HYBRID EFFECTS ON MECHANICAL PROPERTIES OF INJECTION MOLDED NANO-HYBRID COMPOSITES

Y. Arao[1*], H. Suzuki[2], S. Yumitori[3], T. Tanaka[1]. K. Tanaka[4], T. Katayama[4]

[1] *Department of Mechanical and System Engineering, Doshisha University, 1-3 Tatara Miyakodani, Kyotanabe, Kyoto, Japan*
[2] *Graduate School of Doshisha University*
[3] *New Energy and Industrial Technology Development Organization, 1310. Omiya-cho, Saiwai-ku, Kawasaki, Kanagawa, Japan*
[4] *Department of Biomedical Engineering, Doshisha University*
**yoshihiko.arao@gmail.com*

Keywords: Injection molding, thermoplastics, carbon fiber, nanofiller

Abstract

Various kinds of nanofillers were added to improve the mechanical performance of carbon fiber/polypropylene composites. Nanofillers were well dispersed by a twin-screw extruder. The pellets including nanofiller were compounded with carbon fiber in the same condition. The addition of nanofiller significantly affects the modulus and strength of composites. It was found that the effects of nanofillers for the performance of composites depend on the filler species and filler content. Optimum filler content was found around 1 wt%.

1 Introduction

The use of composite materials in the automotive industry is now well accepted and increasing every year. In fact, long glass fiber thermoplastics composite systems had been used for semi-structural and engineering applications. The main idea of using polymeric composite material is reducing the weight of automobile to improve its fuel cost. In addition, thermoplastic composites have recyclability. This characteristic is recognized as a strong driving force for the future application. Recently, carbon-fiber-polypropylene composites systems get a lot of attentions [1]. One of the reasons is that carbon fiber has higher specific stiffness than glass fibers. High specific stiffness contributes the lightweight design of the car. Polypropylene, which is a widely used commodity polymer, is chosen due to its good processibility, low cost and high performance. The cost and strength of these composites depend on the fabrication method. The composites with continuous fiber show the highest mechanical performance, however the productivity is extremely low in the present circumstance. Therefore, composites with continuous fiber are not used for mass production. Short fiber reinforced thermoplastic (SFRP) is usually applied for the car component due to its ease of processing and high productivity through injection molding technique. The problem of SFRP is its low strength and stiffness, even though high strength fibers such as carbon fiber are combined.

SFRP have been well studied by Thomason [2]-[4]. The strength of SFRP is dominated by fiber length, fiber content, and interface strength between fiber and matrix. The interface strength between carbon fiber and polypropylene is distinctly small [5]-[7]. Thomason reported that interfacial shear strength in the GF-PP system is dominated by the residual radial compressive stresses at the interface, and the contribution of chemical bonding is small [5]. To improve the adhesion between fibers and polypropylene, compatibilizers like maleic anhydride grafted polypropylene (MAPP) are generally used in small proportions [8]-[10].

Recently, nanocomposites that includes nanofillers such as carbon nanotubes (CNTs) or clay have been investigated widely. Well dispersed nanofiller can improve the mechanical and thermal properties of resin with low filler loading (typically less than 5%). The use of nanocomposites as matrix material in thermoplastic composites is an interesting new option, since the small particle fit easily between the fiber and the increased modulus could improve the flexural and compressive strength of the composites. A key advantage of the use of nanocomposite instead of other polymers to improve the fibre composite properties is that the properties can be improved without any chage in the processing condition. Therefore, a new type of three-phase hybrid composite has been suggested by lots of authors [11]-[21]. The nanoparticles in the matrix nanocomposites are only intended to improve the matrx-dominated properties of the fibre composites. However, a remarkable result for these three-phase hybrid composites is reported that the nanofiller affects the interface adhesion between fiber and matrix. Mohan et al. reported that the nanoclay improves the fracture strength and wear properties of short glass fiber-reinforced polypropylene composites [11]. Nano silica and alumina particles also showed the positive effects for the mechanical properties of thermosetting composites [16]-[18]. Vlasveld reported that the flexural strength of glass/PA6 composite increased due to the improvement of stiffness of matrix by the addition of nanofiller [14]. On the other hand, he also found that exfoliated layered silicate has the negative effect on the bonding between the glass fiber and PA6 nanocomposites [12]. Istiman et al. also confirmed nanofiller reduced the interfacial shear strength of composites [19],[20]. Conflicted results are found, because the effects of nanofiller depend on the kind of matrix and dispersion state of filler.

