

Morphology and Mechanical Properties of Catalytic Coke/Polypropylene Composites

Kingkan Muangmaithong,¹ Piyasan Prasertthdam,¹ Supakanok Thongyai,¹
Sirirat Wacharawichanant²

¹Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University, Bangkok 10330, Thailand

²Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakorn Pathom 73000, Thailand

Received 3 December 2007; accepted 11 May 2008

DOI 10.1002/app.28705

Published online 7 August 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polypropylene (PP) composites with filler of catalytic coke (CC) or fresh catalyst (FC) of Ni/SiO₂.MgO were prepared by melt mixing technique in a twin screw extruder. The catalytic coke, that has the fibril of carbon, is the waste from petrochemical industry and can be obtained cheaply in high volume. The composites were examined by assessing their mechanical properties, thermal properties, and the morphology of fracture surface of the PP matrix. The improvement of some mechanical properties of the CC filler such as Young's modulus and slightly improvement of tensile strength were observed whereas the elongation at break and toughness decreased with the increase in CC or FC. Both degradation temperature of CC or FC composites decreased with

increased filler content but lesser in the case of CC. The structures of fracture surfaces were supported by the results from mechanical properties measurement. The CC composite in PP matrix (CCPP) exhibits the fibrils and the plastic deformation of the matrix, while the FC composite in PP matrix (FCPP) presents similar fracture roughness as the nascent PP. The catalytic coke can be utilized as the filler to improve the Young's modulus while the fresh catalyst cannot be utilized as filler because of the adverse effects. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2071–2077, 2008

Key words: composites; mechanical properties; morphology; polypropylene

INTRODUCTION

In recent years, polymer based composites reinforced with a small percentages of fillers can significantly improve the mechanical, thermal, and barrier properties of the pure polymer. These composites are now being considered for a wide range of applications including packaging, coating, electronics, automotive, and aerospace industries.^{1,2} Tang et al. investigated melt processing and mechanical property of multi-walled carbon nanotube/high density polyethylene (MWNT/HDPE) composite films.³ The results showed that the stiffness, the yield strength, and the fracture toughness of MWNT/HDPE composite films all increased with increasing MWNT contents. Mahfuz et al. studied the linear low-density-polyethylene (LLDPE) composites by reinforcing carbon nanoparticles/whiskers through an extrusion process.² It was found that with the addition of 2 wt % of carbon nanoparticles/whiskers in LLDPE, the tensile strength and modulus of the composite have increased by 16.9 and 16.37%, respectively. The cross-

linking in the matrix due to infusion, and the alignment of whiskers during the extrusion process enhanced the modulus. Machado et al. studied thermal and mechanical properties of single-walled carbon nanotubes (SWNT)-Polypropylene (PP) composites prepared by shear mixing and then compared the results with nanocomposites containing carbon black (CB) as filler.⁴ They found that at low concentrations of SWNT generally resulted in an increase in Young's modulus and tensile strength, this effect being noticeably higher than that observed for CB/PP composites. At the highest content, both stiffness and strength were significantly reduced. The results of the tensile tests suggest that nanotube incorporation of less than 1 wt % increases tensile strength because of strong interfacial bonding with respect to the unreinforced polymer. Yasmin et al. investigated the different processing techniques and their effects on the mechanical behavior of expanded graphite reinforced polymer nanocomposites consisting of anhydride cured epoxy resin matrix and expanded graphite (EG) with the concentrations of 1–2 wt %. It was found that EG reinforced nanocomposites showed higher elastic modulus than the neat epoxy.⁵

The rationale for selecting PP was because of its widespread industrial applications in housewares, packaging, pipes, and automotive parts e.g., battery

Correspondence to: P. Prasertthdam (piyasan.p@chula.ac.th).

