Mechanical, Flow, and Morphological Properties of Talc- and Kaolin-Filled Polypropylene Hybrid Composites

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Received 19 August 2005; accepted 7 May 2006
DOI 10.1002/app.25535
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polypropylene (PP) hybrid composites have been produced by compounding two types of mineral fillers, viz., talc and kaolin with PP copolymer using a twin screw extruder. The PP hybrid composite was injection-molded into dumbbell specimen for tensile, flexural, and impact properties characterizations. MFI and SEM studies were used to characterize the flow and morphological properties of the PP hybrid composites. The result shows that most of the hybrid composites showed a significant decrease in flow, tensile, flexural, and impact properties compared with the single filler-filled PP composites. However, a hybridization effect was seen for the PPT20K10 hybrid composites, through the synergistic coalescence of positive characteristics from 20 wt % of talc and 10 wt % of kaolin. This hybrid formulation have given an economically advantageous material with the mechanical properties (tensile, flexural, and impact) comparable to those of the talc-filled PP composites. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 434–441, 2007

Key words: polypropylene; hybrid composite; talc; kaolin

INTRODUCTION

Polypropylene (PP) resins have been known for its good mechanical properties, corrosion resistance, low density, low cost, and easy processability to allow it to be used as a versatile matrix for various types of fillers.[1] The introduction of particulate filler into PP improves their mechanical properties and lowers the cost. Particulate-filled thermoplastic composites have proved to be of significant commercial importance in recent years, as industrialists and technologists seek to find new and cost-effective materials for specific applications. There are many types of particulate fillers used to modify properties of filled PP such as talc, kaolin, calcium carbonate, mica, etc.[2–14]

The introduction of talc has been widely known in thermoplastics application, as they used to modify some properties like stiffness, strength, dimensional stability, and crystallinity, but this is usually attained at the expense of impact strength.[2–5] However, these negative effects can be minimized by the use of very fine particles filler. In this respect, introduction of very fine particle-like kaolin has the unique advantage of increasing the impact strength above that of the PP matrix.[6] The use of kaolin is very common practice in the rubber or elastomer industry, but their presence as fillers in thermoplastic industry has not been reported widely. An article by Mareri et al. revealed that the use of surface-treated kaolin with a very fine particle size improved the stiffness and impact properties of PP.[6] Study by Qiu et al. showed that kaolin-filled PP/mPE blend exhibits better impact performance at a low temperature.[7]

Conventional hybrid composites generally consist of different types of fibers and/or fillers in thermoplastic matrix. Hybrid composites are becoming more and more commercially significant in their own right although they were at first developed purely as research tools or model systems for systematic studies of composite structures. There have been numerous studies of hybrid composites using two different kinds of reinforcements in the form of natural fibers, glass fibers, and carbon fibers,[8–11] but only few references are available on particulate fillers-filled PP hybrid composites.[12,13]

The hybrid composite could be developed in manufacturing industry for various reasons including: (i) tailor-made composites to meet specific processing and performance requirements which cannot be satisfied by a single component; (ii) scientific interests by developed new materials with a unique material property characteristic; and (iii) financial or economic advantages in ''diluting'' a more expensive reinforcement or filler with other cheaper dispersive materials.

The effect of individual talc and kaolin-filled PP has been studied in our previous article.[5] The main aim of

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Contract grant sponsor: Ministry of Science, Technology and Innovation, Malaysia; contract grant number: IRPA 6102908.

TABLE I
Material Specifications

Materials	Density (g/cm^3)	Hardness (Moh's scale)	Mean particle diameter (μm)
Talc	2.8	1	6.3
Kaolin	2.6	2	1.7

the present work is to study the effect of talc/kaolin hybrid fillers on PP copolymer matrix. The idea of mixing other fillers with PP/talc composite is to ''dilute'' expensive talc with a controlled percentage of cheaper kaolin for economic advantages. Hence, it would be possible to produce a hybrid composite that has a more favorable balance of properties.

EXPERIMENTAL

Materials

1. Polypropylene copolymer grade Pro-Fax SM240 with melt flow index (MFI) of 25 g/10 min and density of 0.894 g/cm^3 was supplied by Titan PP Polymers (M) Sdn. Bhd (Johor, Malaysia).
2. The two fillers that were used in their as received states are (a) talc grade supplied by Chung Chemicals Sdn. Bhd (Selangor, Malaysia); and (b) kaolin supplied by Finn Chemicals Sdn. Bhd (Kuala Lumpur, Malaysia). (refer to Table I for specification).
3. Additives comprising 0.25 wt % antioxidant (Irganox 1010) and 0.5 wt % ultraviolet stabilizer (Tinuvin 770 DF) both were from Ciba Specialty Chemicals (Switzerland). Both additives were added *in situ* during compounding process.