The hybrid effects with nanofiller possibly compensate the low strength of carbon fiber/polypropylene based SFRP composites. Broad studies for this three-phase hybrid composite have not been yet conducted as far as author's little knowledge. In this study, various nanofiller were added to the carbon fiber/polypropylene composite to find the effective nanofiller for that material system. Hybrid composites were compounded by a twin-screw extruder and were fabricated by an injection molding. Nano-hybrid SFRPs were evaluated by conducting tensile and bending tests. Strengthen mechanism by adding nanofiller was discussed through the investigation of fiber length and interface strength between fiber and nanocomposites.

2 Materials and testing method

2.1 Materials

Polypropylene (PP, J108M) was provided as pellets by Prime Polymer. Its melt flow index was 45 g/10 min at 230 °C and density at room temperature was 0.91 g/cm^3. Carbon fiber (T300) supplied by Toray industries was used as reinforcement of SFRP. Nanofillers prepared in this study were various in forms. The sphere types of fillers are silica particles (TA50C, Admatechs) and alumina particles (TMDAR, Taimei Chemicals). The average diameter of the former is 50 nm and that of latter is 100 nm. Carbon nanotube (VGCF-X, Showa Denko) was used as fiber type nanofiller. The diameter of carbon nanotube (CNT) is 10-15 nm. Platelet clay (Nanomer 1.44P, Sigma-aldrich) was also prepared. To improve the dispersion and adhesion of the filler, MAPP (Youmex 1010, Sanyo Chemical) was used as a compatibilizer.

2.2 Preparation of three-phase hybrid composites.

A corotating twin-screw extrude (ZSK18, Coperion) with a screw diameter of 2 mm and a length-diameter ratio of 35 was used to compound PP/CF/nano filler composites. The screw elements were selected to provide high dispersive mixing. Screw configuration is shown in Fig. 1. It is composed of screw conveying elements and three mixing zones with different configurations of kneading blocks, so as to promote dispersive and distributive mixing. The process temperature was set at 180 °C from the hopper to the die. The screw speed was 150 rpm and throughput *Q*=1 kg/h.

In the first step, PP, nanofillers and MAPP were dry-mixed thoroughly before feeding in to the twin-screw extruder. They were compounded at the condition mentioned above. The nanocomposite extrudates were immediately quenched in water and cooled in air till ambient temperature. Then the extruded strand were chopped into granules and dried. In the second step, the pellets were mixed with carbon fibers using the twin-screw exturder, and compounded under the same condition. The weight content of carbon fiber and MAPP was 20 and 4 wt%, respectively. The weight content of nanofiller was varied from 1 wt% to 4 wt%.

All the specimens were injection molded into dumbbell-shaped tensile bars using a single screw injection molding machine (PLASTR ET-40V, Toyo Machinery & Metal) with a barrel temperature of 210 °C. An end-gated mold was used for molding dumbbell-shaped samples according to JIS K7113. The thickness and width of the specimens are 4 and 10 mm, respectively. The flexural specimens have the same thickness and width with the tensile specimens.

The tensile properties of specimens were determined using 5 samples for each condition with a universal testing machine (AG-100kN, Shimadzu) at a constant cross-speed of 1 mm/min. An extensometer (ST50-10-10, Shimadzu) with gauge length of 50 mm was used for strain measurement. The flexural tests were conducted in the three-point loading mode. The span length and cross-speed were 64 mm and 2 mm/min, respectively.

Fracture surface of the specimens were observed by scanning electron microscopy (JSM-7001FD, JEOL). Prior to SEM observation, all fracture surfaces of the tensile specimens were sputter coated with gold.

