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THERMAL PROPERTIES OF BIO FLOUR-FILLED POLYPROPYLENE BIO-COMPOSITES WITH DIFFERENT POZZOLAN CONTENTS

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In this study, the thermal properties of bio-flour-filled, polypropylene (PP) bio-composites with different pozzolan contents were investigated. With increasing pozzolan content, the thermal stability, 5% mass loss temperature and derivative thermogravimetric curve (DTG_{max}) temperatures of the bio-composites slightly increased. The coefficient of thermal expansion (CTE) and thermal expansion of the bio-composites decreased as the pozzolan content increased. The glass transition temperature (T_g), melting temperature (T_m) and percentage of crystallinity (X_c) of the bio-composites were not significantly changed. The thermal stability, thermal expansion and X_c of the maleic anhydride-grafted PP (MAPP)-treated bio-composites were much higher than those of non-treated bio-composites at 1% pozzolan content due to enhanced interfacial adhesion. X-ray diffraction (XRD) analysis confirmed the crystallinity of pozzolan-added bio-composites. From these results, we concluded that the addition of pozzolan in the bio-composites was an effective method for enhancing the thermal stability and thermal expansion.

Keywords: *bio-composites, bio-flour, pozzolan, thermal properties, thermomechanical properties, X-ray diffraction (XRD)*

Introduction

In recent years, with the rising concerns about increasing environmental degradation and solid waste disposal problems associated with disposable plastics made from non-biodegradable synthetic polymers, eco-friendly natural flour and fibers as bio-fillers have become increasingly recognized as suitable alternatives to inorganic fillers for use as reinforcement in thermoplastics and biodegradable plastics [1–3]. Bio-filler-reinforced thermoplastic and biodegradable plastic composites have many advantages such as low cost, low density, high toughness, lower manufacturing energy, lower manufacturing CO_2 emission, renewability and biodegradability [1, 4, 5]. Bio-composites are derived from partially ecofriendly bio-composites, consisting of bio-filler-filled, petroleum-based plastics (polyolefin) and eco-friendly/green bio-composites, consisting of bio-filler-filled, biodegradable plastic [6]. Polypropylene (PP) is one of the three plastics generally used as the matrix polymer in the bio-composites due to its relatively superior properties such as high melting temperature (T_m), excellent mechanical/thermal properties and low density [7, 8]. Rice husk flour (RHF) and wood flour (WF) have found wide use as completely biodegradable biomass materials and bio-fillers. RHF has the additional advantage of being an agro waste material, which is widely available as a surplus byproduct of the rice production process [3, 9]. Bio-filler-filled, thermoplastic polymer composites are used extensively in various application fields such as decking, siding, window frames, decorative trim, automotive panels, industrial and consumer applications [2, 9].

Improving the thermal stability and reducing the thermal expansion of bio-composites are very important research areas for application of bio-composites to final products. For example, bathroom interiors can suffer thermal deformation due to hot water while automotive interiors are affected by high interior temperatures in summer. Improved thermal stability of bio-composites is also an important factor for application as building interior and automotive interior materials with acceptable fire-retardant characteristics [9]. The idea of adding volcanic pozzolan to the bio-composites has been proposed in order to improve the thermal stability and decrease the thermal expansion.

In this study, we used volcanic pozzolan to increase the thermal stability and reduce the thermal expansion of bio-composites. Pozzolan materials can be used from natural origins or from artificial manufacture due to their worldwide application in recent years to make good quality concrete systems [10–12]. They can be divided into two types: natural and artificial. The natural pozzolan have poorly crystallized materials rich in SiO_2 and Al_2O_3, porous form, and high

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Table 1 Chemical composition of pozzolan mass%

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

*LOI (loss on ignition)

thermal stability [11, 12]. Therefore, we can expect that the high thermal stability and resistance of inorganic volcanic pozzolan will improve the thermal stability and reduce the thermal expansion of bio-composites. The thermal properties and thermal expansion of bio-composites were studied by using a thermal analyzer. Thermogravimetric analysis (TG) can measure the moisture content, thermal decomposition and thermal stability of bio-composite materials [9]. Differential scanning calorimetry (DSC) can be used to measure T_m and the glass transition temperature (T_g) of bio-composite materials [3]. Thermomechanical analysis (TMA) is used to study the dimensional change of a sample as a function of temperature or time [13]. The purpose of this study was to investigate the thermal properties and thermal expansion of bio-flour-filled PP bio-composites with different pozzolan contents. We compared the thermal stability, T_m, T_g and coefficient of thermal expansion (CTE) of pozzolan-added and non-added bio-composites. The crystalline characteristics of pozzolan-added bio-composites were investigated by X-ray diffraction (XRD) over a range of pozzolan content.

