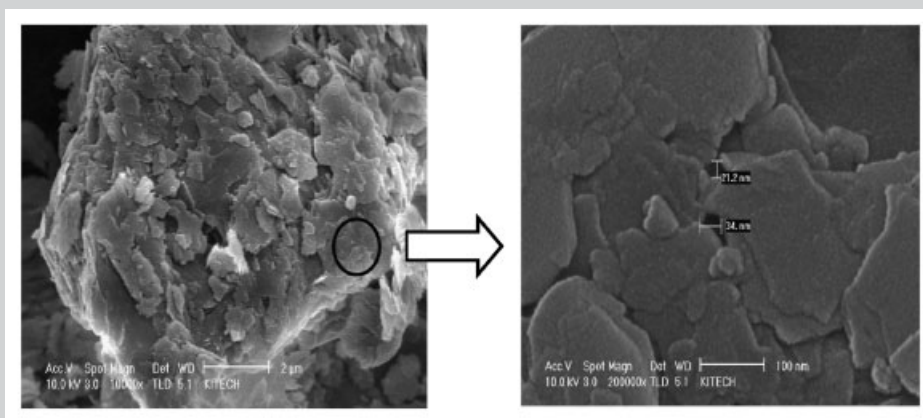**Summary:** This study investigated the physico-mechanical properties, odor and VOC emission of bio-flour filled PP bio-composites with different pozzolan contents. On increasing the pozzolan content, the tensile and flexural strengths of the bio-composites were not significantly changed, whereas the impact strength and water absorption increased slightly and the odor intensity decreased due to the absorption of thermal degradation gases of PP and bio-flour at the pore surface of the pozzolan. The VOC emission of the bio-composites, analyzed by GC-MSD, was mainly due to PP oxidation and the thermal degradation of bio-flour during the extrusion process at high manufacturing temperatures. With increased pozzolan content, other organic compounds of the bio-composites were not significantly changed, but the toluene emission of the bio-composites was decreased. SEM and SEM/EDX mapping techniques were employed to investigate the porous form and the pozzolan distribution in the bio-composites. From these results, we concluded that the addition of pozzolan in the bio-composites was an effective method for reducing their odor and VOC emission without any reduction in mechanical properties.

SEM micrograph of pozzolan (10 000×).

Physico-Mechanical Properties, Odor and VOC Emission of Bio-Flour-Filled Poly(propylene) Bio-Composites with Different Volcanic Pozzolan Contents

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Introduction

Recently, with increasing environmental awareness and expanding global waste problems, eco-friendly bio-fillers have been increasingly recognized as a promising alternative to inorganic fillers in the reinforcement of thermoplastic and biodegradable plastics.[1,2] Bio-fillers have several advantages compared to inorganic fillers, such as a non-hazardous nature, low cost, low density, low energy manufacture (low CO_2 emission), renewability and biodegradability.[1−3] These bio-filler filled thermoplastics and biodegradable plastic composites, commonly called bio-composites and eco-composites, are experiencing fast growth in various applications such as automotive parts, outdoor decking products, window and door frames, consumer products, and so on.[3−5] However, the mechanical and thermal properties of bio-composites remain insufficient to meet the strength requirements of many industrial applications. Therefore, many studies have attempted to improve the mechanical properties and adhesion between bio-fillers and matrix polymers of bio-composites.[1,6] In addition, the importance of reducing the odor produced when bio-composites are used for final material applications has been increasingly recognized. In the melt mixing process of bio-composites using a twin screw extruder, the carbonization odor of the bio-composites is generated due to the high manufacturing temperatures of over 200 °C, which exceed the low degradation temperature of the bio-fillers.[7] Although the manufacturing temperature of the bio-composites is determined by the melting temperature (T_m) of the matrix polymer, this temperature is typically set about 10–30 °C higher than the matrix polymer T_m in order to obtain a smooth mixing process between the bio-fillers and matrix polymers, which is otherwise a problem due to the low compatibility of the two materials.[8] Therefore, obtaining the proper temperature settings in the twin-screw extrusion manufacturing process for bio-composites is important in order to reduce the odor production of bio-composites under the high temperature of the manufacturing process. In recent years, there have been few studies on reducing odor and volatile organic compound (VOC) emission of bio-flour filled thermoplastic bio-composites. With increasing concerns about indoor air quality (IAQ), building and interior materials have become widely recognized as important sources of VOC emissions that contribute to problems of indoor air pollution.[9] The application of bio-composites for building and automotive interior materials has therefore widely increased.[3−5] The VOC emission and odor pro-

duction of bio-composites is therefore an important factor in their increasing applications as building and automotive interior parts. In the present study, we used volcanic pozzolan as an additive to reduce odor production during the manufacturing process and to reduce the VOC emission of the bio-composites. Pozzolan materials can be used in their natural volcanic ash form or as various artificially produced substances resembling pozzolan ash which have been used throughout the world to make good quality concrete systems in recent years.[10,11] Volcanic pozzolan is poorly crystallized in a porous form that is rich in SiO_2 and Al_2O_3, and is highly water absorbent.[11] Therefore, we can expect that the porous form of volcanic pozzolan will absorb the odor and VOCs generated by bio-composites.

