_{12}}{\gamma_0}\cos\delta\right)$, is attributed to the ability of filler particles to store energy [4]. An increase in η^* and G′ under oscillatory shearing would indicate strong interaction between the polymer and filler particles. Strong interaction would result in more resistance to deformation because of a good transfer of stress (caused by shearing) from the filler to the polymer phase [5, 6]. Lozano et al. [7] used oscillatory or dynamic rheological methods to analyse the introduction of vapour grown carbon nano-fiber as a filler in PP. Their results suggest an increase in storage modulus and viscosity with increase in filler loading. This was attributed to a better dispersion of filler in the matrix and enhanced interaction of filler with the polymer matrix. Yuan et al. [8] and Mohanty et al. [9] observed an increase in viscosity upon addition of paper waste or jute to PP and the addition of 5 wt% MAPP increased the viscosity even more.

Thermal study of the composites is another very useful tool in understanding the composite's bulk properties and the interaction of filler and polymer matrix. The bulk properties of semi-crystalline polymeric composites are strongly influenced by their crystalline structure and the relative amounts of amorphous and crystalline phases. Introduction of a second component such as filler into a polymer can provide a nucleating agent that affects both the crystalline and amorphous structure. Generally, the fine spherulitic microstructure produced in PP by adding nucleating agents gives rise to greatly enhanced ductility and strength [10]. The performance of nucleating agents is generally determined by three factors: (a) surface activity of the filler, (b) topology of the filler and (c) surface modification. This was found by Ren et al. [11] where fillers including fumed silica with and without surface modification with silanes were mixed with polymer.

Experimental

Materials

Homopolymer PP (Grade: SM6100, Basell Polymers, Australia), with a melting temperature of 165 °C, and of density: 900 kg/m^3, was used as the polymer matrix for the composites. RHA was supplied by Sunrice (formerly known as Rice Growers Co-operative Ltd.), and is of 98% silica purity. Size reduction from mean particle size of 57–10 µm was done courtesy of Mr. Axel Andrea from Advanced Grinding Technologies, Bayswater, Victoria. The grade of silane used was 3-Aminopropyltriethoxy (APS, density 0.946 g/mL) from Sigma Aldrich Chemicals. The polymer based coupling agent used was MAPP with MA grafted content of 0.55 wt% (Grade: Fusabond PMZ109D) from DuPont, Australia. It had a melting temperature of 162 °C and a melt flow index of 120 g/10 min.

Filler treatment

RHA was first acid washed with hydrochloric acid solution (pH-4.5) to remove impurities such as carbon and trace metal and oven dried at 80 °C overnight. A wet based silanation method was then applied to the RHA. The silane was dissolved in 50 mL of distilled water and stirred for 5 min to allow hydrolysis to occur. RHA was added to the solution while constantly stirring for another 15 min. The solution was then oven dried at 85 °C overnight. Several concentrations of silanes from 0.5 to 15 parts per hundred filler (phf) were used to determine an optimum concentration. However, for clarity only a few concentrations around the optimum region are shown in this paper.

Composite preparation

Compounding of the polymer with RHA was carried out in a batch twin blade Haake mixer using optimum processing conditions. The optimum processing conditions (which was found via a full factorial design of experiments was used with three variables and analysed using Minitab software) were found to be 12 min mixing time at 180 °C at the rotor speed of 60 rpm. Other composites with 30 and 40 phr to matrix and the silanated RHA composites were also prepared using these operating conditions. Each batch was then transferred to a 2 mm thickness mold and compression molded at 180 °C and pressure of 10 KPa for 15 min and then water cooled into plaques.

MAPP application

MAPP was dry blended with filler and PP and then melt mixed in the Haake mixer. Various concentrations (such as 2, 3 and 5 phr were used in these experiments. The mixing was carried out at the previously identified optimum conditions. The resultant mix was then compression molded as described above.

Rheological measurements

A complete rheological characterisation of the system was beyond the scope of this project. This paper reports on an evaluation of η^* and G'. These commonly characterised rheological properties are expected to be sensitive to filler/polymer interaction.