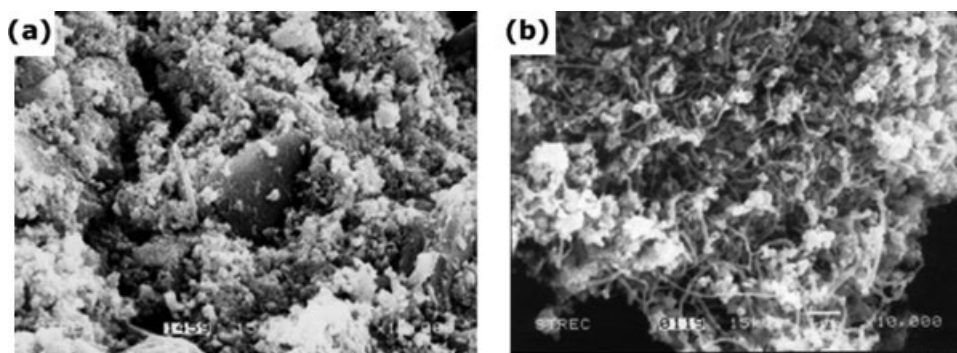


Figure 1 SEM micrographs of (a) FC (b) CC.

cases and bumpers. Moreover, it was resistant to moisture, corrosion, wear, chemical reaction, and extremely low cost.^{4,6,7} Most of fillers for making composite are carbon nanotube, carbon fiber, carbon filament, etc. which have high strength but expensive and complicated production process. Catalytic coke (CC) has the filaments of coke deposit that might be useful to utilize as a filler to improve the mechanical properties of PP. The deactivated catalyst that has a large amount of catalytic coke was the unwanted material in petrochemical industry and can obtain cheaply with high volume. Regarding the catalytic coke, as unwanted product after the reaction, that can be used to increase the value of the PP composite.

In this research, the main purpose is to prepare catalytic coke/PP composites (CCPP) from the reaction of methane and compare with the fresh catalyst/PP composites (FCPP). The dispersion of filler was done by melt processing in a twin screw extruder. The effect of CC on the mechanical properties of composites was investigated. The results were then compared with those obtained for composites containing FC (Ni/SiO₂.MgO catalyst) and nascent PP.

EXPERIMENTAL

Materials

Catalytic coke was synthesized by methane decomposition using Ni/SiO₂.MgO catalyst. In this process Ni/SiO₂.MgO was packed in the middle of tubular quartz reactor located in the electrical furnace. The reactor was evacuated and filled with inert atmosphere of Argon (Ar). Methane (CH₄) and hydrogen (H₂) were introduced into the reactor. The reactor was heated up to 800°C at a rate of 5°C/min. At this temperature the argon gas was switched off and the catalyst was reduced under hydrogen flow (30 cc/min) for 1 h. After the catalyst reduction, the system was purged with argon for 10 min to remove hydro-

gen gas from the system. Then the argon gas was switched to the methane gas at flow rate of 12.5 mL/min. Start to count the time for reaction by changing various reaction times as 60, 80, and 100 min. Then the methane gas was switched to the argon gas. The reactor temperature was held at 800°C for 10 min before the reactor was cooled down. The coke was formed at the surfaces of the catalyst and might create the carbon fiber attached to the catalyst. The Ni/SiO₂.MgO catalyst will totally be covered with the coke and the carbon fiber and after the reaction the deteriorative catalyst with coke will be taken out and hence called catalytic coke (CC). The Ni/SiO₂.MgO catalyst before methane decomposition reaction is called fresh catalyst (FC).

The morphologies of CC and FC were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The vividly different SEM micrographs between CC and FC can be shown in Figure 1. The surface of CC was covered with filamentous coke, in contrast to the clean rough surface seen in FC. The vividly different TEM micrographs of FC and CC can be shown in Figure 2. The micrographs showed that the CC consisted of rod-shaped carbon with diameter about 100 nm, while the FC morphology was spherical in shape and about 44 nm in diameter. A commercial grade of isotactic PP (P602F) were obtained from CCC Chemical Commerce Co., Ltd. The melt flow index and density of PP are 1.0 g/10 min and 0.910 g/m³, respectively. The melting point is 165°C.

