

Effects of Filler Treatments on the Mechanical, Flow, Thermal, and Morphological Properties of Talc and Calcium Carbonate Filled Polypropylene Hybrid Composites

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ABSTRACT: Commercially available neoalkoxy titanate (Lica 12) and organosilane (3-aminopropyltriethoxysilane) coupling agents were used to treat talc and calcium carbonate (CaCO_3) to compare their effects with those of untreated fillers upon their incorporation into polypropylene (PP). Commercial stearic acid treated CaCO_3 was also used to widen the scope of the study. Single-filler PP composites (containing either talc or CaCO_3) and hybrid-filler composites (containing a mixture of talc and CaCO_3) were compounded on a twin-screw extruder and subsequently injection-molded into dumbbells. The silane and titanate treatments dramatically increased the elongation at break for both the single-filler and hybrid-filler composites, whereas stearic acid did not. There was also a moderate improvement in the impact strength of the composites, particularly

those treated with Lica 12. The hybrid composites, through the synergistic coalescence of positive characteristics from talc and CaCO_3 , had exceptionally good impact properties, more so with the aid of the coupling agents. For example, the impact strength value of a Lica 12 treated hybrid composite was the greatest for all the composites studied, overshadowing the superiority of the CaCO_3 -filled PP composites, which predominantly had the highest impact properties. Further investigations of the thermal and morphological properties were also conducted to facilitate the determination of the coupling mechanisms and their interesting effects on the hybrid composites. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 413–426, 2005

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

INTRODUCTION

Polypropylene (PP) filled with particulate fillers has been widely studied, the amount of PP research is still increasing. The versatility of PP and its good processability characteristics have also made it favorable for research and development.

The incorporation of fillers such as calcium carbonate (CaCO_3) and talc in thermoplastics is a common practice in the plastics industry to reduce the production costs of molded products. Fillers are also used to improve the working properties of thermoplastics, such as strength, rigidity, durability, and hardness.¹ Considerable experimental data can also be found in recent studies dealing with the mechanical properties of PP filled with CaCO_3 ,^{2–4} talc,^{5–7} rice husk ash,⁸ and organic fibers.^{9,10}

Particulate-filled polymers must be continuously upgraded to meet the specific requirements of various new applications. One of the possible ways of doing this is the modification of the filler surface to alter the filler–matrix interfacial interaction.⁴ Although the particle size can be changed to modify the interaction, the range is still narrow. Thus, the incorporation of coupling agents onto the filler surface is an obvious way of modifying interactions by a change in the size of the interface or an alteration in the strength of the interaction. Silane and titanate types of coupling agents have been gaining importance in recent time, and many claims and counterclaims have been made about its efficacy. Sharma et al.¹¹ in their article on the effect of a titanate coupling agent on the performance of CaCO_3 -filled PP showed that upon the treatment of the filler with an isopropoxy triisostearoyl titanate coupling agent, a 20% improvement in the impact strength was recorded, whereas the elongation at break of the composite was slightly less than that of virgin PP. They also claimed that this increase in the impact strength was not as evident as reported by Han et al.,¹² who also worked on PP/ CaCO_3 systems previously, even though the fillers were also treated with titanate coupling agents. The elongation at break, as

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TABLE I
List of Coupling Agents and the Amounts Applied for the Surface Treatment

Compound	Formula	Producer	Amount applied (wt %)
3-aminopropyltriethoxy silane	$\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—Si(—O—CH}_2\text{—CH}_3)_3$	Dow Corning	0.4–1.0
Lica 12	$\begin{array}{c} \text{CH}_2\text{—CH—CH}_2\text{O—C—H}_2 \\ \\ \text{CH}_3\text{—CH}_2\text{—C—CH}_2\text{—O—Ti—[O—P(=O)(OCH}_2\text{H}_{17})_2]_3 \\ \\ \text{CH}_2\text{=CH—CH}_2\text{O—CH}_2 \end{array}$	Kenrich	0.5

reported by Han et al., approached that of unfilled PP homopolymer. Demjen,¹³ on the other hand, concentrated on the treatment of CaCO_3 with as many as eight types of silane coupling agents to determine their effect on PP/ CaCO_3 composites. The incorporation of amino-functional silane coupling agents resulted in the reactive coupling of PP and CaCO_3 , both being inactive components; this led to increased strength and decreased deformability. Stearic acid was also used as a surfactant to enhance the filler dispersion of CaCO_3 in PP. However, several workers^{4,14} have branded stearic acid as nonreactive because of its inability to provide effective coupling between the filler and matrix.

Silane and titanate coupling agents have also been used by some workers to treat talc, which is one of the most widely used fillers of PP.¹⁴ Ai Wah et al.¹⁵ reported improved melt flow and filler particle dispersion with the treatment of PP pellets with a commercially available neoalkoxy titanate coupling agent [neopentyl(diallyl)oxy tri(dioctyl)phosphato titanate (Lica 12)]. The chain scission of PP molecules and the plasticizing and lubricating effects of the coupling agent were cited as the main causes of the decrease in the melt viscosity. The tensile and flexural properties of the composites were also reported to decrease, whereas the impact and elongation properties improved, in comparison with those of virgin PP with the incorporation of the coupling agent.

The goal of this article is to report the effects of silane and titanate coupling agents as well as stearic acid on the mechanical, thermal, and morphological properties of talc- and CaCO_3 -filled PP hybrid composites. Previously, various workers have only targeted the effects of filler treatments on a single-filler PP composite. Here, the extent of filler–matrix interactions and filler–filler interactions between two different fillers incorporated into a single matrix, before and after a surface treatment of the fillers, is discussed. The total filler content for all the composites featured in this article was kept constant at 30 wt % because the composites containing 30 wt % talc exhibited the highest tensile strength in previous examinations by Leong

et al.¹⁶ Therefore, the single-filler PP composites consisted of either PP/talc (70/30 w/w) or PP/ CaCO_3 (70/30 w/w), whereas the hybrid composites consisted of PP/talc/ CaCO_3 (70/15/15 w/w/w). The properties of virgin PP as a control specimen were taken from previous works by Leong et al.¹⁷

EXPERIMENTAL

Materials

The PP copolymer (Pro-Fax SM240, Titan PP Polymers, Sdn. Bhd., Johor, Malaysia) had a melt index of 25 g/10 min. The talc filler (Chung Chemicals, Sdn. Bhd., Kuala Lumpur, Malaysia) had an average particle diameter of 6.3 μm and a specific surface area of 1.50 m^2/g , whereas the CaCO_3 fillers (untreated Omyacarb 3-SA and stearic acid treated Omyacarb 3-TSA, Malaysian Calcium Corp., Sdn. Bhd., Selangor, Malaysia) had an average particle diameter of 3.3 μm and a specific surface area of 3.57 m^2/g . The silane coupling agent was 3-aminopropyltriethoxysilane (Z-6011) from Dow Corning (Midland, Michigan). The chemical compositions of the silane compounds are given in Table I. Lica 12, supplied by Kenrich Petrochemicals, Inc. (Bayonne, NJ), was also used as a coupling agent in this compounding. The chemical composition of Lica 12 can also be found in Table I. Other additives, including an antioxidant (Irganox 1010, Ciba, Basel, Switzerland) and an ultraviolet stabilizer (Tinuvin 770 DF, Ciba, Basel, Switzerland), were used to counter the effects of oxidation and ultraviolet degradation on the PP matrix during processing and storage.