A rotational rheometer (ARES from Rheometric Scientific) was used to study the dynamic rheological properties of the RHA filled PP matrix using parallel plate geometry of diameter 25 mm and a gap of 2 mm. Compression molded plaques were cut into specimen disks of diameter 25 mm. The dynamic measurements of the system were carried out at a temperature of 210 °C. This temperature was chosen because it is the processing temperature of this grade of PP. The linear viscoelastic region where modulus is independent of strain was determined using a strain sweep test. The η^* of the samples was measured using dynamic frequency sweep tests in the range 100 to 1 rad/s.

Thermal analysis

Differential scanning calorimetry

Thermal analysis of RHA and PP with and without surface treatment was performed. A DSC (Perkin Elmer 2920 with Thermal Analyst 3100) was used. Helium gas was used as the purge gas (30 mL/min) and nitrogen gas was used as the carrier gas (100 mL/min). The sample was sealed in an aluminium sample pan using an empty aluminium pan with cap as a reference. The data were collected at a heating and cooling rate of 2 °C/min. Samples were cooled to –70 °C then heated to 200 °C, cooled to 30 °C (first run) heated to 200 °C and cooled to 25 °C (second run). The first run erased the sample's thermal history from the compression molding. Only the data from the second run was used for analysis. Some samples were tested twice to determine the test's repeatability. The T_c and T_{co} temperatures were within 1° and the crystallinity within 5%. The stability of any particular system was determined after comparing the crystallisation enthalpy and the temperatures of the first and second cooling curves. Enthalpies of melting and crystallisation, along with the respective temperatures, were obtained using peak integration based on the assumption that ΔH of PP and MAPP is 180 J/g when they are 100% crystalline [9].

Brunauer, Emmett and Teller (BET) surface area analysis

BET surface area analysis was carried out to find the available surface area and porosity of the RHA. The BET surface area value was used to calculate the surface OH number of RHA. A Micrometrics ASAP 2000 surface area analyzer was used to determine the surface area of RHA using isothermal adsorption of nitrogen. The dry sample of RHA was evacuated of all gas and cooled to a temperature of –196 °C, in liquid nitrogen. At this temperature, N_2 was physically adsorbed on the surface of the sample. An adsorption isotherm is usually recorded as volume of gas adsorbed (cc/g @ STP) versus relative pressure (i.e., sample pressure/saturation vapour pressure). The BET multipoint equation (Eq. 1) was used to calculate the specific total surface area. The resultant value mentioned later was then used to calculate the OH number per gram.

$$\frac{1}{W[(P_0/P)-1]} = \frac{1}{W_m C} + \frac{(C-1)}{W_m C}\frac{P}{P_0} \tag{1}$$

where P/P_0 is the relative pressures of adsorption/desorption of nitrogen isotherms at liquid nitrogen temperature and ranges from 0.05 to 1.0, W is the weight of nitrogen adsorbed at a given P/P_o, and W_m the weight of gas to give monolayer coverage and C, a constant that is related to the heat of adsorption. A linear relationship between $1/W[(P_o/P)-1]$ and P/P_0 is required to obtain the quantity of nitrogen adsorbed.

Thermo-gravimetric analysis

TG studies were carried out to estimate the surface OH number of RHA, measure the sample purity and study the silanation efficiency. A Perkin Elmer TG analyzer (TGA7/TAC7DX with Pyris software version 3.81) was used.

Milligram samples (5–10 mg) of silica ash were carefully loaded into a pan and subjected to a constant heating rate of 10 °C/min from 50 °C to 800 °C in an inert atmosphere (N_2). Weight loss against temperature was recorded. Automated baseline correction was used, and the fractional weight loss between two given temperature points was found graphically. Two runs of the same sample of similar mass were run to check repeatability. Weight loss accuracy was found to be 2%. The sample weight loss between 350 °C and 800 °C corresponds to the amount of condensation water lost from OH groups, and these can be used to calculate the number of the OH groups [2, 12, 13]. Because the condensation of two OH groups gives one water molecule, the number of OH groups can be calculated as per Eq. (2) [2].

No. of Silanol groups/ (nm^2),

$$n = \frac{2b * 1,000}{3XW} \tag{2}$$

where X = BET surface area (m^2/g), W = weight of the samples, b = mass of water due to OH condensation.

The assumption with this method is that all OH groups are adjacent and/or in the close vicinity of each other to be able to react and condense to water molecules. The real OH numbers might be slightly higher accounting for the far located OH groups not participating in the condensation reaction. This had not been corrected with our calculated numbers of OH groups.