Sample preparation

Compounding was carried out with a twin-screw extruder (model Haake Rheomex CTW 100). The barrel temperatures of the four zones were 160, 170, 180, and 190°C from the feeding to the die zones. All components were fed into the extruder at once. Compounds were blended at a screw speed of 25 rpm. The extrudates were cooled in a water bath, pulled, and pelletized. Test specimens were injection-molded in a tensile mold using a 35-ton Battenfeld BA 350 CD machine with a Unilog 4000 control system. The injection-molding temperature ranges from 190 to 230°C, while the back pressure is 60 psi. Table II lists compounded formulations.

Sample Characterization

Melt flow index

The processability of the filled PP composites was determined using a Ray-Ran melt flow indexer according to ASTM D1238-90b. A load with 2.16 kg at 230°C was employed in the measurement. All tests were carried out at room temperature (23°C). The average value of five runs was taken for each sample.

Tensile test

The tensile properties were determined with an Instron 5580 100 kN electromechanical tensile testing machine with series IX control system. Tests were conducted in accordance with ASTM D638 using Type 1 test specimen dimensions. The tensile strength, tensile modulus, and elongation at break (EB) values were measured for this test. A crosshead speed of 5 mm/min was employed and the average value of five specimens was taken for each sample. All tests were carried out at room temperature (23°C).

Flexural test

A three-point flexural test was done using the Instron 5580 100 kN electromechanical tensile testing machine with series IX control system. A 3-mm cylindrical surfaces of a three-point loading system were used, and support span length was adjusted to 50 mm. Tests were conducted in accordance with ASTM D790-86 at crosshead speed of 3 mm/min at room temperature (23°C). The flexural strength and flexural modulus values were measured for this test. The average value of five specimens was taken for each sample.

Impact test

Impact testing was done using a Ray-Ran impact pendulum tester at impact energy of 7.5 kJ according to ASTM D256-88. The hammer velocity was set at 2.88 m/s, while the weight of the hammer was 1.811 kg. The Izod impact strength was measured for this test. All tests were carried out at room temperature (23°C). The average value of eight specimens was taken for each sample.

Mode of failure analysis

The mode of fracture was studied by an analysis of the fracture surfaces of tensile samples. This was car-

TABLE II
Sample Formulations for PP Hybrid Filler Composites

Sample formulations	PP loading (wt %)	Talc filler loading (wt %)	Kaolin filler loading (wt %)
PP	100	0	0
PPT30	70	30	0
PPT25K5	70	25	5
PPT20K10	70	20	10
PPT15K15	70	15	15
PPT10K20	70	10	20
PPT5K25	70	5	25
PPK30	70	0	30

ried out with a scanning electron microscopy (SEM) machine (Cambridge S-360, Leica); the fracture surfaces of the tensile test specimens were coated with a thin gold–palladium layer to prevent electrical charge accumulation during the examination.

RESULTS AND DISCUSSION

Flow properties

The melt flow index (MFI) values of single-filler and hybrid-filler filled PP composites are shown in Figure 1. It was noted in previous studies that the incorporation of kaolin resulted lower MFI values when compared with the talc-filled PP composites.[5]

In the case of mineral fillers, the flow properties may be influenced by the interaction between particles and the interaction between particles with the polymer melt. At low filler content, the interaction between the microscopically rough surface of particles and polymer melt played a significant role and decreases the flow ability, resulting in the increase of the viscosity. At higher filler content, the slippage between particles was the dominating effect, resulting in the decrease of the viscosity.[14] Talc and kaolin particles also have the ability to slide against each other during the application of shear force because of their platy shape, which allows an increase in the plastic flow. However, this ability only applies to fillers at certain parts of the composites that are near the die walls, and so, the effect of this ability on MFI is minimal.[5] Furthermore, the incorporation of very fine mineral filler such as kaolin could increase resistance to flow because of the increasing of contact surfaces between particles and matrix, thus resulting and reduction in the increment of viscosity to replace MFI values of the PP composites.

