

Mechanical, Morphological, and Thermal Properties of Polypropylene/Kaolin Composite. Part I. The Effects of Surface-Treated Kaolin and Processing Enhancement

A. Ariffin, A. S. Mansor, S. S. Jikan, Z. A. Mohd. Ishak

School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, Penang, Malaysia

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ABSTRACT: All of the composites were prepared using Brabender internal mixer (50 rpm, 190°C) and molded using compression mold (190°C) to form test samples. The results showed that the tendency of kaolin particles to agglomerate was too strong, resulting in low strength and rigidity but fairly good toughness. To overcome the kaolin agglomerations dilemma, quaternary ammonium compound (QAC), sodium hexametaphosphate (SHMP), sodium hydroxide (NaOH), and polypropylene (PP) grafted maleic anhydride (PPgMAH) surface treatment agents were applied. Better dispersion of kaolin fillers were obtained with reduced size of the agglomerates. It was also found that nonreactive treatments enhanced the toughness of the composite remarkably, because of the

softening effect that promotes plastic deformations. QAC was found to be the most effective dispersing agent of kaolin in PP matrix and contributes to 47% increment in the impact strength value compared to the untreated kaolin composite. QAC-treated kaolin also shows the most remarkable increment in melt flow index (MFI) and degree of crystallization (DOC) beyond other composites. To improve the dispersion and affinity of kaolin fillers to PP matrix, the processing enhancement was conducted at the end of the experiment. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3901–3916, 2008

Key words: talc; kaolin; mechanical properties; thermal properties; morphological properties

INTRODUCTION

Kaolin has been identified as a mineral that shares an analogous microstructure to that of talc. Talc is one of the highly demanded minerals that are fully imported from overseas. In Malaysia, talc plays a dominant role as the most widely used filler in filled polypropylene (PP) for various applications such as automotive components. Composites filled with talc possess greater stiffness, tensile strength, and creep resistance at both ambient and elevated temperatures than other particulate fillers because of its plate-like structure.^{1,2} However, the use of this unique mineral has a trade-off, as talc results in reduction of toughness and it is getting more costly, particularly for importing countries like Malaysia. Thus, it is reasonably viable to use kaolin as an alternative filler to replace talc in PP composite, as it is available abundantly at several locations throughout Malaysia.

Maiti and Lopez³ have studied on the behavior of PP/kaolin composite, which involved tensile and morphological properties. They have found that points of discontinuities were introduced to the matrix due to the presence of bare and nonadherent

kaolin particles and their agglomerates with sharp edges in this composite. To tackle the dispersion problem of kaolin, Mareri et al.⁴ have conducted an in-depth study on the influence of stearic acid and quaternary ammonium cationic treatments on the mechanical properties of PP/kaolin composite. They obtained better particle dispersions with quaternary ammonium treatment and higher impact strength composite. In addition, surprisingly they also discovered an existence of soft interface around each treated particle of kaolin that could act as a shock absorber during impact testing.

Since then, kaolin has somewhat been accepted as mineral filler that could impart toughness. Fellahi et al.⁵ have investigated a modification of epoxy resin using kaolin as a toughening agent. They reported a twofold increase in Izod impact strength through the addition of just 10 phr kaolin compared to the unfilled resin. They also revealed that the prevailing toughening mechanism for the epoxy resin under consideration was localized plastic shear yielding induced by the presence of kaolin particle associated with crack pinning. However, it is worth to note that the improvement was also attributed to the affinity of kaolin filler to the polar matrix of epoxy resin. Various attempts on developing kaolin as filler in polymer have been made later on by several researchers.^{6–10} Some of the initial success in the

Correspondence to: A. Ariffin (azlan@eng.usm.my).

TABLE I
Filler Specifications

Materials	Density (g/cm ³)	Hardness (Moh's scale)
Talc (T)	2.79	1
Kaolin (K)	2.59	2

field of kaolin-filled polymer composite has centered on nylon 6 matrices.^{8,10} Ansari and Gareth⁸ have conducted a study focusing on the measurement of surface energy of kaolin, and reported that the high surface energy of kaolin particles could be lowered using aminosilane coupling agent.

Compounding composite where kaolin particles are dispersed within the polymeric matrix possess significant processing challenges. Relatively there are few studies available in the literature regarding the development of kaolin-filled polymer composite.^{3-8,10} Basically, the authors agree that the overall conclusions for such system are often because of its high surface energy and the presence of polar groups, and that kaolin can be effectively used in association with polar polymer matrix. This conclusion has then been used to partly explain the non-dispersive phenomena of kaolin filler, which resulted in nonuniformity of properties. This research will also expand the potential application of kaolin, which at the moment is confined to the areas such as paper industry and ceramics sector. The evaluation of PP/Talc and PP/Kaolin composites on mechanical and thermal properties will be performed to compare the performance of both composites. As to surmount the aggregation problem of kaolin filler, the effects of kaolin surface treatments and processing enhancement will be investigated.

EXPERIMENTAL

Materials

The polymer matrix used is PP copolymer resin grade SM240 supplied by Titan PP Polymers (M) Sdn. Bhd., Johor, Malaysia. The density of the polymer was specified as 0.894 g/cm³ with the melt flow index (MFI) of 25 g/10 min (2.16 kg at 230°C). Talc and kaolin were supplied by Chung Chemicals Sdn. Bhd., Kuala Lumpur, Malaysia and Finn Chemicals Sdn. Bhd., Selangor, Malaysia, respectively. Tables I and II show the specifications and particles size anal-

TABLE II
Particle Size Analysis

Parameters	Talc	Kaolin
Mean particle diameter d _{50%} (μm)	6.76	1.18
Top cut d _{98%} (μm)	25	25
Specific surface area (m ² /g)	1.8584	8.3291

TABLE III
Surface Area of Fillers Obtained from Brunauer-Emmett-Teller (BET) Nitrogen Method

Fillers	(m ² /g)
Kaolin	19.36
Talc	5.90
QAC-treated kaolin	16.74
SHMP-treated kaolin	18.33
NaOH-treated kaolin	18.88
QAC-treated kaolin milled	17.95

ysis of both fillers, respectively. Whereas, surface area values of talc and kaolin fillers, both treated and untreated are given in Table III. Four types of surface treatment agents were chosen for this study to treat the kaolin fillers. The first type was benzalkonium chloride, later would be referred as quaternary ammonium compound (QAC), supplied by Fluka. Sodium hexametaphosphate (SHMP) [NaPO₃]₆ grade 04267 and sodium hydroxide (NaOH), as a dispersing agent, were supplied by Sigma-Aldrich (M) Sdn. Bhd., Selangor, Malaysia. The final type of surface treatment used was coupling agent maleic anhydride grafted PP (PPgMAH) grade Polybond 3200 supplied by Uniroyal Polybond. All of the surface treatment agents were used as received. Additives added were antioxidant (Irganox 1010) and ultraviolet stabilizer (Tinuvin 770 DF), both were from CIBA.

Filler treatment (QAC, SHMP, NaOH, and PPgMAH pretreatment process)

Surface treatment of the kaolin particle was carried out in an aqueous suspension. The surfactant, QAC with an amount of 2.5 wt % of filler has been shown in the previous work by Mareri et al.⁴ to be the optimum percentage for kaolin treatment. QAC was dissolved in distilled water and stirred for 1 h. Kaolin was then added slowly at room temperature to the stirred aqueous solution. The mixture was continuously stirred for the next 24 h. After treatment, the filler was then dried in an oven at 80°C for 6 h.

Kaolin was pretreated with SHMP. Kaolin was first made into aqueous slurry by adding kaolin and deionized water into a 200-mL beaker with continuous stirring. Note that the deionized water contained SHMP (0.7 wt %) before the addition of kaolin. The kaolin slurry without dispersant appeared to be flocculated, but the suspensions with mixed in dispersant was deflocculated. Stirring continued for 24 h. After treatment, the filler was then dried in an oven at 80°C for 6 h.

Kaolin was first made into aqueous slurry by adding kaolin and deionized water into a 200-mL beaker with continuous stirring. Using pH meter, the pH of the slurry was adjusted to pH 10 by adding 1M NaOH.

TABLE IV
Designation of the Labels

Labels	PP (wt %)	Talc (wt %)	Kaolin (wt %)	QAC-treated kaolin	SHMP-treated kaolin	NaOH-treated kaolin	PPgMAH	Two steps mixing	Milling process
T30	70	30	0	–	–	–	–	–	–
K30UT	70	0	30	–	–	–	–	–	–
K30QAC	70	0	30	x	–	–	–	–	–
K30SHMP	70	0	30	–	x	–	–	–	–
K30NaOH	70	0	30	–	–	x	–	–	–
K30PPgMAH	70	0	30	–	–	–	x	–	–
K30QACPPgMAH	70	0	30	x	–	–	x	–	–
K30QAC2×	70	0	30	x	–	–	–	x	–
K30QACmill	70	0	30	x	–	–	–	–	x

x, treatment/process done on sample.

