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Comparison of the Mechanical Properties and Interfacial Interactions Between Talc, Kaolin, and Calcium Carbonate Filled Polypropylene Composites

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ABSTRACT: Three types of mineral fillers—talc, calcium carbonate (CaCO_3), and kaolin (10–40 wt % filler loadings)—were compounded with polypropylene (PP) with a twin-screw extruder. The composites were injection-molded, and the effects of the filler loading on the mechanical, flow, and thermal properties for the three different types of filled composites were investigated. The aim was to compare their properties and to deduce prospective filler combinations that would yield hybrid PP composites in following studies. The results showed that in most cases, the strength and stiffness of the talc-filled PP composites was significantly higher than those of the CaCO_3 - and kaolin-filled PP composites. However, CaCO_3 , being a nonreactive

filler, increased the toughness of PP. The kaolin-filled PP composites also showed some improvement in terms of strength and stiffness, although the increases in these properties were not as significant as those of the talc-filled PP composites. The effects of interfacial interactions between the fillers and PP on the mechanical properties were also evaluated with semiempirical equations. The nucleating ability of all three fillers was studied with differential scanning calorimetry, and the strongest nucleating agent of the three was talc, followed by CaCO_3 and kaolin. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3315–3326, 2004

Key words: poly(propylene) (PP); composites; fillers

INTRODUCTION

Particulate-filled thermoplastic composites have proved to be of significant commercial importance in recent years, as industrialists and technologists have sought to find new and cost-effective materials for specific applications.¹ The incorporation of fillers such as calcium carbonate (CaCO_3) into thermoplastics is a common practice in the plastics industry, being used to reduce the production costs of molded products. Fillers are also used to modify the properties of plastics, such as the modulus and strength. High filler loadings, however, may adversely affect the processability, ductility, and strength of composites. The incorporation of additives, such as elastomers, coupling agents, compatibilizers, surface agents, antioxidants, and ultraviolet agents, has also been done to further enhance the durability and appearance of composites.²

Studies of mineral fillers such as talc-, kaolin-, mica-, and CaCO_3 -filled plastics are relatively well known.^{3–6} Talc, mica, and kaolin are used to enhance the stiffness and strength of filled plastics, whereas CaCO_3 -filled grades are reported to have higher impact strength. The properties of particulate-filled polymers are determined by several factors, such as the component properties (matrix and filler), composition, and structure. In addition to the component properties, the mechanical characteristics of these materials are significantly influenced by the interfacial interactions, which depend on the size of the interface and the strength of the interaction.⁷

The effect of the structure of fillers usually depends greatly on their shape, particle size, and particle size distribution. There are five major types of particle shapes of mineral fillers: sphere, cube, block, flake, and fibrous. A fibrous filler can usually improve the tensile strength. A sheetlike or platelike filler can improve rigidity, and the improvement depends on the aspect ratio of the filler.⁸ In this study, talc and kaolin are platelet-like, whereas CaCO_3 has an uneven particle shape. The specific surface area is one of the most important characteristics of fillers. It determines the amount of surface contact between the polymer matrix and the filler. Fillers with higher surface areas will contribute to more surface contact between the filler

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and matrix, thus increasing the mechanical properties of the composite. Fillers with fine or small particles have higher surface areas than fillers with big particles. However, the finer the particles are, the greater their tendency is to agglomerate, and this can cause an adverse effect on mechanical properties, especially the impact resistance of composites. The same is true for fillers with big particles, which may act as stress-concentration points or points of discontinuity in composites, thereby promoting crack initiation and propagation.

CaCO₃ is one of the most commonly used inorganic fillers in thermoplastics, such as poly(vinyl chloride) and polypropylene (PP).² At first, CaCO₃ was only used to reduce the cost of expensive resins. The particle size of commercial-grade CaCO₃ is in the range of 1–50 μm . Previous studies² have shown that the enhancement of strength in CaCO₃-filled composites is minimal. This might be due to the lack of surface interactions between the filler and the matrix. Various attempts have been made to improve the surface interactions of CaCO₃, such as the use of stearic acid, titanate, and silane coupling agents.⁷ There are a few theoretical frameworks and models used to explain the toughening mechanism in CaCO₃-filled composites.^{9,10} In addition to these models, several requirements also need to be met to enhance the toughening mechanism:

The dispersion of the filler particles must be sufficiently good to prevent the creation of stress-concentration points through agglomerated particles.

Matrix–filler debonding must occur to allow unhindered plastic deformation around the particles, thereby increasing the ductility of composites.

In the plastic and rubber industry, kaolin has been used widely as a filler because of its great reinforcing effect in mechanical properties, such as stiffness and strength. Mareri et al.⁴ reported that the use of kaolin improved the stiffness of PP. Fellahi et al.¹¹ reported that the modulus and strength of a kaolin-filled epoxy resin increased with increasing filler loading but that the elongation at break (EB) and impact properties decreased. Because kaolin has a platelike structure and a high aspect ratio, the particle size and distribution are very important in determining the mechanical properties of plastic composites. The surface treatment of kaolin can also improve the mechanical properties of plastic composites. Qiu et al.¹² used surface-treated kaolin to improve the mechanical properties of a PP/mPE blend. The results showed that surface-treated kaolin-filled PP could enhance low-temperature impact toughness in comparison with an unfilled blend. This revealed that the surface-treated kaolin had a very good filler–matrix interfacial adhesion, and ka-

TABLE I
Material Specifications

Material	Density (g/cm ³)	Hardness (Moh's scale)	Mean particle diameter (μm)
Talc	2.79	1	6.3
Kaolin	2.59	2	3.0
Untreated CaCO ₃	2.70	3	3.3

olin particles were dispersed in a lamellar form in the kaolin-filled PP/mPE matrix. This may be reason that the kaolin-filled PP/mPE blend exhibited better impact performance at a low temperature.

Demjen et al.⁷ developed and proposed the use of an empirical equation for the quantitative evaluation of the dependence of a composite on the tensile yield stress of particulate polymers. The proposed equation has been used here to quantitatively determine the interaction between the fillers and matrix.

The main aim of this article is to study the effects of the types and loadings of fillers on the mechanical, structural, thermal, flow, and morphological properties of composites. Second, with empirical equations proposed by Khunova et al.,¹ the level of the filler–matrix interaction is investigated and compared with experimental results. This article is the first part of a series of three; part two reports the properties of hybrid composites, and part three discusses the usage of various coupling agents. Although some of the properties for single-filler PP composites presented in this article have been well established and published in various publications, it is important that these data be recollected beforehand to produce an accurate analysis in the following series of articles.