The aim of this study was to investigate the physico-mechanical properties, odor and VOC emission of bio-composites with different volcanic pozzolan contents. We compared the mechanical properties, water absorption and odor emission of pozzolan-treated and non-treated bio-composites. In particular, we measured the VOC emission of the bio-composites with different volcanic pozzolan contents using a gas chromatograph coupled to a mass selective detector (GC-MSD). The dispersion of volcanic pozzolan in the bio-composites was analyzed by scanning electron microscopy (SEM) with energy dispersive X-ray microanalysis (SEM/EDX). To reduced odor production and VOC emission of the bio-composites, we ascertained the optimum pozzolan content.

Experimental Part

Materials

The bio-flours used as the reinforcing filler were rice husk flour (RHF) and wood flour (WF), obtained from Saron Filler Co. and Dongyang CMI Co., South Korea, respectively. The particle size of RHF was 860 to 270 μm and that of WF was 110 μm. Poly(propylene) (PP) was supplied by Hyosung Co., South Korea, with an MFI of 1.7 g · (10 min)$^{-1}$ (190 °C · (2 160 g)$^{-1}$) and a density of 0.91 g · cm^{-3}. Maleic-anhydride-grafted PP (MAPP) was obtained from Eastman Chemical Products, Inc., in the form of Epolene G-3003, which has an acid number of 8 and a molecular weight of 52 300. Pozzolan in volcanic pozzolan ash form and with a particle size of over 70 μm was obtained from AutoWin Co. The chemical composition of pozzolan was determined using an X-ray fluorescence spectrometer (Shimadzu XRF-1700, Japan). Table 1 shows the chemical composition of pozzolan. This tables indicates that pozzolan has a high concentration of SiO_2

Table 1. Chemical composition of pozzolan as percent by weight.

Element	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	LOI[a]
Pozzolan	59.5	17.7	0.9	7.6	1.3	0.2	0.08	4.7	0.1	0.08	5.0

[a] Loss on ignition.

Physico-Mechanical Properties, Odor and VOC Emission of Bio-Flour-Filled Poly(propylene)...

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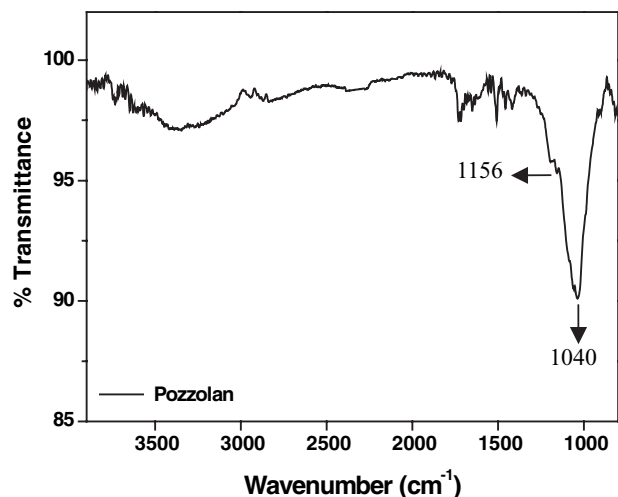Materials and Engineering 1257

Figure 1.   FT-IR spectrum of pozzolan.

and Al_2O_3 elements. FT-IR spectra of pozzolan were obtained using a Thermo Nicolet Nexus 870 FT-IR spectrophotometer from the USA. Figure 1 shows the FT-IR spectrum of the pozzolan. The absorption bands in the region of 3 600–3 100 cm^{-1} were assigned to hydroxyl (OH) groups bonding to the silicon of pozzolan.[11] The absorption band at 1 040 cm^{-1} was attributed to the Si–O(Al)–O vibrations of pozzolan. The shoulder absorption band in the 1 156 cm^{-1} region was due to amorphous silica.[12] These results were confirmed by the functional groups of pozzolan.

Compounding and Sample Preparation

RHF, WF and pozzolan were oven dried at 105 °C for 24 h to adjust the moisture content to 1–3% and then stored in sealed polyethylene bags before compounding. PP was blended with the RHF, WF and volcanic pozzolan in a laboratory-sized, co-rotating, twin screw extruder using three general processes: melt blending, extrusion and pelletizing. The extruder barrel was divided into eight zones with the temperature in each zone being individually adjustable. The temperature of the mixing zone in the barrel was maintained at 190 °C with a screw speed of 250 rpm. The extruded strand was cooled in a water bath and pelletized using a pelletizer. Extruded pellets were oven dried at 80 °C for 24 h and stored in sealed polyethylene bags to avoid unexpected moisture infiltration. The mixtures were prepared with 30 wt.-% filler loading to incorporate the pozzolan at a loading of 0.5, 1 and 3%. Also, to enhance inter-facial adhesion, the 30 wt.-% filler loading was prepared with 1% pozzolan and incorporating 3% MAPP. Extruded pellets were injection molded into tensile (ASTM D638), Izod impact (ASTM D256) and three-point bend test bars (ASTM D790) using an injection molding machine (Bau Technology, South Korea) at 190 °C with an injection pressure of 1 200 psi and a device pressure of 1 500 psi. After injection molding, the test bars were conditioned before testing at 50 ± 5% RH for at least 40 h according to ASTM D 618–99.

Mechanical Property Tests on Bio-Composites

The tensile test for the bio-composites was conducted according to ASTM D 638-99 with a Universal Testing Machine (Zwick Co.) at a crosshead speed of 100 mm · min^{-1} and a temperature of 24 ± 2 °C. Notched Izod impact strength was measured on an impact tester (Dae Yeong Co.) by ASTM method D 256-97 at room temperature. The three point bend tests of the bio-composites were carried out in accordance with ASTM D 790. The specimen had a span to depth ratio of 16:1. The bio-composites were tested at a crosshead speed of 5 mm · min^{-1}. Five measurements were conducted and averaged for the final result.