Experimental

Materials

PP was supplied by Hyosung Co., South Korea, with an MFI of 1.7 g/10 min (190°C/2, 160 g) 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 mass of 52300. Pozzolan, in volcanic pozzolan ash form and with a particle size of over 70 μm, was obtained from AutoWin Co. The surface area of pozzolan was 13.1 m^2 g^{-1}. The chemical composition of pozzolan was determined using an X-ray fluorescence spectrometer (Shimadzu XRF-1700, Japan). The chemical composition of pozzolan, presented in Table 1, indicated a high concentration of SiO_2 and Al_2O_3. The same result is also evident in Fig. 1 based on results from SEM-EDX (a SIRIOM scanning electron microscope, USA) elemental composition analyzer. The bio-flours used as the reinforcing filler were RHF and WF, obtained from Saron Filler Co. and Dongyang CMI Co., South Korea, respectively. The particle size was 860 to 270 μm for RHF and 110 μm for WF. Table 2 shows the chemical constituents of RHF and WF.

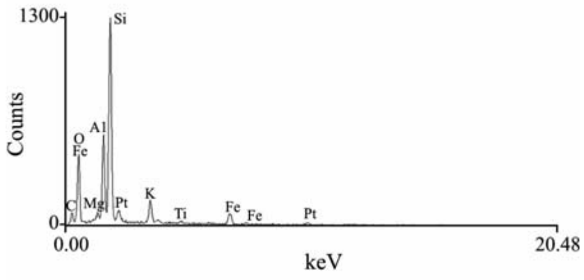

Fig. 1 SEM/EDX spectrum of pozzolan

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 performing 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 mass% filler loading to incorporate the pozzolan at a loading of 0.5, 1 and 3%. Also, to enhance interfacial adhesion, a 30 mass% filler loading was prepared with 1% pozzolan and 3% MAPP.

Methods

Thermogravimetric analysis (TG)

TG measurements were carried out using a thermogravimetric analyzer (TA Instruments, TGA Q500) on 10-mg samples, over a temperature range from 25 to 700°C, at a heating rate of 20°C min^{-1}. TG was conducted with the compounds placed in a high quality nitrogen (99.5% nitrogen, 0.5% oxygen content) atmosphere with a flow rate of 20 mL min^{-1} in order to avoid unwanted oxidation.

Table 2 Chemical constituents of WF and RHF [3]

	Others	Holocellulose	Lignin	Ash
RHF	6.5	59.5	20.6	13.2
WF	10.9	62.5	26.2	0.4

Thermomechanical analysis (TMA)

The thermal expansion and CTE tests of the bio-composites were conducted using a thermomechanical analyzer (TMA 2940, TA Instruments) from ambient temperature to 120°C at a heating rate of 2°C min^{-1} in a high quality nitrogen atmosphere. Expansion mode with a constant compression load of 0.05 N was applied to the specimen in the testing process. The specimens were cut to the shape of a rectangular prism of size 5×5×3.2 mm.

Differential scanning calorimetry (DSC) analysis

DSC analysis was carried out using a TA Instrument DSC Q 1000 (NICEM at Seoul National University) with samples of mass 5~8 mg. Each sample was scanned as the temperature was ramped from –80 to 200°C at a heating rate of 10°C min^{-1} and then cooled at the same rate under a nitrogen atmosphere. Thermal properties, T_m and T_g, were determined from the second scan. T_m was considered to be the maximum of the endothermic melting peak from the heating second scan and T_g to be where the deflection of the baseline can be observed from the cooling second scan.

The specimens' relative percentage of crystallinity (X_c) was calculated according to the following equation:

$$X_c = \frac{\Delta H_f 100}{\Delta H_f^0 w}$$

where ΔH_f is the heat of fusion of the PP and bio-composites, ΔH_f^0 is the heat of fusion for 100% crystalline PP (ΔH_{100}=138 J g^{-1}) [14] and w is the mass fraction for PP in the bio-composites.