Results and discussion

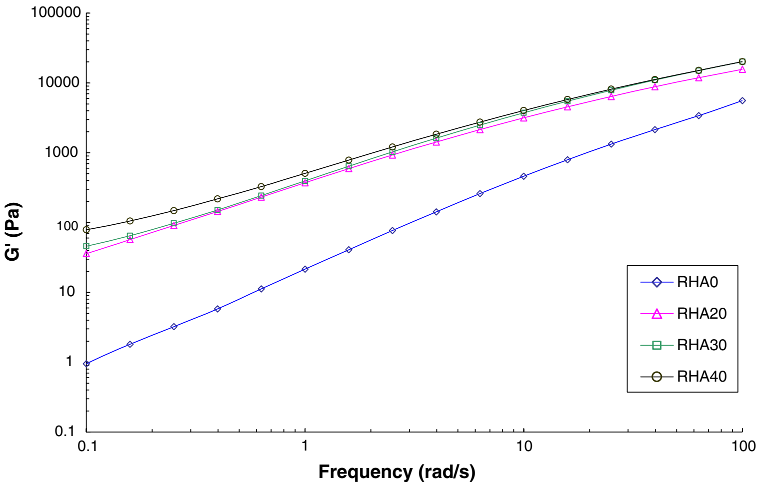
Rheological linear viscoelastic region

In this study, a rotational viscometer with a parallel disc configuration was chosen to examine the rheological behaviour of the composites. The advantage of using the parallel plate geometry is that it can be used for filled polymer systems of extremely high viscosity and elasticity. The oscillation method can be used to study the dispersion of filler in the matrix and the elasticity of the composites [7]. All oscillatory testing as a function of frequency was conducted within the linear viscoelastic range. The linear viscoelastic region of all samples in this study was determined prior to dynamic shearing at the temperature of 210 °C. The linear viscoelastic region for PP was found to be up to a strain of 15%, and for 20, 30 and 40 phr composites, it was up to 7%. APS silanated samples of 1, 1.5 and 2 phf were similar to the non-silanated samples. The maximum of the linear viscoelastic region of the samples with MAPP ranged between 5% and 9% and hence tests were carried out at strains lower than this.

Effect of filler loading on rheological properties

The G′ was obtained from the frequency sweep tests. Figure 1 shows the variation of G′ with frequency for RHA-filled PP with increasing filler loading at temperature of 210 °C. It can be seen that G′ increases significantly with the addition of 20 phr filler over the studied frequency range, as expected. However the increase in G′ with filler load was not linear and similar results were obtained for 20, 30 and 40 phr. The optimum used in this study is 20 phr. Son et al. [14] and Maiti and Hassan [15] observed similar results in wood flour filled PP, where the viscosity and elastic response with increasing filler loading increased up to a certain loading and plateaued thereafter over the frequency range studied. The polymer melt viscosity of a composite initially increases due to the obstruction to deformation produced by filler particles [7]. However, they also introduce discontinuities into the polymer matrix and the number of discontinuities increases with increase in filler loading. Above a particular filler level (the threshold level) an excess of discontinuities would occur, and this

Fig. 1 G′ plotted as a function of frequency for different loadings of RHA at 210 °C



could prevent further stress transfer so there would be no further increase in the viscous and elastic response [7]. RHA particles are porous and irregular in shape [2], which might lower the threshold level compared to other fillers.

Effect of silane on rheological properties

RHA is hydrophilic filler and is not compatible with the hydrophobic PP. Surface treatment of RHA was carried out to improve the filler matrix compatibility. Its surface was treated with a di-functional chemical compatibilisers from the silane group. Silanes contain two functional groups on each end capable of undergoing reactions with hydrophilic fillers and hydrophobic thermoplastics and thus act as a bridge connecting filler and matrix. As mentioned earlier the coupling agent used was amino silane "3-aminopropyltriethoxy" APS. This silane is compatible with PP because of it's chemical functionality. Three different concentrations of this silane (1, 1.5 and 2 phf) were used to produce 20 phr RHA composites and the rheological measurements were carried out at 210 °C.