The treated kaolin was continuously stirred overnight. The treated kaolin was then dried for 6 h at 80°C.

PPgMAH in pellet form was applied using *in situ* method during the compounding of the composite. The amount used in this research was fixed at 0.5 wt %.

Composite preparation

Melt compounding of the PP/talc/kaolin composites was done using Brabender Plasticoder model PLE 331 internal mixer with temperature of 190°C at 50 rpm for 12 min. The formulations for untreated and treated PP/Kaolin and PP/Talc composites are listed in Table IV. Samples of compounded PP were then molded compressed in an electrically heated hydraulic press. The hot press procedure involved preheating at 190°C, followed by compressing at the same temperature, and subsequent cooling under pressure. Molded samples were then cut into test shape specimens.

Two steps mixing (2×)

A two-step mixing process was employed to aid the fillers dispersion in the PP matrix. In the first step, mixing was allowed to continue for 8 min. Upon completion of the mixing cycle, the molten mix was taken out and passed through the two-roll mill (2.0-mm nip setting). The sheet obtained was cut into small strips and charged back to the mixer to ensure homogeneous mix, and mixed for another 2 min at the same temperature and rotor speed. The molten mix was then removed and sheeted again as before.

Mechanical testing

The tensile and flexural properties were measured with Instron 5582 100 kN electromechanical testing machine with series IX control system. Tensile test were carried out according to ASTM D 638-98 Type 1 at a testing speed of 50 mm/min. Three-point flexural tests were performed in accordance to ASTM D 790-98. Tests were conducted at a crosshead speed of

3 mm/min. Izod impact strength of unnotched samples were measured using an impact-testing machine, Pendulum Impact Tester Zwick 5101. At least five samples from each formulation were tested. All the tests were carried out at room temperature (27°C).

Morphological studies

Morphological studies were performed with a scanning electron microscope (SEM) machine model Leica Cambridge S-360. Observations were made on fracture surfaces of tensile samples. The test specimens were coated with a thin gold-palladium layer to prevent electrical charge accumulation during the examination.

Thermal analysis

The melting and crystallization behavior of the composites were studied using a Perkin-Elmer DSC-6 in a nitrogen atmosphere with a heating and cooling rate of 20°C/min. The samples were heated from 50 to 220°C, held at that temperature for 1 min to eliminate thermal history, then the nonisothermal crystallization process was recorded from 220 to 50°C, and a standard status of crystallization was created.

Melt flow index

The processability of the filled PP composites was determined with a Kayeness Polymer Test Systems Series 4000 Melt Flow Indexer according to ASTM D 1238-99b. A load of 2.16 kg at 230°C was used in the measurement.

RESULTS AND DISCUSSION

Mechanical properties

Effect of surface-treated kaolin on tensile and flexural properties

Figures 1 and 2 show the effect of fillers on tensile and flexural strength of PP. The performance of talc-

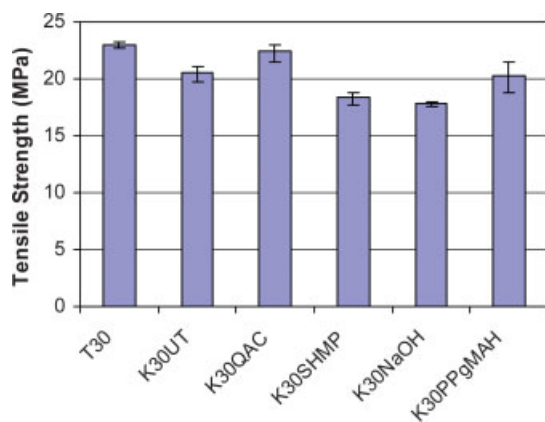


Figure 1 Tensile strength of PP composites as a function of filler surface treatments. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

filled PP (T30) composite was higher than kaolin-filled PP (K30 UT). This could be attributed to several reasons, such as particle size, filler-matrix interactions, and aggregations. With respect to particle size, there are two different arguments regarding the correlation of particle size with the strength of a composite. As shown in Table II, the particle size of kaolin is smaller than that of talc. According to Verbeek,¹¹ smaller particle size filler requires more polymers for effective binding, resulting in a lower tensile strength of the composite. In contrast, Li et al.¹² claimed that interfacial stresses of filler particle increase as the particle size increases. This means, damage initiates distinctively around particles with larger size compared to the smaller size. Therefore, smaller particle size would result in higher strength composite. In this case study, the latter argument^{13,14} was likely to be accepted, as filler with smaller particle size are likely to have larger surface area,¹³ therefore, it is known to increase the strength of the composite.

Although theoretically kaolin smaller particle size would strengthen the composite, the contrary was observed in this research. To understand this result, which seems to be inconsistent, the behavior of filler-matrix was studied. Previous studies^{3,8} reported a similar trend of decreased strength for kaolin-filled polymer composite. Maiti and Lopez³ claimed that the presence of kaolin particles interferes with stress transfer, particularly in the absence of specific adhesion between PP and kaolin. These interferences are due to the generation of discontinuity in the PP matrix resulting in early failure of the composite at small deformation.

Moreover, kaolin has a very strong tendency for severe aggregations due to its high surface area.^{15,16} In PP matrix, kaolin are poorly dispersed and formed a lot of agglomerations. This will be shown

later in SEM micrograph of the composite. The agglomerates act as crack initiation sites,^{17,18} consequently resulting in low tensile and flexural strength of the composite. Whereas, the superior mechanical performance of talc-filled composite may be attributed to the homogeneously dispersed talc particles. It has also been well documented that talc acts as reinforcing fillers,^{19,20} and therefore a high composite strength was expected.

Another possible reason for inferior strength of kaolin-filled PP compared to talc-filled PP composites might be due to the nature of particle size distribution of the fillers. Largely scattered distribution of kaolin particle size created points of discontinuity in the PP matrix, resulting in premature failure. This is due to the fact that broad particle size distribution causes greater interfacial stresses than narrow particle size distribution, which may lead to early failure of the composite.¹²

It is interesting to note that slight improvements in tensile and flexural strength were achieved with surface-treated kaolin (treated with PPgMAH) compared to the untreated kaolin. Usually the capability of matrix to transfer stress depends on a great extent upon the interfacial strength between fillers and matrix.²¹ A high interfacial strength corresponds to a high composite strength.²² The increment of strength for PPgMAH-treated composite might be attributed to this factor. Through macromolecular entanglement, PPgMAH made the PP matrix hydrophilic while the maleic anhydride attacked the polar surface of kaolin. Such strong interfacial interactions are formed across the interface between the two components and account for the adhesion in the system. This mechanism was suggested by numerous researches.^{23–25} An increase in filler-matrix interactions also enable more stress to be transferred from the matrix to the fillers during external loading.

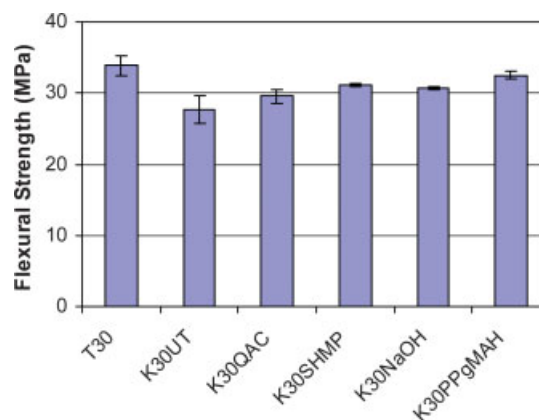


Figure 2 Flexural strength of PP composites as a function of filler surface treatments. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

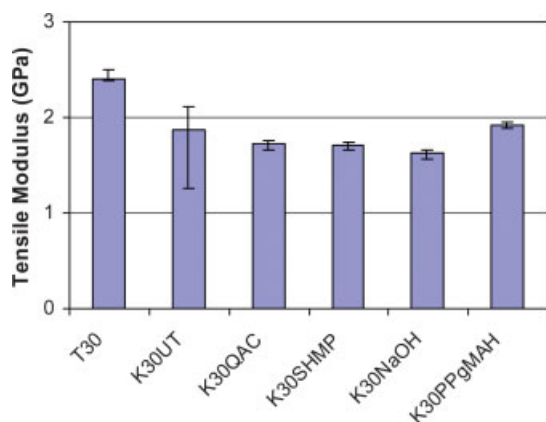


Figure 3 Tensile modulus of PP composites as a function of filler surface treatments. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

On the other hand, in the case of QAC, SHMP, and NaOH, the surface treatments applied was principally to reduce the interparticle forces of kaolin, thus improving the overall dispersion in PP matrix. There are several studies that focused also on the surface characterization of mineral fillers treated with surfactant.^{26–30} It was reported that both the dispersion component of the surface tension and the surface polarity decrease as an effect of the surface treatment. However, kaolin treated with SHMP and NaOH show a decrease in tensile strength compared to the untreated kaolin composites. It can be concluded that the surface treatments applied did not promote strong interfacial interaction between kaolin and PP, resulting in a weak interfacial bonding. Furthermore, the introduction of a surfactant also reduces particle–matrix interactions, which gives rise to increase in particle–matrix debonding, thereby reducing the strength of the composite.¹³

Nevertheless, the slight increment in flexural strength behavior of nonreactive (QAC, SHMP, and NaOH) kaolin treated composites compared to the untreated composite is best described by reduced crack initiation sites as a result of better filler dispersions. Published results proved that aggregates act as fracture initiation sites, thus leading to reduction in strength and fracture resistance.^{17,31} In addition, QAC has also been proven⁴ as an effective dispersing agent in promoting uniform filler distributions and reducing the size of kaolin aggregates, hence lowering the amount of stress concentration points in the composite. This explains the improvement in tensile and flexural strength of the QAC-treated composite compared to the untreated composite.