Water Absorption Test for Bio-Composites

Rectangular specimens with a size of $37 \times 12 \times 3$ mm^3 were used in the water absorption tests. Samples were immersed in distilled water at 25 °C for up to 47 d. At each testing time, the samples were removed from the water and patted dry. The mass change of samples was recorded using an electronic balance at each testing time. The water absorption of the bio-composites was obtained from the weight difference and was reported as the percentage increase in the initial weight.

Odor Intensity Test for Bio-Composites

To measure the odor intensity of the bio-composites, extruded pellets (150 g) were stored in sealed polyethylene bags according to their different volcanic pozzolan contents. The odor intensity was measured at room temperature and 80 °C after 1 h using the extruded pellets. The odor intensity was measured using five selected people who smelled each extruded pellet in the sealed polyethylene bags. The odor emission scale used to measure the odor intensity of the bio-composites is presented in Table 2. Five measurements were conducted with each sample and averaged for the final result.

Table 2.   Odor emission scale to measure the odor intensity of the bio-composites.

	High			Middle			Low		
	High	Middle	Low	High	Middle	Low	High	Middle	Low
Point	9	8	7	6	5	4	3	2	1

High odor emission

Low odor emission

GC-MSD Analysis

The GC-MSD analysis of bio-composites was performed on a CP-3800 gas chromatograph/Saturn 2000 MSD with a CP SIL 5CB capillary column. Helium was used as the carrier gas with a flow rate of about $1.2\,ml \cdot min^{-1}$. The oven temperature of the GC was initially held at 35 °C for 5 min, then raised to 250 °C at a rate of $8\,°C \cdot min^{-1}$ and maintained at that temperature for 30 min. The bakeout time was increased to 30 min with a constant temperature of 200 °C. MS acquisition parameters included scanning from $m/z = 30$–650 amu in the electron impact (EI) mode automatically. The seven bio-composites were stored in odorless polyester bags containing injected, high quality, nitrogen gas and maintained at room temperature for 24 h, after which the VOC emission of the bio-composites was analyzed by GC-MSD.

SEM/EDX Analysis

SEM was used to measure the porous surfaces of the pozzolan using a SIRIOM scanning electron microscope (FEI Co.) from the USA. In addition, a SEM equipped with an EDX elemental composition analyzer was used to analyze the bio-composites with 3% pozzolan content. The acceleration potential used during this investigation was 20 kV. The total scanning time during elemental map generation was 20 min. Prior to the measurement, the specimens were coated with gold (purity, 99.99%) to eliminate electron charging. The elements C, O, Al and Si were selected for mapping on the basis of the data obtained in single particle analysis. The images showed the distribution of C, O, Al and Si elements of pozzolan in the bio-composites.

Results and Discussion

Mechanical Property Tests

Figure 2(a) and 2(b) show the tensile and flexural strengths of PP-RHF and PP-WF bio-composites with different pozzolan contents. On increasing the pozzolan content, the tensile and flexural strengths of the bio-composites were not
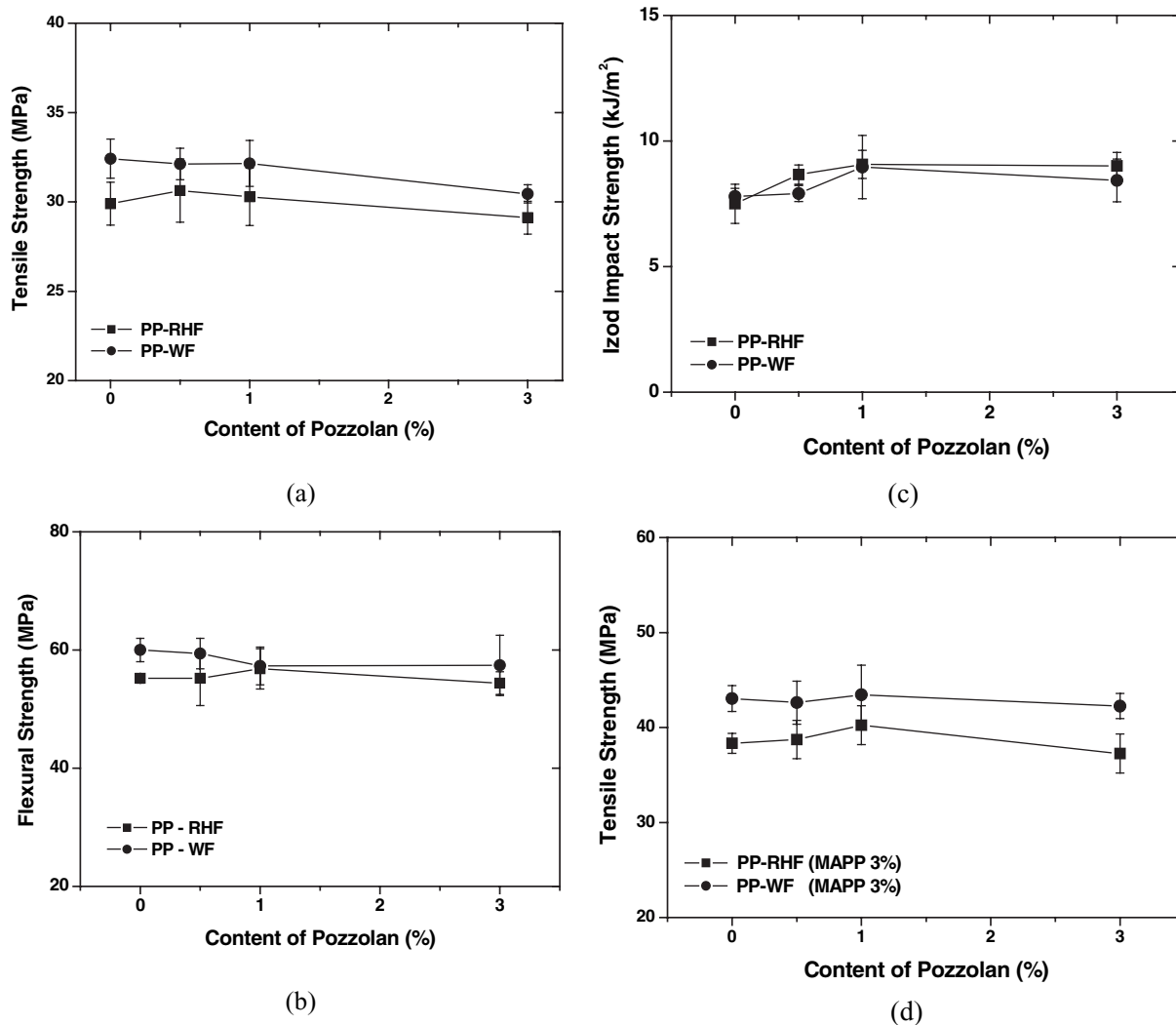