From Fig. 2 below it can be seen that G′ increased with addition of more than 1.5 and 2 phf APS over the frequency range studied. However at 1 phf APS, G′ decreased below the system with no silane. This is attributed to the porosity of the RHA. The silane molecules travelled inside the pores reacting with OH groups in the pores and not available to reach and react with the polymer molecules. Polymer chains being larger molecules could not penetrate in the pores and access silane molecules. This caused a rather lubricating effect reducing the G′ even below the 0 phr APS. When used in higher concentrations of 1.5 and 2 phf, some may have reacted with OHs in the pores but there will be some to react with OH groups on the surface. This led to increase in G′ for higher phf APS and was attributed to enhanced interfacial bonding and restricted dissipation of viscoelastic energy. The data suggest that the saturation concentration for this silane is around 1.5 phf APS, as the graph tends to plateau at 2 phf APS. This suggests that there is a limited number of OHs that is sufficient to undergo reaction with silanols of 1.5 phf silane. This is confirmed by TGA studies as well as rheological studies for systems with MAPP discussed below. Qing Lui et al. [16] suggested that any loosely adsorbed silane could migrate into the polymer matrix and form polymer-filler bonds more readily than tightly bonded silane. It may be that at low concentrations the APS is more tightly bonded to the available OH groups in a single layer on the silica surface while at higher concentrations (≥1.5 phf) APS molecules are more loosely bonded into multiple layers of silane. This would result in stronger bonds between the filler and matrix by loosely bonded silanes being free to migrate into the polymers chains and form entanglement or bonds, so a system with a higher APS level would have a higher viscosity and elasticity. However, with the further increase in the silane concentration to 2 phf, there were no more improvements. This suggests that when there is an excess of silanes molecules to the available OH groups on the tightly bonded silane layer, the tightly bonded layer will no longer be able to hold the loosely bonded layer. This would cause slip between the tightly bonded and excess silane molecules so even if the molecules have migrated to the polymer matrix, it would not enhance the bond between the filler and the matrix. These silanes are more likely to cross link with each other or with the matrix. Further work with TGA was carried out to confirm this.

Effect of MAPP on the rheological properties

MAPP is often used as a coupling agent in composites where PP is the base matrix. The presence of anhydride

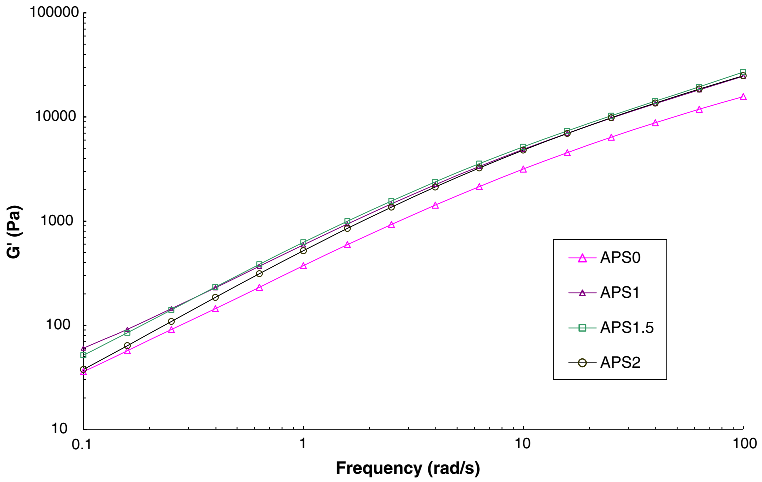


Fig. 2 G′ plotted as a function of frequency for different loadings of APS for 20 phr RHA at 210 °C

groups on the MAPP chain allows for molecular attraction between MAPP and silica surface hydroxyls. The chain also either entangles itself with PP chains and/or chemically attaches itself to PP as they have the same backbone polymeric structure. Addition of MAPP was expected to increase the viscous as well as elastic response of the system by improving the filler-matrix interaction [8]. Three different concentrations of MAPP (2, 3 and 5 phr) and 100% MAPP were used to produce 20 phr RHA composites. Rheological measurements were carried out at 210 °C.

Figure 3, 4 shows that G′ increased significantly with addition of MAPP initially but tended to decrease above 3 phr. The trend was similar for the studied frequency range. This suggests that the saturation concentration of MAPP is ∼3 phr. This is in the lower part of the range recommended by the manufacturer (2–5%) and is lower than the optimum (5%) found by Yuan et al. [8] in a system with 10 phr filler. The low saturation level in the composites under study was attributed to the very low number of OH on the silica surface (0.56 silanols/nm^2 discussed below). So only, a low concentration of MAPP is needed to react with all the available hydroxyls from the RHA surface and any further increase in MAPP concentration causes an excess in the system. Excess MAPP in the system causes a decrease in η^* and G′ because MAPP is a low molecular weight polymer as a result of chain scission occurring during the grafting process [14]. This is more clearly shown in Fig. 3 by the lowest values of η^* and G′ being found for the 100% MAPP sample.