As can be seen in Figure 1, the MFI values have decreased with increasing content of kaolin talc. These results show that the flow properties of hybrid filler-filled PP composites are significantly influenced by the natural properties of the filler itself. Although both fillers have plate-like particle shape, the aspect ratio, particles size and particles size distribution is totally different. All of these properties are believed to influence the flow properties as well as reduce the MFI values of the PP hybrid composites.

Tensile and flexural properties

Tensile and flexural properties of PP filled with single and hybrid filler loading are shown in Figures 2–4. The sample formulation listing the composition of talc replacing kaolin is shown in Table II. The mechanical properties of the composites filled with a single filler of talc were first investigated to optimize the appropriate ratio of fillers. The results of a previous study[5] have shown that with an increase of the talc content, the tensile modulus increased, the EB decreased, while the tensile strength exhibited a maximum value at a weight ratio of 30 wt % used. Since the composites containing 30 wt % of talc exhibited the highest tensile strength, the total filler content afterward was kept constant at 30 wt %, and kaolin was used to gradually replace talc (compare Table II).

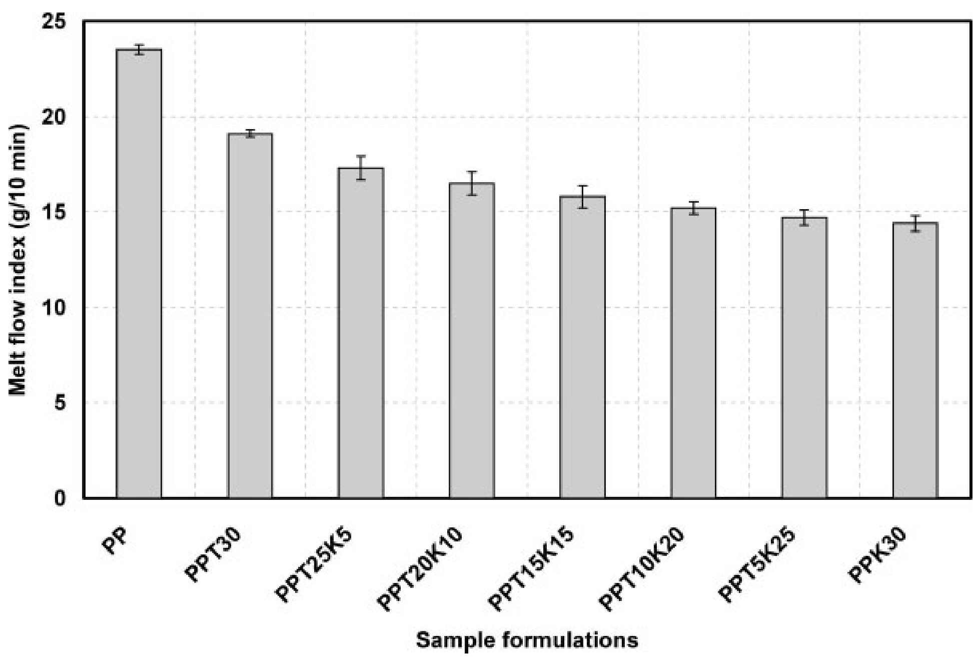

Figure 1 Melt flow index for various compositions of the PP hybrid composites.