EXPERIMENTAL

Materials

Copolymer-grade PP (Pro-Fax SM240), with a melt index of 25 g/10 min and a density of 0.894 g/cm³, was supplied by Titan PP Polymers (M) Sdn. Bhd.

Three types of fillers were incorporated into PP: talc (Chung Chemicals Sdn. Bhd.), untreated CaCO₃ (Omyacarb 3-SA, Malaysian Calcium Corp. Sdn. Bhd.), and kaolin (Finn Chemicals). Table I lists the specifications.

The additives included an antioxidant (Irganox 1010) and an ultraviolet stabilizer (Tinuvin 770 DF), both from Ciba.

Sample preparation

The compounding was performed with a Rheomex CTW 100 twin-screw extruder (Haake). The barrel temperatures of the four zones were 160, 170, 180, and 190°C, from the feeding zone to the die zone. The

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 with a Niigata AN 50 50-ton injection-molding machine. The injection-molding temperature ranged from 190 to 230°C, and the back-pressure was 60 psi.

Mechanical testing

The tensile and flexural properties were measured with a Testometric M500-25 kN tensile machine in accordance with ASTM D 638 and ASTM D 790-86 with type 1 test specimen dimensions. For tensile tests, a crosshead speed of 5 mm/min was used, and the average value of at least five specimens was taken for each sample. For flexural tests, a three-point loading system was used, and the support span length was adjusted to 50 mm. The crosshead speed was 3 mm/min. All tests were carried out in an air-conditioned room (27°C).

Impact testing was performed with a Ray-Ran impact pendulum tester at an impact energy of 7.5 kJ according to ASTM D 256-88. The hammer velocity was set at 2.88 m/s, and the weight of the hammer was 1.811 kg.

Mode of failure analysis

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

Density determination

The density (ρ) of the test specimens was determined according to the ASTM 792 water displacement method (method A) with the following equation:

$$\rho = [W_1/(W_1 - W_2)]\rho_w \quad (1)$$

where W_1 and W_2 are the sample weights in air and water, respectively, and ρ_w is the density of water.

Melt-flow index (MFI)

The flow behavior of the filled PP composites was determined with a Ray-Ran melt-flow indexer according to ASTM D 1238-90b. A load of 2.16 kg at 230°C was used in the measurement.

Thermal analysis process

The crystallization behavior and melting characteristics of the composites were studied by differential scanning calorimetry (DSC) with a PerkinElmer DSC-6 in a nitrogen atmosphere at a heating and cooling rate of 20°C/min. In the first heating and cooling scans, the samples were heated from 50 to 220°C and held at that temperature for 1 min to eliminate the thermal history; then, the nonisothermal crystallization process was recorded from 220 to 50°C, and a standard status of crystallization was created. A second heating was also performed at 20°C/min from 50 to 220°C.

Filler content determination

As some filler might be loss during processing, a polymer burn-off test or ashing was performed to determine the final filler content in the composites after the injection-molding process was completed. Dumbbells were randomly selected and burnt off in a furnace with the temperature set at 600°C. The filler residue was then weighed, and the corresponding weight fraction of the filler (W_f) was converted into the volume fraction of the filler (V_f) with the following formula:

$$W_f = \frac{\rho_f}{\rho_c} V_f \quad (2)$$

where ρ_c and ρ_f are the densities of the composite and the filler, respectively.

RESULT AND DISCUSSION

Determination of the filler content by ashing

The exact filler content of various formulations was determined by the polymer component being burnt off, which left the fillers. The fillers were then cooled before the weighing. W_f , V_f , ρ_c , and ρ_f are listed in Table II.

MFI

The MFI values of various composites are shown in Figure 1. Because the incorporation of fillers hinders plastic flow and increases the viscosity of a polymer melt, a reduction of MFI with the filler loading is expected. The overall MFI of CaCO₃-filled PP is higher than that of the other composites, and this may signify that CaCO₃ has the ability to increase the plasticity and processability of the polymer. Talc and kaolin particles also have the ability to slide against each other during the application of shear forces because of their platy shape, which allows an increase in the plastic flow. However, this ability only applies to fill-

TABLE II
Filler Contents of Various Formulations

Sample code	Measured W_f	ρ_c (g/cm ³)	Calculated V_f
UCC10	0.09	0.85	0.03
UCC20	0.18	0.97	0.06
UCC30	0.24	1.02	0.09
UCC40	0.39	1.14	0.17
T10	0.09	0.95	0.03
T20	0.19	1.02	0.07
T30	0.29	1.11	0.12
T40	0.37	1.20	0.16
K10	0.08	0.96	0.03
K20	0.16	1.01	0.06
K30	0.25	1.09	0.10
K40	0.34	1.19	0.16

UCC = untreated CaCO₃; T = talc; K = kaolin.

ers at certain parts of the composites that are near the die walls, and so the effect of this ability on MFI is minimal.

Thermal properties

Talc has been labeled as a strong nucleating agent in various publications,^{13–17} and this can be measured by DSC. Figure 2 shows the exothermic crystallization peaks of unfilled PP and filled PP composites at 30% filler loadings. On the basis of the decreasing height of the peaks for filled PP with respect to unfilled PP, it appears that the incorporation of the fillers reduced the crystallinity of PP. A careful examination of the DSC curves, however, reminds us that the curves have been normalized only in terms of the initial masses of the samples tested and not in terms of the actual PP

fractions of the samples. Naturally, as the filler content increases, the PP mass fraction decreases proportionately, and only the PP component contributes to the crystallization peak (because the bond-forming process during the crystallization of PP releases heat; i.e., it is exothermic).