X-ray diffraction (XRD) analysis

The XRD analysis of pozzolan, PP, and bio-composites was conducted in an Xpert-Pro diffractometer (Panalytical B.V. Co.) with Ni filtered CuK_α radiation (λ=1.54 Å). The applied voltage and current of the X-ray tubes were 40 kV and 100 mA, respectively. 2θ was scanned between 5 and 80° at 2° min^{-1}. All the bio-composite samples were injection molded into 75 mm×12 mm×3 mm plaques for XRD measurements.

Results and discussion

Thermogravimetric analysis (TG)

Figures 2 and 3 show the dynamic TG curves of PP–RHF and PP–WF bio-composites, respectively, with different pozzolan contents. The mass loss of pozzolan was about 3.8% throughout the temperature range. The mass loss of pozzolan was attributed to the gradual evaporation of moisture below 100°C and the loss on ignition to the organic materials above 340°C [12, 15]. In the TG curves, the thermal degradation of the PP–RHF and PP–WF bio-composites occurred in a two-step degradation process, which was also confirmed by the presence of two peaks for the derivative thermogravimetric curve (DTG_{max}) temperatures in Tables 3 and 4. The first thermal degradation step was attributed to the hemicellulose, cellulose and lignin constituents in RHF and WF, and the second one to thermal degradation of PP. This result demonstrated that the thermal stability and degradation temperature of PP was higher than that of bio-flour [9, 16]. Tables 3 and 4 show the 5% mass loss temperature, DTG_{max} temperatures and mass residue of pozzolan, for the PP–RHF and PP–WF bio-composites, respectively, with different pozzolan contents. With increasing pozzolan content, the 5% mass loss temperature and DTG_{max} temperatures of both bio-composites were slightly increased and the mass residue (ash) content of the bio-composites also increased. These results are also seen in Figs 2 and 3. The incorporation of pozzolan in the bio-composites increased the thermal

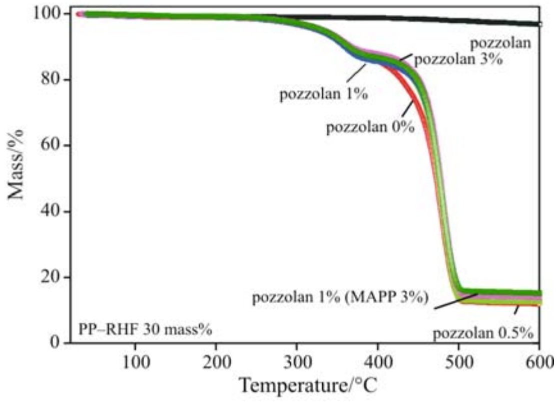

Fig. 2 TG curves of PP–RHF bio-composites at different pozzolan contents

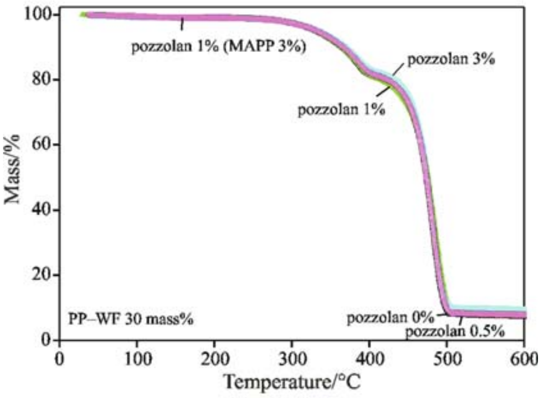

Fig. 3 TG curves of PP–WF bio-composites at different pozzolan contents

Table 3 Summary of 5% mass loss temperature, DTG_{max} degradation temperature and ash content of PP–RHF bio-composites with different pozzolan contents

PP–RHF 30 mass%	5% mass loss temperature/°C	DTG_{max} temperature/°C		Mass residue/% ash
		first peak	second peak	
Pozzolan 100%	nd	487.14	nd	96.2
Pozzolan 0%	326.9	359.8	480.9	12.3
Pozzolan 0.5%	328.5	361.5	481.4	12.6
Pozzolan 1%	328.7	362.9	482.6	14.9
Pozzolan 3%	334.1	364.6	484.2	15.5
Pozzolan 1% (MAPP 3%)	331.1	363.6	483.5	14.3