Filler treatment

The required amount of silane was calculated as follows:

$$\text{Amount of silane (g)} = \frac{[\text{Amount of filler (g)} \times \text{Surface area of filler (m}^2/\text{g)}]}{\text{Minimum coating area of silane coupling agent (ws)}} \quad (1)$$

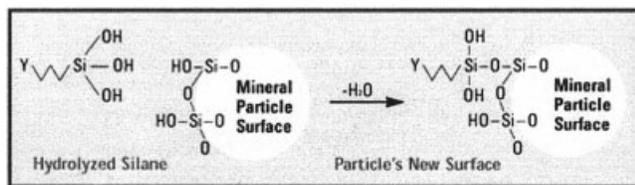


Figure 1 Schematic of the condensation of silanol (hydrolyzed silane) with reactive groups on the filler surface.

The minimum coating area of the type of silane used was 353 μm^2 . The surface treatment was performed by deposition from an aqueous alcohol solution. For complete surface wetting, the following amounts were required per kilogram of talc: 4.2 g of silane diluted in 205.8 g of an ethanol solution (95% ethanol/5% water solution adjusted to pH 4.5–5.5 with acetic acid) to yield a 2% final concentration. The treatment requirements per kilogram of CaCO_3 were as follows: 10 g of silane diluted in 490 g of ethanol. The 2% silane/ethanol solution was left for 5 min to prehydrolyze the silane to activate the silane group. Once it was activated (hydrolyzed), the resultant silanol groups condensed with other silanols or with reactive groups on the surface of the filler, as shown in Figure 1. The ability of a silane to bond to a surface is generally determined by the concentration of such sites on the surface of the filler. After the treatment, the fillers were then dried in an oven at 110°C for 24 h. The dried fillers were rinsed again with ethanol to drive away any residual silane before the fillers were dried again at the same temperature and for the same period.

Unlike silanes, the amount of Lica 12 to be incorporated did not depend on the surface area of the fillers. According to the reference manual supplied with Lica 12,¹⁸ the recommended dosage of Lica 12 is either 0.5 wt % of the total filler or 0.2 wt % of the resin, whichever provides the greater absolute amount of titanate. Because all the composites in this study were filled with 30% filler, the incorporation of 0.4 wt % titanate was chosen for both talc and CaCO_3 . Toluene was

TABLE II
Compositions of Compounded Formulations Containing Untreated Fillers

Formulation	PP (wt %)	Untreated talc (wt %)	Untreated CaCO_3 (wt %)
PP	100	—	—
UCC30	70	—	30
T30	70	30	—
T15:UCC15	70	15	15

used as a solvent to reduce the viscosity of the titanate. The ratio of the solvent to toluene was fixed at 3:1. The solvent was added into a vessel, and the titanate was blended mechanically into the solvent for approximately 30 min. The filler was then added to the vessel, and the slurry was mixed until a good dispersion was achieved. The slurry was then poured into a tray and dried in an oven at 80°C for 5 h. The fillers were washed again with toluene to drive off excess titanate and dried again for the same period of time at the same temperature.

Sample preparation

Compounding was carried out with a twin-screw extruder (Rheomex CTW 100, Haake, Karlsruhe, Germany). The barrel temperatures of the four zones were 160, 170, 180, and 190°C from the feeding to die zones. The compounds were blended at a screw speed of 25 rpm. The extrudates were cooled in a water bath, pulled, and pelletized. The test specimens were injection-molded into a tensile mold with a Niigata AN 50 50-ton injection-molding machine (Niigata, Japan). The injection-molding temperature ranged from 190 to 230°C, whereas the back-pressure was 0.4 MPa. Tables II and III list the compounded formulations containing untreated and treated fillers, respectively.

Mechanical testing

The tensile and flexural properties were measured with an Instron 5582 100 kN electromechanical tensile

TABLE III
Compositions of Compounded Formulations Containing Treated Fillers

Formulation	PP (wt %)	Untreated talc (wt %)	Silane-treated talc (wt %)	Lica 12 treated talc (wt %)	Stearic acid treated CaCO_3 (wt %)	Silane-treated CaCO_3 (wt %)	Lica 12 treated CaCO_3 (wt %)
TCC 30	70	—	—	—	30	—	—
STUCC 30	70	—	—	—	—	30	—
LTUCC 30	70	—	—	—	—	—	30
STTALC 30	70	—	30	—	—	—	—
LTTALC 30	70	—	—	30	—	—	—
T15 : TCC15	70	15	—	—	15	—	—
T15 : STUCC15	70	—	15	—	—	15	—
T15 : LTUCC15	70	—	—	15	—	—	15

testing machine (Instron, Canton, MA) with a series IX control system in agreement with ASTM D 638 and ASTM D 790-86 with type 1 test specimen dimensions. For the tensile tests, a crosshead speed of 5 mm/min was used, and an average value of at least five specimens was taken for each sample. For the 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 (Ray-Ran, Warwickshire, UK) at an impact energy of 7.5 kJ according to ASTM D 256-88. The hammer velocity was set at 2.88 m/s, whereas the weight of the hammer was 1.811 kg.

Mode of failure

The mode of fracture was studied through an analysis of the fracture surfaces of the tensile samples. This was carried out with a Leica Cambridge S-360 scanning electron microscopy (SEM) machine (Leica Cambridge, Cambridge, UK). 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 (ρ) determination

ρ of the test specimens was determined according to the ASTM D 792 water displacement method (method A) as follows:

$$\rho = [W_1 / (W_1 - W_2)] \rho_w \quad (2)$$

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

Thermal analysis process

The crystallization behavior and melting characteristics of the composites were studied with differential scanning calorimetry (DSC) with a PerkinElmer DSC-6 (PerkinElmer, Boston, MA) 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 thermal history, the nonisothermal crystallization process was recorded from 220 to 50°C, and a standard status of crystallization was created.

Chemical structural analysis with fourier transform infrared (FTIR) spectroscopy

FTIR analyses were performed for treated fillers to determine the chemical structures before and after the filler treatments. About 5 mg of the fillers was mixed

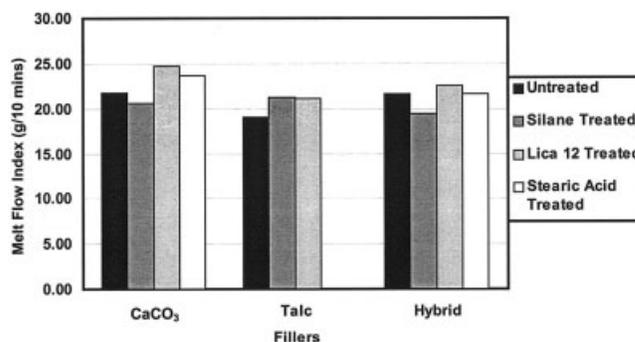


Figure 2 MFIs of composites with treated and untreated fillers.

with about 95 mg of potassium bromide (KBr) before they were compacted into thin pellets with a hydraulic press with 8 tons of force and maintained there for about 3 min. The pellets were then inserted into a Nicolet Avatar 360 FTIR spectrophotometer (Nicolet Avatar, Karlsruhe, Germany) and scanned with Omnic software.

Melt-flow index (MFI)

The processability 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 for the measurements.

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:

$$W_f = \frac{\rho_f}{\rho_c} V_f \quad (3)$$

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

RESULTS AND DISCUSSION

MFI

The effect of the silane and titanate coupling agents on the melt-flow behavior is shown in Figure 2. The MFIs for the PP composites filled with Lica 12 and stearic acid treated fillers increased slightly over those of the

untreated fillers. This trend agreed with the work of Ai Wah et al.,¹⁵ who reported an increase in MFI with the incorporation of Lica 12 into talc-filled PP. This increase in the melt flow was due to molecular chain scission or a change in the molecular weight distribution, or there might have been a lubricating or plasticizing effect induced by the coupling agent. This lubricating effect of the coupling agent was also found to be true by others.^{12,18} Han et al.¹² found that the reduction in the melt viscosity with the presence of a coupling agent might result from the surface modification of the filler particles. In other words, the coupling agent might have acted as a surface modifier, so that, under shear stress, there could be far less frictional resistance to flow with the treated filler particles than would have been possible with the untreated filler particles. This, however, implies that there is no true coupling (in the chemical sense) between the coupling agent and the polymer matrix. There is also a possibility that the coupling agent might have diffused into the polymer matrix, thus acting as an internal plasticizer, and this would have increased the melt flow of the polymer phase. Moreover, the titanate increased the MFI of CaCO₃-filled PP to a level very similar to that of virgin PP (25 g/10 min). Han et al.¹² reported a similar trend. This seems to indicate that the coupling agent Lica 12 effected some changes in the structural arrangement between the polymer matrix and the CaCO₃ particles.