In contrast with the factor influencing the strength of the composite, normally interfacial adhesion is not highlighted with modulus measurements.¹³ Figures 3 and 4 exhibit the tensile and flexural modu-

lus of PP composites, respectively. Obviously, talc-filled PP (T30) possesses higher modulus compared to kaolin-filled PP (K30). This finding again contradicts to the assumption made before with respect to particle size. Though smaller particle size and harder rigidity of kaolin compared to talc were expected to be an additional factor to favor in stiffening the composite,³² this behavior could not be achieved due to agglomeration problems. The tendency of kaolin fillers to agglomerate provide site for microcrack to initiate, thus raising the possibility of the composite to fracture at early stage. As a result, lower tensile modulus was obtained.

A factor that contributes to higher tensile and flexural modulus of talc would be the effect of good filler wetting by PP matrix. Better wetting of talc particles were due to talc's organophilic characteristics. A likely explanation for talc's affinity to PP matrix is that the position of oxygen atoms on the surface of the talc platelet (oxide groups) corresponds to the carbon bonds on the surface of PP crystal.³³ Good wetting will result in less porosity, which would increase the modulus of the material.¹¹ Several studies also demonstrated that talc could enhance the rigidity of the PP composites.^{34,35}

From Figures 3 and 4, it can be seen that surface-treated kaolin composite possessed lower tensile and flexural modulus than T30 and K30UT composite. The above results factually reflect the contradiction between the stiffening effect of the rigid particles and the softening effect of the soft interlayer of surface-treated kaolin (this scenario will be explained later in the impact strength discussion). The softening of PP can be observed with the addition of non reactive surface treatment agent and particularly of QAC.⁴ As the composites were filled with 30% kaolin, the treatment percentage in the matrix was so significant that the softening effect seemed to be

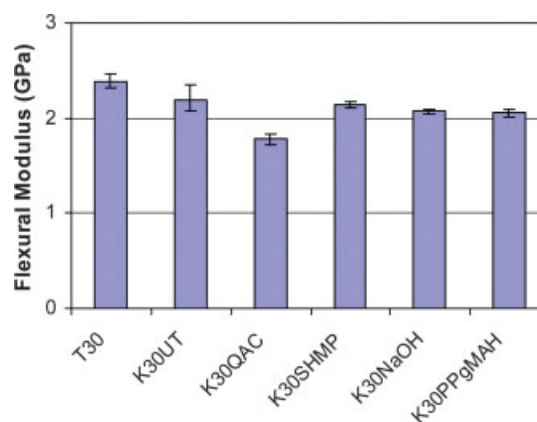


Figure 4 Flexural modulus of PP composites as a function of filler surface treatments. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

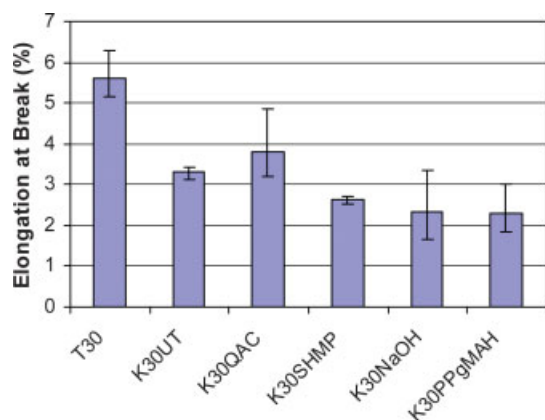


Figure 5 Elongation at break of PP composites as a function of filler surface treatments. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

prevalent, leading to a weaker tensile and flexural modulus.

The effect of kaolin fillers on the elongation at break of PP composite is shown in Figure 5. The reduction in the elongation at break value could be attributed to the rigidity of kaolin mineral particle and extensive kaolin agglomerations. According to Li et al.,¹² interfacial stresses between particle and matrix surface in particulate-filled composite increased slightly with hard particles and decreased slightly with soft particles. It has been shown in Table I previously that kaolin Moh's hardness (value: 2) is particularly higher than talc (value: 1). This might be the reason for lower elongation at break of kaolin compared to that of talc.

In addition, Maiti and Lopez³ stated that the analysis of the tensile stress data showed the occurrence of significant stress concentration in the structure due to the incorporation of kaolin fillers into PP. The defect in the structure is caused by discontinuity in stress transfer or stress concentration at the interface of the dispersed phase and the matrix. To understand the correlation of interfacial stresses and point of discontinuity in the elongation of polymer matrix, it seems to be appropriate to discuss the possible explanation proposed by Hadal et al.³⁶ on the deformation of particulate-filled composites. They suggested that when the fibrils associated with the polymer matrix are pulled along the tensile axis, the restrained plasticity increased the localized stresses associated with the mineral particles. The particles act as stress concentrators and restrict the enhanced stretching of polymer matrix, thus resulting in lower elongation at break value. With respect to the rigid particle of kaolin, the combined effect of high interfacial stress and the discontinuity of stress transfer increased the highly stressed localized region, therefore leading to lower elongation at break. The

kaolin-filled PP composites with respect to surface treatments, QAC exhibited an improvement in elongation at break values, whereas PPgMAH, SHMP, and NaOH showed a reduction. This is due to a fact that the interfacial adhesion might result in an additional barrier for the motion of the macromolecules, thus yielding a reduction in elongation at break.

The possible role of aggregation was mentioned several times during the previous discussion of kaolin filled composites. Although the kaolin fillers have been subjected to various surface treatments, the influence of aggregates is unambiguous. From the tensile tests conducted earlier, it is reasonable to conclude that QAC suspension treatment was the most efficient treatment for kaolin with respect to optimum strength and toughness balanced performance. But still, it is interesting to investigate how far the properties of the QAC-treated composite would be improved if the kaolin particles were dispersed individually throughout the PP composite, and whether modified PP matrix would enhance the properties to a greater extent. Thus, processing enhancement was conducted to improve the dispersion and affinity of kaolin fillers to PP matrix.

Effect of processing enhancement on tensile and flexural properties

Figures 6 and 7 show the tensile and flexural strength properties of QAC-treated kaolin composites with different processing enhancements. For QACPPgMAH composite, the strength of the composite decreased compared to QAC-treated kaolin composite. In contrast, Liao et al.³⁷ reported that the tensile strength of PE blended with diblock copolymer PE-PEG and MMT treated with alkylammonium ions is higher than PE blended with treated MMT. This was due to good affinity of the fillers to the

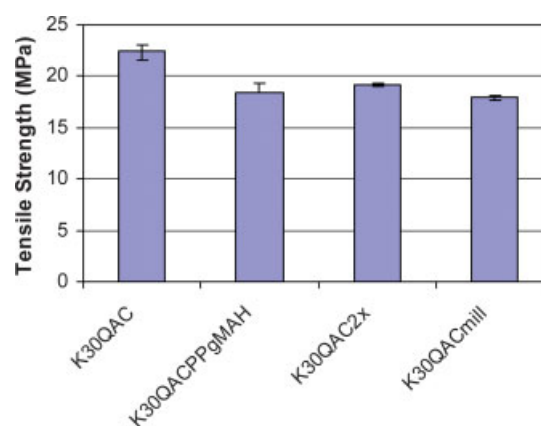


Figure 6 Effect of processing enhancements on tensile strength of PP/QAC-treated kaolin composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