Table 4 Summary of 5% mass loss temperature, DTG_{max} degradation temperature and ash content of PP–WF bio-composites with different pozzolan contents

PP–WF 30 mass%	5% mass loss temperature/°C	DTG_{max} temperature/°C		Mass residue/% ash
		first peak	second peak	
Pozzolan 0%	332.9	388.1	483.7	7.7
Pozzolan 0.5%	333.4	389.4	484.9	8.1
Pozzolan 1%	334.1	389.9	485.8	8.3
Pozzolan 3%	335.8	391.4	487.1	9.7
Pozzolan 1% (MAPP 3%)	335.1	390.5	486.7	8.2

stability which may be attributed to quartz and the formation of metal oxides in pozzolan such as aluminium, ferrum and magnesium on the PP and bio-flour surface [7, 17].

Above 550°C, the ash content of the PP–RHF bio-composites was much higher than that of the PP–WF bio-composites, due to the higher ash content of RHF relative to WF (Table 2). The 5% mass loss and DTG_{max} temperatures of the PP–WF bio-composites were slightly higher than those of the PP–RHF bio-composites, indicating the superior thermal stability of the former due to the higher cellulose and lignin content of WF (Table 2) [16]. As seen in Tables 3 and 4, the 5% mass loss and DTG_{max} temperatures of MAPP-treated, 1% pozzolan bio-composites were slightly higher than those of the non-treated bio-composites, due to the improved compatibility and interfacial adhesion between the bio-flour and matrix polymer at the interface. The enhanced interfacial adhesion of MAPP-treated bio-composites could be attributed to the formation of an ester bond with maleic anhydride (MA) to react with the OH groups of the bio-flours which increased the thermal stability of the bio-composites [2, 4, 14]. These results suggested that incorporation of inorganic materials and MAPP as compatibilizing agents enhanced the thermal stability of the bio-composites.

Thermal expansion

TMA expansion curves of the PP–RHF and PP–WF bio-composites are shown in Figs 4 and 5, respectively, and the CTE values of both bio-composites at different pozzolan contents are shown in Table 5. The TMA method for measurement of CTE is useful for understanding the dimensional changes of bio-composite materials as well as the thermal stresses caused by increasing temperature [9, 18]. A lower CTE value of the bio-composites indicates that the bio-composites undergo lower dimensional change when exposed to cold or warm atmospheric change [9]. The CTE value of pure PP, $197.7\cdot10^{-6}$ °C^{-1}, was decreased to 163.7 and to $193.1\cdot10^{-6}$ °C^{-1} by adding 30 mass% RHF and WF, respectively in the PP matrix. This result is also evident in Figs 4 and 5, indicating that incorporation of bio-flour in the matrix polymer is suitable for preventing the thermal expansion of bio-composites at high temperature due to the lower thermal expansion of the bio-flour. In addition, the CTE values of the PP–RHF bio-composites were much lower than those of the PP–WF bio-composites. The particle size of RHF (860 to 270 μm) is higher than that of WF (110 μm). Lee *et al.* [18] reported that the CTE value of pure polybutylene succinate (PBS) is significantly reduced from $294\cdot10^{-6}$ to $46\cdot10^{-6}$ °C^{-1} by the addition silk fiber with particle size of 12.7 mm (30 mass%) in the PBS. Similarly, the CTE values of PP–RHF and PP–WF bio-composites were decreased

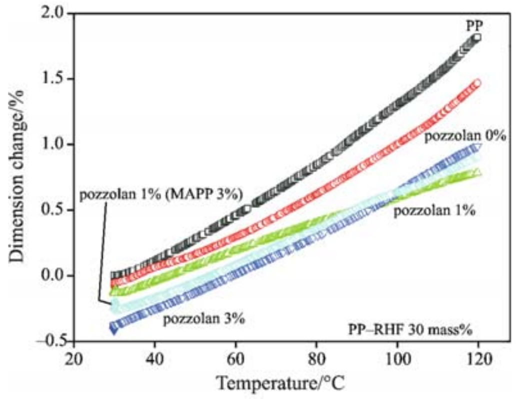

Fig. 4 TMA curves of the dimensional change of PP–RHF bio-composites at different pozzolan contents