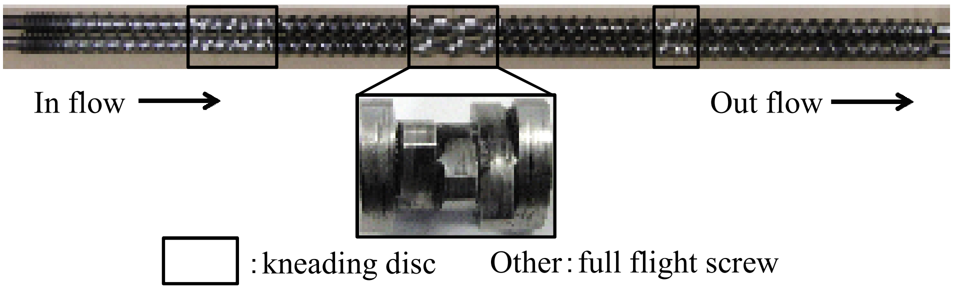


Figure 1. Screw configuration used in this study.

3 Experimental results

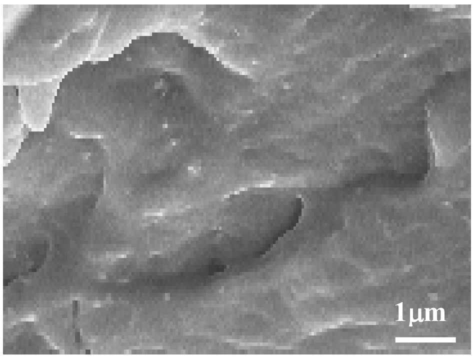
3.1 Dispersion state of nano fillers

The effects of nanofillers on the mechanical properties of composites depend on the dispersion state of nanofillers. Figure 1 shows the dispersion states for each hybrid composites (1 wt%). The nanofillers usually agglomerates due to strong interaction between the fillers. However, alumina particles were well dispersed in the polypropylene. Silica particles were detected as small aggregates of different forms, containing 3-10 particles. The silca particles used in this study is smaller than alumina particles. Therefore, dispersion state of silica particles was worse than that of alumina particles. The dispersion state of CNTs was worst in the nanofiller. Agglomerates with the size less than 1μm was observed for CNT based hybrid composites. The dispersion state of CNTs was nearly equal compared to the results reported by other literatures [21]. For nanoclay composite, the clays were not detected by SEM. It is deduced that the clay exfoliate well, but it's not completely exfoliated structure. This is because completely exfoliated clay in PP was extremely difficult and hasn't been achieved yet. The compounding method used in this study can disperse the nanofillers well when the filler content is low, such as 1 wt%.

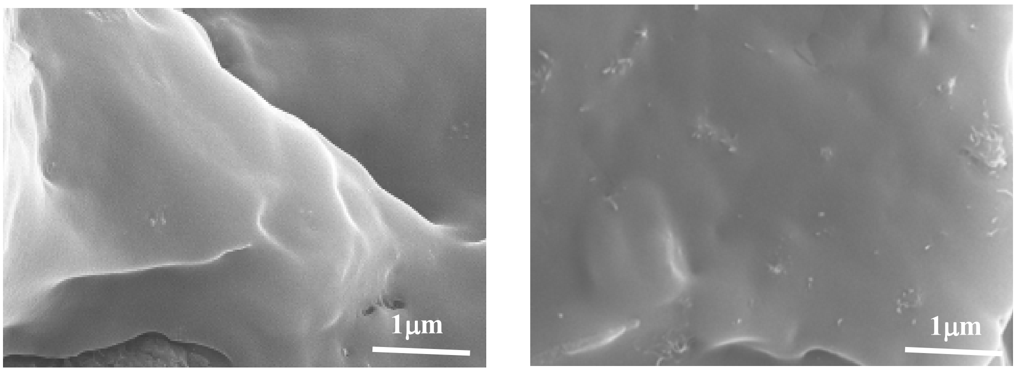
3.2 Tensile test

Figure 3 shows the stress-strain (S-S) curves of the composites. The strength of CF/PP without MAPP was approximately 34 MPa. This value is the same with the strength of PP. The length of carbon fiber is too short to strengthen the composites. Fu et al. found that failure strain decreases with the reduction of fiber length. Matrix crack occurs at the ends of fibers because the stress concentrates at the ends. When the fiber length decreases, the number of fiber ends proportionally increases. Carbon fibers in composites suffered high shear stress during the compounding process in twin-screw extruder. Short carbon fibers do not contribute the strength of composites due to low stress transfer efficiency and facilitation of matrix crack at the ends of fibers. Failure strain and maximum stress increased by adding MAPP. Good adhesion between fiber and matrix can suppress the debonding between them and improve the stress transfer efficiency.