The effect of the silane coupling agent on the melt flow of PP composites is also shown in Figure 2. The treatment of the fillers with silane reduced the overall MFIs of all the composites, except for talc-filled PP. These results indicated that the effect of the silane coupling agents on the melt flow of the filled systems depended on the polymer/filler combination employed. Different fillers might have different surface interactions with the coupling agent, and so the effect of the silane treatment on the filler-matrix and filler-filler interactions could also differ according to the types of fillers used, especially when hybrid fillers were used. Therefore, the reduction in MFI for CaCO₃-filled PP could be attributed to the coupling effect between the filler and matrix, which hindered polymer melt flow. Stearic acid, on the other hand, has been proven to enhance the particle dispersion of CaCO₃.¹⁴ Because the reduction in agglomerated particles reduces hindrance to polymer melt flow, an enhancement of the MFI can be expected. Therefore, with the correct combinations of polymers, fillers, and filler treatments, it is possible to change the melt-flow properties of filled polymeric systems.

Thermal analysis

DSC thermograms were recorded during the melting process for all composites containing treated and un-

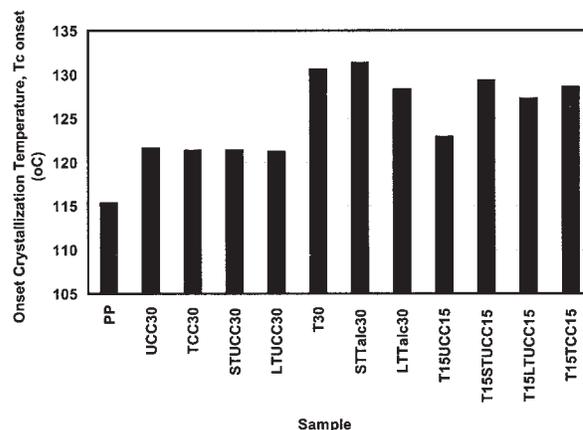


Figure 3 $T_{c \text{ onset}}$ for various formulations.

treated fillers to determine the effect of the surface treatment on the crystallization behavior of the polymer matrix. Premphet and Horanont¹⁹ also used DSC to investigate the effect of stearic acid coatings on the crystallization properties of CaCO₃-filled PP/ethylene-octane copolymer blends.

Figure 3 shows the onset crystallization temperatures ($T_{c \text{ onset}}$'s) obtained from DSC thermograms of various PP composites filled with single and hybrid fillers, with or without filler surface treatments. The incorporation of CaCO₃ treated with stearic acid and both titanate and silane coupling agents into PP did not render any significant improvement in the crystallization kinetics over those of its untreated counterpart. However, all CaCO₃ fillers, whether they were treated or untreated, had some level of nucleating effect on PP according to the higher onset temperatures recorded for all CaCO₃-filled PP composites in comparison with that of neat PP. The $T_{c \text{ onset}}$ values were proportional to the amount of the crystalline phase.¹⁴ Nucleation increased the number of crystalline units, such as spherulites and lamellae, in the material, and this resulted in a reduction of their size. Thus, the size of the crystalline units could also be measured indirectly through the studies of $T_{c \text{ onset}}$.

The talc-filled PP composites had an even higher $T_{c \text{ onset}}$ than neat PP, and this suggested that the nucleating effect of talc was much stronger than that of CaCO₃. Pukanszky¹⁴ found similar trends and claimed that the nucleation effect of CaCO₃ was lacking in comparison with that of talc. These results also showed that the crystallinity and crystalline units of PP changed considerably upon the incorporation of talc. These changes in the crystalline structure could possibly affect the properties of the composites, although other factors such as particle orientation could also play important roles.²⁰ Unlike CaCO₃, the treatments of talc particles showed some effects on $T_{c \text{ onset}}$ of PP. The Lica 12 treatment of talc slightly reduced the crystallization kinetics of PP. A slight increase in

$T_{c \text{ onset}}$ of STTalc30 was also detected. However, because the increase and decrease in $T_{c \text{ onset}}$ for both samples were less than 3°C, the overall effect of the Lica 12 and silane treatments on the crystallinity of PP was not significant.

The treatments, on the other hand, were very effective in inducing better crystallization kinetics when they were used for hybrid composites. All filler treatments increased $T_{c \text{ onset}}$ of hybrid composites. Alonso et al.²¹ showed some evidence in their work that the orientation of talc particles was higher when the filler was treated with organosilanes. Monte¹⁸ reported that a titanate coupling agent reacted with hydroxyl groups present at the filler surface to form a monomolecular layer that increased the compatibility between the filler and matrix. Water of hydration could be present at the surfaces of inorganic fillers, giving the fillers a high tendency to agglomerate. The agglomeration of particles could cause air pockets to be trapped between the particles. The treatment of a titanate coupling agent was reported to eliminate the water of hydration by replacing it with organofunctional titanate, causing the surface of the filler to be more compatible with the polymer matrix. Because of enhanced filler–matrix compatibility, the polymer matrix thereby displaced the trapped air pockets, and this resulted in deagglomeration of the particles, thus improving filler dispersion. Filler orientation and dispersion could affect the rearrangement and growth of crystalline units, and good dispersion and improved particle orientation reduced the hindrance of the particles and allowed better spherulite growth and rearrangement. Thus, it is believed that a better filler dispersion of the hybrid fillers was obtained with filler treatment, and as a result, the crystallization activity of hybrid composites increased with the treated fillers. Because the overall crystallization temperatures of talc-filled PP were the highest of the samples, we deduced that talc possessed a stronger nucleating ability than CaCO_3 , as proven earlier by several workers.^{14,16,21} As for the hybrid-filler composites, the lower overall $T_{c \text{ onset}}$ values, in comparison with those of talc-filled PP composites, were due to the lower talc content in the hybrid composites.

Chemical structural analysis with FTIR spectroscopy

The 4000–500 cm^{-1} wave-number ranges of the difference spectra of talc and CaCO_3 fillers treated with different coupling agents are presented in Figures 4 and 5, respectively.

The appearance of the SiO group ($\sim 1300 \text{ cm}^{-1}$) could be used to confirm the presence of the silane coupling agent. Figure 4 shows that the treatment of silane on talc could be detected, and this suggested that the condensation of silane on the surface of the

filler took place during the drying process. Apart from the SiO group, the bands at 1376–1652 cm^{-1} showed the presence of Si–N, $\text{NH}(\text{C}_2\text{H}_5)\text{—OCH}_3$, and $\text{CH}_3\text{—NH—COCH}_3$,²² all of which were characteristic groups of the amino silane used during hydrolysis in ethanol. The Lica 12 treatment, on the other hand, affected the spectrum of talc at approximately 2200–2500 cm^{-1} , signifying the presence of phosphate groups.