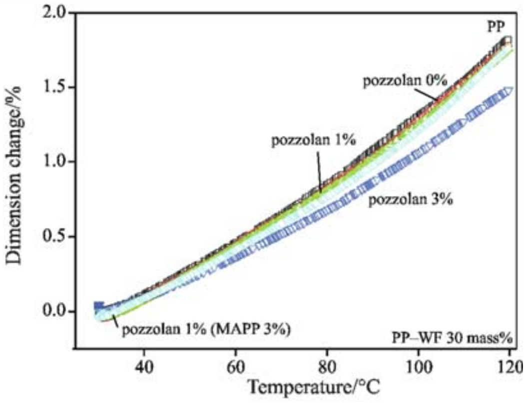

Fig. 5 TMA curves of the dimensional change of PP–WF bio-composites at different pozzolan contents

with increasing pozzolan content, suggesting that the addition of pozzolan in the bio-composites improved their dimensional stability because any dimensional change of the bio-composites was restricted by the pozzolan inorganic material. As seen in Table 5, the use of 3% MAPP as a compatibilizing agent decreased the CTE values of both bio-composites at the same 1% pozzolan loading, which was attributed to the enhanced interfacial adhesion between the hydrophilic bio-flour and the hydrophobic matrix. These results suggested that the addition of pozzolan and MAPP in the bio-composites is an effective method for reducing the thermal expansion and dimensional change of bio-composites.

Table 5 Comparison of the coefficients of thermal expansion (CTE) of bio-composites with different pozzolan contents

Specimen	40–100°C (10^{-6}/°C)
PP	197.7
PP–RHF 30 mass%	163.7
Pozzolan 1%	162.9
Pozzolan 3%	146.3
Pozzolan 1%, MAPP 3%	138.5
PP–WF 30 mass%	193.1
Pozzolan 1%	191.8
Pozzolan 3%	178.1
Pozzolan 1%, MAPP 3%	185.6

DSC analysis

The effect of pozzolan content on the thermal properties of the bio-composites was examined in non-isothermal DSC experiments. Figure 6 presents the second heating curves for pure PP and WF-filled, PP bio-composites at different pozzolan contents. In addition, Table 6 lists the thermal properties of T_g, T_m, ΔH_f and X_c for PP, and RHF- and WF-filled, PP bio-composites at different pozzolan contents. As the pozzolan content increased, X_c of the bio-composites was not significantly changed. It may be assumed that the addition of bio-flour and pozzolan to PP did not generate the formation of suitable nucleation sites and did not significantly affect the crystallization properties of the PP matrix [19]. Moreover, T_m and T_g of the bio-composites were unaffected by pozzolan addition as demonstrated by the lack of any significant change with increasing pozzolan content. Table 6 shows that the addition of MAPP in the bio-composites at 1% pozzolan content had little effect on T_m, and T_g but that X_c was slightly increased. Increased X_c of the

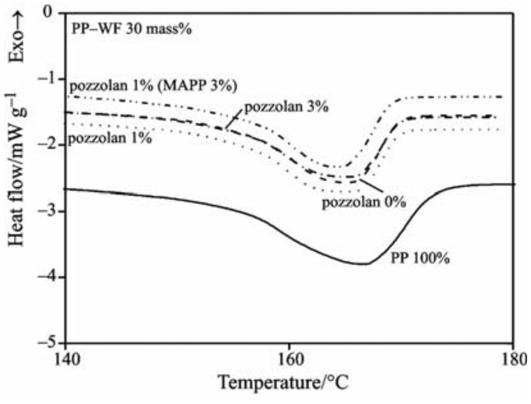

Fig. 6 DSC heating curves of PP–WF bio-composites at different pozzolan contents

Table 6 DSC test results of the bio-composites with different pozzolan contents

Specimen	T_g/ °C	T_m/ °C	ΔH_f/ J g^{-1}	X_c/ %
PP	–2.8	166.6	78.2	56.6
PP–RHF 30 mass%	–3.1	166.9	52.8	54.7
Pozzolan 1%	–2.9	166.7	53.1	54.9
Pozzolan 3%	–2.8	166.6	52.4	54.2
Pozzolan 1%, MAPP 3%	–2.3	166.2	56.1	58.1
PP–WF 30 mass%	–3.4	166.3	52.5	54.3
Pozzolan 1%	–2.5	166.9	53.2	55.1
Pozzolan 3%	–2.7	165.7	54.1	56.0
Pozzolan 1%, MAPP 3%	–2.0	166.7	56.5	58.5

bio-composites may have arisen from enhanced interfacial adhesion due to the chemical bond between MAPP (anhydride group) and bio-flour (OH group) that formed an ester linkage at the interface [14].