Figure 2. Tensile strength (a), flexural strength (b), Izod impact strength (c) and tensile strength of non-treated and MAPP-treated (d) RHF and WF filled PP bio-composites at different pozzolan contents.

significantly changed. However, at 3% pozzolan content, the tensile strength of the bio-composites was slightly decreased. This was mainly attributed to the low compatibility and interfacial interaction between hydrophilic pozzolan and hydrophobic PP matrix. The Izod impact strength of bio-flour filled PP bio-composites with different pozzolan contents is shown in Figure 2(c). With increasing pozzolan content, the impact strength of the bio-composites slightly increased, possibly due to the pozzolan preventing crack propagation on impact.[12] Therefore, more energy was required to fracture the impact specimen with increasing pozzolan content.

The tensile strength of MAPP-treated bio-composites with different pozzolan contents is shown in Figure 2(d). As seen in Figure 2(a) and 2(d), the tensile strength of MAPP-treated bio-composites was much higher than that of non-treated bio-composites. This was due to enhanced compatibility and interfacial adhesion between the bio-flour and the matrix polymer. The excellent tensile strength of MAPP as a compatibilizer in the bio-flour filled PP bio-composites could be attributed to the ability of MA to react with the OH groups of the bio-flours and the high compatibility of the MA-grafted PP copolymer chains with the PP matrix.[1,8,13] To increase the industrial application of bio-composites, the most important factor is gaining good mechanical properties and interfacial adhesion between the two phases. Furthermore, the tensile strength of MAPP-treated bio-composites was not affected by pozzolan content. Therefore, we could conclude that the addition of pozzolan in the manufacturing process to reduce odor emission and VOC emission of the bio-composites did not affect the mechanical properties of the bio-composites.

Water Absorption Test

Figure 3 and 4 show the effect of pozzolan on the water absorption curves of PP-RHF and PP-WF bio-composites
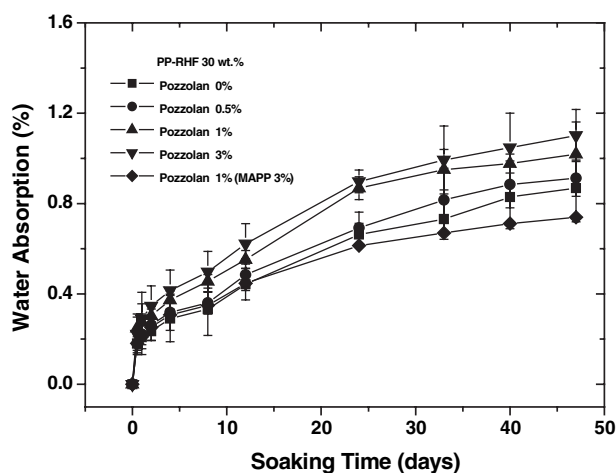

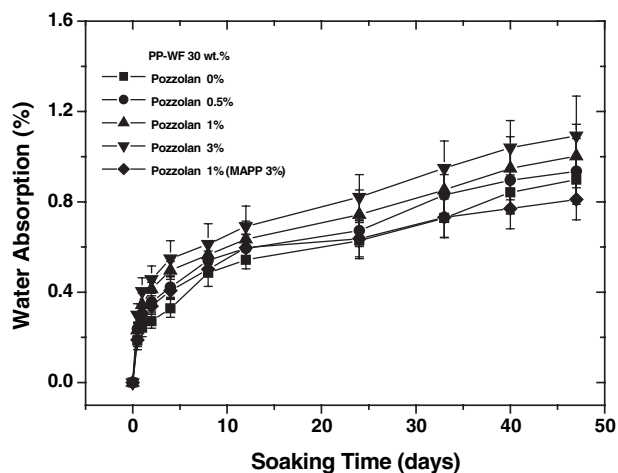Figure 3. Water absorption curves of RHF filled PP bio-composites.