The physical characteristics of the crystallization peak (Fig. 3) can be used to deduce the crystallinity of a polymer.¹⁸ As shown in Figure 2, both the onset temperature (T_o) and the crystallization temperature (T_c) increased with the incorporation of fillers into the PP matrix. The increase in these temperatures could be attributed to the formation of nuclei at an earlier stage and at a higher temperature during the cooling process. T_o corresponds to the temperature at which nucleus formation starts to occur; this releases heat as the process continues until it reaches a maximum at T_c . T_o reflects the nucleating ability of a nucleating agent: strong nucleating agents will substantially increase the value of T_o .¹⁹ Therefore, from Figure 2, it can be deduced that all the fillers used have nucleating effects on the PP matrix, the strongest nucleating agent being talc and the weakest being kaolin. Strong nucleation will modify and change the crystalline structure of PP from β spherulites, which are weaker, into the stronger α form.¹³ With an increase in the crystallinity of the polymer matrix, the composite is expected to obtain a higher modulus, better dimensional stability, and increased strength.²⁰ Therefore, the larger increase in strength for the talc-filled PP composite is partly due to increased crystallinity of the polymer matrix. The effect of crystallinity on the mechanical properties of CaCO₃- and kaolin-filled PP composites, however, is minimal, as both these fillers show only

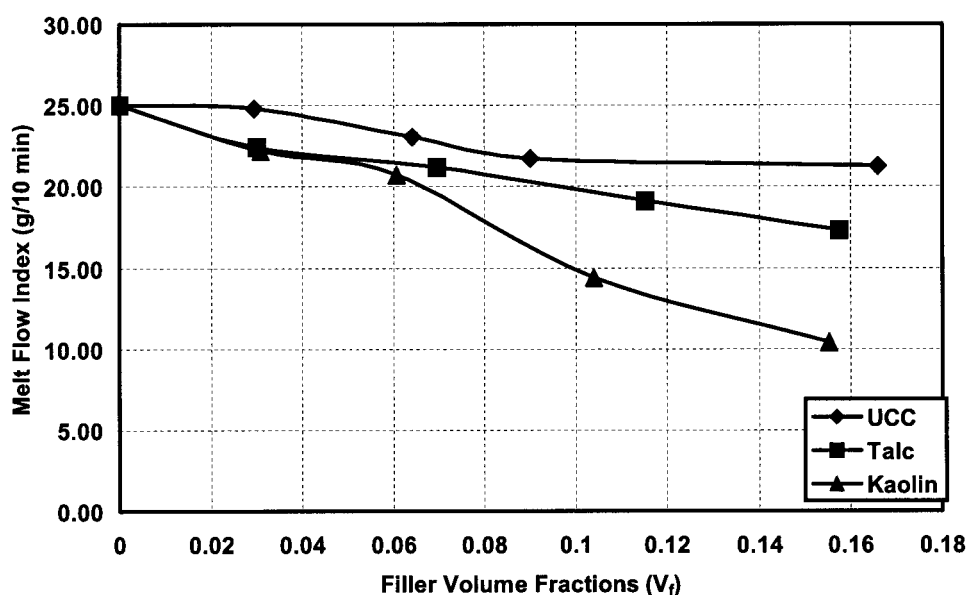


Figure 1 Effects of the filler loading on the MFI.

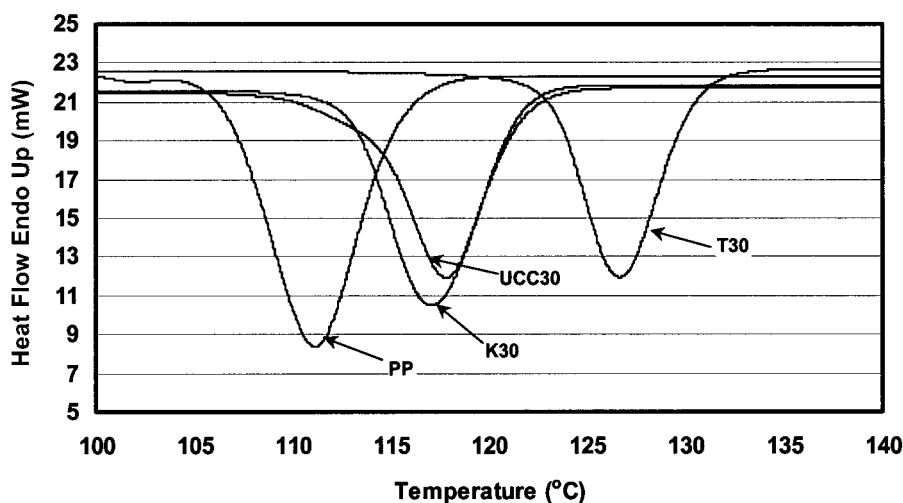


Figure 2 Exothermic crystallization peaks for filled and unfilled PP.

weak nucleating abilities in comparison with talc. Therefore, the mechanical properties of these composites must be affected by other factors, which were given due consideration in earlier parts of this study.

Effect of the filler loading on the mechanical properties

Tensile properties

Figure 4 shows the tensile modulus of talc-, CaCO_3 -, and kaolin-filled PP composites. 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 due to the fact that 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.

Figure 5 shows the tensile strength of talc-, CaCO_3 -, and kaolin-filled PP composites. An increase in the tensile strength was observed for talc up to a maximum at $V_f = 0.15$. Kaolin-filled PP showed an increase from $V_f = 0.05$ to $V_f = 0.12$, after which the strength started to deteriorate. For CaCO_3 -filled PP, a reduction in strength was observed with increasing filler loading. The initial increase in strength for talc- and kaolin-filled PP composites was mainly due to good filler-matrix interactions, which were largely due to the platy nature of the fillers. Platy fillers have high aspect ratios, and this increases the wettability of the fillers by the matrix, thus creating fewer microvoids between the fillers and matrix.²¹ Increased filler-matrix interactions also enable more stress to be transferred from the matrix to the fillers during external loading.

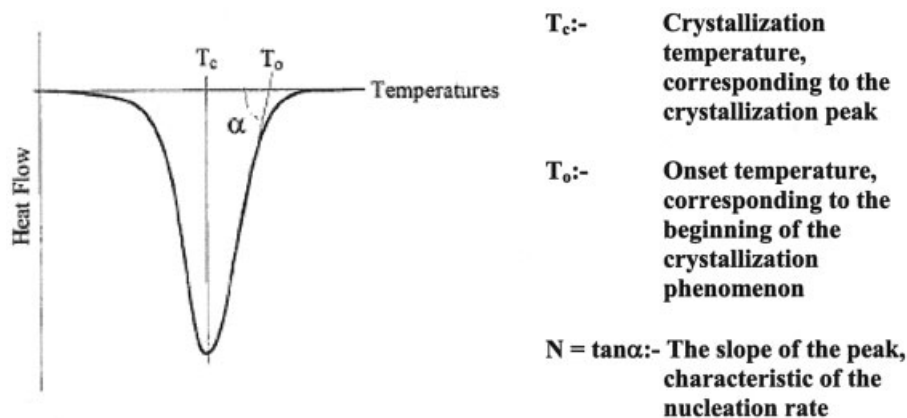


Figure 3 Physical characteristics of the crystallization peak.