XRD analysis

Figure 7 shows an XRD diffractogram of the pozzolan which was analyzed for peaks over the 2θ range from 10 to 55°. Pozzolan showed strong diffraction peaks at 2θ of 8.8 and 26.5°, which were attributed to biotite and quartz of pozzolan, respectively [10, 11, 20]. This result was further confirmation that pozzolan was mainly composed of Al_2O_3 and SiO_2.

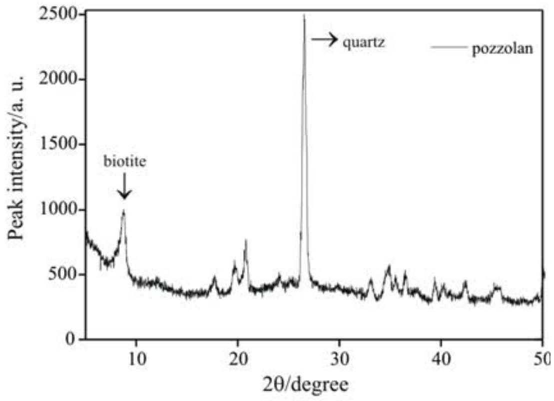

Fig. 7 XRD diffraction curve of pozzolan

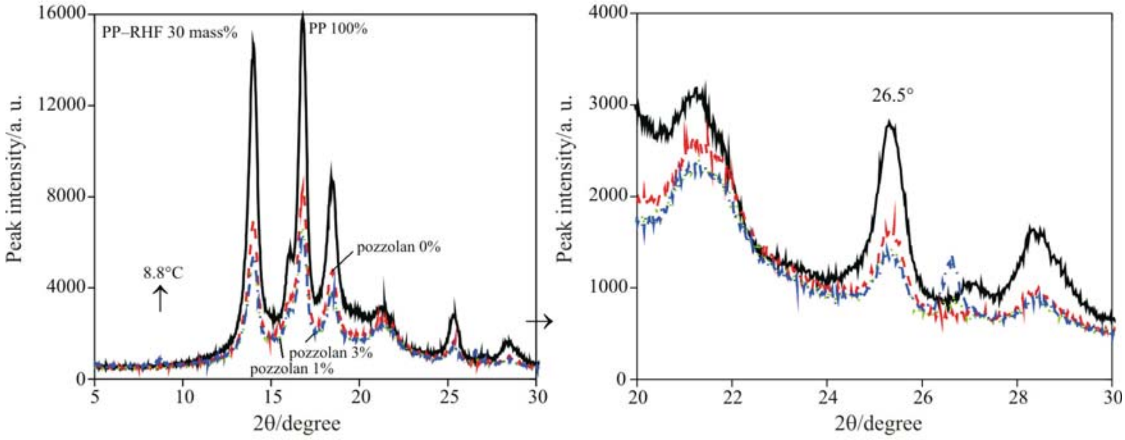

Fig. 8 XRD diffraction curve of PP–RHF bio-composites at different pozzolan contents