Figure 4. Water absorption curves of WF filled PP bio-composites.

over a period of 47 d. The water absorption is related to its rate of diffusion into the bio-composites.[14] As seen in Figure 3 and 4, the water absorption of bio-composites was very low due to the encapsulation of the hydrophilic bio-flour and pozzolan by the hydrophobic matrix polymer. With increasing water absorption time, a rapid rate of water absorption was observed for all the bio-composites during the first days of soaking, but this rate decreased gradually afterwards and reached a plateau.[15] The increased water absorption of the bio-composites was firstly due to hydrogen bonding between the hydroxyl (OH) groups present in the bio-flour and the water molecules, and secondly to the diffusion of water molecules into the bio-flour/matrix interface through voids.[3,8,15] The water absorption of the bio-composites increased with increasing pozzolan content because of the hydrophilic character and porous form of pozzolan.[11] Use of 3% MAPP as a compatibilizer decreased the water absorption of the bio-composites at the same pozzolan loading, which was attributed to the reduced water absorption of the bio-flour due to the ability of the MA group on MAPP to form hydrogen or covalent bonds with some of the free hydroxyl groups of bio-flour.[3]

Odor Intensity Test

Figure 5 presents the odor intensity of PP-RHF and PP-WF bio-composites at room temperature and 80 °C, respectively. We measured the odor intensity of the bio-composites described in Table 2. Odor production of bio-composites can be caused by the matrix polymer or the bio-filler, or by a combination of both. The matrix polymer and compatibilizer (MAPP) can emit unwanted odors, caused by residual monomers or by decomposition products that occur in the production process of bio-composites due to non-optimized heating temperatures.[16] In addition, the bio-flour can emit odors, caused by thermal degradation of
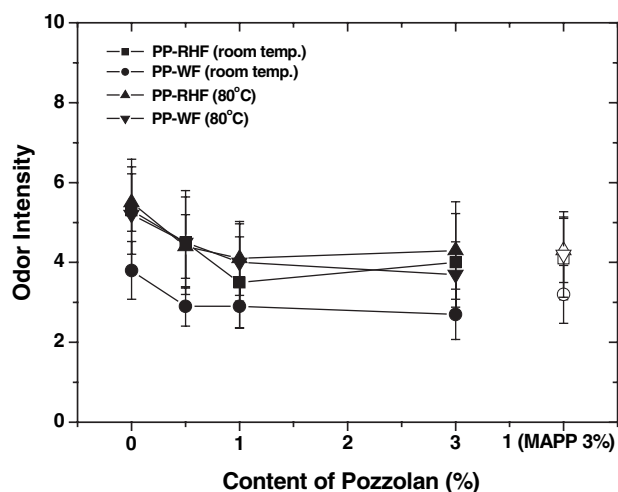
Figure 5. Odor intensity of RHF and WF filled PP bio-composites kept at room temperature and 80 °C for 1 h.

bio-flour surfaces and extruder smoke due to low thermal stability and thermosensitive bio-flour during the high temperature manufacturing process. With increasing pozzolan content, the odor intensity of the bio-composites decreased. This result suggested that the thermal degradation gases from the matrix and bio-flour were absorbed at the pore surface of the pozzolan, thereby preventing them from migrating into the final products.[17] The odor intensity of PP-RHF bio-composites was much higher than that of PP-WF bio-composites at room temperature and 80 °C, indicating that the thermal stability of RHF was lower than that of WF and that RHF produced a larger amount of thermal degradation gases and products than WF during the extrusion process.[18] In addition, the odor intensity of bio-composites at 80 °C was much higher than that of bio-composites at room temperature, due to the increasing odor emission of the matrix and bio-flour at high temperature. The emitted odor of the bio-composites was measured at 80 °C to determine the suitability for application as automotive interior materials in summer environments. Therefore, we could conclude that the reduced odor emission of the bio-composites was an important factor for their application as building interior and automotive interior materials.

GC/MSD Analysis

Table 3 and 4 list the emission levels, as detected by GC-MSD, of various VOCs from the bio-composites with different pozzolan contents at room temperature. The VOC emission of the bio-composites mainly confirmed the oxidation of PP and the thermal degradation of the bio-flour during extrusion in the twin-screw extruder barrel through reaction with oxygen present at high manufacturing temperatures.[19] As seen in Table 3 and 4, acetaldehyde emission of the bio-composites was observed in the range

Table 3. VOC emission levels of PP-RHF bio-composites (unit: ppb).

VOC	Pozzolan content				
	%				
	0	0.5	1	3	1 (MAPP 3%)
Acetaldehyde	3	2	3	3	5
Dichloromethane	1	1	1	2	3
3-Methylfuran	1	0	1	1	1
Ethyl acetate	1	1	4	1	0
Tetrahydrofuran	1	2	1	3	1
Toluene	57	55	40	52	44
Furfural	1	1	1	1	1