Composites preparations

To obtain the good homogeneity of the composite, two steps mixing of CC or FC with PP were performed and the obtained composite called as CCPP and FCPP, respectively. First, to uniformly disperse the CC in PP matrix, the manual mixing of 10 wt % CC with nascent PP on digital hot plate at 200°C for 10 min was performed. The resulted blend of CCPP

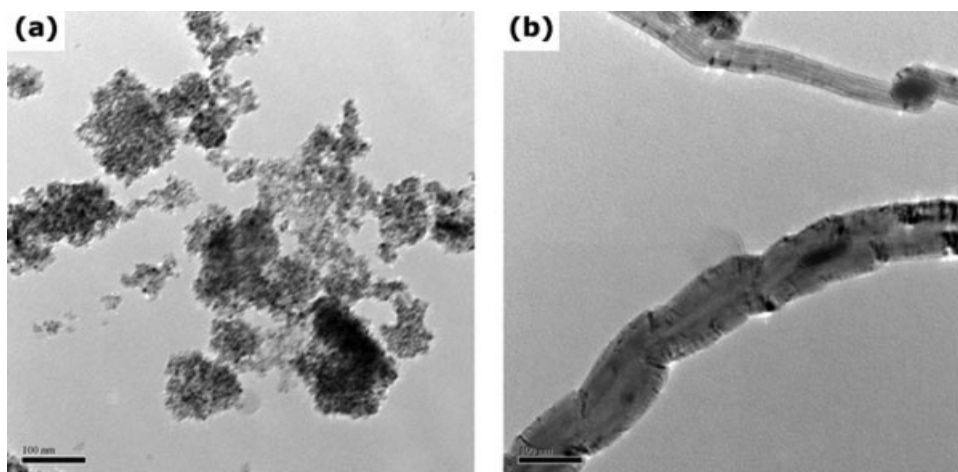


Figure 2 TEM micrographs of (a) FC (b) CC.

was compressed to form a thin film form and cut to pieces to make the master batch of CCPP.

Last, to prepare the PP composites of the desired CC content, the nascent PP and master batch from the first step was weighted and mixed before compounding using a Haake twin screw extruder model Rheocord 300p screw diameter is 15 mm with L/D of 25 : 1. The operating temperatures of the twin screw extruder were set at 150, 160, 175, 185, 195, and 210°C, respectively, and the screw speed was set at 60 rpm. The CC/PP composites (CCPP) of 1.0, 2.0, and 3.0 wt % CC and the FC/PP composite (FCPP) of 1.0, 2.0, and 3.0 wt % FC were made accordingly by mixing with CC or FC, respectively. All PP composites pellets were dried at 100°C for 1 h and further melt and compressed at 200°C under the pressure of 1500 psi for 7 min and left to cool down to room temperature to form the sheet of composite which can be cut to obtain standard specimen for mechanical properties tests.

Composites characterization

The tensile tests were performed at room temperature according to ASTM standard D882 by Universal Testing Machine, Instron model 5567. The tensile tests were performed at crosshead speed of 50 mm/min. The average tensile strength of five samples was undertaken.

The morphologies of the CC, FC, and the tensile-fractured surfaces of the composites (CCPP and FCPP) were examined by using a JSM-5800LV, JEOL scanning electron microscope, and a JEOL JEM-2100 transmission electron microscope, operated at 80–200 keV.

Thermal properties were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA samples were cut and

mechanically grind into small pieces of 5–15 mg. TGA of TA Instruments, Inc. was carried out under flow of oxygen at the heating rate of 10–750°C/min.