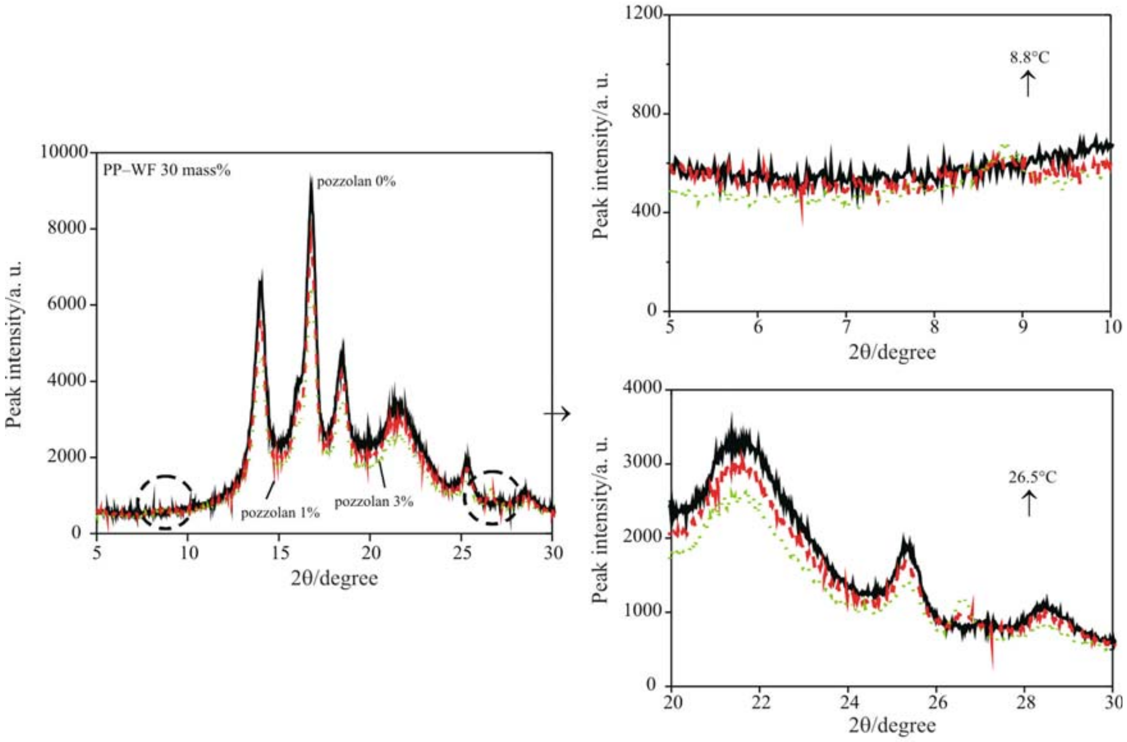

Fig. 9 XRD diffraction curve of PP–WF bio-composites at different pozzolan contents

The XRD diffractograms of PP–RHF and PP–WF bio-composites at different pozzolan contents are shown in Figs 8 and 9, respectively. PP, both bio-composites and pozzolan-added bio-composites all showed strong characteristic diffraction peaks at 2θ of 14.2, 16.7, 18.5 and 21.3°, which were assigned to the (110), (040), (130) and (111) diffraction planes of the monoclinic α-form of PP crystals, respectively [21, 22]. Furthermore, a shoulder diffraction peak shown at 2θ of 16° was determined to be the crystal plane (300) of the hexagonal β-form of PP [20]. With addition of bio-flour and pozzolan in the PP, the intensity of this peak slightly decreased, suggesting that the incorporation of bio-flour and pozzolan did not induce crystallization and did not act as a nucleating agent of PP. In Figs 8 and 9, two new characteristic peaks of pozzolan-added PP–RHF and PP–WF bio-composites are evident at 2θ of 8.8 and 26.5°, due to biotite and quartz structures of pozzolan in the bio-composites [10, 11, 20], respectively. The diffraction peak intensity of biotite (8.8°) and quartz (26.5°) of both bio-composites was slightly increased with increasing pozzolan content.

Conclusions

With increasing pozzolan content, the 5% mass loss temperature, DTG_{max} temperatures and thermal stability of PP–RHF and PP–WF bio-composites slightly increased due to quartz and metal oxides in the pozzolan. The CTE values and thermal expansion of PP–RHF and PP–WF bio-composites decreased with increasing pozzolan content, indicating that pozzolan addition in the bio-composites improved their dimensional stability. The T_m, T_g and X_c of the bio-composites showed no significant change with increasing pozzolan content, presumably because pozzolan addition to PP did not generate the formation of suitable nucleation sites and did not significantly affect the T_m and T_g of the bio-composites. The 5% mass loss, DTG_{max} temperatures, thermal stability, thermal expansion and X_c of MAPP-treated bio-composites were higher than those of the non-treated bio-composites at 1% pozzolan content due to enhanced interfacial adhesion. From the XRD analysis, we could be confirmed by two new characteristic peaks of pozzolan-added bio-composites being evident at 2θ of 8.8° (biotite) and 26.6° (quartz). Also, the crystallinity of PP was not influenced by the addition of bio-flour and pozzolan.

Acknowledgements

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