1–5 ppb, indicating that the oxidized degradation product of the matrix polymer was produced during the manufacturing process. However, with increasing pozzolan content, the acetaldehyde, dichloromethane, ethyl acetate and furfural emission levels of the bio-composites were not significantly changed. Furfural can be produced from agro-raw or waste materials rich in pentosan polymers such as cellulosic and lignocellulosic materials.[20] Furfural emission was only observed in the PP-RHF bio-composites, indicating that the pentosan polymer of PP-RHF bio-composites was much higher than that of PP-WF bio-composites. The emission of 3-methylfuran and tetrahydrofuran from the PP-RHF bio-composites is listed in Table 3. This could be attributed to hemicellulose degradation products of the bio-composites during the extrusion process.[21] Bio-flour is mainly composed of cellulose, hemicellulose and lignin. Hemicellulose is one of the main constituents of bio-flour and has a low thermal stability and degradation temperature, compared to cellulose and lignin, due to its low molecular weight.[22,23] 3-Methylfuran and tetrahydrofuran emissions were not detected from the PP-WF bio-composites, possibly because the main hemicellulose constituents of RHF and WF are different. In addition, the VOC emission of RHF filled PP bio-composites was detected with greater variety than that of WF filled PP bio-composites. The variation in VOC emissions of PP-RHF bio-composites could be attributed to the higher content of organic acids, pectins, fat, and wax in RHF compared to WF.[7] The toluene emission of the bio-composites clearly decreased with increasing pozzolan content, indicating that the porous structure of pozzolan could absorb the toluene emission of

Table 4. VOC emission levels (ppb) of PP-WF bio-composite.

VOCs	Pozzolan content				
	%				
	0	0.5	1	3	1 (MAPP 3%)
Acetaldehyde	2	2	2	3	1
Toluene	58	56	48	27	40
m-Xylene	49	56	49	50	50

the bio-composites that was generated during the manufacturing process.[11,12] Therefore, our results provide convincing proof that the thermal degradation and oxidation gases and toluene emissions of bio-composites were absorbed by pozzolan, as shown schematically in Figure 6. These results suggest that the addition of pozzolan is an effective method to reduce the toluene emission of bio-composites and that the most effective pozzolan contents were 1% PP-RHF bio-composites and 3% PP-WF bio-composites.

SEM/EDX Analysis

SEM micrographs of pozzolan are presented in Figure 7. The SEM micrograph of pozzolan in Figure 7(a) shows a rough and irregular surface. Figure 7(b) clearly shows the porous form of the pozzolan surface with pore sizes. This porous pozzolan structure was considered to act by capturing and absorbing toluene, thereby reducing the odor emission of the bio-composites during the manufacturing process. These results were confirmed by the reduced toluene and odor emissions of the bio-composites with increasing pozzolan content. Figure 8 and 9 show SEM micrographs and elemental maps of the impact fracture surface of RHF and WF filled PP bio-composites at 3% pozzolan content. The C, O, Al and Si elemental maps of the bio-composites are presented. The C and O elemental signals of the bio-composites were mainly due to PP, RHF and WF. The elements of the PP main chain have a C–C bonding structure. RHF and WF are complex materials consisting of cellulose, hemicellulose and lignin which contain C–C, C–O and C=O bonding structures. In addition, two new characteristic Al and Si elemental signals of the bio-composites were observed due to the poorly crystallized pozzolan material which is mainly composed of SiO_2 and Al_2O_3.[11,12] This result confirmed that pozzolan was well dispersed into the bio-composites. The differences in
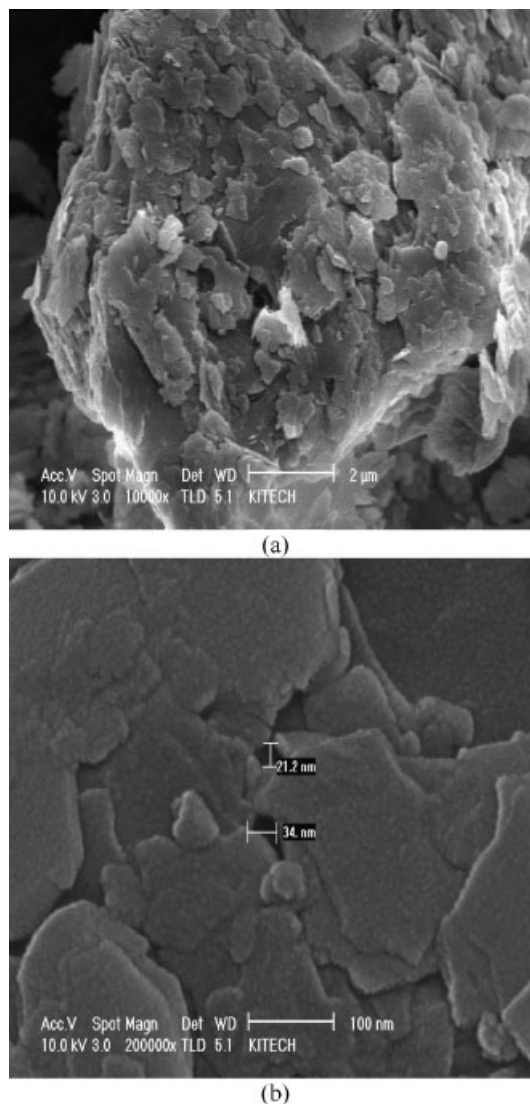

