Preparation of Organosilane Treated Microcrystalline (SiMCC) and SiMCC/Polypropylene Composites

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Abstract

In this study, the silane treated microcrystalline cellulose (SiMCC)/polypropylene composite was prepared. In the first step, the surface modification of microcrystalline cellulose (MCC) with various concentrations of hexadecyltrimethoxysilane was carried-out in order to obtain the SiMCC having good compatibility with PP matrix. Characterizations including SEM, FT-IR, TGA and DSC were employed to analyze the structure of SiMCC. SEM revealed that MCC surface morphology was changed from rod shape into rough particles after silane treatment. In the next step, the obtained SiMCC was mixed with PP powder using twin-screw extruder. Based on TGA results, it was found that the addition of SiMCC led to thermal stability enhancement of PP matrix during melting process. As a result, it was claimed that SiMCC could be an effective heat stabilizer for polymer melt process. Also, the compatibility was achievable, as supported by the gradual degradation of SiMCC observed in TGA thermograms.

Keywords : Microcrystalline cellulose, Organosilane, Organosilane treated MCC, Polypropylene composite , Thermal stability.

Introduction

Cellulose /polymer composites are the important branches in the field of composite materials.[1-7] Compared with conventional inorganic fillers, cellulose provide many advantages such as abundance and low cost, flexibility during processing and less resulting machine wear, desirable fiber aspect ratio, low density, minimal health hazard and biodegradability. One of the most used reinforcement fillers is microcrystalline cellulose (MCC). It is easy to prepare by reacting cellulose with aqueous solution of strong mineral acid at boiling temperature for a period of time. The hydrolysis reaction removes amorphous cellulose and reduces the degree of polymerization (level -off degree of polymerization, LODP) of the cellulose chain. MCC exists in rod shaped particles having a large particle size distribution. Due to MCC particle having high aspect ratio, it is one of interesting reinforcement fillers for the preparation of polymer composites. Basically, its chemical structure consists of repeating unit (anhydroglycoside unit (AGU)). Due to the high degree of crystallinity, microcrystalline cellulose is not swollen in water, stable to temperature and pH variations when compared to cellulose. Moreover, MCC is hydrophilic and tends to result in phase separation when incorporated into polymer matrix, causing poor compatibility. To solve this problem, surface modifications of MCC are practically required. Surface modifying agents include maleic anhydride based polyolefins,[1] maleic anhydride grafted

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polycaprolactone, [2] epoxy silicone oil, [3] organosilanes. [6-7] Methods of modification were reported in details.

The aim of this work was to prepare SiMCC/PP composites containing SiMCC having various silane to MCC ratios. The properties of the obtained composites were presented.

Materials and Experimental Procedures

Materials

Cellulose fiber was obtained from local textile fiber spinning factory. Hexadecyl triethoxysilane (DYNASLAN 9116) was kindly provided by Evonik Industries. Polypropylene powder (MFI = 19.8 g/min) was supported by HMC Polymers (Thailand) co., Ltd. Tween-80 (non-ionic surfactant) was bought from Acros Organic Co., Ltd. IrganoxR® B 215 (heat stabilizer) was purchased from Ciba Inc., Switzerland.

Methodology

Microcrystalline cellulose (MCC) was prepared by acid hydrolysis of waste cotton fabric with 2.5 N hydrochloric acid at temperature of 100 ^{O}C for 3 hours. The white residue obtained was washed repeatedly with distilled water to obtain acid-free MCC. The MCC was then dried in a vacuum oven to constant weight and ground into fine powder. Then, the MCC was swollen in urea solution before coupling with hexadecyl triethoxysilane at 80 ^{O}C, 1 h. Silane to MCC mole ratios of 1: 1, 1: 2, 1: 3, and 1:4 were employed. Hydrochloric acid was used to adjust pH to 1. The silane treated microcrystalline cellulose (SiMCC) was characterized by Fourier transform infrared spectroscopy (FTIR) in the range 450–4000 cm^{-1}, The MCC/PP composite and SiMCC/PP composites were prepared by twin screw operating at 180-210 oC and 100 rpm using co-rotating mode. Melt flow index (MFI) was determined by melt flow index

tester (XRL-400 series) from C.B.N. Engineering Ltd. (China). Scanning electron microscopy (SEM) using Philips XL 30 CP was used to observe the morphology. Thermogravimetric analysis (TGA) using Mettler model Toledo TGA/SDTA 851 and Differential Scanning Calorimetry (DSC) using NETZSCH DSC 200 F3 were performed to study the thermal behavior.