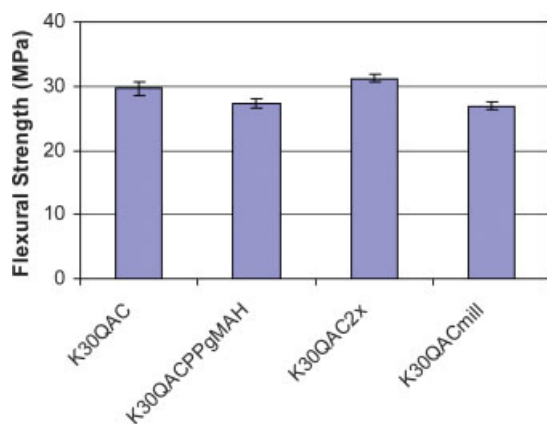


Figure 7 Effect of processing enhancements on flexural strength of PP/QAC-treated kaolin composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

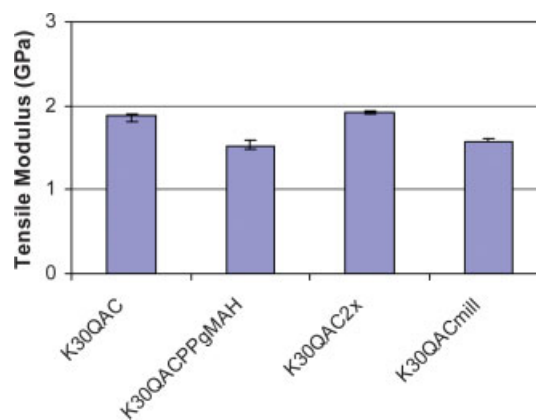


Figure 9 Effect of processing enhancements on tensile modulus of PP/QAC-treated kaolin composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymer matrix. A possible reason for this contradiction is that the MMT clay treated with alkylammonium exhibits different characteristics with alkylammonium-treated kaolin clay. Therefore, the synergistic effect of dispersing agent and coupling agent was not attained in kaolin-filled PP composite.

A reduction in tensile strength was also obtained for K30QACmill and K30QAC2 \times composites. As discussed earlier, the particle matrix interaction plays a vital role for the strength behavior of a composite. QAC-treated kaolin promotes the dispersion of fillers, but reduces the filler-matrix interaction, therefore resulting in low strength in K30QACmill composite albeit better dispersion of filler was obtained (refer to SEM result). However, for K30QAC2 \times composite, this finding is in agreement with the result of Cantero et al.³⁸ The decrement observed in two steps mixing method was attributed to degradation.

Figure 8 gives a comparison of elongation at break for QAC-treated kaolin with different processing methods. There is no significant improvement from any of the three methods. K30QACPPgMAH retained the elongation at break value without further increment. On the other hand, a decrement in the elongation at break was observed for QAC-treated kaolin compounded with two steps mixing method. This is in agreement with the tensile strength results and may again be attributed to the degradation of the PP matrix. This result also indicates that the QAC2 \times composite exhibited brittle failure behavior. A slight decrease in K30QACmill composite could be attributed to better distribution of rigid kaolin fillers, which led to restriction of macromolecular movement, thereby reducing the elongation at break value.³⁶

The significance of two steps mixing method becomes clearer when comparing the rigidity of the composites. Figures 9 and 10 show the tensile and

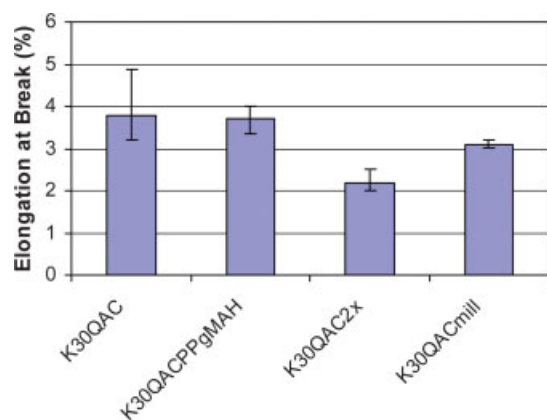


Figure 8 Effect of processing enhancements on elongation at break of PP/QAC-treated composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

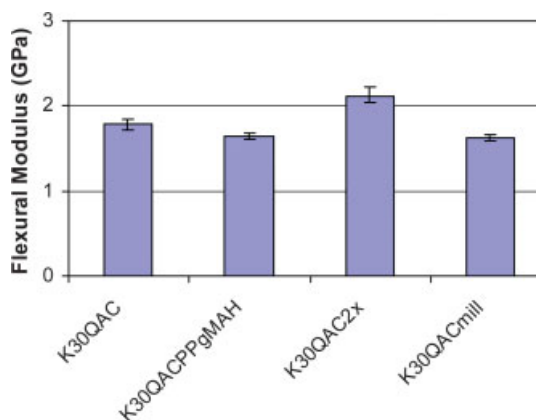


Figure 10 Effect of processing enhancements on flexural modulus of PP/QAC-treated kaolin composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

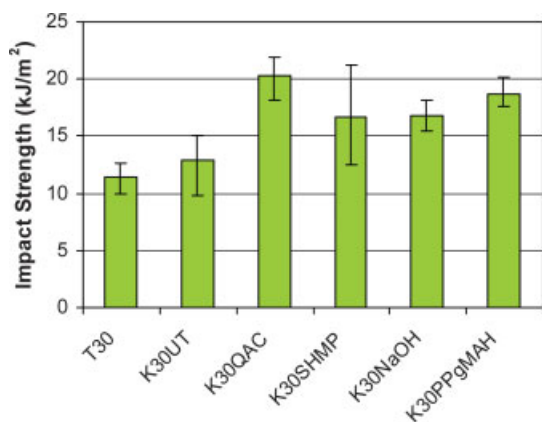


Figure 11 Effect of different surface-treated kaolin on impact strength of single-filler composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

flexural moduli of the composites, respectively. Both modulus of K30QACPPgMAH and K30QACmill marked a decrement. On the other hand, an increment of both modulus was observed for K30QAC2× composite, which was more pronounced in flexural modulus (Fig. 10). This property enhancement indicates better fillers dispersion, as Silva et al.¹⁷ reported that a homogeneous composite would result in higher rigidity behavior.

Effect of surface-treated kaolin on impact property

Figure 11 gives the impact strength of the single-filler composites. Clearly, both untreated and treated kaolin particles exhibit the toughening ability compared to PP/talc composite. Impact strength of kaolin was higher than talc due to smaller particle size and larger surface area of kaolin particles as reported in Tables II and III, respectively. A similar effect had been reported by Bakar.¹⁸ Considerable improvement relating to the effect of kaolin filler on the toughness property of polymer matrix^{4,5,7,8} signifies the ability of kaolin to impart toughness to PP composite.

With respect to talc, its particle size is larger than kaolin. As particle size increased, unnotched impact energy decreased, mainly as a result of crack initiation. The larger particle sizes provide higher stress concentrations where a crack can be initiated more easily. Therefore less energy is required to initiate the crack, which dominates over the higher energy needed to propagate the crack.^{4,12} This argument holds true for the lower impact strength of talc compared to kaolin. The relevance of surface-treated kaolin also becomes clear when comparing the impact strength of treated and untreated composites. This finding is in agreement with previous research,⁸ which proved that the incorporation of kaolin into

nylon changed the mechanical properties and raised the modulus and toughness of the materials. Thus better results were achieved for the treated kaolin if compared to that of untreated counterpart. As discussed earlier in tensile modulus, a softening of PP is observed in the presence of SHMP and NaOH. In this case, the softening effect promotes toughness. Toughness is the major factor that controls the impact strength. There was also an apparent increment in impact strength for K30PPgMAH composite that might be due to good filler/matrix interaction. It has been noted in previous study⁷ that the surface-treated kaolin particles showed a better impact toughness because of the good interfacial adhesion with the matrix.

From Figure 11, it can be seen that the increment is most pronounced in K30QAC composite, which provide the highest impact strength. This improvement might be attributed to the enhancement in filler dispersion and softening effect of QAC. During the fracture of a composite in which the mineral filler is fine and well dispersed, the stress will be transferred effectively throughout the composite, therefore higher stress is needed to crack the composite.³⁹

According to Mareri et al.,⁴ surface treatment agent was introduced into the PP matrix on the kaolin surfaces, which leads to an assumption that there was an interphase around each particle. Therefore, the matrix volumes are affected by the treatment around the fillers. The presence of these supple zones which are affected by the nonreactive treatments could explain the decrease in the composite modulus (Figs. 3 and 4), or explained earlier as the softening effect. Furthermore, these zones might also act as shock absorbers during impact tests.⁴ The presence of a soft interphase improves the impact strength by absorbing the impact energy through plastic deformation. The evidence of this plastic deformation is provided by SEM micrographs that will be shown later. This plastic deformation can dissipate a large amount of energy and consequently enhance the toughness of the composite. Furthermore, the combined effect of evenly distributed kaolin particles and the larger plastic deformation lead to a synergistic increase of impact strength.³¹ From these findings, it is reasonable to infer that positive effect on toughness could be obtained from PP/kaolin composite for both treated and untreated kaolin fillers.