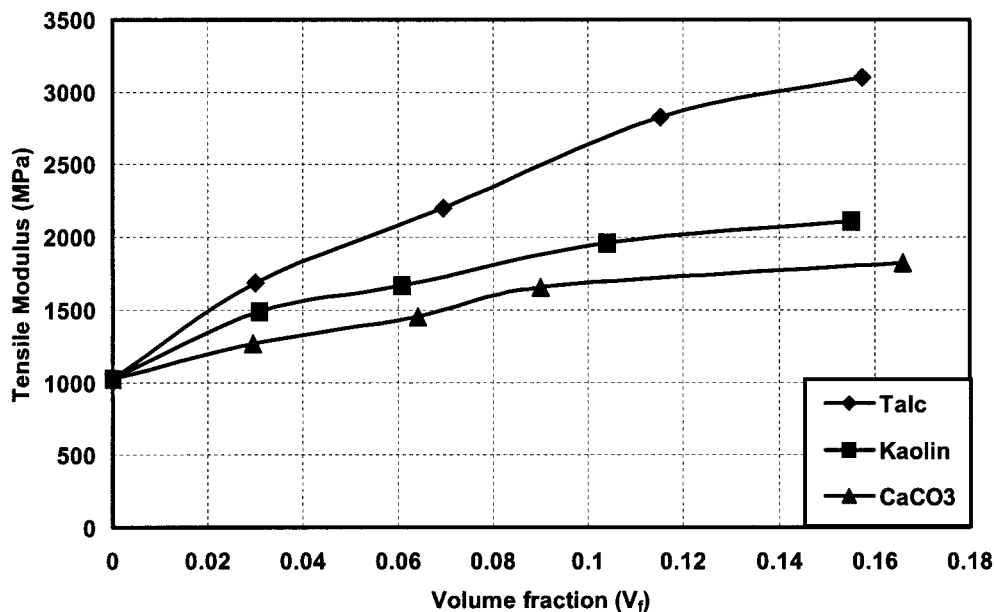


Figure 4 Effect of the filler loading on the tensile modulus of talc-, kaolin-, and CaCO₃-filled PP composites.

It has also been reported that nontreated fillers have high-energy surfaces.¹³ During the melt-mixing process, polymer chains are adsorbed onto the active sites of the filler surface. The adsorption of polymer molecules leads to the development of a layer, which has properties different from those of the matrix polymer. Because of the preferred adsorption of large molecules, the dimensions of the crystalline units, which depend on the molecular mass of the polymer, will usually decrease. Therefore, too much of an increase in the amount of the filler will reduce the mobility of the chains and also affect the kinetics of crystallization.

Kinetic hindrance leads to the development of small, imperfect crystallites. Therefore, the crystallinity of the polymer may not necessarily increase, although talc has been cited as a strong nucleating agent in various publications.^{16,15} Pukanszky et al.¹⁷ also proved that changing the crystalline structure has a much smaller effect on the properties than the particle orientation of the fillers. Kim and White²² suggested that talc particles tend to orient with the plane surface parallel and perpendicular to the flow direction at the sample skin and core, respectively. However, Figure 6 shows that talc particles only orient parallel to the

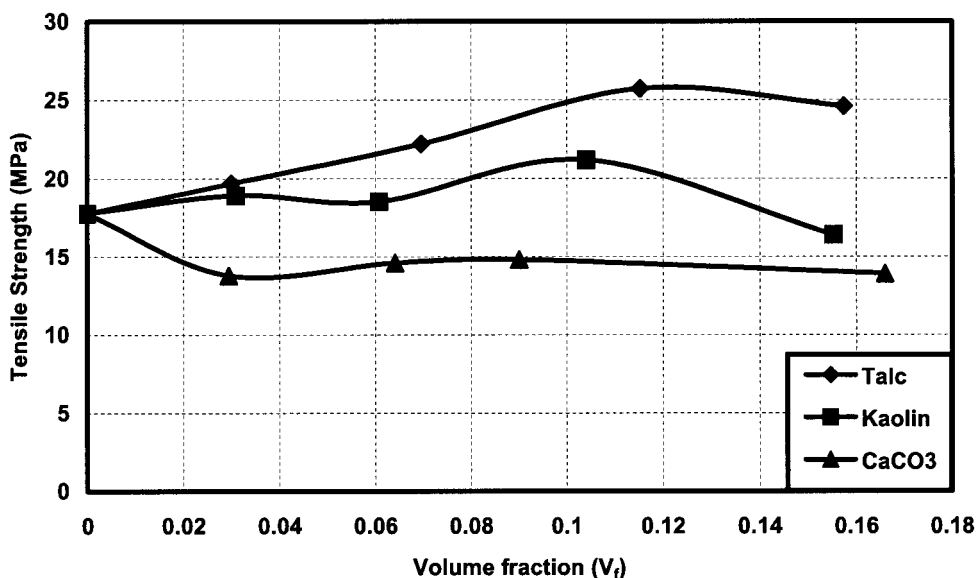


Figure 5 Effect of the filler loading on the tensile strength of PP.

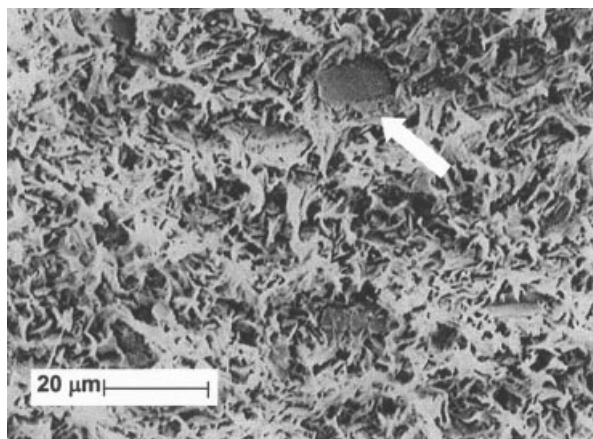


Figure 6 SEM micrograph of 30 wt % talc-filled PP. Filler particles are embedded into the matrix, with very few exposed at the fracture surface, as shown by the arrow.

flow direction throughout the composite. Moreover, large plastic deformation occurs during fracture, whereas talc filler particles are deeply embedded into the fracture surface; this also signifies good interactions between the filler and matrix. Filler dispersion is good, and no large void presence can be seen between the particles and the matrix. The tensile strength of kaolin- and talc-filled composites decreases at higher filler loadings because the matrix continuity is replaced by particle–particle contact. Therefore, mechanical coherence, except for some agglomeration, will disappear.²³

CaCO₃ shows a moderate drop in the tensile stress with the filler loading in comparison with other filled PP composites. This may be because CaCO₃ is known to promote craze formation in deformed polymers before fracture.²³ The interaction strength changes over a very limited range because PP itself has very low surface energy and the polar component of surface tension is very close to zero, as mentioned by Pukanszky.¹³ This causes dewetting of CaCO₃ particles from the PP matrix. Dewetting becomes more evident as the concentration of the filler increases, but dewetting also occurs at lower filler concentrations at high elongations.²⁰ In Figure 7, exposed CaCO₃ particles at the fracture surface can be observed. Very few broken CaCO₃ particles can be seen, and this indicates that the filler–matrix adhesion is relatively weak, allowing debonding to occur before fully developed plastic deformation and, therefore, the formation of cavities. The particle size of CaCO₃ is large, in that it has isometrically shaped particles. Large particle sizes lead to greater stress concentration and contribute to the formation of larger cavities and voids, and so the decrease in the tensile strength is completely normal. Critical strain debonding also caused the yielded specimens to exhibit opacity.