It is obvious that adding CNT to the CF/PP composite improves the maximum strength and reduces the failure strain compared to the CF/PP with MAPP. It means the SFRP becomes less ductile after incorporation of CNT. This tendency was observed for other hybrid composites. Figure 3 shows the maximum tensile strength against nanofiller content. The maximum strength of the composites increased by adding MAPP. It is worth noting that the strength of composites further improved by adding nanofiller. Except for clay hybrid composites, adding nanofiller showed positive effects for the tensile strength of composites.



(a) Alumina particles (1wt%)



(b)Agglomerate of silica (1wt%) (c) Agglomerate of CNT (1wt%)

Figure 2. SEM observation of the fracture surface of hybrid composites

CNT and alumina particles were the most effective at 1wt % of nano filler, thought the CNT was agglomerated. It is expected that the addition of CNT enhances the strength of composites more, when dispersion of CNT is improved. Strength of hybrid composites decreased when the weight fraction of filler increased from 1 wt% to 4 wt%. Interparticle distance of nano fillers decreased with increasing the weight fraction of nano fillers. Small interparticle distance facilitates the agglomeration of fillers. It is presumed that the growth of agglomeration of filler reduces the strength of hybrid composites. The optimum weight fraction of nanofiller exists around 1 wt% for these material systems.

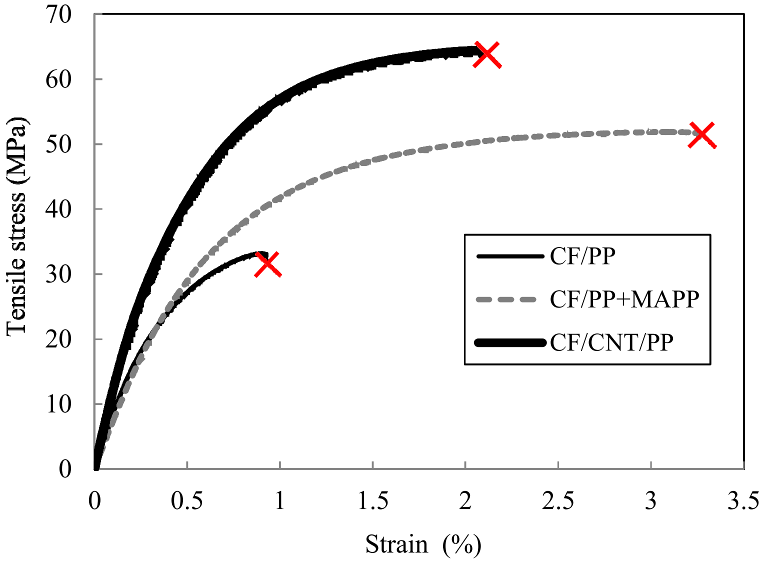


Figure 3. Stress-strain curves for CF/PP and CF/CNT/PP composites. 1 wt% of CNT was added to the CF/PP composites.