In Figure 5, the broad carbonate band (at ca. 1500 cm^{-1}) shows that a small part of CaCO_3 survived the hydrolysis. The condensation of the silane coupling agent should be visible at 1000–1300 cm^{-1} . Although there are a few peaks in the 1000–1200- cm^{-1} range, the broad band of the carbonate seems to have masked some of the bands of the silane, especially the SiO group ($\sim 1300 \text{ cm}^{-1}$), rendering it indistinguishable from the spectrum of the untreated fillers. The drying treatment of the silane coupling agent on the filler surface, which could result in the evaporation of a fairly large amount of the agent, as proven by Nakatsuka et al.,²³ could contribute to the weak peak of the silanes. The stearic acid treatment also altered the CaCO_3 spectrum in the 2800–3000- cm^{-1} region. More phosphate groups could be seen in the Lica 12 treated CaCO_3 , with the presence of peaks at 2874 and 2983 cm^{-1} .

Effect of the surface treatment on the mechanical properties of CaCO_3 and talc PP

The effect of the surface treatment on the tensile modulus of the PP composites can be seen in Figure 6. Stearic acid, titanate, and silane treatments did not have a significant influence on the moduli of the composites. Young's modulus was measured during the process of elastic deformation in the composites; the movement at the filler–matrix interfaces was very limited. In the polymer filled with rigid particles, the polymer itself solely contributed to the elasticity of the composite. Therefore, the modulus could not be used to characterize the strength of the filler–matrix interactions, and so the value of the modulus should not have been affected even if strong filler–matrix interactions existed because of filler surface modification.¹⁴

The effects of filler surface modification on the tensile strength of the composites are depicted in Figure 7. Generally, almost all the composites with surface-treated fillers studied here experienced a slight decrease in the tensile strength in comparison with the composites with untreated fillers. The stearic acid treatment was mainly to improve the overall dispersion of the CaCO_3 fillers in the polymer matrix, and it did not act as a coupling agent, as proven previously.^{13,15,17} An improvement in the dispersion by stearic acid was reported to be due to its ability to reduce the filler–filler interaction. Initially, it was

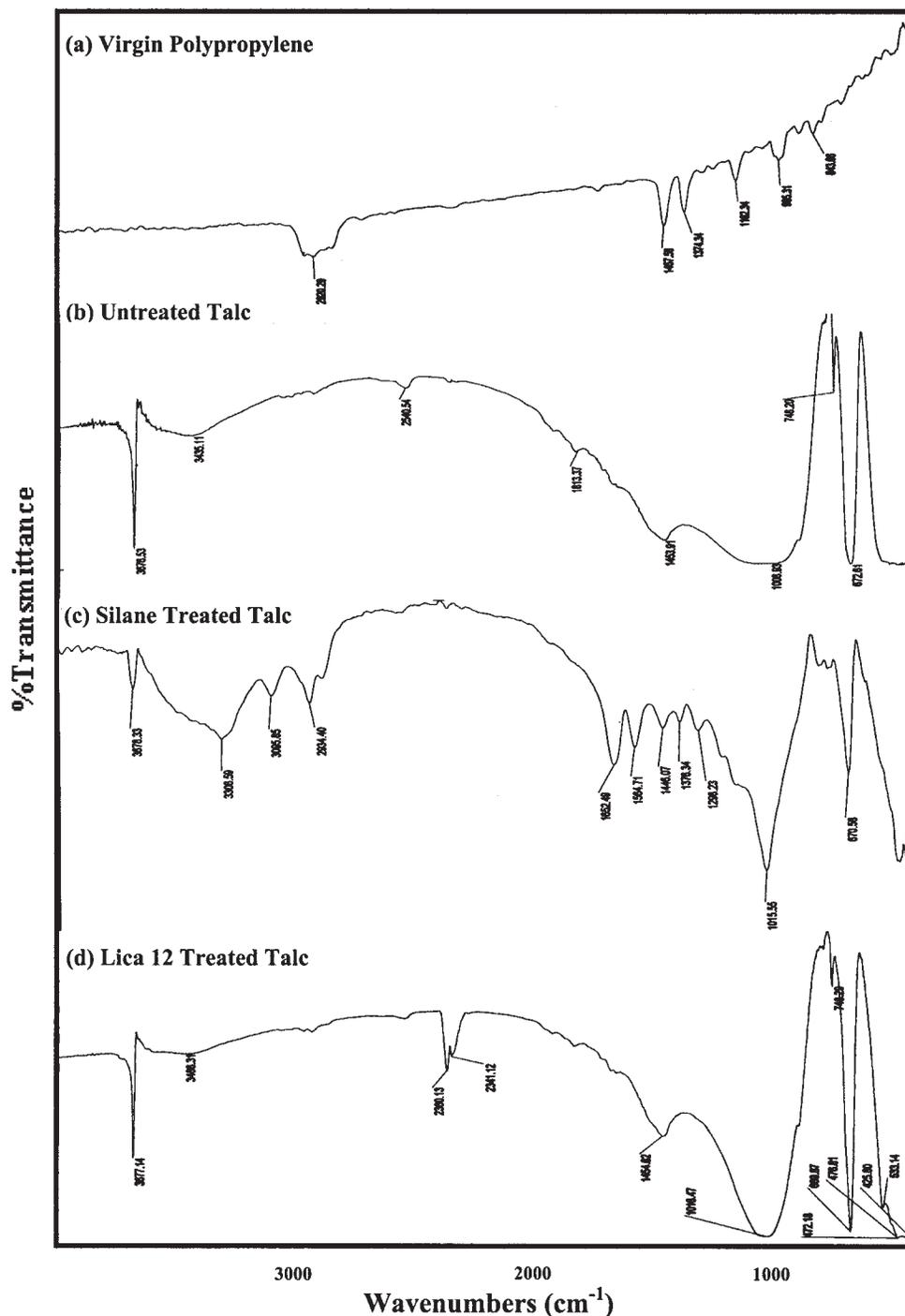


Figure 4 FTIR difference spectra of virgin PP and talc fillers treated with silane and Lica 12 coupling agents.

thought that an improved filler dispersion could enhance the strength and toughness of a composite because both properties are very susceptible to filler particle agglomeration. However, closer examinations by Pukanszky¹⁴ and Demjen¹³ revealed that stearic acid also indirectly reduces the filler–matrix interaction, and so stearic acid has been branded as a non-reactive surfactant. Therefore, the tensile strength in the composites with stearic acid treated fillers could re-

main the same or experience a reduction, in comparison with that of the composites with untreated fillers. Furthermore, the composites with stearic acid treated fillers also experienced a severe decline in the deformability in comparison with untreated composites, as shown in Figure 8. Thus, it is believed that the stearic acid treatment did contribute to some embrittlement of the polymer matrix, especially at the filler–matrix interfaces.