The particle size of kaolin is smaller than that of talc. Although fillers with small particles have been known

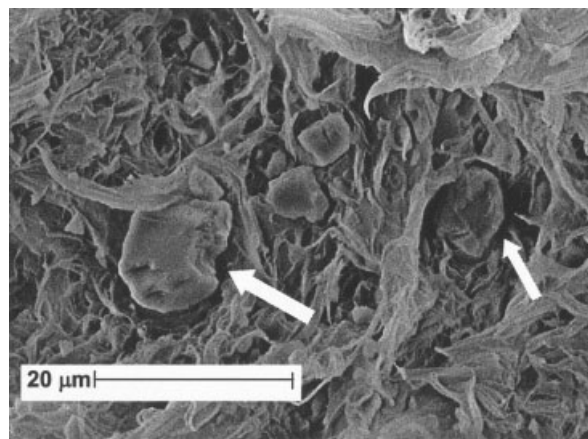


Figure 7 SEM micrograph of 30 wt % CaCO₃-filled PP. The bonding of the filler to the matrix is very weak because of the formation of cavities around filler particles, as shown by the arrows.

to increase the tensile strength,²⁰ it is evident from Figure 8 that the kaolin used in this study possesses the worst possible distribution, having a small particle fraction with a strong tendency for severe aggregation. The continuous sheet structure produces thin particles, which are often found in nature as overlapping flakes. These are informally called *books* because of their resemblance under magnification to stacks of paper. Kaolin books are bound via hydrogen bonding of the octahedral-layer hydroxyl face of one flake to the tetrahedral-layer oxygen face of the adjacent flake. The separation of books into individual clay flakes is, therefore, difficult, especially in a polymer matrix.²⁴ Therefore, kaolin books are known as aggregates, made up of particles held together by strong forces, and not as agglomerates, which are made up of particles held together by weak forces.²⁰ These books debond easily from the matrix and tend to reduce the strength of the material, even though the agglomerate

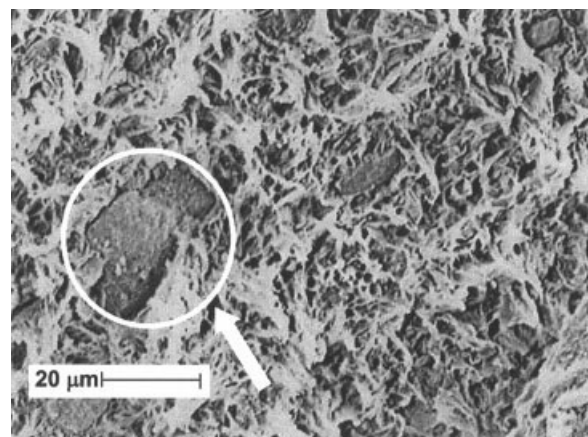


Figure 8 SEM micrograph of 30 wt % kaolin-filled PP. The arrow shows aggregated kaolin books in the PP matrix.

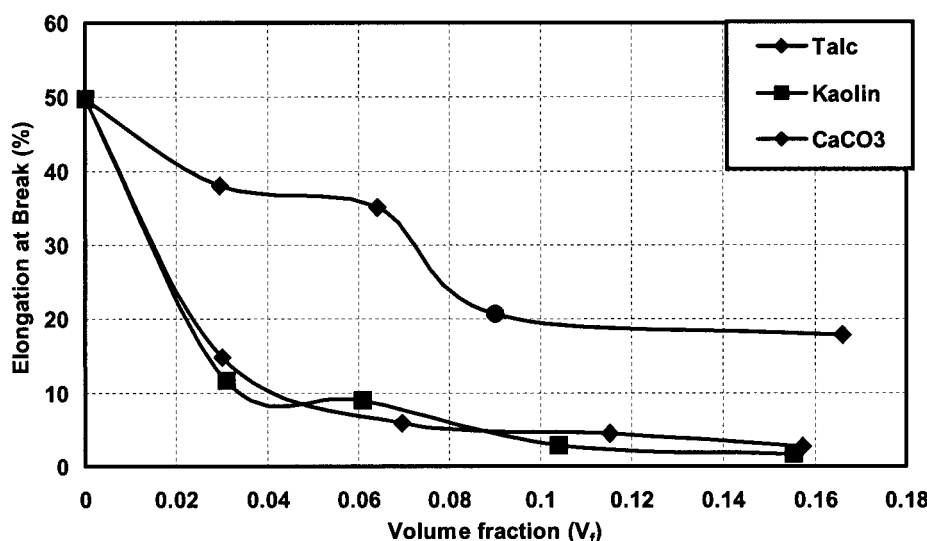


Figure 9 Effect of the filler loading on EB of talc-, kaolin-, and CaCO₃-filled PP composites.

may be strong enough to increase the initial modulus.²⁰ Aggregates are weak points in the material and break fairly easily when stress is applied. A broken kaolin aggregate then behaves as a strong stress concentrator, leading to a decrease in the tensile strength of kaolin-filled PP.

Figure 9 shows the effect of the filler loading on EB of various types of filled PP composites. In all cases, the incorporation of fillers resulted in significant drops in EB of PP. This indicates that the incorporation of a filler changes the mode of failure of PP from ductile behavior to brittle behavior. This reduction in the deformability of PP can be attributed to extensive filler agglomeration, which leads to insufficient homogeneity, and also to the rigidity of particulate fillers. Under the effect of an external load, the inhomogeneity of local stress distribution initiates deformation at particular locations in a composite. At a higher filler loading ($V_f = 0.12$ – 0.15), EB of kaolin- and talc-filled PP decreased in comparison with that of CaCO₃-filled PP. The minimal decrease in EB for CaCO₃-filled PP indicates that there is also some degree of brittle–ductile transition during the development of plastic deformation, as proposed by Wu.⁹ The weak adhesion of fillers to the matrix allows sufficient debonding of the filler from the matrix, which allows more plastic deformation to occur before failure and leads, therefore, to the higher EB value of the composite.