Result and Discussion

Silane treated microcrystalline cellulose was characterized by FTIR spectroscopy as shown in Figure 1. The sharp peaks at 2800-3000 cm^{-1} is attributed to the -CH$_2$- and -CH$_3$ group that are not observed in FTIR spectrum of MCC. Therefore, these findings lead to conclude the presence of organosilane in the SiMCC. The band at 1134 cm^{-1} is assigned to the stretching of Si-O-Si bonds. The Si-O-C bond was expected to be found in the region of 1015-1095 cm^{-1}. Unfortunately, the fingerprint of this band is present in the same range of cellulose bands. The morphology of SiMCC is obviously different from those of MCC as shown in Figure 2. As seen, the modification of MCC with organosilane results in the transformation of MCC from fibrous shape into agglomerate particle with no aspect ratio. The particle sizes of MCC and SiMCC at various mole ratios was shown in table 1. Change in shape was evident in case of higher ratios of silane to MCC, indicating the completeness of MCC transformation. This is due to the fact that the urea swollen cellulose was able to completely react with organosilane, thus preventing it converting back into the original form.

As a result of hydrophobicity characteristic of SiMCC, this filler is more compatible with polypropylene than MCC as shown in Figre 3. As seen, the composites with SiMCC having more organosilane content exhibit the better compatibility, judged by the invisibility of phase separation between filler and matrix.
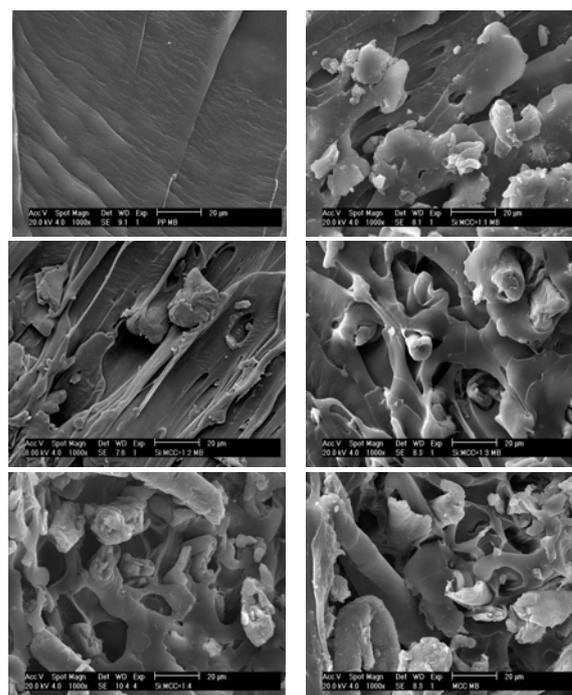
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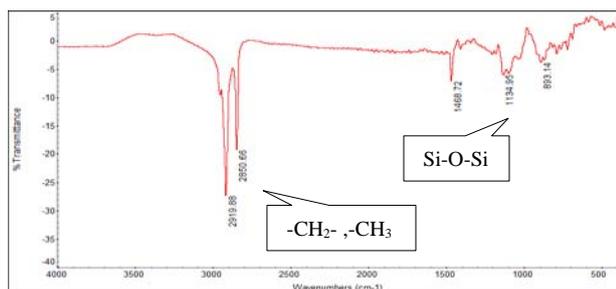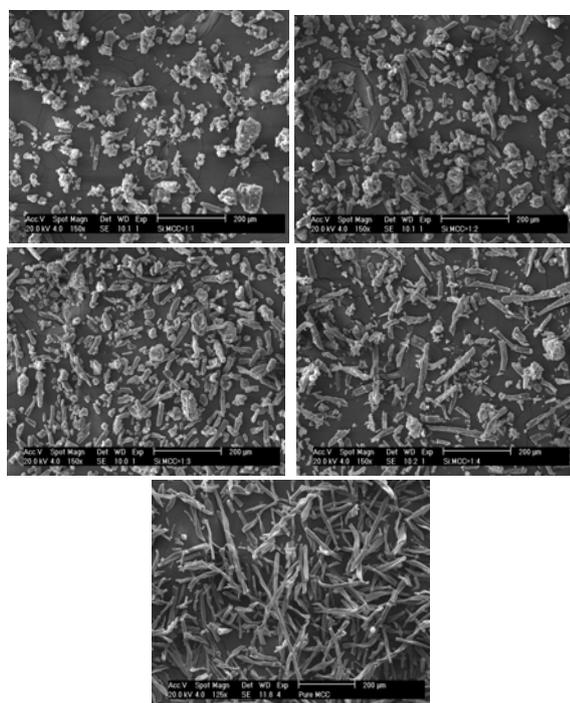