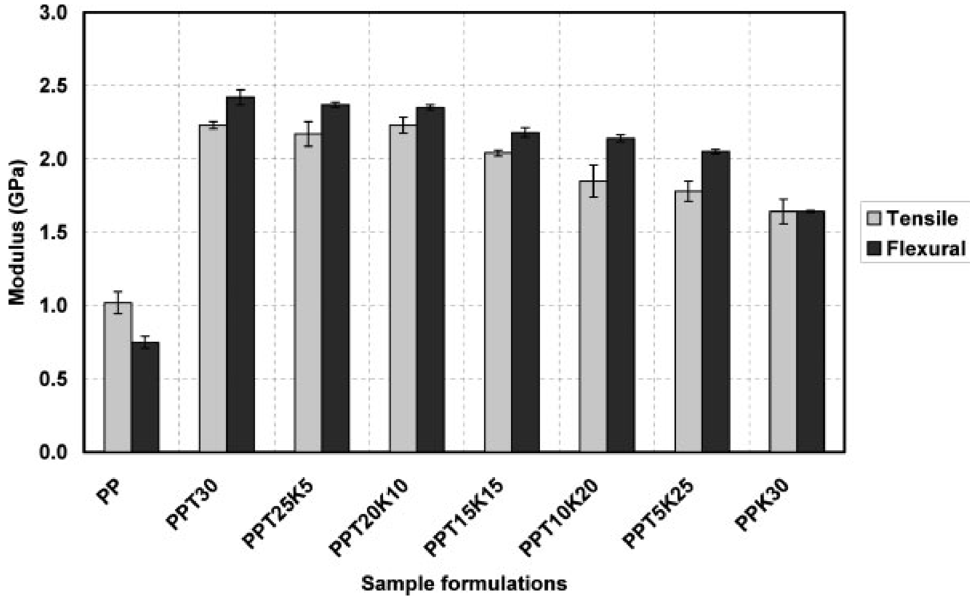

Figure 2 Tensile and flexural modulus for various compositions of the PP hybrid composites.

According to our first publication,[5] a significant and almost linear improvement in the modulus of PP can be observed, especially for talc-filled PP. This indicates that the tensile modulus has only a very weak dependence on the specific surface area and particle shape of the fillers. This is because the modulus is measured before any significant plastic deformation takes place and so does not take into consideration the interaction between the fillers and the polymer matrix. Therefore, the increase in the modulus of PP can only be caused by (1) the substitution of PP by the largely more rigid filler and (2) the filler restricting the mobility and deformability of the matrix by introduction of a mechanical restraint.

As expected, the tensile and flexural modulus of the composites decreased (Fig. 2) with the increasing replacement of talc by kaolin. However, the overall moduli of the composites are higher than unfilled PP because of many factors such as rigidity of fillers and filler particle orientation.[4–6] There is a synergistic effect in the case of the hybrid filler composite when compared with the single-filler composites. It can be seen that the tensile modulus of the PPT20K10 hybrid composites is comparable to that of 30 wt %

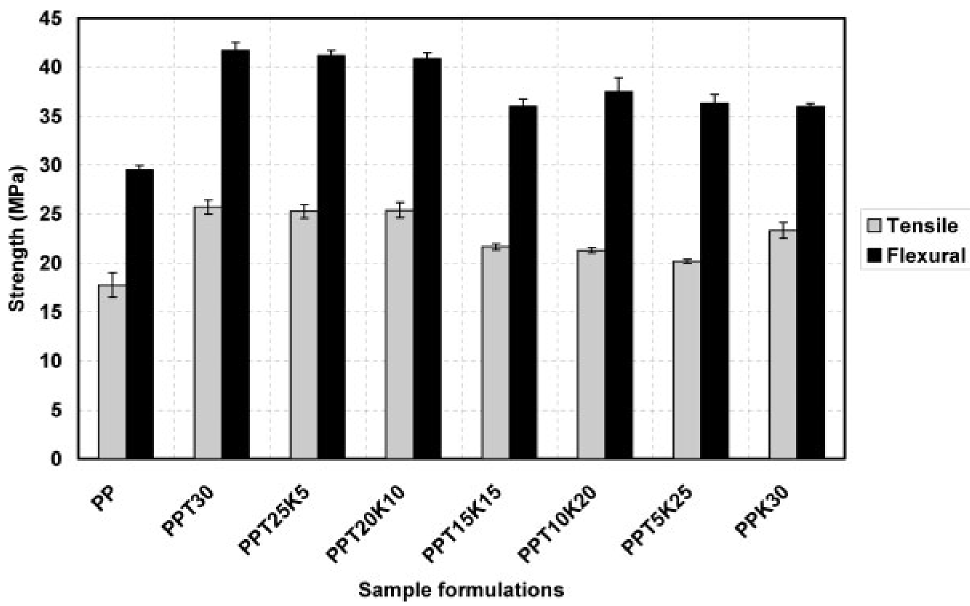

Figure 3 Tensile and flexural strength for various compositions of the PP hybrid composites.