Thermal analysis and surface area analysis results

Effect of RHA on the crystallisation

From Table 1, below, it can be seen that the crystallisation temperature (T_c) of PP is $T_c \sim 127$ °C. This is within the range of published values [10, 11]. Addition of RHA in the system increased the T_c of PP to ∼130 °C. The degree of crystallinity of the composites decreased with increasing filler loading, as expected, linearly ($R^2 = 0.97$) or quadratically ($R^2 = 0.99$) when normalised for filler loading. Similar results were observed by other researchers where crystallinity decreased for systems of filled PP with

Fig. 3 G′plotted as a function of frequency for different loadings of MAPP for 20 phr RHA at 210 °C

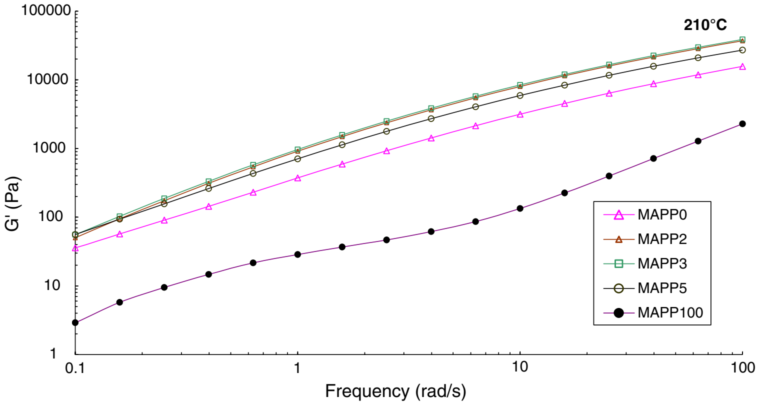


Fig. 4 TGA of untreated silica ash and 1, 1.5, 2 phf APS treated silica ash at inert atmosphere

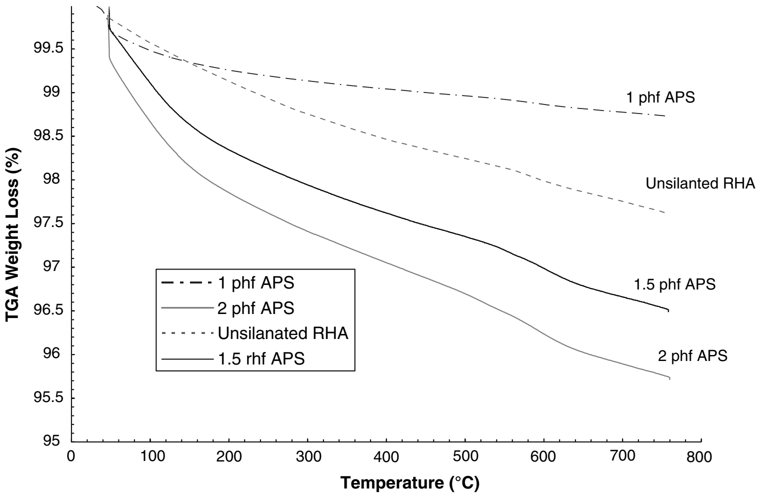


Table 1 Summary of results from DSC studies

Sample name		% crystallinity	T_{co} (°C)	T_c (°C)
Pp	100%	51.4	131.6	126.9
MAPP	100%	36.6	132.6	129.0
MAPP:PP	5–95	34.05	132.51	128.3
phr RHA				
20 RHA	20	33.0	133.8	130.0
30 RHA	30	25.7	132.3	129.1
40 RHA	40	22.3	134.6	130.6
Phr MAPP (20 phr RHA)				
20 RHA	0	33.0	133.8	130.0
2 phr MAPP	2	39.0	138.3	134.0
3 phr MAPP	3	34.2	138.1	133.8
5 phr MAPP	5	35.5	135.9	131.9
phf APS (20 phr RHA)				
20 RHA	0	33.0	133.8	130.0
1 phf APS	1	35.2	133.7	130.3
1.5 phf APS	1.5	35.3	132.4	129.1
2 phf APS	2	31.7	133.0	129.6