Figure 1. The representative of subtractive FTIR spectrum of SiMCC obtained from Silane to MCC mole ratios 1 : 4

Table 1. Particle sizes of MCC and SiMCC at various Si:MCC mole ratios.

Filler	Fibrous shape length (μm)	Agglomerate particle diameter (μm)
MCC	25-500	-
Si:MCC=1:1	25-125	12.5-75
Si:MCC=1:2	25-125	12.5-62.5
Si:MCC=1:3	25-125	12.5-75
Si:MCC=1:4	25-212.5	12.5-62.5

Figure 2 . SEM images of SiMCC at various mole ratios (A) Silane: MCC = 1:1 (B) 1:2 (C) 1:3 (D) 1:4 and (E) MCC
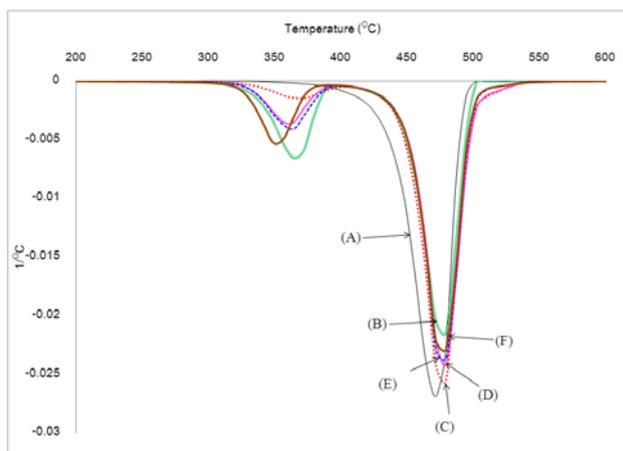

Figure 3. SEM images of (A) PP, SiMCC/PP composites at various mole ratios of Silane : MCC (B) 1:1 (C) 1:2 (D)1:3 (E)1:4 and (F) PP/MCC composite.
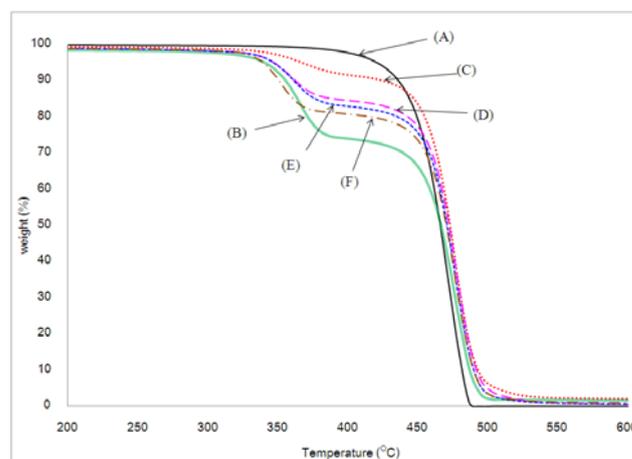

Figure 4. TGA Thermograms of PP (A), SiMCC/PP composites at various mole ratios of Silane : MCC (B) 1: (C) 1 : 2 (D) 1 : 3 (E) 1 : 4 and (F) PP/MCC composite.

Figure 5. DTG Thermograms of PP, SiMCC/ PP composites at various mole ratios of Silane : MCC (B) 1:1 (C) 1:2 (D) 1:3 (E) 1:4 and (F) PP/MCC composite.