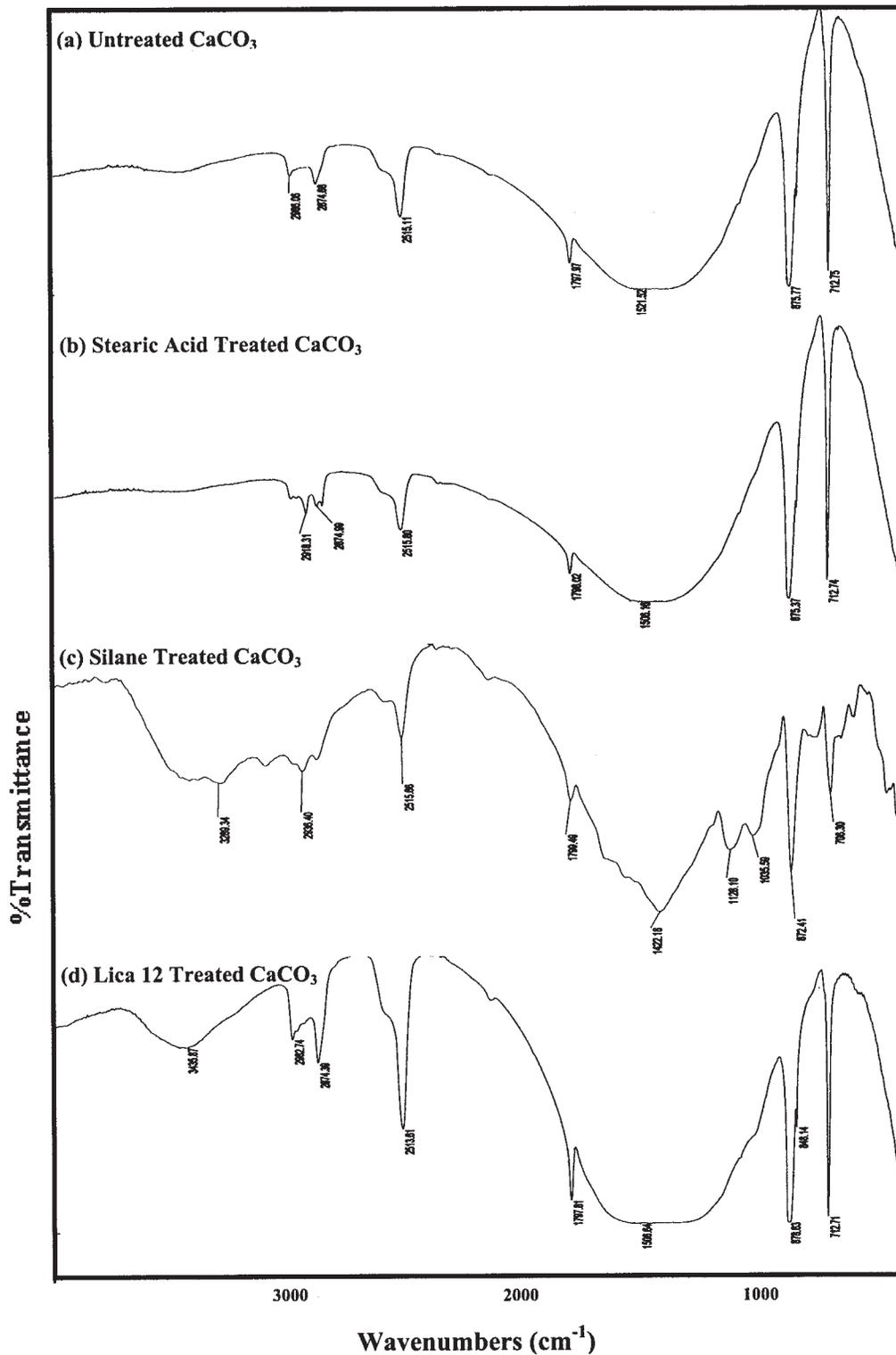


Figure 5 FTIR difference spectra of CaCO_3 fillers treated with silane and Lica 12 coupling agents.

The reduction of the strength of the composites filled with Lica 12 treated fillers, which agreed with the results obtained by Ai Wah et al.,¹⁵ was due to the role of the titanate coupling agent in acting as a plasticizer in the filled system.^{12,18} The chain scission of

the polymers upon the Lica 12 treatment could also have contributed to the decline in the strength of the composites. However, the elongation at break of the titanate-treated filled PP composites improved drastically over that of the untreated filled PP, and this

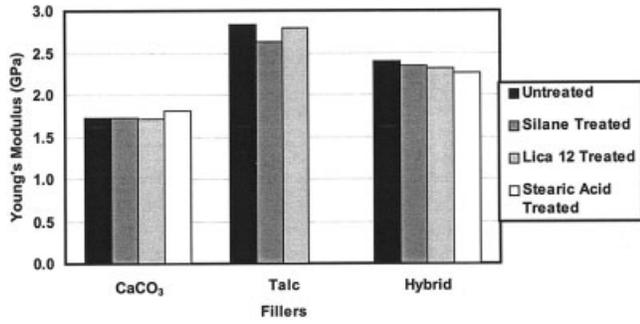


Figure 6 Young's modulus for single-filler and hybrid composites with and without the filler surface treatment.

could be attributed to the plasticizing effect of the titanate treatment.

For composites filled with silane-treated fillers, the decrease in the tensile strength contradicted past reports,^{4,12,14} in which workers reported positive coupling effects of the silane on both PP and the fillers. The silane treatment in this study seemed to have the same effect as the titanate treatment; it reduced the strength and increased the deformability of the composites. This contradiction is still unclear; perhaps it is worth mentioning that the recommended dosage of the silane might not be correct for an effective treatment of the fillers to obtain adequate coupling ability. Underdosage of the silane could lead to inhomogeneity and inadequate coupling between the fillers and matrix, whereas overdosage could cause severe particle agglomeration.²⁴ Therefore, a correct dosage of a coupling agent is vital for the optimum advantages to be gained. The elongation at break for these composites also increased tremendously for all silane-treated composites, for single-filler and hybrid-filler composites, as shown in Figure 8. This drastic improvement in deformability further suggests that the coupling between the filler and matrix was not strong enough because the fillers failed to hinder plastic deformation of the polymer matrix.

Unlike the tensile modulus, the flexural modulus of the composites was much more affected by the filler

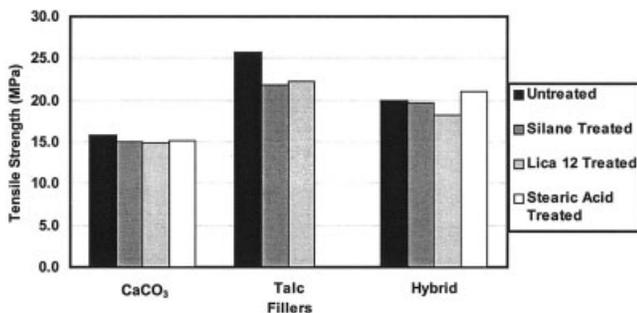


Figure 7 Tensile strength for single-filler and hybrid composites with and without the filler surface treatment.

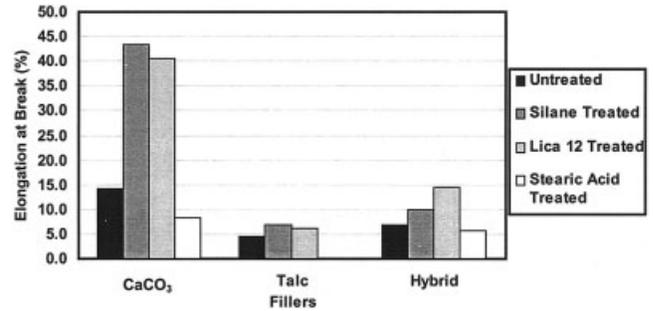


Figure 8 Elongation at break for single-filler and hybrid composites with and without the filler surface treatment.

treatments. Most of the formulations with treated fillers experienced retained, if not increased, flexural modulus, as shown in Figure 9. Flexural tests were more sensitive to the surface skin of the injection-molded samples, which were richer in polymer content as a result of being molded against a surface. Restrictions imposed by the mold walls rendered excess polymer to the surface of the samples.²⁵ Therefore, the increase in the flexural modulus for the formulations with treated fillers could be solely attributed to the higher crystallinity of the polymer, as proven earlier with thermal analysis. There were also some positive changes in the flexural strength of the PP composites because of the filler treatment, as shown in Figure 10. The most obvious increase in the flexural strength was found for the treated hybrid composites; with the filler treatment, the flexural strength approached that of the talc-filled PP composites. This increase in the strength with the hybrid composites far exceeded the theoretical value that could be calculated by the rule of mixtures. The most likely reasons behind the strength increase of the treated hybrid composites were the sensitivity of the flexural tests for detecting the increased crystallinity of the polymer and the improved orientation of the treated fillers, which could impart more resistance on bending.