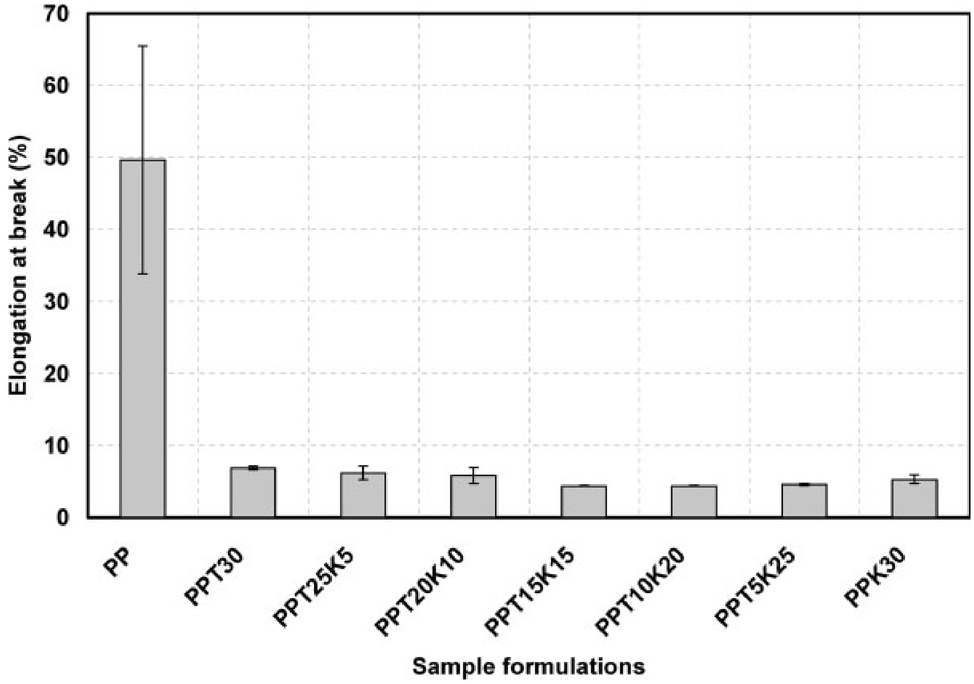

Figure 4 Elongation at break (EB) for various compositions of the PP hybrid composites.

of talc-filled PP single-filler composite. This result suggests that the replacement of 10 wt % of talc with kaolin is sufficient to achieve stiffness for hybrid PP composites, comparable to the talc-filled PP single-filler composites. The retaining in modulus of the PPT20K10 hybrid composite might be due to the difference in particle size between talc and kaolin, since the particle size of kaolin is four times smaller than that of talc.[15]

Figure 3 showed that, the tensile and flexural strength also gradually decreased with increasing kaolin content. Nevertheless, both tensile and flexural strength of the PPT20K10 hybrid composite are retained when compared with other formulation as well as talc-filled PP single-filler composite. This comparable value suggests that the replacement of 10 wt % of talc with kaolin does not affect both the tensile and flexural strength of the hybrid composite. The retaining in strength of the hybrid composite at lower kaolin content (less than 10%) can be attributed to the homogenously dispersed talc and kaolin particles, since the well-dispersed particles made the crack propagation path longer, absorbed a portion of the energy, and enhanced plastic deformation. However, tensile and flexural strength of the hybrid composites decreased with the increase of filler content as well as kaolin, replacing talc from 15 to 25 wt %. This behavior can be related to the probable tendency to form aggregates or agglomerates, resulting in a poor dispersion of the fillers on the PP matrix. Hence, the agglomeration of the filler particles results in a decrease in mechanical strength due to low strength of the agglomerates themselves. This agglomeration of kaolin particles can be seen clearly in SEM micrograph as it will be discussed later (compare Fig. 10).

When compared with kaolin, talc is a stronger reinforcing filler due to its thin platy or flaky nature and possesses the capability to orientate to the polymer flow during processing.[5,16–18] Talc has a high aspect ratio, which increases the wettability of the filler by the matrix, thus creating less microvoids and increasing interaction between filler and matrix.[19] The preliminary study has also shown that talc is the strongest crystallization agent compared to calcium carbonate and kaolin.[5] Strong nucleation will modify and change the crystalline structure of PP from β spherulites, which are weaker, into the stronger α form.[17] With the increase in crystallinity of the polymer matrix, the composite is expected to obtain higher modulus, better dimensional stability as well as increased strength.[2–4] As discussed in previous study,[5] the incorporation of kaolin in PP contributes to the reduction of tensile strength due to the worst distribution of kaolin which can be seen in SEM micrograph (Fig. 8).

Figure 4 shows the effect of hybridization on the EB of the composites. It can be seen that the incorporation of fillers into PP resulted in a drastic drop in the EB. It appears that the failure mode of the PP matrix has shifted from ductile to brittle with the incorporation of the fillers. This can be attributed to the presence of the fillers, which suppressed the ability of the PP matrix to undergo a plastic deformation process. The EB of the hybrid composite is slightly lower than the single-filler composite.