The DSC of Perkin–Elmer were performed to measure the glass transition temperature (T_g) and Crystalline melting temperatures (T_m) by heating the 3–9 mg samples from –40 to 200°C at a heating rate of 40°C/min in flow of N_2 . The samples were further cooled down from 200 to –40°C at a cooling rate of 40°C/min. Subsequently, the second heating was performed by raising the temperature to 200°C at a rate of 40°C/min and the T_g and T_m were detected.

RESULTS AND DISCUSSION

Thermal properties

The effects of CC and FC on the degradation temperature of all composites are shown in Figure 3.

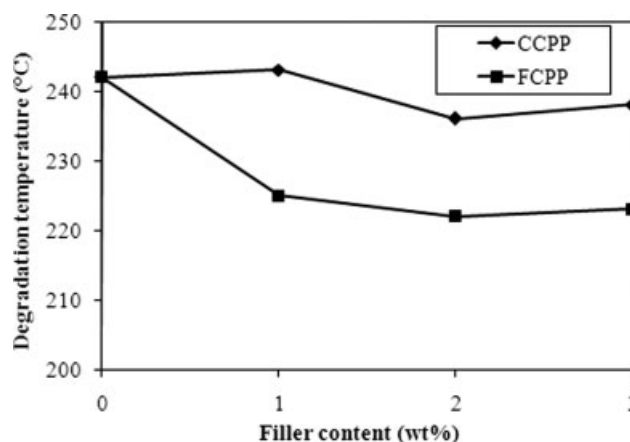


Figure 3 Degradation temperatures of the FCPP and CCPP at various filler contents.

TABLE I
The Variation of T_g and T_m of Pure PP and Composites at Various Filler Contents and Filler Types

Material	T_g (°C)	T_m (°C)
Pure PP	-8.8	160.0
1.0 wt % of CCPP	-8.1	161.4
2.0 wt % of CCPP	-8.1	161.3
3.0 wt % of CCPP	-8.0	161.4
1.0 wt % of FCPP	-10.8	155.3
2.0 wt % of FCPP	-10.2	156.6
3.0 wt % of FCPP	-8.9	157.9

The composites degradation temperatures at 5% weight loss were measured by TGA. It can be seen that the degradation temperature decreased with increasing filler contents. The thermal stability of pure PP was better than all composites. In comparison of FCPP with CCPP, the CCPP had the higher thermal stability than FCPP. This might be because of the difference between compositions of the filler that affected the stability. Usually CC will have more carbon deposit while FC will not have. Moreover, the size of the filler might affect the stability. The CC has larger sizes because of the carbon deposit and so this filler is harder distributed through the matrix than FC. In other aspect, the agglomeration of the FC also response for the poor migration in the matrix, so the degradation temperature will be lower.

Table I shows glass transition temperature and melting temperature of pure PP and its composites at various filler contents. The obtained results showed that the melting temperature (T_m) and glass transition temperature (T_g) were not abruptly changed when CC was incorporated in the polymer matrix. However, T_m tend to decrease when FC was incorporated in the polymer matrix, while T_g were slightly increased. The decrease in T_m of the matrix might result from the agglomeration of the FC which reduced the interfacial bonding between fillers and matrix at the interfaces.⁸ Regarding the effect of the filler content on the T_m and T_g , no significant differences were observed.

TABLE II
Tensile Strength of the FCPP and CCPP at Various Filler Contents and Filler Types

Material	Tensile strength (MPa)
Pure PP	28.81
1.0 wt % of CCPP	29.05
2.0 wt % of CCPP	30.08
3.0 wt % of CCPP	29.24
1.0 wt % of FCPP	28.98
2.0 wt % of FCPP	29.02
3.0 wt % of FCPP	27.26

TABLE III
Young's Modulus of the FCPP and CCPP at Various Filler Contents and Filler Types

Material	Young's modulus (MPa)
Pure PP	1160.10
1.0 wt % of CCPP	1215.22
2.0 wt % of CCPP	1362.48
3.0 wt % of CCPP	1385.63
1.0 wt % of FCPP	1286.98
2.0 wt % of FCPP	1288.39
3.0 wt % of FCPP	1260.80