As the ductility of the composites increased, we expected the toughness of the composites to also in-

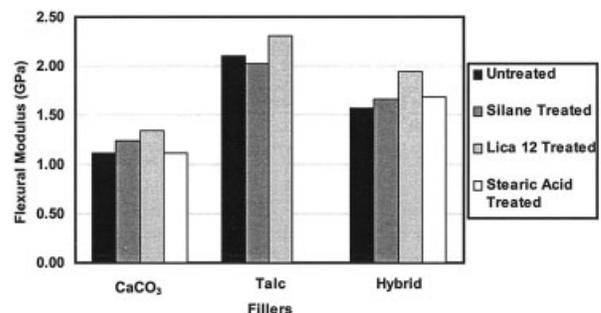


Figure 9 Flexural modulus for single-filler and hybrid composites with and without the filler surface treatment.

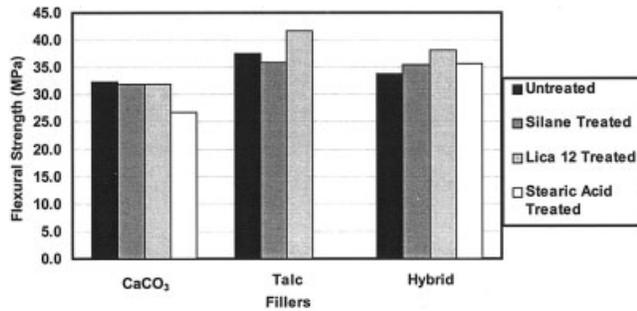


Figure 10 Flexural strength for single-filler and hybrid composites with and without the filler surface treatment.

crease, as reported in the literature;^{4,13,21} hence, a high impact strength was expected for the composites. Therefore, it was only logical that the increase in the elongation at break for the silane- and titanate-treated composites should be accompanied by an increase in the impact strength as well. There was indeed an apparent increase in the impact strengths of LT-TALC30 and T15LTUCC30, both being titanate-treated, whereas STTALC30, T15STUCC15, and T15TCC15 only showed a marginal increase, as shown in Figure 11. The hybrid composites experienced a moderate but commendable improvement in the impact strength with the incorporation of treated fillers. This was particularly true for titanate-treated T15LTUCC15; the impact strength recorded for this formulation exceeded the values recorded for untreated and even treated CaCO₃-filled PP composites. Previous studies¹⁶ have shown that CaCO₃ should be a better filler for imparting impact strength than talc or hybrid fillers. The better impact properties of the titanate-treated talc-filled PP and titanate-treated hybrid-filler composites could be attributed to the improved dispersion and orientation of the filler particles and the plasticizing effect of the titanate coupling agent.^{14,15,18} Better filler dispersion reduced stress concentration sites, which were very sensitive to impact stresses, whereas the plasticizing effect operated in conjunction with interfacial adhesion between the

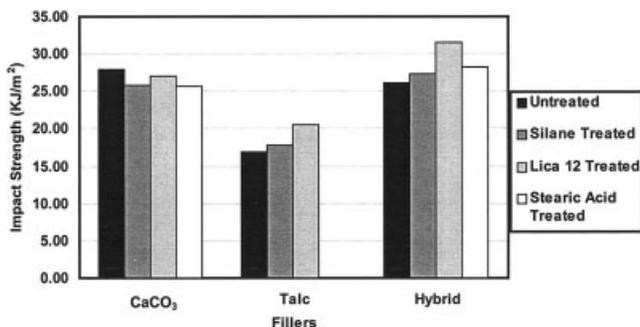


Figure 11 Impact strength for single-filler and hybrid composites with and without the filler surface treatment.

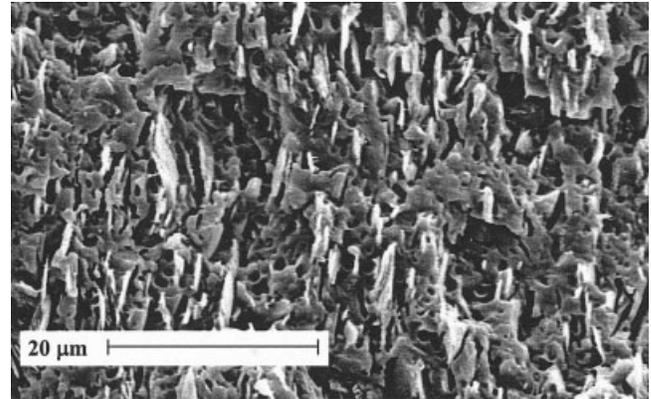


Figure 12 SEM micrograph of a T30 untreated single-filler composite fracture surface.

filler and matrix to yield an increase in the toughness of the composites. STUCC30 and LTUCC30, however, did not record a significant increase in the impact strength, although the elongation at break for these samples showed considerable improvement. Perhaps the titanate coupling agent was needed only to improve the dispersion of the CaCO₃ particles and did not participate in the toughening process of the CaCO₃-filled PP composites. The optimum dosage of the silane coupling agent was not determined beforehand, and this might have led to severe aggregation of the fillers,²⁴ which was detrimental to the impact strength.

Morphology

SEM micrographs of the tensile fractured surfaces of PP composites filled with untreated and treated fillers are shown in Figures 12–19. An examination of the micrographs for PP filled with untreated talc and CaCO₃ (Figs. 12 and 13, respectively) reveals very different fracture surface morphologies. A preferred

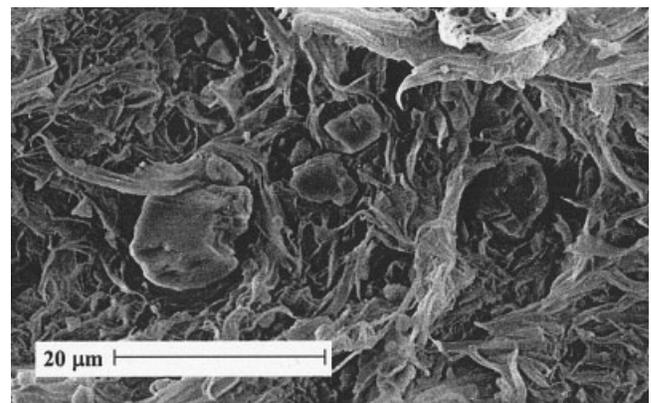


Figure 13 SEM micrograph of a UCC30 untreated single-filler composite fracture surface.

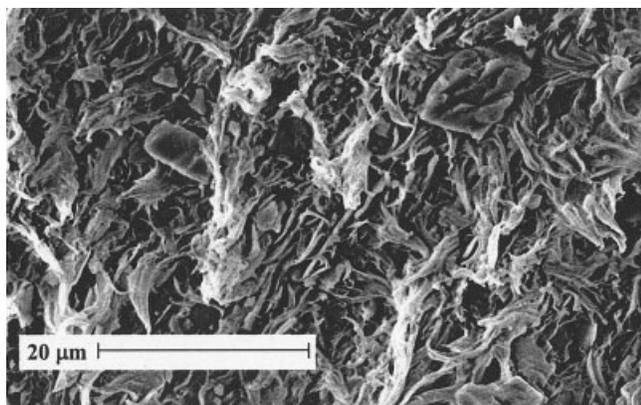


Figure 14 SEM micrograph of a T15UCC15 hybrid-filler composite fracture surface.

orientation of talc particles can be clearly seen, with the basal sheet planes mostly parallel to the surface of the injection molding (Fig. 12). This unique organization of particles was the result of the platelike structure of talc and its motion in a viscous medium during the injection process. Plastic deformation is not evident, and this suggests brittle failure of the composite. Most of the talc particles are clearly visible, and they tended to be embedded inside the polymer matrix. CaCO_3 particles, however, tended to be exposed and loosely spread on the fracture surface, with large cavities surrounding the particles. This clearly indicates that the filler–matrix interaction of talc-filled PP was far better than that for CaCO_3 -filled PP composites, even without any form of filler treatment. Signs of long polymeric fibrils clearly indicate that severe plastic deformation occurred before fracture in CaCO_3 -filled PP.