increasing loading of $BaSO_4$, $CaCO_3$, talc and fumed silica [11]. The decrease in crystalline phase was attributed to it being a highly filled system; the motions of polymeric chains are limited by the presence of filler. The change in the onset temperature of crystallisation T_{co} is a good indicator of the nucleation effect of the fillers [11]. Table 1 shows that adding 20 phr RHA to PP increased the T_{co} as well as the T_c, but increasing RHA further had no further significant effect. This indicates that the RHA is a nucleating agent at low loadings (<20 phr). The change was only a few degrees so it can be considered to be only a weak nucleating agent. This can be attributed to the incompatibility of polar hydrophilic filler and a hydrophobic matrix leading to weak interfacial adhesion. With increased concentration of RHA from 20 to 40 phr, the nucleation efficiency is worsened due to increased polar hydrophilicity and increased interparticle interaction.

Effect of coupling agents on the crystallisation

Surface treatments/coupling agents were added to improve the surface adhesion of PP and RHA. Cocrystallisation is the driving force of compatibilisation between crystalline/crystalline components of the same kind [8]. This suggests that PP segments of MAPP will form miscible blends with the PP through cocrystallisation. The thermal properties of PP, MAPP and blend of MAPP/PP (5:95) were measured (Table 1). The results for T_c, T_{co} and % crystallinity for PP and MAPP were very similar to literature values [17]. With the addition of only 5 phr MAPP to PP, the degree of crystallinity reduced significantly and the T_{co} and T_c increased. This indicates a nucleation effect suggesting that anhydride groups hinder the chain mobility by cross linking or entanglement.

Addition of MAPP into the composite of RHA/PP increased rate of crystallisation as T_{co} and T_c were increased significantly for all MAPP concentrations when compared to 0 phr MAPP. The increase with 2 and 3 phr MAPP was attributed to an increased interaction between the RHA and PP promoting faster crystallisation [8]. The degree of crystallinity of the system also increased significantly with addition of 2 phr MAPP. This was attributed once again to the low OH groups available on RHA surface, which is sufficient for the MAPP concentration of up to 2 phr. There was a plateauing effect with increasing MAPP concentration up to 5 phr, while the 100% MAPP sample had a lower T_{co} and $T_{c.}$ The decrease in T_c and T_{co} with the increase from 5% to 100% MAPP samples was attributed to the anhydride groups in MAPP. An excess of anhydride groups (during melt mixing) allows them to react with each other causing cross linking and entanglements [8].

The degree of crystallinity increased with addition of APS then decreased: the maximum was around 1 phf (Table 1). This may be attributed to the low OH numbers of RHA, sufficient up to around 1.5 phf APS. The excess silanols in the 2 phf APS sample may crosslink, inhibiting chain motion and decreasing crystallinity. However, there was no significant effect on T_c and $T_{co.}$ This suggests no significant increase in interaction between filler and polymer, suggesting this coupling agent is not effective in this system. It is unusual for surface treating agents to have no effect on T_c and T_{co} but Valesco et al. [10] observed similar results for one system of talc filled PP.

TGA and surface area analysis results

Silanation efficiency

TGA was carried out on silane treated and untreated silica ash. Weight loss was used to calculate surface OH group

Table 2 Summary of results from TGA

phf APS	Total weight loss %	First stage (% weight loss)	Second stage (% weight loss)
	50–760 °C	50–250 °C	500–750 °C
0	2.4	0.98	0.61
1	1.3	0.5	0.22
1.5	3.5	1.56	0.81
2	4.3	1.74	0.93

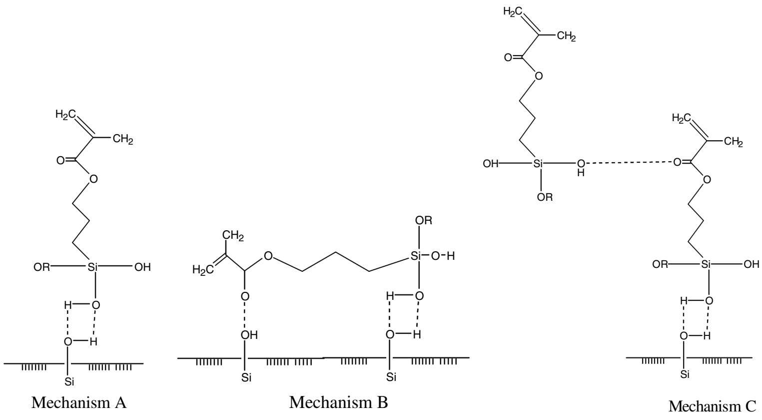


Fig. 5 Different mechanisms of silanes reacting to the silica surface (Redrawn from Lui et al. [16])