Mechanical properties

The effect of CC and FC on tensile strength, Young's modulus, elongation at break of all composites at various filler contents are shown in Tables II–IV. From Table II, it can be seen that the tensile strength was not significantly changed with increasing filler content, because the polar nature of filler and non-polar nature of polymer causes the poor interaction and dispersion between filler and polymer which may hardly effect the tensile strength.^{9–12}

From Table III, it can be seen that Young's modulus of CCPP increased with increasing filler content. This may be due to the increased interfacial area in the composite with filler, with promotes the stress transfer efficiency with in small strain range.¹³ Moreover, it may be caused the brittle characteristics of fillers. The CCPP had the higher Young's modulus than FCPP. An increase in Young's modulus of the composites with increasing filler content has also been observed in other filler-PP composites.^{4,9,14–16}

From Table IV, the elongation at break of PP composites decreased with increasing filler content. This result indicated that the increasing filler content caused less ductility or more brittle because the addition of filler led to the higher stiffness. A decrease in elongation at break of the composites with increasing filler content was also observed in other studies of filler-PP composites.^{9,14,17}

In consideration of the effect of filler types in Tables II–IV, it can be seen that the CCPP exhibited higher Young's modulus than FCPP. This result indicated that CCPP exhibited higher stiffness than

TABLE IV
Elongation at Break of the FCPP and CCPP at Various Filler Contents and Filler Types

Material	Elongation at break (%)
Pure PP	4.97
1.0 wt % of CCPP	4.39
2.0 wt % of CCPP	3.95
3.0 wt % of CCPP	3.65
1.0 wt % of FCPP	4.33
2.0 wt % of FCPP	4.07
3.0 wt % of FCPP	3.33

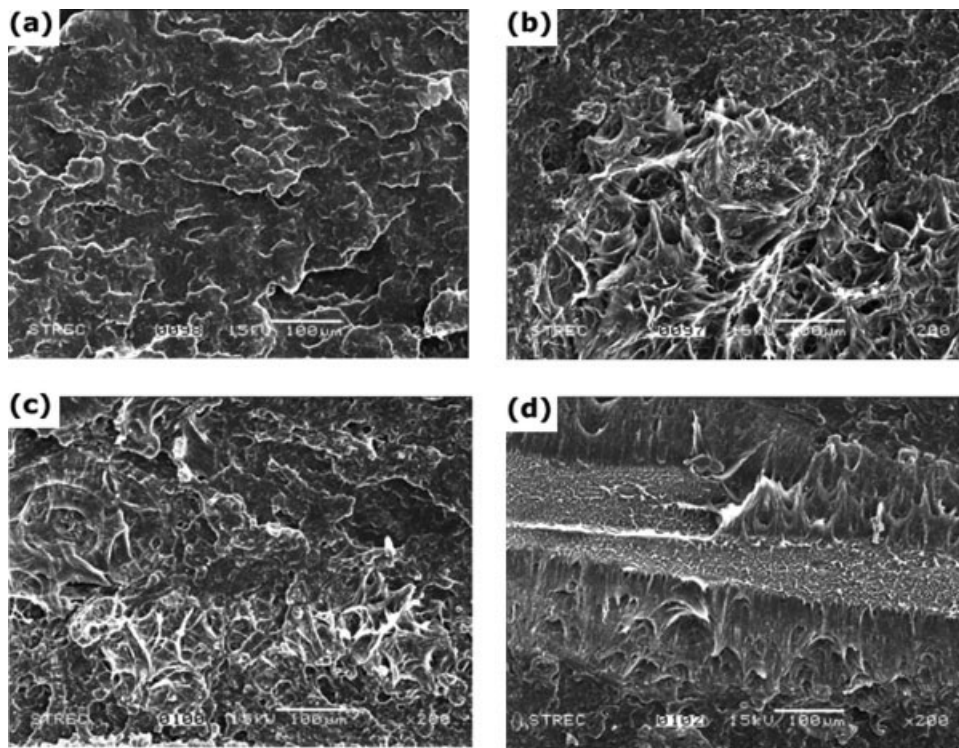


Figure 4 SEM micrographs of the tensile-fractured surface of (a) Neat PP (b) 1.0 wt % CCPP (c) 2.0 wt % CCPP, and (d) 3.0 wt % CCPP.