Figure 14 shows the fracture surface of the T15UCC15 hybrid composite. Obvious polymeric fibrils can be seen, and this suggests the occurrence of

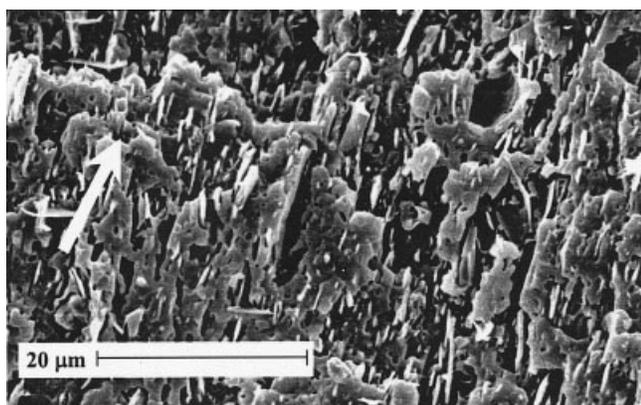


Figure 15 SEM micrograph of an LTTALC30 fracture surface. The arrow shows the direction of the orientation of the talc particles. The layers of the polymer matrix can be seen peeling off.

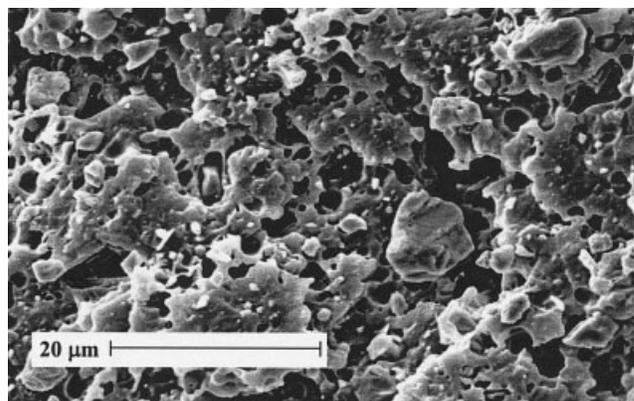


Figure 16 SEM micrograph of an LTUCC30 composite fracture surface.

plastic deformation. Loose, unattached CaCO_3 particles can be seen lingering on the fracture surface. Talc particles can hardly be spotted on the fracture surface, and this suggests that they could be embedded deeply into the matrix and were indistinguishable from the long polymer fibrils because of the platy nature of the filler. Obviously, this could also mean that the interactions between the talc particles and the matrix were considerably better than those of CaCO_3 particles.

The tensile fractured surface morphology of LT-TALC30 is presented in Figure 15. The orientation of the talc particles according to the polymer melt flow can be observed, and it played a vital role in strengthening the polymer matrix. There was also no severe agglomeration of particles, and this suggests that Lica 12 could help with the filler dispersion. There is no significant formation of long and sharp polymeric fibrils, as observed in Figure 14, whereas layers of the polymer matrix tightly bonded by the fillers can be seen peeling off from the fracture surface; this suggests quite good filler–matrix interactions and adhe-

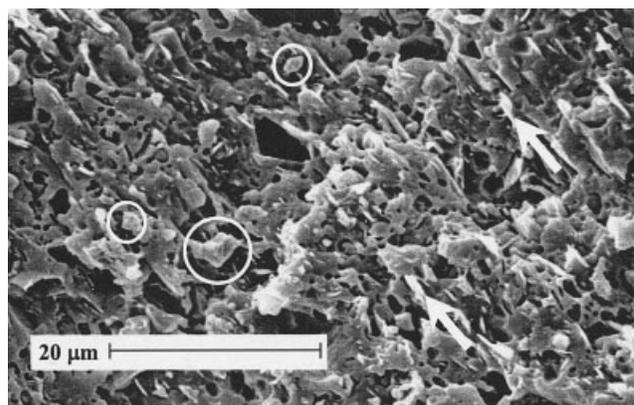


Figure 17 SEM micrograph of a T15LTUCC15 hybrid composite fracture surface. The arrows show talc particles, and the circles show CaCO_3 particles.

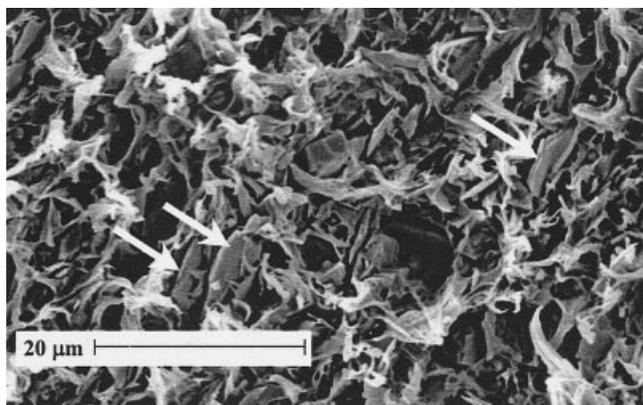


Figure 18 SEM micrograph of an STTALC30 fracture surface. Talc particles, depicted by the arrows, follow a certain orientation.

sion, although brittle fracture was expected. Because the fillers were still tightly bound to the matrix, the strength of the corresponding composite should have been quite high, as shown earlier with the tensile strength data.

The fracture surface morphology of PP filled with Lica 12 treated CaCO_3 is shown in Figure 16. The fracture surface represents a seemingly brittle failure mode. However, upon closer examination, deep valleys can be found, and this is believed to have been caused by pulled-out layers of the polymer, whereas numerous holes left behind by CaCO_3 particles can be seen accompanying these layers. Although it is still unclear how these formations of valleys could occur, the high elongation at break recorded for LTUCC30 suggests that large plastic deformations could have occurred between these polymer layers. The huge shearing force exerted by the pulling between these layers could cause the filler particles to be detached from the surfaces of those layers and this leave behind holes. This unique phenomenon could probably be achieved only when the polymer had sufficient plasticity and high filler–matrix adhesion. Because the treatment of the PP composites with Lica 12 was proven to increase the plasticity of PP and improve filler–matrix adhesion,^{15,18} this unique morphology could be said to exist only with the Lica 12 treatment. Moreover, improved filler–matrix adhesion prevented the reduction of the strength of LTUCC30, even though the elongation at break recorded by the composite was very high.

Figure 17 shows an overall brittle fracture surface of PP filled with Lica 12 treated hybrid fillers. Although there was a mix of incorporated fillers with completely different dimensions (CaCO_3 was isometric, and talc was platy), the dispersion of the fillers in the polymer matrix was fairly homogeneous. The anisotropic orientation of talc can still be seen and clearly shows that neither the CaCO_3 fillers nor the filler treatments in-

terfered with talc particle orientation. Therefore, the talc particles could still play a certain role as a reinforcement, whereas the CaCO_3 particles independently enhanced the toughness of the overall system. This could well explain the good retention of impact properties for the hybrid composites in comparison with the single-filler composites.

Figure 18 shows a more ductile fracture surface morphology of a silane-treated talc-filled PP composite, which is contrary to the morphology depicted in Figure 12 for the untreated filler composite. Although the visibility of talc particles is quite poor, it can still be seen that most of the talc particles were oriented to a certain direction, as shown by the arrows in Figure 18.