density per area, and the difference between the untreated and silane treated RHA was used to determine the silanation efficiency. The results are tabulated in Table 2. Figure 4 is a thermogram of untreated and silane treated silica ash in the inert (N_2) atmosphere. BET surface area measurements were carried out and used to calculate the OH number per gram.

The weight loss of RHA in an inert atmosphere tends to occur in two stages. The first stage (50–250 °C) weight change is due to the loss of physically absorbed water molecules and the second stage (500–750 °C) is due to loss of chemically made water molecules from the condensation reaction of two silanol (OH) molecules from the RHA surface [2]. The surface silanol group density for the untreated silica ash was calculated as described in the method section and it was found to be 0.56 OH groups/nm^2. This is low compared to previously reported silanol numbers of 9, 4.5 and 16/nm^2 for fumed and precipitated silica and another type of silica ash, respectively [2].

The silanol number per gram based on the BET surface area (49 m^2/g) for the silica ash used in this study is $32 \times 10^{18}/g$. This is also low compared to the previously reported silanol number of $320 \times 10^{18}/g$ for another silica ash, one with a coarser structure, with a surface area of 29 m^2/g and to $450 \times 10^{18}/g$ and $900 \times 10^{18}/g$ reported for precipitated and fumed silica respectively with surface areas in the range of 150–300 m^2/g [2]. Hence, it was concluded that this silica ash has a significantly lower number of silanol groups on its surface than other silicas.

There was an increase in the weight loss with increasing silane concentration for most samples. The weight change for the silanated samples also mainly occurred in two stages. The first weight change (50–250 °C) was attributed to the loss of physically adsorbed water as well as loosely adsorbed silane and increased with increase in silane concentration. The second stage weight change at around 500–750 °C was attributed to the condensation of silanol groups present in silane molecules that were loosely absorbed onto RHA surface.

The 1 phf APS sample showed a decrease in weight loss compared to the untreated sample. A decrease in the second stage weight loss of silane treated RHA might indicate that the OH groups had undergone a reaction with silane functional groups and hence were no longer available for a condensation reaction. However, these groups may also take up moisture and/or interact among themselves to neutralize one another and cause filler agglomeration.

The second stage weight loss of the 1 phf APS was also lower than the 1.5 and 2 phf APS samples. This is consistent with the rheological behaviour for the same sample that found a plateau at ~1.5 phf APS and further suggests that the 1 phf APS sample is more tightly bonded. This variation in behavior depends on how the silane reacts with the silica. Lui et al. [16] postulated that APS can be adsorbed onto the surface of silica from solvent in three possible forms (Fig. 5), i.e., through hydrogen bonding between silanol groups of APS and silica (mechanism A), through hydrogen bonding of C=O and silanol groups (mechanism B), or by forming multilayers through hydrogen bonding (mechanism C). At lower silane concentrations, silane molecules will be adsorbed onto the surface of silica mainly via mechanism A or B. With increased silane concentration, form C occurs more readily where the upper layer of multilayer silane is only loosely bonded. In the case of the 1 phf APS samples after drying at 85 °C temperature, the surface hydrogen bonded silane (mechanism A) may be converted to covalently bonded silane through the condensation between silanol groups of the silane and the surface silanol group of the silica. This covalently attached silane would then be part of the tightly bonded silane to the RHA surface.

The 1.5 and 2 phf APS samples had a higher weight loss than the 1 phf APS, in the second stage of 500–750 °C, which was attributed to the condensation reaction between the silanol groups of the loosely bonded silanol, suggesting that they have a combination of tightly and loosely bonded silanes.

Conclusions

In this research, the effect of RHA as filler in PP matrix was studied. From its interaction with the matrix and the rheological response of the composite, RHA can be environmentally friendly filler at end-of-use in polymeric materials to minimise environmental pollution rather than produce strong reinforcing.