FCPP. This may be due to difference in a polarity miss match of fillers and polymer matrix. Therefore, FC has higher surface area than that of CC. This

may induce agglomeration and poor adhesion between FC and polymer matrix and subsequently decrease the stiffness. Moreover, it can be seen that

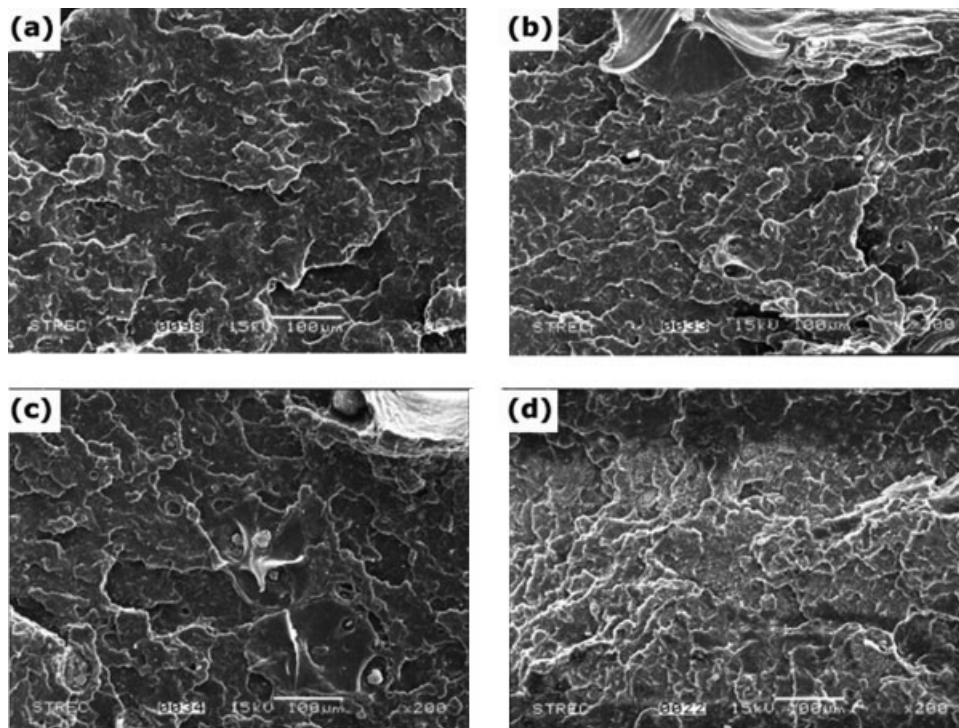


Figure 5 SEM micrographs of the tensile fracture surface of (a) Neat PP (b) 1.0 wt % FCPP (c) 2.0 wt % FCPP, and (d) 3.0 wt % FCPP.