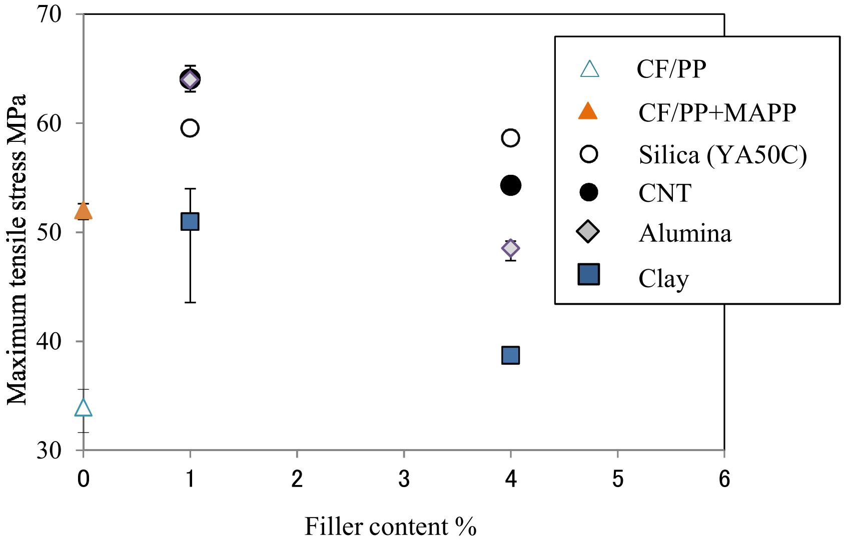


Figure 4. Maximum tensile stress of composites against nano filler content.

3.2 Flexural test

Figure 5 shows the elastic modulus measured by three-point bending test. Elastic modulus of CF/PP didn't change by adding MAPP. However, addition of nanofillers increased elastic modulus of composites. Elastic modulus of composites increased approximately 1GPa by adding 1wt % of CNT or alumina particles. It is reported that addition of 1wt% of nanofiller slightly increases the modulus of polypropylene about 0.2-0.6 GPa [22, 23]. Some synergy effects possibly exist for these hybrid composites. It is worth noting that modulus and strength for only the hybrid composite with silica nano particle showed sharp enhancement by adding 4 wt% of filler. It is conflicted results for the concept of agglomeration. One of the potential factors is the improvement of matrix crystallization. A small amount of well-dispersed nanofiller can act the effective nucleating agent to accelerate the crystallization of PP matrix and thus promote the mechanical performance of hybrid composites. Further study is needed to interpret this result. The flexural strength (Fig. 6) showed almost same tendency with the results of tensile strength. The strength of clay based composite decreased with increasing the addition of clay.

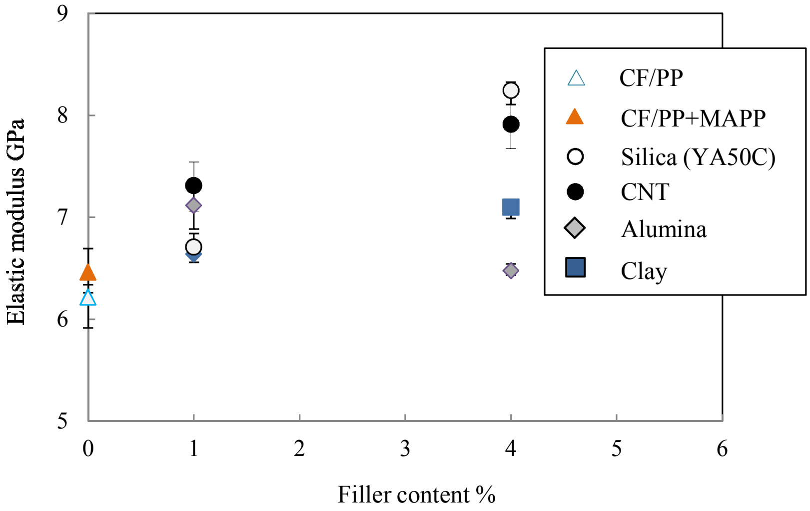


Figure 5. Improvement of elastic modulus by adding nano filler.