The decomposition of PP shows one degradation step with peak mass loss Td of 464 °C. PP/MCC composite and various SiMCC/PP composites decomposed in 2 steps as seen in Figure 4 and 5 and summarized in Table 2. The first step corresponds to the decomposition of SiMCC and the second represents the polypropylene matrix degradation. In the first onset temperature step, MCC/PP composite shows the highest degradation temperature, indicating the high thermal stability of untreated cellulose. After surface modification as represented by SiMCC, the corresponding onset temperature reveals that an increase in the silane to MCC ratio results in a gradual decrease in the first onset temperature. This is likely related to the gradual degradation of silane moiety present on SiMCC; the more the amount of silane content the lower the onset degradation temperature. The gradual decomposition can be indicative of compatibility of SiMCC in PP matrix. For the 2nd onset degradation temperatures which represent the onset temperature of PP matrix, it can be seen that the SiMCC/PP composites exhibit higher onset temperature than MCC/PP, indicating that silane treated MCC behaved as heat stabilizer for polypropylene. Moreover, in case of

SiMCC/PP composites, char residue was observed, indicating flame retardancy property. The mechanism of char formation might be related to the formation of 'active' cellulose as shown in Scheme 1. From the degradation mechanism, it is believed to be associated with scission of glycosidic bonds, caused by transglycosylation. Cellulose undergoes depolymerization but this does not involve mass loss. The second step consists of dehydration of pyranose rings, producing anhydrocellulose and resulting in mass loss. Further degradation of pyranose produces CO_2, various volatile gases and unsaturated cyclic compounds.[8] A comprehensive study of cellulose char obtained by thermal degradation of microcrystalline cellulose in an inert atmosphere at temperatures between 190 and 390 °C has been investigated. The abundance of aromatic building blocks (furans, alkylbenzenes and alkylnaphthalenes) increases with the temperature of degradation. It was concluded that up to about 250 °C a highly ordered ß-l,4 - polyglucan is principally maintained, while above this temperature a new polymer containing furanoid, hydroxyaromatic and unsaturated hydrocarbon entities, and a high number of carboxyl and carbonyl groups is formed. With increasing temperature of degradation, further dehydration takes place, and above 320 °C disproportionation and elimination of volatiles (CO, CO2) occurs, resulting finally in a highly condensed aromatic polymer.[9,10]
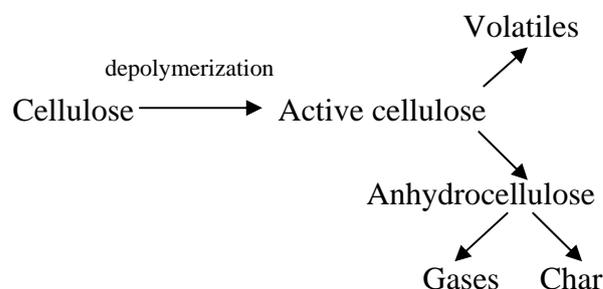
Scheme 1. The thermal degradation mechanism of cellulose

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Table 2. Degradation temperatures of MCC / PP and SiMCC / PP composites analyzed by TGA.

Composite	1st Onset Temp. (^{o}C)	2nd Onset Temp (^{o}C)	Td (^{o}C)	% char
PP	-	443	464	0
PP/MCC	343	443	479	1.48
1:1 SiMCC/PP	341	453	479	2.02
1:2 SiMCC/PP	337	453	479	0.67
1:3 SiMCC/PP	337	453	479	0.53
1:4 SiMCC/PP	332	453	479	0.93

The modification of microcrystalline cellulose using organosilane is found to increase the degradation temperature of PP, indicating that SiMCC was capable of thermally stabilizing polypropylene matrix during melt processing. As a result, the degradation of polypropylene was minimized. In contrast, MCC alone failed to behave this function as its presence did not result in an increase in 2nd onset temperature. In all cases of SiMCC fillers, the corresponding 2nd onset degradation temperatures are recorded at 453 ^{o}C, meaning that varying organosilane ratios exhibit no difference in their capability of stabilizing polypropylene referring to Table 2. The stabilization effect is partly due to the addition of foreign particles which favorably induce the crystallization of polypropylene matrix, leading to higher crystallinity of a polymer composite. This reason is also confirmed by DSC results. Figure 6 (a) and (b) show melting and crystallization behavior of PP and various composites. In addition, the percent weight loss in Table 3 obtained at 479 ^{o}C further confirms that the addition of SiMCC significantly reduces the weight loss of PP when compared to MCC and virgin PP. Favorably, the presence of the MCC had little effect on the melting temperature of PP as seen in Table 4. Another advantage of SiMCC and MCC addition is that the percent

crystallinity of SiMCC/PP composites and PP/MCC composite are higher than PP as seen in Table 5. Finally, the addition of MCC as well as SiMCC results in a slight increase in Tc since the average particle size of the filler is too big to induce the rate of PP crystallization.