Effect of processing enhancement on impact property

In contrast, no significant improvement was attained in the composites with different processing methods. Figure 12 illustrates the impact strength of these composites. With the exception of K30QACmill

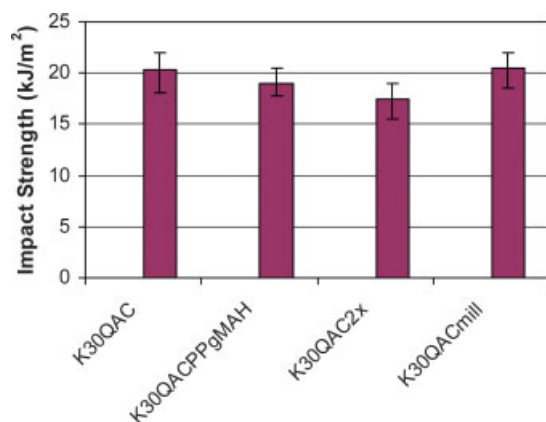


Figure 12 Effect of different processing enhancements on impact strength of single-filler composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

which possesses similar strength as K30QAC, while K30QACPPgMAH and K30QAC2 \times show a reduction in the impact strength values. Analogous to the behavior of elongation at break, the improved adhesion between kaolin filler and PP matrix in K30PPgMAH composite might be the reason for this decrement.²² Whereas, the reduction in impact strength of K30QAC2 \times may be attributed to a certain degradation of PP matrix during the second mixing stage.³⁸

Morphological properties

Effect of surface-treated kaolin on morphological property

The fractured surfaces of the composites were examined using SEM to investigate the effect of dispersion and to relate morphology to the mechanical properties. Good dispersion of fillers in the matrix, effective wetting of fillers by matrix and strong interfacial adhesion are required to obtain composite materials with satisfactory mechanical properties. However, this is not valid for untreated kaolin-filled PP. Because of the hydrogen bonds formed between untreated kaolin particles and the wide difference in character between untreated kaolin and the PP matrix, the filler tend to agglomerate and become unevenly distributed throughout the matrix.⁴⁰ This is shown in Figure 13. The large agglomerate size gives rise to greater stress concentration, which leads to poor strength of PP/kaolin composite.

Figure 13 reveals the existence of holes and subsequent plastic deformation in the morphology of kaolin-filled composite. The study of Xu et al.⁴¹ had reported that during the deformation process of particulate-filled polymer composite, the most common failure mechanism is debonding at the filler-matrix interface. From the micrograph, debonding process

of kaolin aggregates created large holes, which means that kaolin filler can be pulled out completely from the PP matrix through the interfacial failure as the filler-matrix adhesion is relatively weak. The reason for poor adhesion between kaolin and PP was probably because of the difference in surface free energy (or polarity).

The degree of interaction at filler-matrix interfacial zone changes in a very limited range, since PP itself has very low surface energy and the polar component of surface tension is very close to zero, as mentioned by Pukanszky and Maurer.²² This causes dewetting of high-surface energy kaolin particles from the PP matrix. The dewetting process of kaolin aggregates allowed debonding to occur prior to fully develop plastic deformation. According to Renner et al.,¹⁴ easy debonding and the formation of large voids lead to premature failure. They also claimed that if debonding is the dominating deformation mechanism and if a large number of particles separate from the matrix under the effect of external load, decrement in the tensile strength is expected. Thus, detailed analyses of the results presented earlier (effect on tensile strength) clearly revealed such effects.

Apparently, the volume affected by the micromechanical deformation processes, mainly debonding and some shear yielding is much larger in K30 (Fig. 13) than in T30 (Fig. 14). Pukanszky and Maurer²² quoted that plastic deformation of the matrix is the main energy-consuming process during fracture both in blends and composites. Meanwhile, the large agglomerates size of kaolin gives rise to greater stress concentration and contributes to the formation of larger cavities and voids (indicated by arrows in Fig. 13). Cavitations of the PP matrix around the filler particles were also reported to be the main toughening mechanism.⁴² These findings further

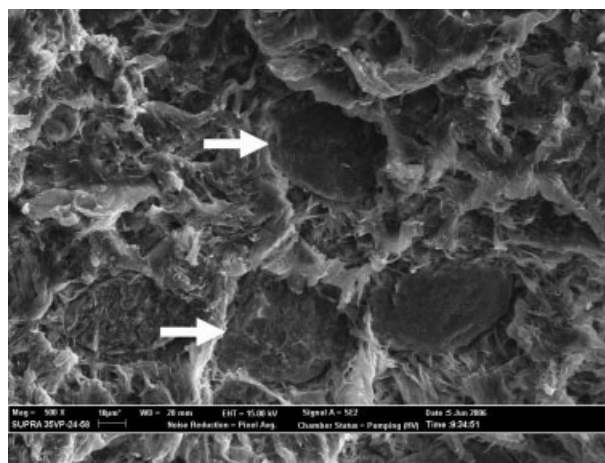


Figure 13 SEM micrograph of the fractured surface of 30 wt % kaolin-filled PP (K30) ($\times 500$).

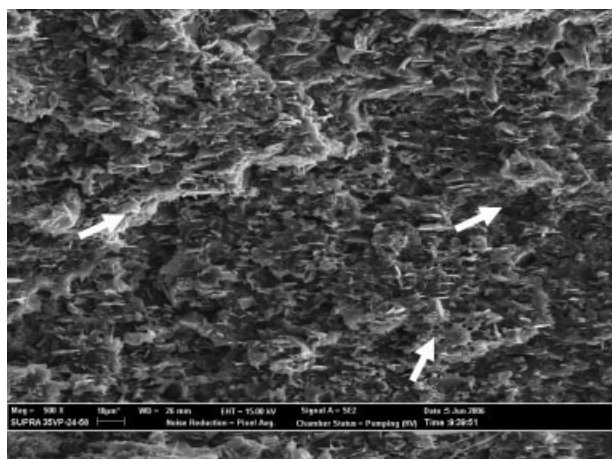


Figure 14 SEM micrograph of the fractured surface of 30 wt % talc-filled PP (T30) ($\times 500$).

support the increment of impact strength exhibited by K30 composite.

On the contrary, talc fillers are well dispersed with few being loosely exposed at the fractured surface (indicated by arrows in Fig. 14). This suggested that the filler particles are deeply embedded into the PP matrix, which signifies good interaction between the filler and matrix. It has been well documented that strong interaction exists between talc filler and PP matrix.^{29,34} It can also be observed that there is no large void presence in between the filler and the matrix. The dispersion homogeneity of talc fillers (Fig. 14) leads to a good strength and rigidity of PP/talc composite. Furthermore, it could be seen that the surface was relatively smooth, indicating brittle fracture behavior. This morphology held responsible for the drastic decrease in toughness of this composite. Similar finding has been reported elsewhere.⁴³

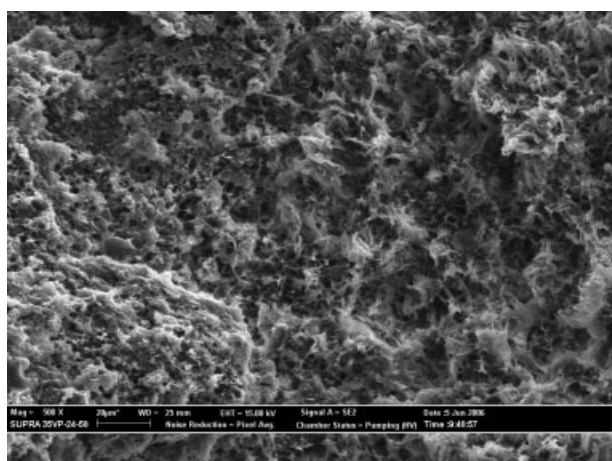


Figure 15 SEM micrograph of the fractured surface of 30 wt % QAC-treated kaolin-filled PP (K30QAC) ($\times 500$).

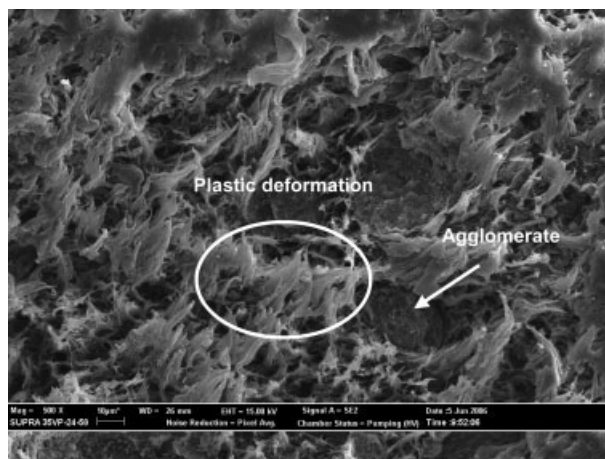


Figure 16 SEM micrograph of the fractured surface of 30 wt % SHMP-treated kaolin-filled PP (K30SHMP).