The PP matrix most certainly retained its ductility when it was incorporated with silane-treated CaCO_3 , as shown in Figure 19. This further shows that the ductility and morphology of the polymer matrix depended not only on the type of coupling agent used but also on the type of filler that the coupling agent was treating. According to the DSC data, the crystallinity of STUCC30 was also quite low, and this helped to preserve the ductility of the matrix as well. The surfaces of some fillers were still attached to the polymeric fibrils, as shown by the arrows in Figure 19, and this indicated quite good filler–matrix adhesion. This evidence was crucial for proving that the silane treatment could still provide good filler–matrix adhesion, although the dosage was believed to be insufficient for effective coupling to instill greater strength to the composite.

Figure 20 shows the morphology of mostly brittle fracture surfaces for the T15STUCC15 hybrid composite. From earlier observations, we deduced that the brittleness of the matrix was contributed by the increased matrix crystallinity due to the treatment of CaCO_3 with the silane coupling agent; this was supported by the DSC data. Talc particles can be seen very clearly here; the overall filler orientation was not disturbed, although there were some parts in which the

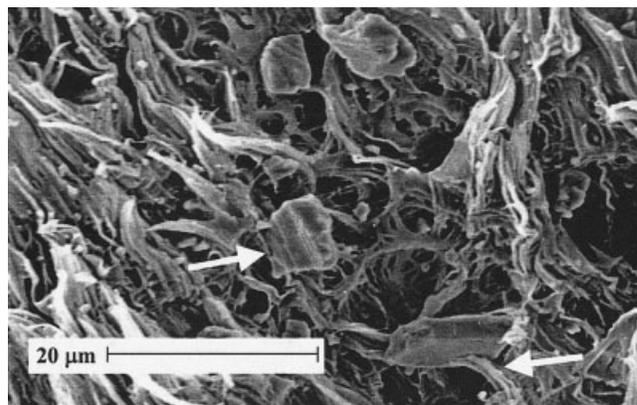


Figure 19 SEM micrograph of an STUCC30 fracture surface.

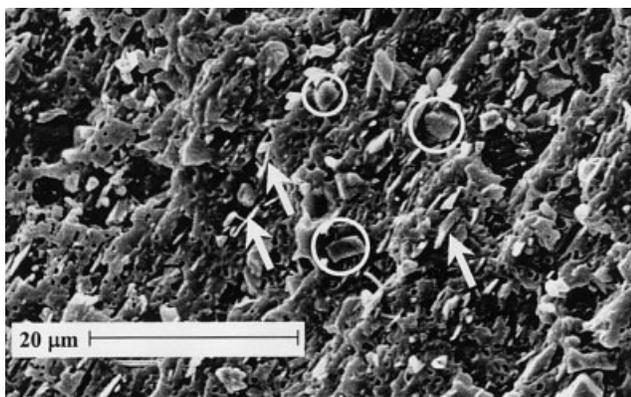


Figure 20 SEM micrograph of a T15STUCC15 hybrid composite fracture surface. The arrows show talc particles, and the circles show CaCO_3 particles.

talc particles had to give way to large CaCO_3 particles. Some voids and cavities left behind mostly by the CaCO_3 filler are still visible. Most of the CaCO_3 particles can be seen embedded in the PP matrix, with only a fraction of those straddled loosely on the surface. Here, silane treatment was proved to be an active surface treatment for improving filler–matrix bonding.

The stearic acid treatment was conducted solely on CaCO_3 for the purpose of improving its dispersion in the matrix. Figure 21 shows that the filler dispersion in TCC30 was quite homogeneous, although some large CaCO_3 particles were present. Some polymeric fibrils, indicating plastic deformation, can be observed on the fracture surface, although the elongation at break for the composite was rather low in comparison with that of the untreated CaCO_3 -filled PP. This further confirms the theory that matrix embrittlement occurs more toward the filler–matrix interfaces at which the concentration of stearic acid is highest.

The fracture surface shown in Figure 22 of T15TCC15 was very brittle, and this undoubtedly was the main reason for the low elongation at break re-

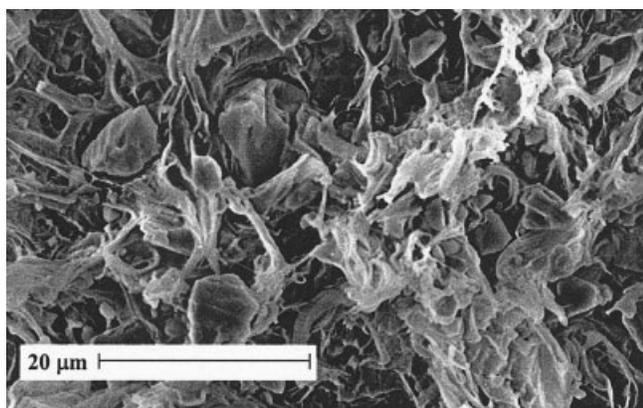


Figure 21 SEM micrograph of a TCC30 fracture surface.

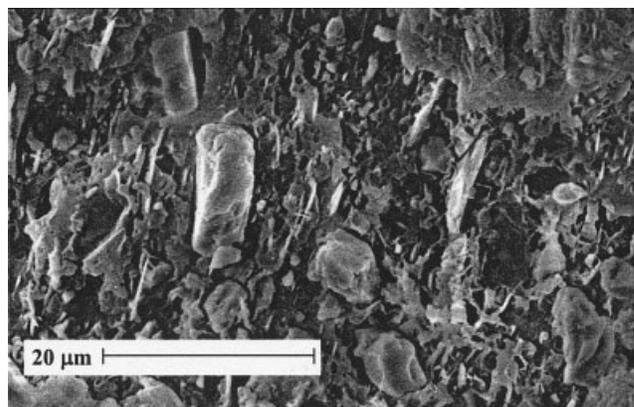


Figure 22 SEM micrograph of a T15TCC15 hybrid composite fracture surface.

corded for this composite. Because stearic acid was only necessary to improve the dispersion of CaCO_3 , it might not have the same effect on talc. In fact, as shown in Figure 22, talc was not as oriented as in other samples, and this indicated that stearic acid, while improving the dispersion of the fillers, could also reduce the particle orientation of talc. However, this somehow did not much affect the strength of the composite, and this shows that good filler dispersion is more vital to the enhancement of composite strength.

CONCLUSIONS

A study of the effects of three different kinds of filler treatments (stearic acid, 3-aminopropyltriethoxysilane, and Lica 12 coupling agents) has revealed that the silane treatment inhibits melt flow and that the others do not. The silane treatment increases both the filler–matrix and filler–filler interactions, and these interactions can hinder the polymer melt flow. However, the strength of the composites treated with silanes was either the same or lacking in comparison with that of the untreated composites, despite the improvement in the filler–matrix interactions. It is thus believed that the silane dosage still needs to be optimized before it can provide just the right amount of coupling.

The treatment with stearic acid, on the other hand, improved the filler dispersion of the composites and thus increased the MFI. Contrary to the silane treatments, the stearic acid treatment reduces filler–filler interactions and provides a better dispersion of the fillers, particularly CaCO_3 . Nevertheless, this form of treatment also reduces filler–matrix interactions and consequently results in decreased composite strength and ductility.

Titanate treatments also increased the elongation at break and MFI of all the composites studied here, and

this can be attributed to chain scission of the polymer matrix or the indirect role of the coupling agent as a plasticizer or lubricant. Moreover, the titanate-treated T15LTUCC15 hybrid composite had superb impact strength, overshadowing the superiority of CaCO₃-filled PP, which, in its untreated form, was thought to have the best impact characteristics of all. Although the true mechanistic details of the interactions in T15LTUCC15 are still elusive, it is believed that the treatment of Lica 12 can induce better filler orientation, dispersion, and interaction with the PP matrix to achieve this synergistic effect.

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