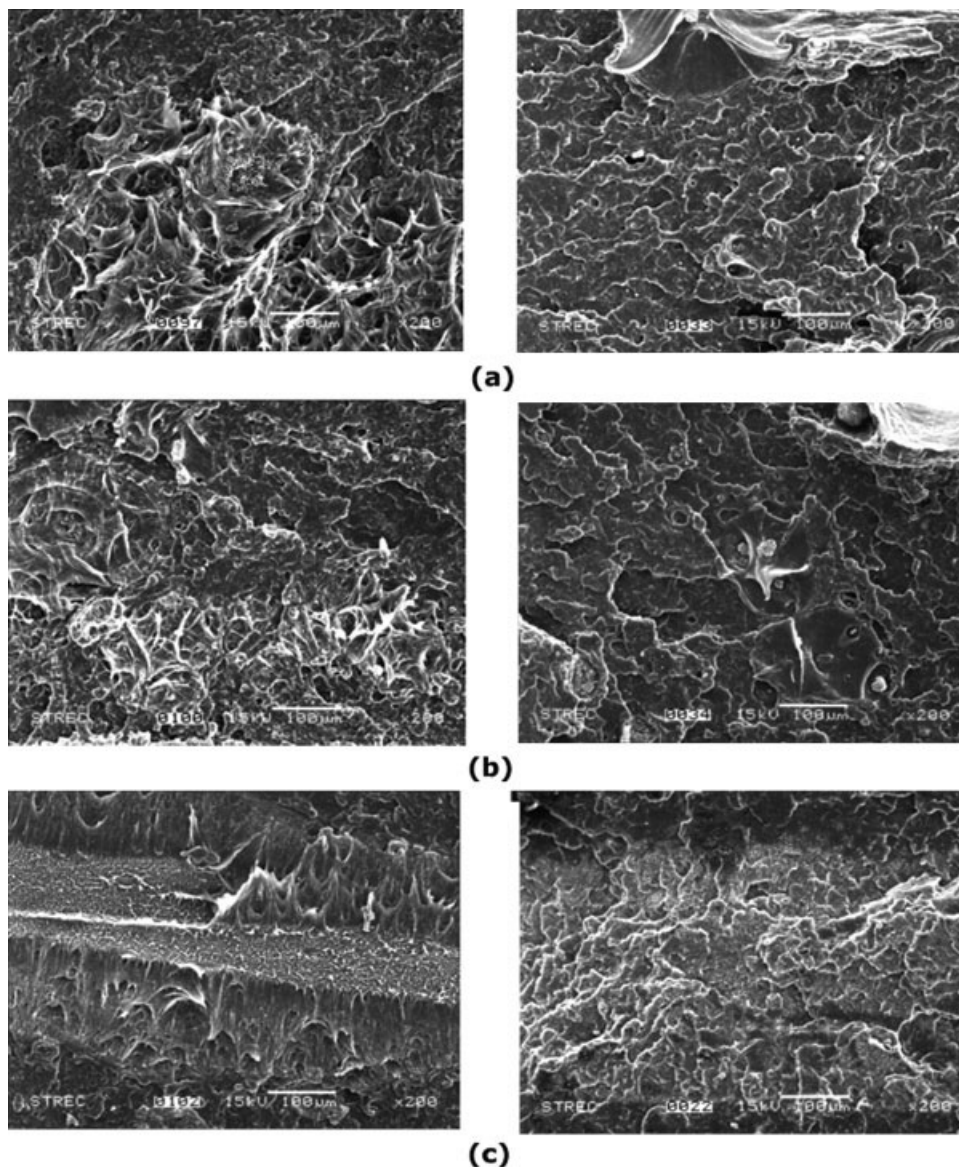


Figure 6 Compared to SEM micrographs of the tensile fracture surface between CCPP and FCPP at (a) 1.0 wt % (b) 2.0 wt % and (c) 3.0 wt %.

tensile strength and elongation at break of CCPP and FCPP were not largely different.

Morphological properties

From Figure 4, the SEM micrographs of the tensile-fractured surfaces of CCPP at various filler contents and pure PP exhibit the fibrils and the plastic deformation of the matrix polymer. There is a greater amount of plastic deformation of the matrix polymer in the CCPP than in the pure PP. This appearance reveals the good adhesion between PP matrix and CC. Moreover, it could be expected that the composite had higher stiffness than pure matrix. Moreover, the tensile tests of CCPP represented the higher stiffness than PP because of the properties of the CC filler.