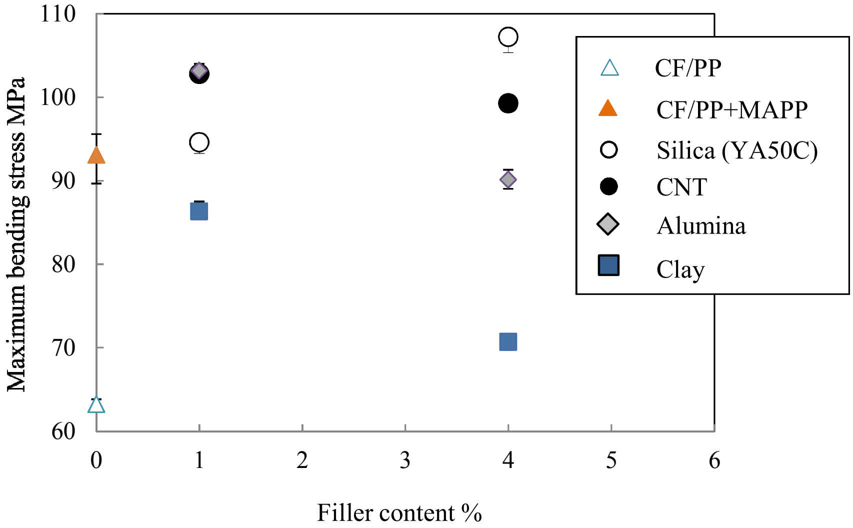


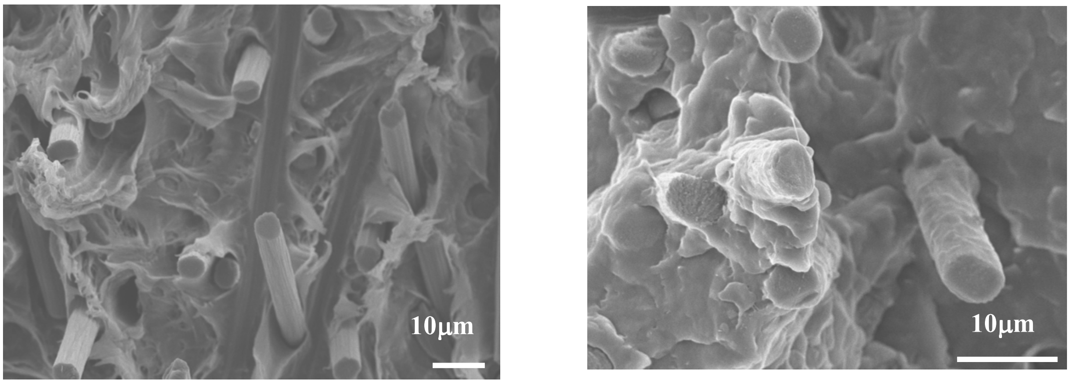
Figure 6. Maximum bending stress against nano filler content.

3.3 Fractography

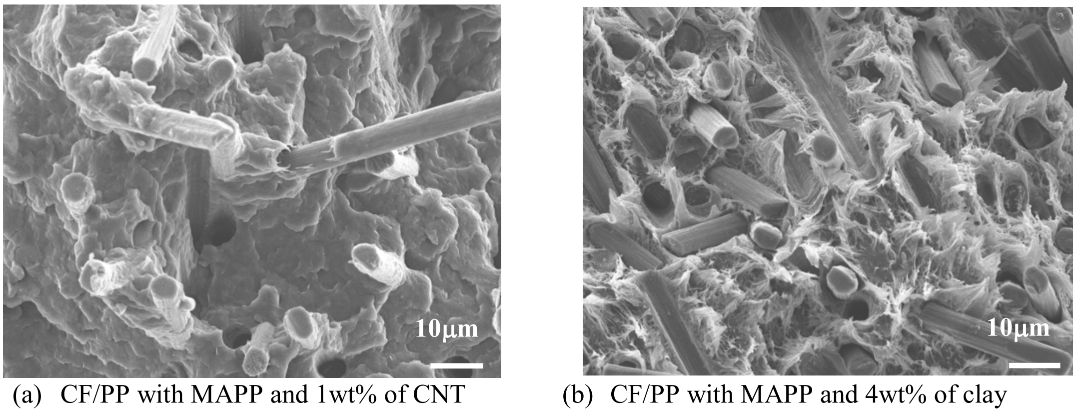
The SEM micrographs of the fracture surfaces of CF/PP and hybrid composites are shown in Fig. 7. For the fracture surface of CF/PP composites without PP, The surface of carbon fiber was very smooth, and the fiber was pulled out directly. Fiber-matrix deboning was also seen. It implies that the adhesion between carbon fiber and PP is weak without the comatibilizer. Weak interface strength is due to the hydrophobic nature of PP molecules, which gives a big problem in enhancing the adhesion between hydrophilic fiber and hydrophobic PP matrix. Addition of MAPP improves the adhesion of carbon fiber and matrix. Fig .7(c) demonstrates that the surface of carbon fiber gets impregnated in the resin. However, most of fibers were pulled out from the matrix. The fiber length of carbon fiber was not enough to achieve the fiber fracture. In this case, the reinforcement efficiency of fiber is quite small.