Figure 7. SEM micrographs of the pozzolan: (a) 10 000×; (b) 200 000×.
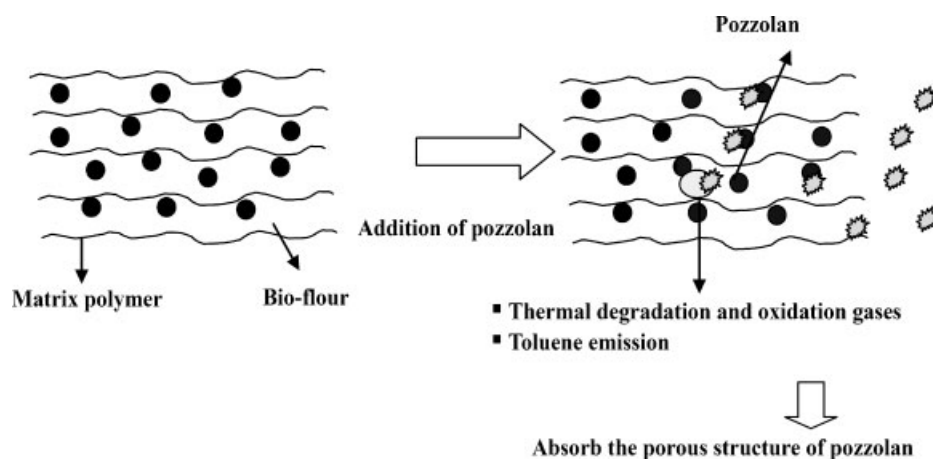

Figure 6. Schematic diagram of the adsorption effect of the porous surface of pozzolan on the thermal degradation and oxidation gases and toluene emission of bio-composites.
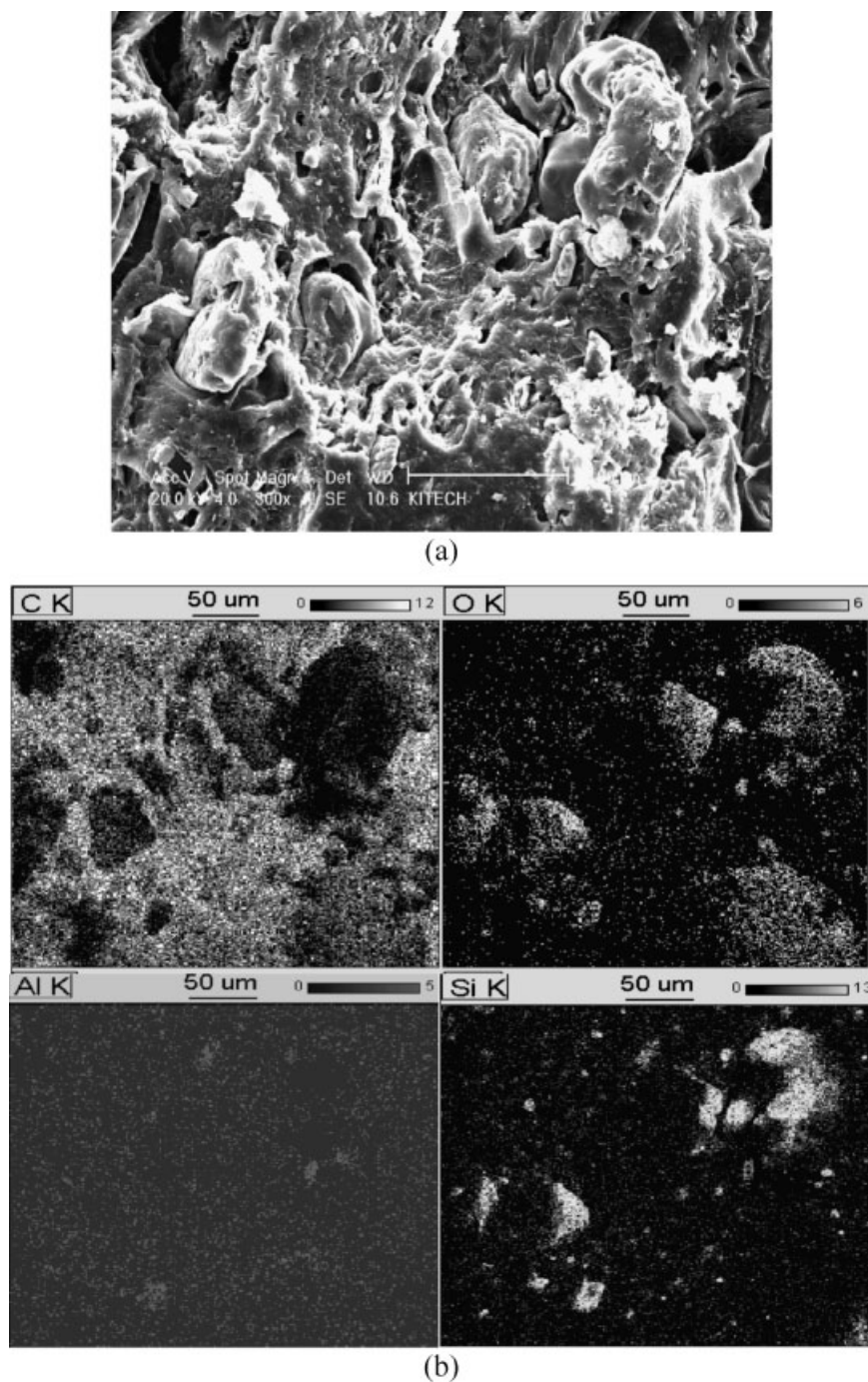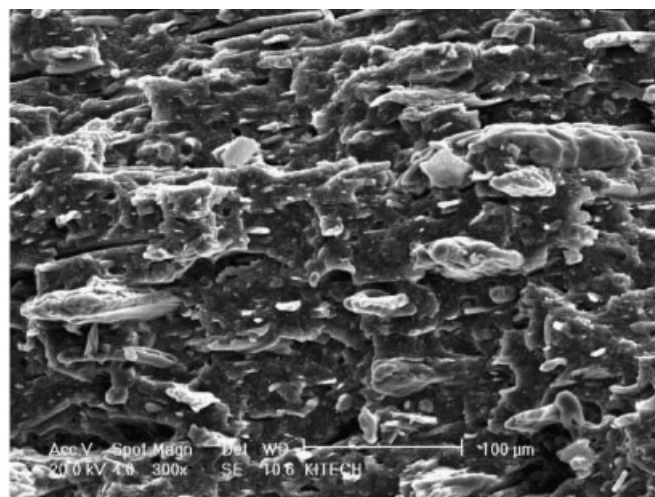
(a)