Flexural properties

Figure 10 shows the flexural modulus of talc-, CaCO₃-, and kaolin-filled PP composites. Just like the tensile modulus (Fig. 4), the flexural modulus of all the samples increased almost linearly with increasing filler loading. Again, it is a well-known fact that the incor-

poration of rigid particulate fillers improves the stiffness of plastic matrices.² The higher enhancement observed in platy talc and kaolin can be attributed to the higher aspect ratio and particle orientation of both these fillers, in comparison with CaCO₃. Talc shows better improvement than kaolin, and this may be due to the better filler orientation of talc particles. In addition, kaolin tends to agglomerate because of its fine particles, thereby increasing the mobility of the polymer matrix and consequently reducing the overall stiffness of the composites. Generally, the flexural modulus of the composites is lower than the tensile modulus. This could be due to a surface skin that is rich in polymer because of molding against a surface.²⁰ Because of the restrictions imposed by the walls of molds, the surfaces of composites have an excess of polymer. Therefore, in flexural tests in which the maximum stress is at the surface, the properties of the surface are emphasized at the expense of the interior, and so the measured values of the modulus are low. This error decreases as the particle size decreases.

Figure 11 shows the flexural strength of talc-, CaCO₃-, and kaolin-filled PP composites. In the case of talc-filled PP composites, there was a significant increase in the flexural strength with increasing filler loading until a maximum filler loading was reached ($V_f \approx 0.05$); thereafter, the value decreased. The improvement of the flexural strength with the incorporation of kaolin only slightly increased at a filler loading of $V_f = 0.04$ but decreased at higher filler loadings ($V_f > 0.03$). For CaCO₃-filled PP, the flexural strength increased moderately until around $V_f = 0.05$, after which a decrease was recorded.

The higher flexural strength of talc-filled PP further confirms that talc is a better reinforcement than the other fillers. Both the aspect ratio and particle orien-

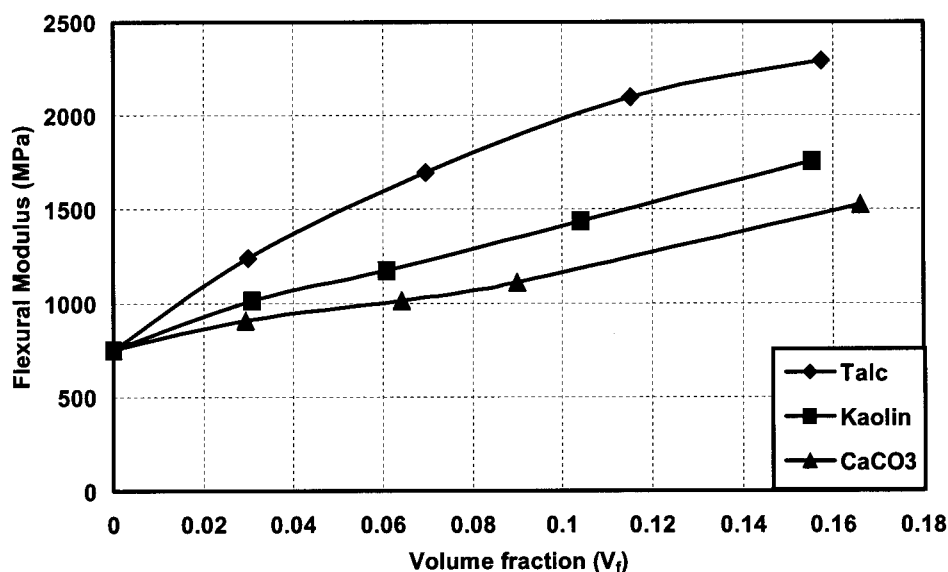


Figure 10 Effect of the filler loading on the flexural modulus of talc-, kaolin-, and CaCO₃-filled PP composites.

tation contribute to the high flexural strength of this particular composite. The orientation of talc particles takes place during melt flow and the application of stress while tests are performed. Kaolin, though having a higher surface area due to its small particle size, tends to agglomerate, and this results in the reduction of surface interactions between the PP matrix and the filler. This explains the reduction in the flexural strength of kaolin-filled PP at higher filler loadings. CaCO₃, however, does not agglomerate as much as kaolin because of its larger particle size. The weak bonding between the CaCO₃ filler and the matrix monotonously reduces the strength of the composite even

at a very low filler loading. Thus, the only true reinforcing filler is talc.

Impact properties

The impressive impact properties of CaCO₃-filled PP have long been established and recognized.² The impact strength has a direct correlation to the adhesion of the filler to the PP matrix. As expected, an increase in the impact properties can be observed with increasing filler loading, as shown in Figure 12, because of the weak adhesion of CaCO₃ to the PP matrix, which has been proved with SEM micrographs (see Fig. 7). The

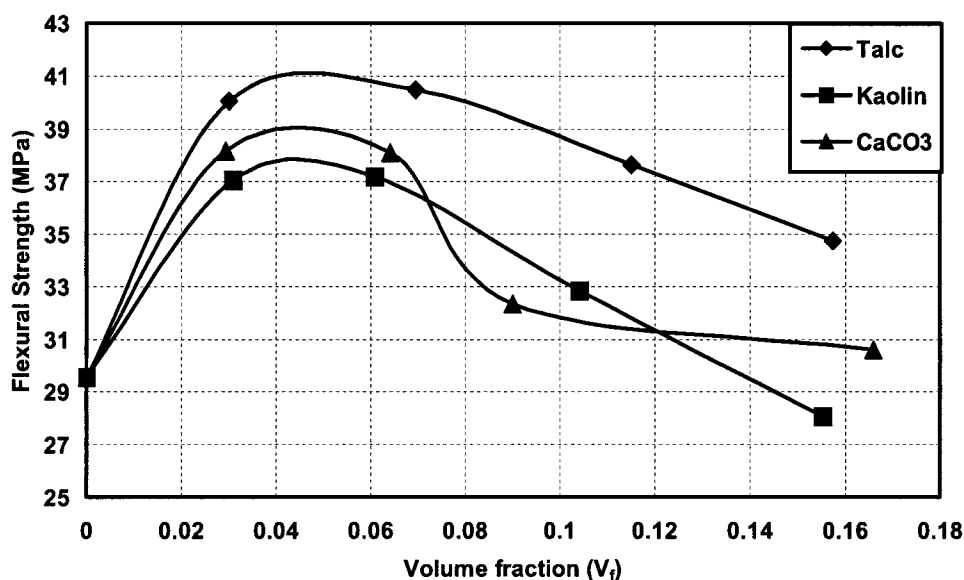


Figure 11 Effect of the filler loading on the flexural strength of talc-, kaolin-, and CaCO₃-filled PP composites.