The carbon fibers on the fracture surface were coated by resin for the hybrid composites. It was concerned that most of MAPP were used to improve the adhesion of nanofiller and it possibly reduced the adhesion between fiber and resin. However, the fibers were coated by resin and adhesion seems to be good for CF/CNT/PP composites. The adhesion of CF/PP/clay composites was weak as shown in Fig. 7(d). Fiber-matrix debonding was observed, and fibers were not coated by resin. This leads to the strength reduction for CF/clay/PP hybrid composites. In general, MAPP has a very low molecular weight, which allows its highly mobilized short chains to interact actively with a great number of clay platelets in large clay surface areas during melt blending. This facilitates good clay dispersion and can achieve the effective intercalation [24]. It is deduced most of MAPP was incorporated to the interlayer of clays, and it reduced the adhesion between carbon fiber and polypropylene. It is reported that clay has negative effects for the interfacial properties of other materials systems. The intercalation, which has the traction force into the interlayer of clay, also possibly reduces the interfacial strength of fiber and matrix. Completely exfoliated structure might be required to improve the mechanical properties of clay based hybrid composites.

The strength of SFRP is successfully predicted by Kelly-Tyson model [3]. For hybrid composites, it is assumed that the main reinforcement is fibers and nanofiller only changes the properties of matrix. Therefore, the mechanical properties of hybrid composites are usually predicted by some models with the consideration of matrix modification. In this assumption, fiber length and interface strength are dominant factors for the mechanical performance of hybrid composites. The effects of nanofiller on fiber length and interfacial properties of hybrid composites will be discussed in the future work.



(c) CF/PP without MAPP (d) CF/PP with MAPP



(a) CF/PP with MAPP and 1wt% of CNT (b) CF/PP with MAPP and 4wt% of clay

Figure 7. SEM micrographs of fracture surface after tensile test.

References

[1] F. Rezaei, R. Yunus, N.A. Ibrahim, E. S. Mahdi. Development of short-carbon-fiber-reinforced polypropylene composite for car bonnet. *Polymer-Plastics Technology and Engineerin*g, **47**, 351-357, (2008)

[2] J. L. Thomason, M.A. Vlug. Influence of fibre length and concentration on the properties of glass fibre-reinforced polypropylene: 1. Tensile and flexural modulus *Composite Part A*, **27**, 477-484, (1996)

[3] J.L. Thomason, M.A. Vlug, G. Schipper, H.G.L.T. Krikor. Influence of fibre length and concentration on the properties of glass fibre-reinforced polypropylene: 3. Strength and strain at failure. *Composite Part A*, **27**, 1075-1084, (1996)

[4] J. L. Thomason. Influence of fibre length and concentration on the properties of glass fibre-reinforced polypropylene: 5. Injection moulded long and short fibre PP. *Composite Part A*, **33**, 1641-1652, (2002)

[5] L. Yang, J.L. Thomason. Temperature dependence of the interfacial shear strength in glass-fibre polypropylene composites. *Composites Science and Technology*, **71**, 1600-1605, (2011)

[6] J.L. Thomason. Micromechanical parameters from macromechanical measurements on glass reinforced polypropylene. *Composites Science and Technology*, **62**, 1455-1468, (2002)

[7] S. Y. Fu, B. Lauke, E. Mader, C.Y. Yue, X. Hu. Tensile properties of short-glass- and short-carbon-fiber-reinforced polypropylene composites. *Composite Part A*, **31**, 1117-1125, (2000)