(b)

Figure 8.   SEM-EDX mapping of the impact fracture surface of RHF filled PP bio-composites: (a) SEM image (300×); (b) EDX mapping of pozzolan.

the elemental map of Si between the RHF and WF filled PP bio-composites were thought to be associated with the difference in the inorganic materials of RHF and WF. RHF is a lignocellulosic material which commonly has a much higher ash content than WF. The RHF ash content was about 10% and mainly consisted of silica (SiO_2: 96%).[13] Due to the high SiO_2 content in the RHF, the Si elemental map of the bio-composites showed considerable variance.
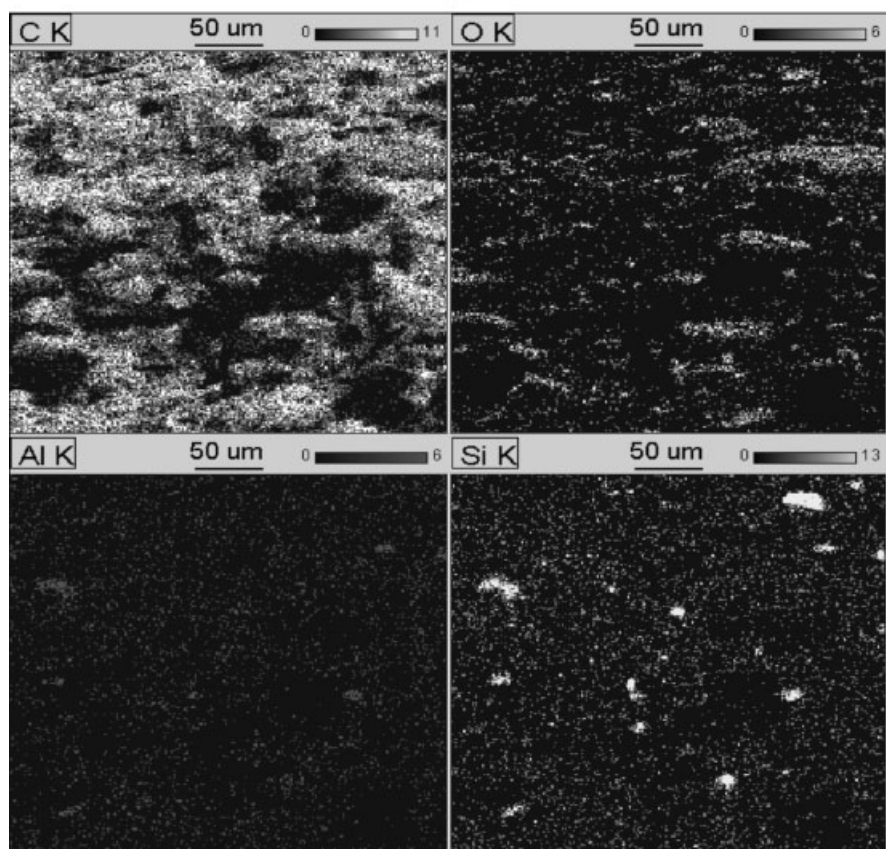
Conclusion

With increasing pozzolan content, the tensile and flexural strengths of the bio-composites and the tensile strength of the MAPP-treated bio-composites were not significantly changed. However, the Izod impact strength of the bio-composites was slightly increased. With the addition of pozzolan in the bio-composites, the water absorption of the

Figure 9.   SEM-EDX mapping of impact fracture surface of WF filled PP bio-composites:
(a) SEM image (300×); (b) EDX mapping of pozzolan.

bio-composites was slightly increased due to the hydrophilic character and porous form of pozzolan. The addition of 3% MAPP as a compatibilizer decreased the water absorption of the bio-composites at the same pozzolan loading, which was attribute to the reduced water absorption of the bio-composites due to the increased interfacial adhesion between the bio-flour and matrix at the interface.

Odor production of bio-composites can be caused by the matrix polymer or the bio-flour, or by a combination of both that can occur in the production process of the bio-composites when run at non-optimized heating temperatures. With increasing pozzolan content, the odor emission of the bio-composites decreased because the thermal degradation gases of the matrix and bio-flour were believed

to have been absorbed at the pore surface of the pozzolan, thereby preventing them from migrating into the final products. The levels of various VOCs emitted from the bio-composites were measured using GC-MSD system. With increasing pozzolan content, the emission levels of other organic compounds of the bio-composites were not significantly changed but the toluene emission of the bio-composites decreased because the porous pozzolan structure was able to absorb the toluene emitted from the bio-composites. The porous form and pore size of the pozzolan surface were confirmed by SEM. Finally, the results from the SEM/EDX analyzer clearly exhibited the two new characteristic Al and Si elemental signals of pozzolan in the bio-composites at 3% pozzolan content. This result provided convincing proof that pozzolan was well dispersed into the bio-composites. The results presented here have clearly supported the addition of pozzolan to bio-composites as an effective method to reduce the odor and VOC emission of bio-composites without any reduction in mechanical properties.

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