SEM micrographs illustrating the effect of surface treatment on dispersion of kaolin fillers are presented in Figures 15–18. As discussed earlier, surface treatments of kaolin fillers are meant to overcome the tendency of particles to agglomerate, thus promoting good dispersion. Figure 15 provides an indication for the better dispersion of kaolin in the QAC-treated kaolin composite (K30QAC). No visible agglomerates can be observed from the micrograph. There were small voids left behind as a result of detachment of the agglomerated particles, suggesting that the QAC treatment had effectively reduced the sizes of agglomerates compared to the untreated composite (Fig. 13). It has been well documented that failure concentrates in agglomerated regions; hence, smaller agglomerates are therefore beneficial.¹² From Figure 16, it can be seen that SHMP possessed the worst dispersions of kaolin particles of all the treatments applied. However, it is worth noting

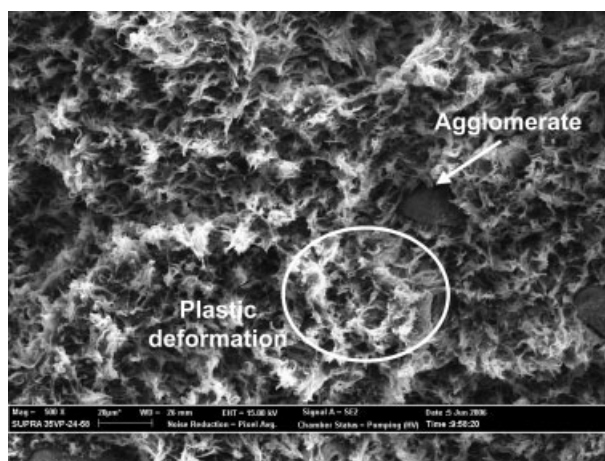


Figure 17 SEM micrograph of the fractured surface of 30 wt % NaOH-treated kaolin-filled PP (K30NaOH).

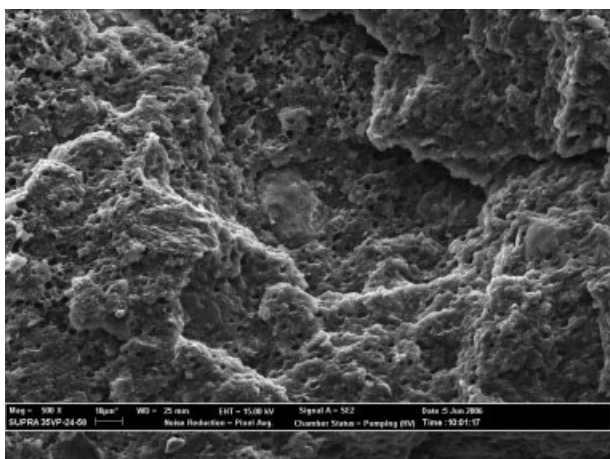


Figure 18 SEM micrograph of the fractured surface of 30 wt % PPgMAH-treated kaolin-filled PP (K30PPgMAH).

that the dispersions of SHMP-treated kaolin fillers were fairly better than untreated composite. The NaOH treatment successfully reduced the size of kaolin agglomerates, but the dispersions were poor compared to QAC (Fig. 17).

The fracture surface observations of QAC, SHMP, and NaOH-treated kaolin composites (Figs. 15–17) exhibit that plastic deformation and fibrillation occur in the composite systems. These provide qualitative evidences that the nonreactive surface treatments on the kaolin particles enhanced the dissipation of energy through plastic deformation. Such a deformation process would certainly consume more energy than that dominated only by debonding as shown in Figure 13 (K30). Pukanszky and Maurer²² revealed that the major energy absorbing process is the plastic deformation of the matrix, which is enhanced by the presence of the surface modifier. Evidently, the inherent softening effect of nonreactive treatments of kaolin has made an important contribution. As analyzed earlier, all of the composites maintained a high level of impact strength. Furthermore, plastic flow of the matrix are clearly visible, indicating that the flow properties of kaolin-filled PP could be increased with nonreactive surface treatment. This is in agreement with the results of MFI behavior.

Figure 18 shows the morphology of PPgMAH-treated kaolin composite. Better dispersions of kaolin fillers were achieved as there is no visible kaolin agglomerate. This finding provides an explanation for the improvements in strength and rigidity of PPgMAH composite (Figs. 1–4). It is also important to note that there is no indication of plastic deformation observed from the micrograph. This suggests that enhanced interaction of PPgMAH-treated kaolin composite's interface was successfully achieved. The enhancement of the interface can be explained by the coupling effect of PPgMAH between filler and

matrix,^{23,24,44} which leads to the improvement of affinity between kaolin and PP. The improvement of adhesion between kaolin particles and PP led to higher modulus and strength, but lower toughness of the composite as obtained in the mechanical test results. Furthermore, as there is no indication of plastic flow, the decrease in MFI was expected (refer to MFI section).

From the overall mechanical properties analyses and morphological observations, it can be concluded that the efficiency of surface treatment agent has an order of QAC > PPgMAH > SHMP > NaOH. Thus, QAC-treated kaolin composite has been chosen to undergo the processing enhancement to study better dispersion of kaolin particles.

Effect of processing enhancements on morphological property

The effect of processing enhancements on the dispersion of kaolin fillers were studied by examining the tensile fractured surfaces of K30QACmill, K30QAC2 \times , and K30QACPPgMAH composites (Figs. 19–21). From the micrographs, it can be observed that the dispersion of kaolin particles in the composites were more or less the same with conventional method of compounding QAC-treated kaolin composite. Therefore, close examinations on the morphology of the matrix phase are important to further discuss the effect of processing enhancements. High magnification SEM micrograph could portray the type of fracture (brittle or ductile) exhibited by the matrix phase, which would provide some explanations to the strength, rigidity, and toughness behaviors of the composite.

Figures 22–25 present the fractured surface of K30QAC, K30QACPPgMAH, K30QACmill, and K30QAC2 \times composite with higher magnification

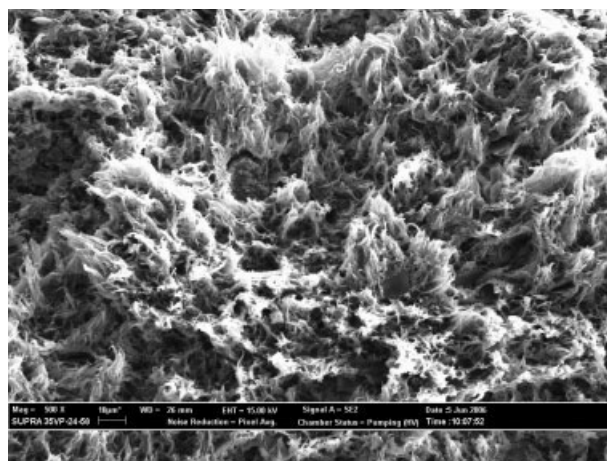


Figure 19 SEM micrograph of the fractured surface of 30 wt % milled QAC-treated kaolin-filled PP (K30QACmill) ($\times 500$).

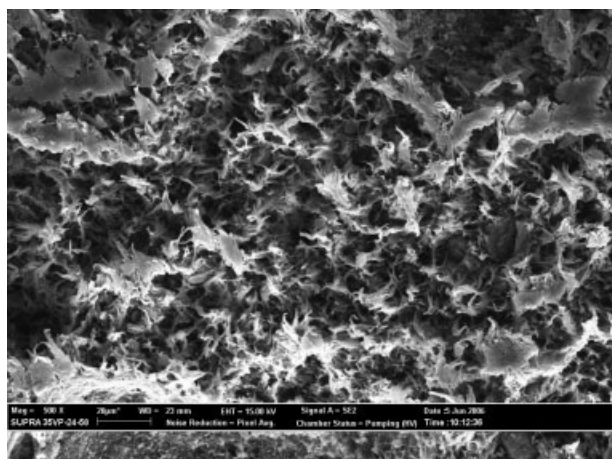


Figure 20 SEM micrograph of 30 wt % QAC-treated kaolin-filled PP composite prepared by two steps mixing method (K30QAC2 \times) (\times 500).

SEM micrographs. SEM fractograph of the composite filled with 30 wt % QAC-treated kaolin shown in Figure 22 reveals the existence of kaolin agglomerates, which were only visible at higher magnification SEM (1500 \times). In comparison with the images taken at lower magnification, no kaolin agglomerations were observed probably shielded by the plastic deformations.