[8] N.G. Karsli, A. Aytac. Effects of maleated polypropylene on the morphology, thermal and mechanical properties of short carbon fiber reinforced polypropylene composites. *Materials and Design*, **32**, 4069-4073, (2011)

[9] M.S. Kumar, A.K. Ghosh, N. Bhatnagar. Mechanical properties of injection molded long fiber polypropylene composite, Part 1: Tensile and flexural properties. *Polymer Composites*, **28**, 259-266, (2007)

[10] X. Fu, B. He, X. Chen. Effects of compatibilizers on mechanical properties of long glass fiber-reinforces polypropylene. *Journal of Reinforced Plastics and Composites*, **29**, 936-949, (2010)

[11] T.P. Mohan, K. Kanny. Influence of nanoclay on rheological and mechanical properties of short glass fiber-reinforced polypropylene composites *Journal of Reinforced Plastics and Composites*, **30**, 152-160, (2011)

[12] D.P.N. Vlasveld, P.P. Parlevliet, H.E.N. Bersee, S.J. Picken. Fibre-matrix adhesion in glass-fbre reinforced polyamide-6 silicate nanocomposites, *Composites Part A*, **36**, 1-11, (2005)

[13] Y. Yoo, M.W. Spencer, D.R. Paul. Morphology and mechanical properties of glass fiber reinforced Nylon 6 nanocomposites. *Polymer*, **52**, 180-190, (2011)

[14] D.P.N. Vlasveld, H.E.N. Bersee, S.J. Picken. Nanocomposite matrix for increased fibre composite strength. *Polymer*, **46**, 10269-10278, (2005)

[15] J. Njuguna, K. Pielichowski, S. Desai. Nanofiller-reinforced polymer nanocomposites. *Polymer for Advanced Technologies*, **19**, 947-959, (2008)

[16] C.M. Manjunatha, A.C. Taylor, A.J. Kinloch, S. Springer. The tensile fatigue behavior of a silica nanoparticle-modified glass fibre reinforced epoxy composite. *Composites Science and Technology*. **70**, 193-199, (2010)

[17] O. Akinyede, R. Mohan, A. Kelkar, J. Sankar. Epoxy/fiberglass composites hybridized with alumina nanoparticle. *Journal of Composite Materials*, **43**, 769-781, (2009)

[18] L. Tang, H. Zhang, X. Wu, Z. Zhang. Improvement and mechanism of the interface strength between fiber and epoxy resin filled with the alumina nanoparticles. *Proceedings of ICCM-18* (2011)

[19] N.A. Isitman, M. Aykol, C. Kaynak. Nanoclay assisted strengthening of fiber/matrix interface in functionally filled polyamide 6 composites. *Composite Structures*, **92**, 2181-2186, (2010)

[20] N.A. Isitman, M. Aykol, C. Kaynak. Interactions at fiber/matrix interface in short fiber reinforced amorphous thermoplastics composites modified with micro- and nano-fillers. *Journal of Material Science*, **47**, 702-710, (2012)

[21] K. Prashantja, J. Soulestin, M.F. Lacrampe, P. Krawczak, G. Dupin, M. Claes. Masterbatch-based multi-walled carbon nanotube filled polypropylene nanocomposites: Assessment of rheological and mechanical properties. *Composites Science and Technology*, **69**, 1756-1763, (2009)

[22] R.J. Zhou, T. Burkhart. Mechanical properties and morphology of microparticle and nanoparticle-filled polypropylene composites. *Journal of Material Science*, **45**, 3016-3022, (2010)

[23] M. Ganb, B.K. Satapathy, M. Thunga, R. Weidisch, P. Potschke, D. Jehnichen. Structural interpretations of deformation and fracture behavior of polypropylene/multi-walled carbon nanotube composites. *Acta Materialia*, **56**, 2247-2261, (2008)

[24] Y. Dong, D. Bhattacharyya. Effects of clay type, clay/compatibiliser content and matrix viscosity on the mechanical properties of polypropylene/organoclay nanocomposites. *Composites: Part A*, **39,** 1177-1191, (2008).