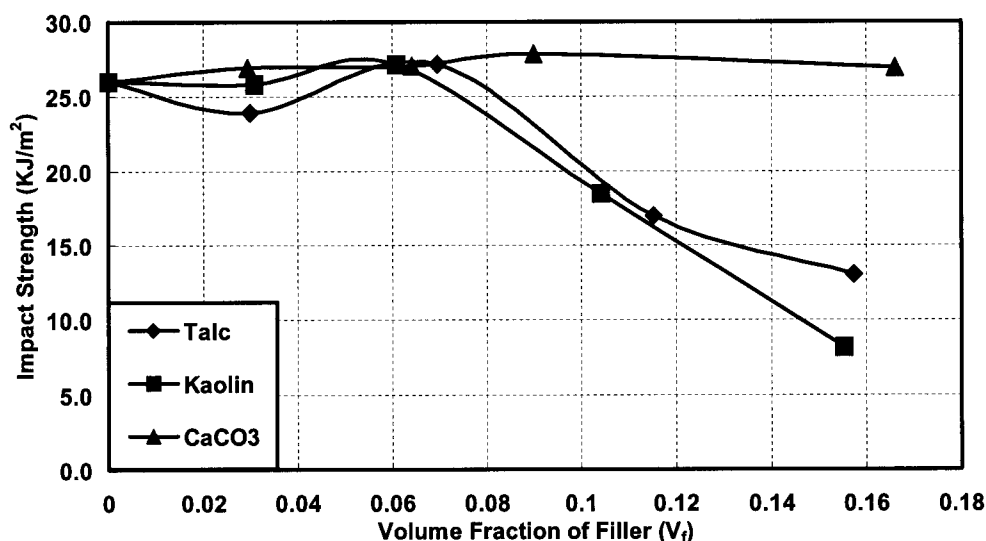


Figure 12 Effect of the filler loading on the Izod impact strength of talc-, CaCO_3 -, and kaolin-filled PP.

toughening effect of CaCO_3 on PP has been studied, and several theories have been used to explain this phenomenon:

1. Wu⁹ developed the critical interparticle distance concept. It predicts that the transition of a composite from a brittle state to a ductile state can occur if the interparticle distance is lower than a certain critical value.
2. Muratoglu et al.²⁵ added that when the interparticle distance is short enough, a preferential orientation of crystal planes of the lowest shear resistance occurs between filler particles. This crystallographic orientation can lower the local plastic resistance, thus allowing more plastic deformation to occur and leading to the higher toughness of the composite.

The toughening effect of talc and kaolin is not pronounced, although an increase in the impact strength at the initial stages of filler loading has been observed for both fillers (see Fig. 12). Impact properties drop drastically at moderate filler loadings ($V_f > 0.06$) for both fillers for several reasons:

1. For talc-filled PP, anisotropic particle orientation throughout the composite also increases the resistance of local plastic deformation of the matrix, thus making the composite more brittle. Although crack-initiation sites or voids might not be abundant—they can hardly be detected from SEM micrographs (see Fig. 6)—crack propagation is very quick because of the lack of the ability of the composite to absorb the impact energy through plastic deformation. Furthermore, the adhesion of the PP matrix to talc is

exceptionally good because of the embedding of the talc filler into the PP matrix. Moreover, neat PP possesses high impact properties. Therefore, at a higher filler loading, the amount of the PP matrix available becomes scarcer, and this leads to a decrease in the toughness and impact resistance of the composite.

2. Kaolin, however, is neither an active nucleating agent nor a good reinforcement for the PP matrix. The initial increase in the impact resistance at lower filler loadings is due to the lack of filler adhesion to the matrix, although there is good dispersion of the filler. However, at higher filler loadings, severe agglomeration of the filler due to its high surface energy creates many crack-initiation and stress-concentration sites, which are very sensitive to impact stresses and cause detrimental effects on the impact properties of the composite.

Quantitative evaluation

A quantitative evaluation was performed through the substitution of the yield and tensile strengths of the composite into eqs. (3) and (4). Subsequently, Figures 13 and 14 were plotted in a linearized form according to eq. (4). Parameter B , characterizing the particle-matrix interaction, was calculated from the slopes of the graphs, and the values were compared and evaluated. It can be observed from both figures that this model is applicable because a good linear correlation can be obtained in most cases. The intersections at the y axis, which are $\ln \sigma_{y0}$ and $\ln \sigma_0$ for Figures 13 and 14, respectively, correspond to the values of the polymer matrix. A small difference exists in the slopes (i.e., $B_{\sigma y}$) in Figure 13, indicating the presence of different inter-

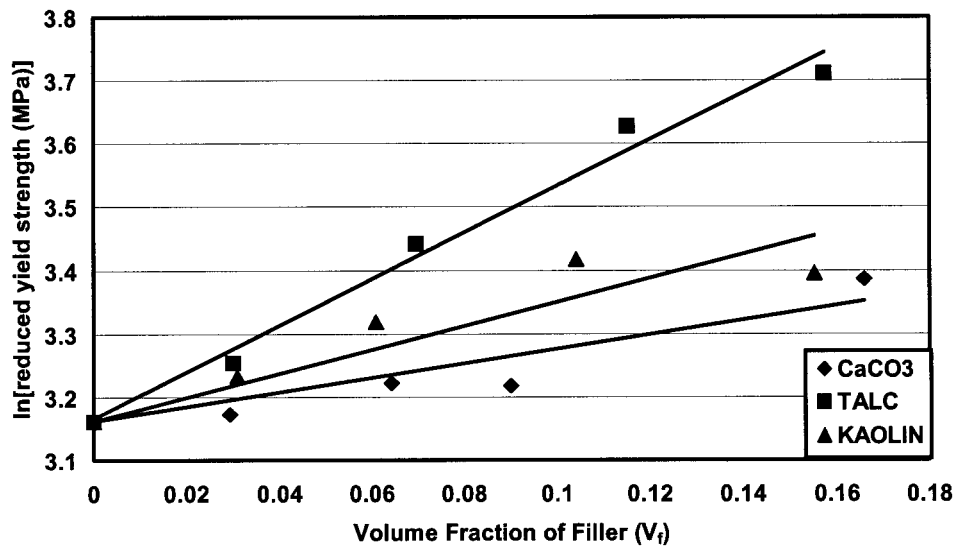


Figure 13 Reduced tensile yield strength of talc-, kaolin-, and CaCO₃-filled PP composites plotted in a linearized form of eq. (4).