The SEM micrographs of the tensile-fractured surfaces of FCPP at various filler content and pure PP are represented in Figure 5. The SEM micrographs show that the dispersion of the FC on the polymer surface was nonuniform. This nonuniform dispersion led to local agglomeration of FC within the polymer. FCPP and pure PP present similar fracture features is surface roughness. It can be seen that, there was good adhesion inside FCPP. These observations support the results of the tensile tests where the FCPP displayed higher stiffness than the pure PP.

From Figure 6, the SEM micrographs of the tensile fracture surfaces of CCPP compared with FCPP at various filler content. It can be seen that CCPP had higher plastic deformation of polymer than FCPP. These observations support the results of the tensile

tests where the CCPP displayed higher stiffness than the FCPP.

CONCLUSIONS

The degradation temperature of CCPP and FCPP decreased with increasing filler contents. In addition, the degradation temperature of CCPP was higher than of FCPP. T_m and T_g were not largely different when filled with CC. On the contrary, the T_m of PP composites decreased when filled with FC, while the T_g increased. The pure PP, CCPP and FCPP with increasing filler contents showed no significant change in tensile strength. Young's modulus of CCPP and FCPP increased with increasing filler contents. The elongation at break of CCPP and FCPP decreased with increasing filler contents. The CC can be utilized as a filler to increase the Young's modulus of PP while maintaining T_g , T_m , and tensile strength of the matrix while FC can not utilize as a filler because of the adverse effects.

References

1. Wu, C. L.; Zhang, M. Q.; Rong, M. Z.; Friedrich, K. *Compos Sci Technol* 2002, 62, 1.
2. Mahfuz, H.; Adnan, A.; Rangari, V. K.; Jeelani, S.; Jang, B. Z. *Compos A* 2004, 35, 519.
3. Tang, W.; Santare, M. H.; Advani, S. G. *Carbon* 2003, 41, 2779.
4. Machado, M. A. L.; Valentini, L.; Biagiotti, J.; Kenny, J. M. *Carbon* 2005, 43, 1499.
5. Yasmin, A.; Luo, J. J.; Daniel, I. M. *Compos Sci Technol* 2006, 66, 1179.
6. Wang, Y.; Chen, F. B.; Li, Y. C.; Wu, K. C. *Compos B* 2004, 35, 111.
7. Ding, C.; Jia, D.; He, H.; Guo, B.; Hong, H. *Polym Test* 2005, 24, 94.
8. Kim, H. S.; Kim, S.; Kim, H. J.; Yang, H. S. *Thermochim Acta* 2006, 451, 181.
9. Premalal, H. G. B.; Ismail, H.; Baharin, A. *Polym Test* 2002, 21, 833.
10. Suarez, J. C. M.; Coutinho, F. M. B.; Sydenstricker, T. H. *Polym Test* 2003, 22, 819.
11. Yang, H. S.; Wolcott, M. P.; Kim, H. S.; Kim, S.; Kim, H. J. *Polym Test* 2006, 25, 668.
12. Rattanasom, N.; Saowapark, T.; Deeprasertkul, C. *Polym Test* 2007, 26, 369.
13. Wu, C. L.; Zhang, M. Q.; Rong, M. Z.; Friedrich, K. *Compos Sci Technol* 2005, 65, 635.
14. Ismail, H.; Edyham, M. R.; Wirjosentono, B. *Polym Test* 2002, 21, 139.
15. Mwaikambo, L. Y.; Martuscelli, E.; Maurizio, A. *Polym Test* 2000, 19, 905.
16. Ruksakulpiwat, Y.; Suppakarn, N.; Sutapun, W.; Thomthong, W. *Compos A* 2007, 38, 590.
17. Karmarkar, A.; Chauhan, S. S.; Modak, J. M.; Chanda, M. *Compos A* 2006, 38, 227.