The system is not compatible as RHA is hydrophilic and PP is hydrophobic. To improve the interfacial compatibility, two types of coupling agents, amino propltriethoxy silane and maleic anhydride grafted polypropylene were used. The effect of the RHA on the PP matrix and its coupling efficiency with the coupling agents were studied using a parallel plate rotational rheometer, TGA and DSC.

The following conclusions were drawn:

- The rheological properties and storage modulus (G′) increase with the addition of RHA across a range of frequencies. A plateau was reached at 20 per RHA.

Addition of coupling agents generally increases the rheological properties suggesting they increase interaction between PP and RHA. Silane increases G′ up to 1.5 and MAPP up to 3 MAPP, which is a relatively low level, attributed to low OH numbers. G′ decreases significantly thereafter, attributed to slip in silanated samples and low molecular weight in MAPP samples.

- DSC studies show that the addition of RHA to PP reduces the degree of crystallinity, attributed to filler particles limiting chain mobility. However, RHA increases the crystallisation rate so it is a weak nucleating agent at low concentrations.

Addition of APS increases the degree of crystallinity only at low concentrations. It had no effect on crystallisation rate. Addition of MAPP increased the degree of crystallinity at low concentration, the optimum being at 2 phr MAPP. It also increased the crystallisation rate at low levels.

- The increased rheological properties and effects on crystallinity and crystallisation rate with addition of silane and MAPP to PP/RHA composites suggests enhanced interaction between filler and polymer. MAPP had more effect than the silane, suggesting it is the better coupling agent. Effects were more pronounced at low concentrations.
- TG studies were used to determine the OH numbers on the RHA surface as well as in understanding the bonding mechanism of silane molecules to RHA. The OH number was estimated to be 0.56 OH/nm^2. This is lower than values published for other grades of silica. Composites with low silane levels had significantly lower weight loss than other samples suggesting silane formed a tightly bonded layer onto the RHA surface by reacting with OH groups. In composites with higher silane levels, the tightly bonded layer was topped with a loosely bonded layer reacting mainly with the silanol groups of the tightly bonded silane layer. The low optimum silane level of one phr filler is consistent with the low OH numbers on RHA.
- The effect of coupling agents is more pronounced at lower concentrations, both for rheological and thermal properties. For APS, the optimum is 1.5 phf, for MAPP 2–3 phr. These relatively low levels reflect the low OH numbers: the few available OH groups are quickly bonded and the remaining coupling agent becomes excess.

References

1. Kalapathy U, Proctor A, Shultz J (2002) Bioresour Technol 85:285
2. Chaudhary DS (2004) In: School of civil and chemical engineering. Royal Melbourne Institute of Technology, Melbourne
3. Fuad M, Zaini MJ, Ishak ZAM, Omar AKM (1995b) Eur Polym J 31(9):885
4. White JL, Czarnecki L, Tanaka H (1998) Rubber Chem Technol 53:823
5. Boira MS, Chaffey C (1977) Polym Eng Sci 17:715
6. Han CD, Weghe VD, Shete P, Haw JR (1981) Polym Eng Sci 21:196
7. Lozano K, Yang S, Zeng Q (2004) J Appl Polym Sci 93:155
8. Yuan X, Zhang Y, Zhang X (1998) J Appl Polym Sci 71:333
9. Mohanty S, Nayak SK, Verma SK, Tripathy SS (2004) J Reinforced Plastics Compos 23(6):632
10. Velasco JI, De Saja JA, Martinez AB (1996) J Appl Polym Sci 61:125
11. Ren Z, Shanks RA, Rook TJ (2001) J Appl Polym Sci 79(11):1942
12. Mueller R, Kammler HK, Wegner K, Pratsinis ES (2003) Langmuir 19:160
13. Zhao XS, Lu GQ, Whitetaker AK, Millar GJ, Zhu HY (1997) J Phys Chem 101:6525
14. Son J, Gardner DJ, O’Neill S, Metaxas C (2003) J Appl Polym Sci 89:1638
15. Maiti SN, Hassan M (1989) J Appl Polym Sci 37(7):2019
16. Liu Q, Ding J, Chamabers DE, Debnath S, Wunder SL, Baran GR (2001) J Biomed Mater Res 57(3):384
17. Yoon HK, Lee HW, Park OO (1998) J Appl Sci 70:389