This might be due to the agglomeration tendency between talc/talc or talc/kaolin or kaolin/kaolin filler particles.

Impact properties

Figure 5 shows the impact strength of the single and hybrid filler-filled PP composites. The slight decrease in impact strength of talc-filled PP (PPT30) can be attributed to the nature of their particle. Talc used in this study has a large particle size and high aspect ratio compared with kaolin. Large particles act as flaws, which can initiate cracks, while high aspect ratio particles have large stresses near their edges, which facilitate failure.[20] According to Griffith's theory, a large aggregate is a weak point, which lowers the stress required for the composite to fracture.[6] On the contrary, the usage of kaolin with a very fine particle size provides a positive contribution toward an improvement of impact strength of the PP composites. According to Riley et al.,[20] the impact strength depends on both the size and the shape of the filler and is also affected by micromorphology. Impact strength is enhanced by small, low aspect ratio filler particles and good particle dispersion in polymer matrix.[12,20] According to Nakagawa and Sano, the presence of fine particles dispersed within the matrix make plastic deformation easier. So, during the fracture of a composite in which the mineral filler is fine and well dispersed, the stress will have to be larger to start the micro crack on a particle, and the impact energy will largely be absorbed by the exhibited plastic deformation, which occurs more easily around the particles.[6] Hence, when considering all these factors, the impact strength of kaolin-filled PP (PPK30) is higher than talc-filled PP (PPT30) at the same filler loading.

The result of hybrid filler loading showed that the Izod impact strength of PP hybrid composites drastically decreased with incorporation of kaolin, replacing talc from 15 to 25 wt %. On the other hand, it can be seen that the impact strength of the PPT20K10 hybrid composites is comparable to that of talc-filled PP (PPT30), but is slightly decreased when compared with the kaolin-filled PP (PPK30) single-filler composite. This behavior can be explained by the fact that in a single-filler system, the filler particles are dispersed homogeneously in the PP matrix. Thus, the impact energy is more uniformly distributed giving rise to higher impact strength.[12] However, in a hybrid system, the mixing of two different types of fillers possibly worsens the particle distribution, which increases the tendency of particles to form aggregates or agglomerates. This is especially true for the kaolin dominant system. Further discussion on this subject will be given later.

Morphology

Figure 6 shows a ductile fracture surface morphology of unfilled PP (SM240) matrix. The presence of plastic deformation in the form of matrix fibrillation on the fracture surface is believed to be responsible for the higher values in toughness properties such as EB and

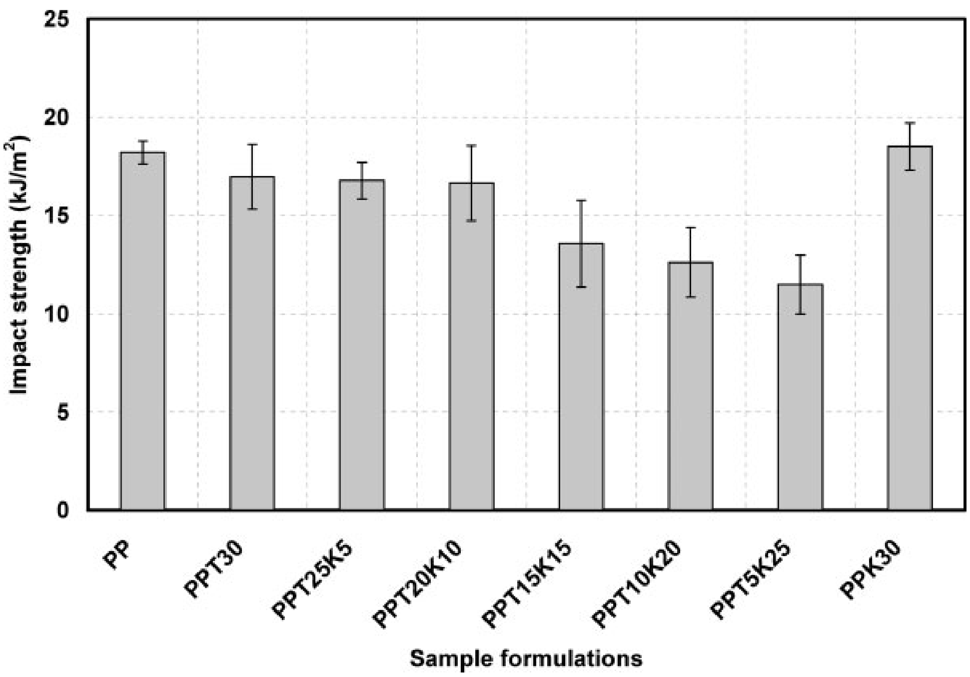

Figure 5 Impact strength for various compositions of the PP hybrid composites.