Processing enhancements had successfully improved the dispersions of kaolin fillers as evidenced in Figures 23–25. The arrows (Figs. 22–25) show the reduction in size of QAC-treated kaolin agglomerates in PP composites with different processing methods. Furthermore, with respect to K30QACmill and K30QAC2 \times composites (Figs. 24 and 25), it is clear that the plastic deformation of the composites indicating ductile fracture is higher than that of the others. These suggest that the appearan-

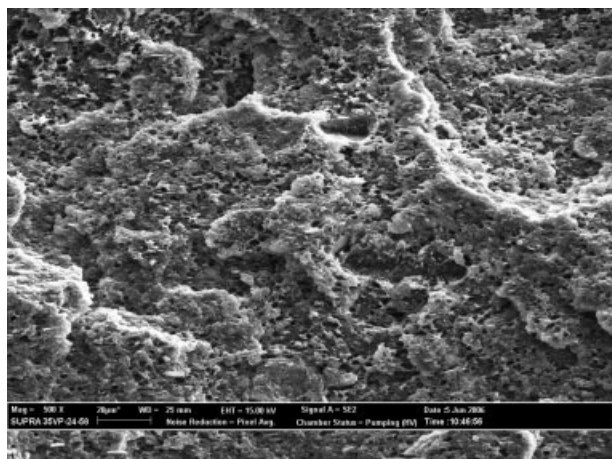


Figure 21 SEM micrograph of 30 wt % QAC-treated kaolin-filled PP modified with PPgMAH (K30QACPPgMAH) (\times 500).

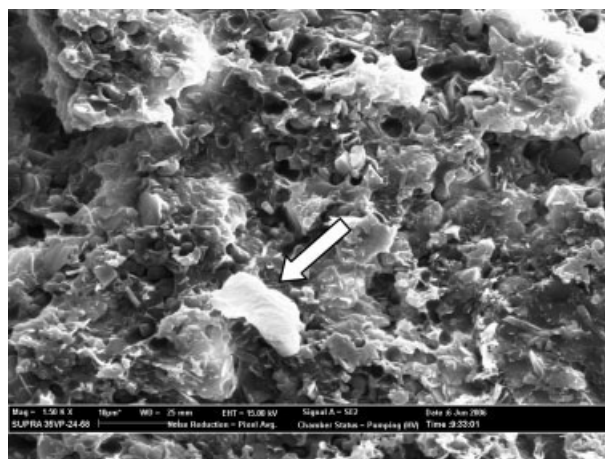


Figure 22 SEM micrograph of the fractured surface of 30 wt % QAC-treated kaolin-filled PP (K30QAC) (\times 1500).

ces of the fibrillated matrix are probably the result of a successive debonding of the kaolin particles from the matrix accompanied by the tearing of the matrix. However, the improvement of filler dispersions and extension of plastic deformations were insufficient to enhance the mechanical properties of these composites. As discussed earlier, possible reasons for the drawbacks are due to the decrease in filler-matrix interactions, the degradation of PP matrix and the absence of synergistic effect between dispersing agent and coupling agent.

Melt flow index determination

MFI provides valuable information about the flow behavior of materials. The MFI of single-filler composites with different surface treatments are shown in Figure 26. As can be seen, talc shows higher MFI than untreated kaolin. This is due to its ability to act as a flow promoter. Talc is the softest known min-

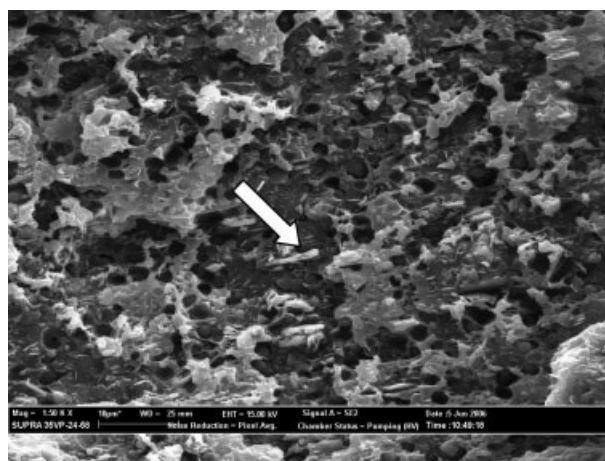


Figure 23 SEM micrograph of the fractured surface of K30QACPPgMAH composite (\times 1500).

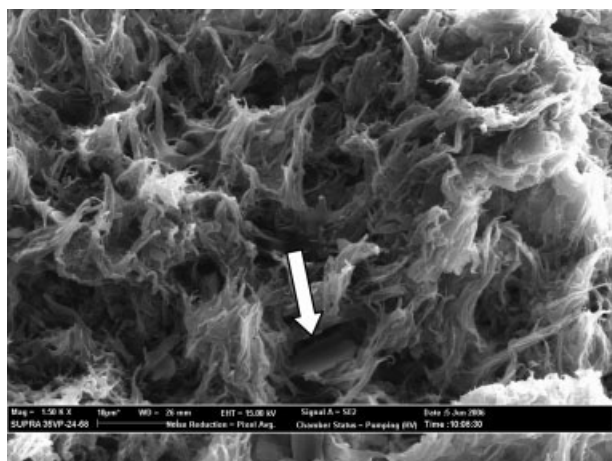


Figure 24 SEM micrograph of the fractured surface of K30QACmill composite ($\times 1500$).

eral on earth as adjacent talc layers are held together only by weak van Der Waals type forces.³⁴ These layers slide over each other with considerable ease when shearing action is applied to the mineral, which allows an increase in the plastic flow. In contrast, incorporation of kaolin fillers with strong interparticle forces¹⁵ would hinder plastic flow as well as increase the viscosity of PP melt,¹⁸ thus a decrease in MFI is expected.

An increase in flow properties of PP/kaolin composite was obtained with the aid of QAC surface treatment agent. The softening effect induced by this surface treatment agent might play a role in promoting such behavior. In agreement with many studies,^{18,29,45} the reduction in melt viscosity in the presence of surface treatment agent may have resulted from the surface modification of the filler particles. QAC might have acted as a surface modifier, consequently, under shear stresses, there could be far less

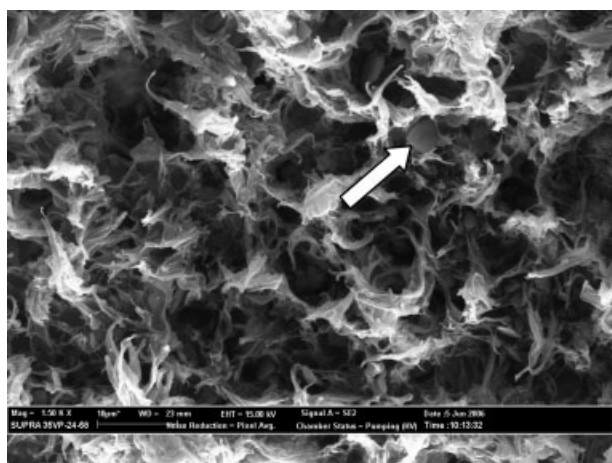


Figure 25 SEM micrograph of the fractured surface of K30QAC2 \times composite ($\times 1500$).

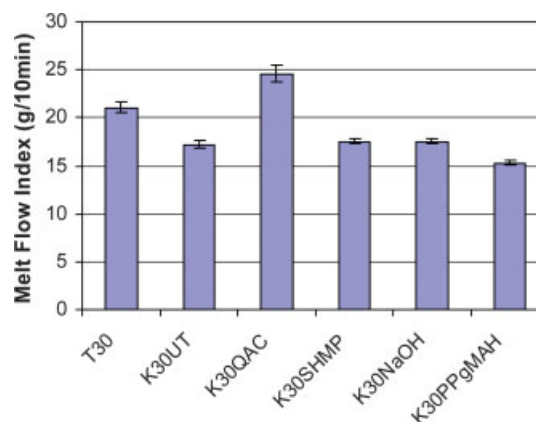


Figure 26 Effect of surface treatments on melt flow index of PP composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

frictional resistance to flow with the treated filler particles compared to that of the untreated filler particles. Furthermore, Kim et al.⁴⁶ in their study of stearic acid-treated CaCO_3 had reported that nonreactive surface treatment agent could increase processability of composite. Hence, the results obtained from MFI values signify the ability of QAC surface-treated kaolin to increase plasticity and processability of the polymer comparable to talc-filled PP composite. However, the above-mentioned scenarios occur only in the presence of QAC-treated kaolin, whereas SHMP- and NaOH-treated kaolin show similar MFI value compared to that of untreated kaolin. It is believed that SHMP and NaOH treatments fail to promote softening effect to the composite systems, thus no significant effect can be seen in the MFI value.