Table 3. Second decomposition of PP, MCC/PP and SiMCC/PP composites at various Si: MCC mole ratios in composites analyzed by TGA.

Composite	Onset temperature (^{o}C)	Degradation temperature, Td (^{o}C)	% wt loss at 479 ^{o}C	% Residue
PP	443	464	85	0
MCC/PP	453	479	76	1.48
1:1 SiMCC/PP	453	479	67	2.02
1:2 SiMCC/PP	453	479	67	0.67
1:3 SiMCC/PP	453	479	70	0.53
1:4 SiMCC/PP	454	479	71	0.93

Table 4. Melting temperature (Tm) and crystallization temperature (Tc) of PP, PP / MCC and SiMCC / PP composites at various Si:MCC mole ratios in composites analyzed by DSC.

Composite	Melting temperature (^{o}C)	Crystallization temperature (^{o}C)
PP	155	119
MCC/PP	158	129
1:1 SiMCC/PP	153	120
1:2 SiMCC/PP	155	121
1:3 SiMCC/PP	156	122
1:4 SiMCC/PP	157	123

Table 5. Enthalpy of fusion (ΔH_f) and percentage of crystallinity of PP, PP / MCC and SiMCC / PP composites with various Si:MCC mole ratios analyzed by DSC.

Composite	ΔH_f (J/g)	% Crystallinity
PP	77.83	37.43
MCC/PP	64.05	44.10
1:1 SiMCC/PP	64.98	44.74
1:2 SiMCC/PP	68.00	46.82
1:3 SiMCC/PP	67.84	46.71
1: 4 SiMCC/PP	64.89	44.67
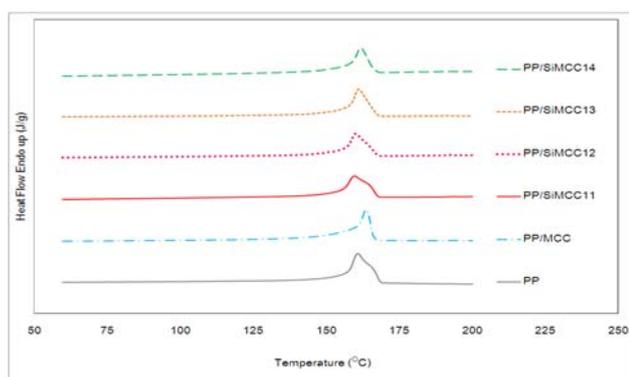
(A)
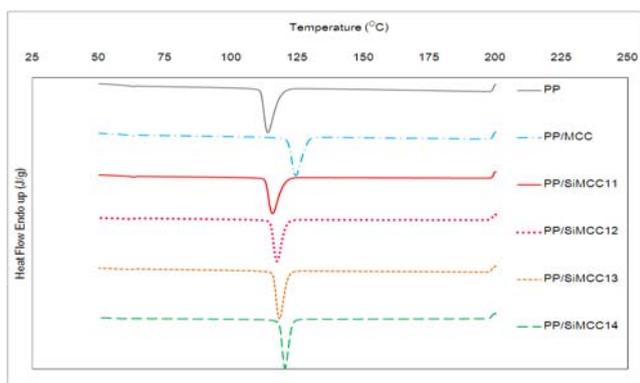
(B)

Figure 6. Heat capacity curves of PP, PP / MCC and SiMCC / PP composites at various Si : MCC mole ratios in composites, (A) melting endotherm and (B) crystallization exotherm.

Conclusions

Silane treated microcrystalline cellulose (SiMCC) was successfully prepared. The higher organosilane to MCC ratio resulted in the higher SiMCC particle content with agglomerate form. The complete MCC transformation (from rod to agglomerate) was achieved when 1:1(or higher) silane to MCC ratio was employed. As a result of hydrophobicity, SiMCC particles as filler additive were more compatible to PP matrix than original MCC. SiMCC/PP composites were found to exhibit improved thermal stability responsible to the presence of SiMCC fillers. The addition of SiMCC into to PP matrix also led to an increase in the percentage of crystallinity due to the effect of the presence of SiMCC as foreign particles.

Acknowledgements

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