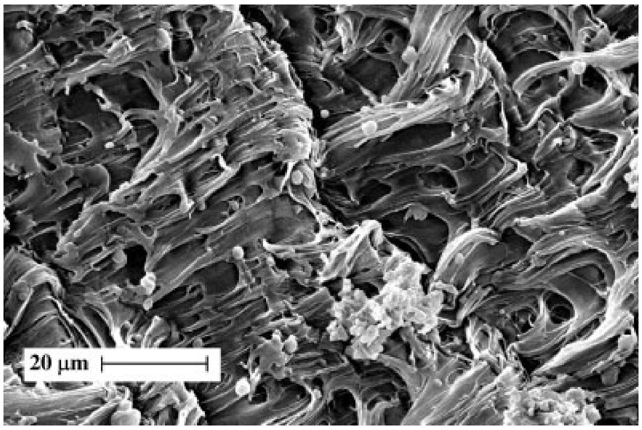

Figure 6 SEM micrograph of unfilled PP at 1000× magnification.

impact strength as can be seen from the result in Figures 4 and 5.

Figure 7 shows SEM micrographs of the tensile fractured surfaces of 30 wt % of talc-filled PP (PPT30) composites. A preferred orientation of talc particles can be clearly seen, with their basal sheet planes mostly parallel to the surface of the injection-molding. This unique organization of particles is the consequence of the plate-like structure of talc and its motion in a viscous medium during the injection-molding process. Most of the talc particles are clearly visible, well dispersed, and tend to be embedded inside the PP matrix. Thus, it is not surprising for the PPT30 composites to exhibit better strength and stiffness in comparison with PPK30 (Figs. 2 and 3).

Figure 8 shows the fracture surface morphology of PPK30 composite. There is a big form of agglomeration indicating a poor dispersion of kaolin in the PP matrix. The very fine particle size of kaolin would increase particle–particle interaction and result in the agglomeration of kaolin particles. Filler agglomeration

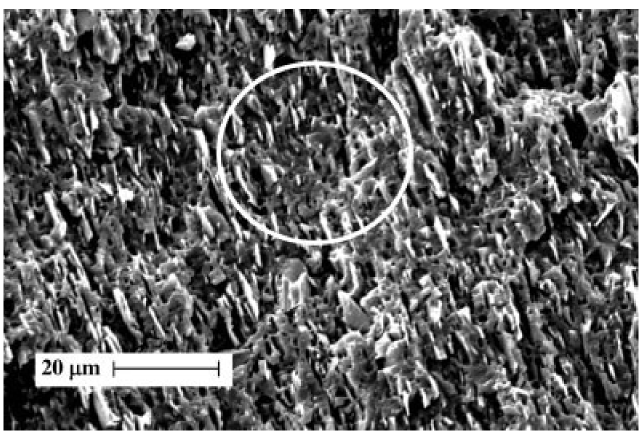

Figure 7 SEM micrograph of PPT30 single-filler composite fracture surface at 1000× magnification. Circle shows dispersed talc particles.

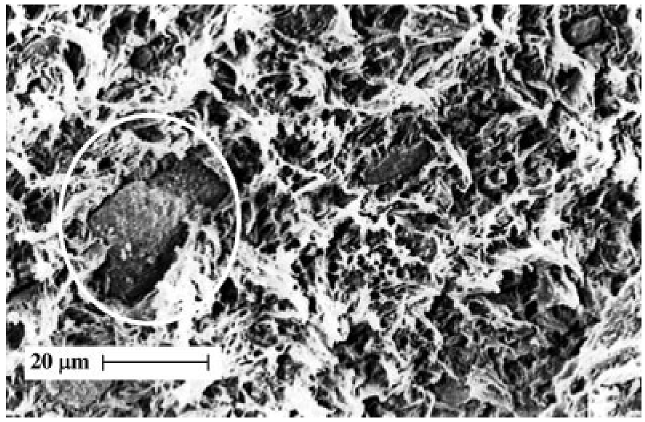

Figure 8 SEM micrograph of PPK30 single-filler composite fracture surface at 1000× magnification. Circle shows agglomerated kaolin particles.

would act as stress concentration points or weak points, which would reduce the mechanical properties especially EB (Fig. 4).