QAC shows the most remarkable increment in MFI beyond T30 and K30UT composite, which could signify that QAC has the ability to increase the plasticity and processability of the composite. Moreover, the significantly larger MFI of QAC-treated kaolin-filled PP composite also indicates a more homogeneous composite. The study of Pukanszky and Maurer²² reported that composite with larger MFI was a result of homogeneous component of the composite. On the other hand, the PPgMAH treatment reduced the MFI value of the PP/kaolin composite. As discussed earlier, PPgMAH act as a coupling agent that promotes strong interaction between fillers and matrix.^{23,44} Hence, the reduction in MFI value for PPgMAH-treated kaolin-filled PP could be attributed to the coupling effect between fillers and matrix, which hinders polymer melt flow.

The effect of processing enhancements on PP/kaolin composite was further evidenced through MFI. From Figure 27, a slight increment in the flow properties of K30QACmill and K30QAC2 \times could be

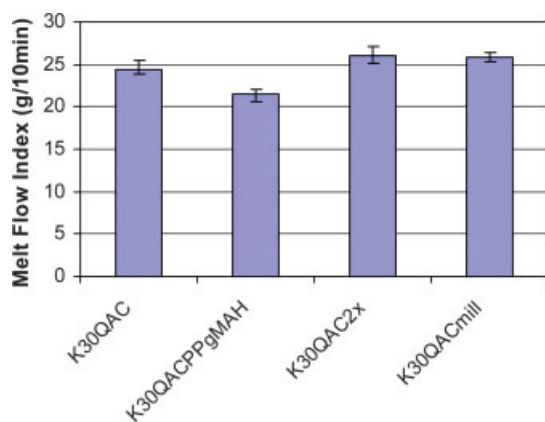


Figure 27 Effect of processing enhancements on the MFI of QAC-treated kaolin/PP composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observed. The reduction in agglomerated particles and better fillers homogeneity which were attained in those composites are believed to be responsible in increasing the polymer melt flow. According to Wei,²⁹ less agglomerated particles would promote the polymer matrix to flow at ease. Therefore, an enhancement of MFI was obtained.

Thermal properties

Table VI summarizes differential scanning calorimetry (DSC) results for single-filler composites. It is evident that for the onset of melting temperature, $T_{m \text{ onset}}$, there were very little difference between PP/talc and PP/kaolin composites, for both untreated and treated kaolin fillers. $T_{m \text{ onset}}$ of the composite represents the thermal stability of the composite. The results (Table VI) indicate that the thermal stability of the composites were comparable with each other. Similar results were also obtained for T_m , as kaolin fillers, untreated and treated with different types of surface treatment agents had almost no influence on the temperature of the melting peak, T_m . Enhanced processing method of K30QAC composites also were insuffi-

cient to provoke a significant change in the thermal properties.

Crystallization behavior of talc-filled PP and kaolin-filled PP were also studied to determine the effect of the fillers on the crystallization properties of PP composite. The crystallization peak was interpreted according to the method given in the previous works.^{47,48} It may be noted from the values that the crystallization in talc-filled PP starts at a temperature greater than kaolin-filled PP, implying acceleration of the crystallization process in the presence of talc fillers. This is undoubtedly due to the enhanced nucleation in the presence of talc, as it is well documented that talc has high nucleating ability.^{35,36,48} Additionally, surface-treated kaolin composites and processing enhancements exhibit crystallization at higher temperature ($T_{c \text{ onset}}$, T_c) than untreated PP/kaolin composite. This is presumably because of enhanced dispersion of kaolin fillers. According to Mareri et al.,⁴ the improved particle dispersion obtained with surface treatment would lead to a much greater number of nucleation sites, inducing crystallization at higher temperature.

Hadal et al.³⁶ quoted that the increase in heat enthalpy of cooling is a direct indication of higher percentage of bulk crystallinity in PP composites. From Table VI, it can be observed that kaolin fillers, with or without surface treatment exhibit enhanced crystallization in comparison to talc-filled PP composite. Using a value of heat enthalpy for 100% crystalline PP of 207.15 J/g,⁴⁸ the percentage of crystallinity of PP composites are estimated (Table V) and presented in Table VI. From the results tabulated, it can be deduced that the kaolin fillers used have increased the degree of crystallinity (DOC) of PP matrix. The DOC calculations revealed that QAC composite exhibit highest DOC compared to other composites. The study of Velasco et al.⁴⁸ reported that surface treatment agent which improves fillers dispersion as well as wetting and act as internal lubricants for filled PP by reducing the melt viscosity could slightly raise the crystallinity of the PP matrix. The composite is expected to obtain higher modulus, better dimensional properties stability, as

TABLE V
Physical Characteristics of the Crystallization Peak^{2,4}

1. T_c	The crystallization temperature corresponding to the maximum of the crystallization peak.
2. $T_c \text{ onset}$	The onset temperature corresponding to the beginning of the crystallization phenomenon.
3. Slope from $T_c \text{ onset}$ to T_c	The slope of the peak characteristic of the germination rate or the nucleation rate
4. $T_c \text{ onset} - T_c$	Inversely proportional to the rate of spherulite growth.
5. DOC	Degree of crystallinity
ΔH_c , heat of fusion; ΔH_f , heat of fusion for 100% crystalline; W_f , weight fraction	$\% \text{DOC} = \frac{\Delta H_c}{\Delta H_f} \times 100\%$ for neat or unfilled polymer
	$\% \text{DOC} = \frac{\Delta H_c}{\Delta H_f(1-W_f)} \times 100\%$ for composite

TABLE VI
Thermal Properties of the Composites Derived from DSC Scan Thermogram

Composite	Melting (from heating scans)		Crystallization (from cooling scans)					
	T_m onset (°C) ± 2	T_m (°C) ± 2	T_c onset (°C) ± 2	T_c (°C) ± 2	T_c onset - T_c (°C)	Nucleation rate (mW/°C)	ΔH_c (J/g)	DOC %
T30	151.4	164.3	127.6	121.8	5.7	2.7	34.7	55.9
K30UT	151.6	166.2	118.7	112.8	5.9	3.0	37.5	60.3
K30QAC	150.7	164.9	124.1	119.9	4.2	6.8	51.6	83.0
K30SHMP	151.2	164.7	121.5	115.9	5.6	3.3	43.8	70.5
K30NaOH	149.6	165.2	120.6	115.8	4.8	2.9	48.6	78.0
K30PPgMAH	152.4	165.6	121.3	113.9	7.4	2.7	48.5	78.0
K30QACPPgMAH	150.9	165.1	121.2	115.9	5.3	4.7	45.5	73.3
K30QAC2×	152.3	166.3	122.6	117.3	5.3	5.3	48.6	78.3
K30QACmill	150.4	165.3	123.9	119.9	3.9	7.6	49.9	80.4

well as increased strength with the increase in crystallinity of the polymer matrix.⁴⁴ However, in this work, this finding did not reflect the strength behavior of the PP/kaolin composite as the influence of filler agglomerations and weak interfacial interaction contribute more than the crystallization factor of PP matrix.

Nevertheless, it is reasonable to infer that the crystalline structure of the matrix plays a critical role in toughening behavior. This could be correlated with the results of the impact tests obtained for the surface-treated composites. Wang et al.⁴⁴ supported this phenomenon. They had reported that the modified interface between PP matrix and filler particles increases the nucleating ability of the fillers and retards the motion of the PP chains. This leads to the formation of PP crystals with imperfection and smaller size in the matrix and promotes plastic deformation of the matrix after the debonding occurs. These effects, combined with the effective stress distribution throughout the composite by filler particles, resulted in the increment of toughness.

CONCLUSIONS

The incorporation of kaolin in PP matrix resulted in composite with fairly good impact strength, which is enhanced with the aid of nonreactive surface treatment agents. SEM studies indicate better dispersion with less agglomerations and smaller aggregates for treated kaolin composites. At high kaolin loading of 30 wt % in PP composite, various surface treatments of kaolin were only able to reduce the size of aggregates, but unable to break the aggregates and thus failed to disperse the particles individually. Nonreactive treatments yielded composites with larger plastic deformation compared to untreated and PPgMAH-treated kaolin-filled composites. This signifies the ability of nonreactive treatments to promote toughness in PP-filled composite. Nevertheless, this

morphology was also held responsible for the decrease in strength and stiffness of PP/kaolin composite. With respect to the processing enhancement aspect, dispersions homogeneity of the composites filled with QAC-treated kaolin was attained. However, this was insufficient to provoke significant improvement in the mechanical properties except for the impact strength of the composites due to the decrease in filler-matrix interactions and the degradation of PP matrix.

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