actions between different particle fillers and the matrix. The equation used is as follows:

$$\sigma_y = \sigma_{y0} \frac{1 - \phi_f}{1 + 2.5\phi_f} \exp(B_{\sigma y}\phi_f) \quad (3)$$

where σ_y and σ_{y0} are the yield stresses of the composite and the polymer matrix, respectively; ϕ_f is the volume fraction of the filler in the composite; and $B_{\sigma y}$ is the parameter characterizing interaction. The term $(1 - \phi_f)/(1 + 2.5\phi_f)$ takes into consideration the reduction in the effective load-bearing cross-section

area due to the introduction of the filler into the polymer matrix. Because the elongation of the specimens at fracture is always less than 20%, the factors that take into account the changing dimensions of the specimen during the test can be neglected. As a result, the engineering tensile strength (σ) can also be substituted into eq. (3) instead of σ_y for the calculation of B . Thus, eq. (3) can be linearized into

$$\ln \sigma_{y\text{red}} = \ln \left[\sigma_y \frac{1 + 2.5\phi_f}{1 - \phi_f} \right] = \ln \sigma_{y0} + B_{\sigma y}\phi_f \quad (4)$$

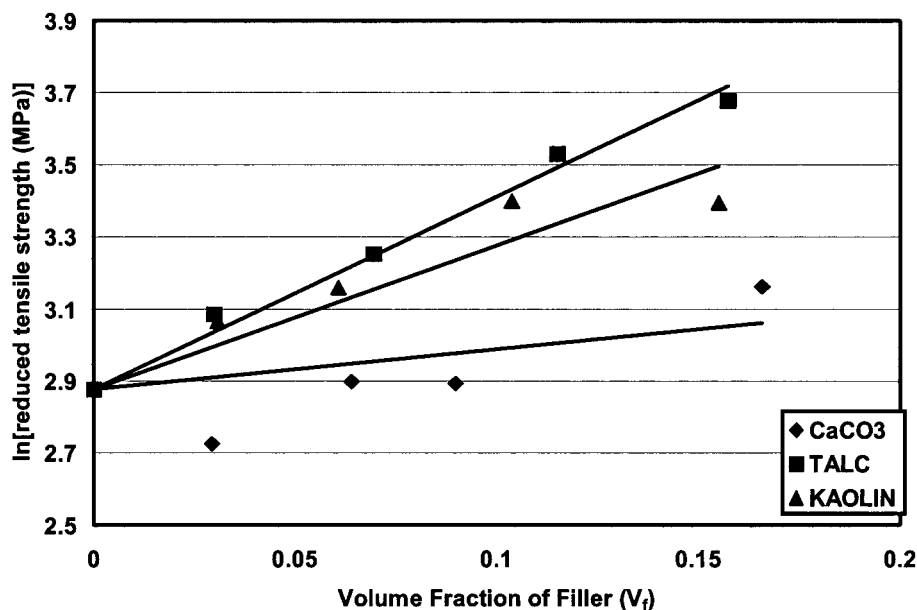


Figure 14 Reduced tensile strength of talc-, kaolin-, and CaCO₃-filled PP composites plotted in a linearized form of eq. (4).

TABLE III
Comparison of the Interaction Parameters of Various
Fillers with the PP Matrix Obtained Through
Measurement of Their Tensile Properties

Filler	Yield strength ($B_{\sigma y}$)	Tensile strength (B_{σ})
Talc	3.68	5.34
Kaolin	1.89	3.99
CaCO ₃	1.44	1.12

Once graphs of $\ln \sigma_{y \text{ red}}$ and $\ln \sigma_{\text{red}}$ versus the composition, ϕ_f , are plotted, the slopes $B_{\sigma y}$ and B_{σ} , respectively, can be obtained. The intersections of the y axis, $\ln \sigma_{y0}$ and $\ln \sigma_0$, give quantitative values characterizing the polymer matrix.

A larger deviation of the slopes (i.e., parameter B_{σ}) can be observed in Figure 14. The calculated B parameters are shown in Table III. Both parameters, $B_{\sigma y}$ and B_{σ} , show that the interaction between talc and PP is the strongest, followed by the interactions of kaolin and CaCO₃ with PP. Therefore, we can also conclude that this quantitative evaluation is consistent with the theories evaluated previously in tensile, flexural, and impact tests and can be used as yet another characterization method for polymer composites.

CONCLUSIONS

Various tests have been performed on talc-, kaolin-, and CaCO₃-filled PP composites to compare their mechanical properties. Generally, talc and kaolin have been proved to be reinforcing fillers for PP on the basis of increases in the tensile and flexural strength with the filler loading. However, talc tends to agglomerate at higher filler loadings, and this causes the strength and toughness of talc-filled PP composite to decrease substantially. Talc is also a strong nucleating agent, thus increasing the crystallinity of the polymer matrix. The increased crystallinity of talc-filled PP composites has also given added strength and stiffness to the composite, which can titrate the effect of the filler agglomeration on the mechanical properties.

Kaolin-filled PP, at high filler loadings, possesses the worst possible distribution, as can be seen in SEM micrographs. Because of severe agglomeration and lack of homogeneity, the strength of kaolin-filled PP composites deteriorates even at moderate filler loadings. The agglomeration of kaolin is due to the small particle size, high filler surface energy, and a tendency of the filler to absorb moisture during processing. The impact property of kaolin-filled PP is also among the

lowest because of stress-concentration points created by large filler agglomerates.

CaCO₃-filled PP composites, however, possess very high impact strength. SEM micrographs clearly show that CaCO₃ fillers are poorly bonded to the matrix; this allows the formation of microscopic cavities, which lead to local microplastic deformation and an increase in the overall toughness of the composite. However, the increase in the impact toughness of PP-CaCO₃ composites comes at the expense of the tensile and flexural strength.

A quantitative evaluation with an empirical formula has provided an indication of the interactions between the fillers and the PP matrix. The results suggest that the filler-matrix interactions are strongest for talc-filled PP, followed by those for kaolin-filled PP composites and CaCO₃-filled PP composites.

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