Figure 9 shows the fracture surface morphology of talc/kaolin-filled PP (PPT20K10) hybrid composite. It can be seen that PPT20K10 hybrid composite exhibits a brittle failure mode. The talc particles can hardly be spotted on the fracture surface, suggesting that they are well embedded deep into the matrix, while kaolin particles seem to be dispersed well around the PP matrix. This SEM micrograph proved that the replacement of 10 wt % of talc with kaolin is sufficient to have a balance in stiffness, strength, and toughness properties to that of talc- and kaolin-filled PP single-filler composite.

Figure 10 shows the fracture surface morphology of talc/kaolin-filled PP hybrid composites (PPT15K15) where the replacement of talc with kaolin is more than 10 wt %. The appearance of large kaolin particle (~ 25 μm) in PP matrix seems to highlight its tendency

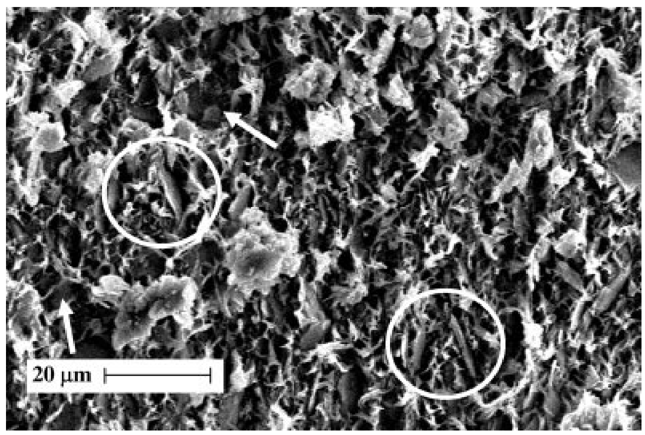

Figure 9 SEM micrograph of PPT20K10 hybrid-filler composite fracture surface at 1000× magnification. Arrows point to kaolin particles, while circles show talc particles.

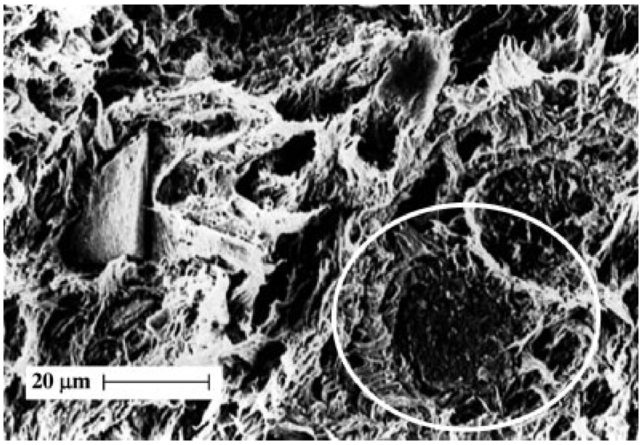

Figure 10 SEM micrograph of PPT15K15 hybrid-filler composite fracture surface at 1000× magnification. Circle shows agglomerated kaolin particles.

to form aggregates or agglomerates. The severe filler agglomeration would act as a stress concentration point which contributed toward the deterioration in the ultimate properties of hybrid composites especially tensile strength, EB, and impact strength.

CONCLUSIONS

The incorporation of both talc and kaolin into the PP matrix has notably given a true picture of how the different fillers interact with each other and with the PP matrix. Most of the hybrid composites show a significant decrease in flow and mechanical properties; since this depended on the type of filler that is more dominant and the influence of the individual filler itself on properties of PP. However, a hybridization effect was seen for PPT20K10 hybrid composite when 10 wt % of talc was replaced with kaolin, as there was a more balance or comparable results in stiffness (tensile and flexural modulus) and strength (tensile, flexural, and impact) properties compared with the other hybrid compositions. The morphological studies have demonstrated that an aggregation or agglomeration tendency of fillers were clearly seen in the PP matrix when more than 10 wt % of talc was replaced with kaolin, which contributed toward the reduction in the mechanical properties of hybrid composites, especially EB and impact strength.

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