

Mechanical Properties of i-PP/CaCO₃ Composites

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SYNOPSIS

Tensile and impact behavior of CaCO₃-filled polypropylene was studied in the composition range 0–60 wt % filler. Tensile modulus increased while tensile strength and breaking elongation decreased with increase in CaCO₃ content. The modulus increase and elongation decrease were attributed to increased filler–polymer interaction resulting in reduction in molecular mobility, while increased amorphization and obstruction to stress transfer accounted for the tensile strength decrease. Analysis of tensile strength data showed introduction of stress concentration in the composites. Izod impact strength at first increased up to a critical CaCO₃ content, beyond which the value decreased. Surface treatment of CaCO₃ with a titanate coupling agent LICA 12 enhances the adhesion of the filler and polymer, which further modifies the strength properties. Scanning electron microscopic studies indicated better dispersion of CaCO₃ particles upon surface treatment, which effected the changes in the strength properties of the composites.

INTRODUCTION

Composites of polymers with particulate fillers have generated considerable interest owing to desirable improvement in certain properties for various applications.^{1–7} When filled with limestone, polypropylene becomes a keen competitor for engineering thermoplastics with properties approaching those of ABS and other high-cost materials. The interest in developing such mineral-filled polypropylene composites is primarily to widen the range of application of the polymer. In such highly filled polymer systems, a major problem is nonuniformity of properties due to poor dispersion of the filler in the matrix. Surface treatment of the dispersed phase by a suitable coupling agent has been of much help in overcoming the dispersion problem. In recent times, the titanate types of coupling agents have been found to be very effective and their modifying effects on the rheological and mechanical properties of filled polymers have been extensively studied.^{7–9} The effect of a titanate coupling agent on the crystallization behavior of CaCO₃-filled polypropylene and its cor-

relation with mechanical properties has been reported by the authors.¹⁰

In this paper, we report a study on the mechanical properties of isotactic polypropylene (i-PP)/CaCO₃ composites with and without a titanate coupling agent. Tensile modulus, yield stress, and elongation-at-break data have been analyzed on the basis of theoretical predictions for two-phase systems. The degree of discontinuity in the structure is assessed on the basis of the stress concentration factor. Izod impact strength values have also been evaluated. Scanning electron microscopic studies have been made to characterize the discontinuity in the structure.

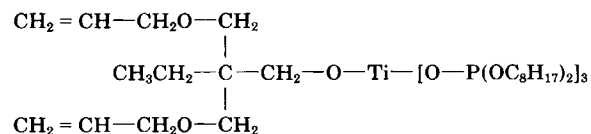
EXPERIMENTAL

Materials

Isotactic polypropylene (i-PP) used was Koylene M0030 (MFI 10, density 0.89 g cm⁻³) obtained from Indian Petrochemicals Corporation Ltd. Calcium carbonate used was a British Drug House product (density 2.70 g cm⁻³) obtained from Glaxo Laboratories, India. The average particle diameter of CaCO₃ particles determined by hydrometer analysis was 5.5 μm. Calcium carbonate was surface-treated with a liquid titanate coupling agent (LICA 12)

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neopentyl (diallyl) oxy, tri(dioctyl) phosphatoteitanate:



which was obtained from M/s Kenrich Petrochemicals, Bayonne, N.J., USA.

Surface Treatment of CaCO₃

In toluene solution of LICA 12 (0.5 wt % on the basis of CaCO₃), a requisite quantity of the filler was added with continuous stirring. The slurry was air-dried for 24 h and then vacuum-dried at 110°C for 4 h. The fillers developed hydrophobicity, confirmed by the floating test on water. A similar technique for filler surface treatment was used by other authors^{11,12} as well.

Preparation of the Composites

Vacuum-dried i-PP and CaCO₃ (both untreated and treated) were compounded at 160°C on a two-roll mill for 10 min to prepare thin sheets containing 0–35 vol % (0–60 wt %) filler. Several plies of these sheets were then compressed in a mold at 200°C using a pressure of 10.35 MPa to make sheets of 1 and 3 mm thickness. Dumbbell-shaped tensile specimens were machined from the 1 mm sheets, while rectangular bars for impact specimens were machined from 3 mm sheets. Unfilled i-PP samples were also prepared under identical conditions of mixing and molding.

Measurements

Tensile properties were measured on an Instron Universal Testing Machine (Model 1121) according to the ASTM D638-82 test procedure at an extension rate of 100% (initial crosshead separation 5 cm and crosshead speed 5 cm/min). Izod impact strength values were estimated on notched samples on an FIE instrument (Model IT-0.42) according to the ASTM D256-73 test procedure. At least five samples were tested for each composite composition, and the average value is reported. Tests were performed at ambient temperature (30 ± 2°C).

Scanning electron microscopic (SEM) studies of cryogenically fractured tensile samples were carried out on a Cambridge Stereoscan (Model S4-10). The acceleration voltage used was 20 kV.

RESULTS AND DISCUSSION

Tensile Properties

Tensile properties evaluated from the stress-strain curves (not shown) are presented in Figures 1–4 in the form of plots of the ratio of the property of the composite (subscript *c*) to that of the unfilled i-PP (subscript *p*) against volume fraction ϕ_F of CaCO₃.

The variation of relative tensile moduli (E_c/E_p) with ϕ_F is shown in Figure 1. The modulus of untreated CaCO₃-filled composites show a steady increase with filler concentration; at maximum ϕ_F (35.4%), the value is almost double that of i-PP. Surface treatment of the filler with the coupling agent brings about a dramatic change in the modulus values. The modulus increases to about double that of i-PP at ~ 4 vol % filler; beyond this ϕ_F , the increase is only marginal. The modulus data were compared with some theoretical predictions for two-phase composites that take into account the shapes, packing fraction, and adhesion between the inclusion and the polymer matrix (Fig. 1). Curve "A" is the plot of Einstein's equation without adhesion^{13,14} [eq. (1)], curve "B" represents Einstein's equation with adhesion^{13,14} [eq. (2)], whereas curve "C" exhibits the modified Kerner's equation^{13,15} with adhesion [eq. (3)] for filled polymer composites with the Poisson ratio γ_p of i-PP taken as 0.35:

$$E_c/E_p = (1 + \phi_F) \quad (1)$$

$$E_c/E_p = (1 + 2.5\phi_F) \quad (2)$$

$$E_c/E_p = 1 + \frac{15(1 - \gamma_p)}{8 - 10\gamma_p} \cdot \frac{\phi_F}{1 - \phi_F} \quad (3)$$

The data for untreated CaCO₃-filled composites fit the Einstein model without adhesion up to $\phi_F = 0.17$, while beyond this ϕ_F , the model predicts lower values and the data tend to fit the upper-bound equation with adhesion. The agreement of the data with the no-adhesion model at low ϕ_F range seems quite expected because i-PP/CaCO₃ composites are of the no-adhesion type in view of the fact that there is no chemical interaction of inorganic CaCO₃ with organic polyolefin i-PP. Any interaction operative would only be physical, e.g., surface adsorption. The polymeric matrix is, however, stiffened by the particulate second-phase CaCO₃. The particles restrict the mobility and deformability of the matrix by introducing a mechanical restraint, the degree of which depends on the particulate spacing and the properties of the particle and the matrix.¹⁶ Other works^{17–19} also showed a modulus increase in poly-

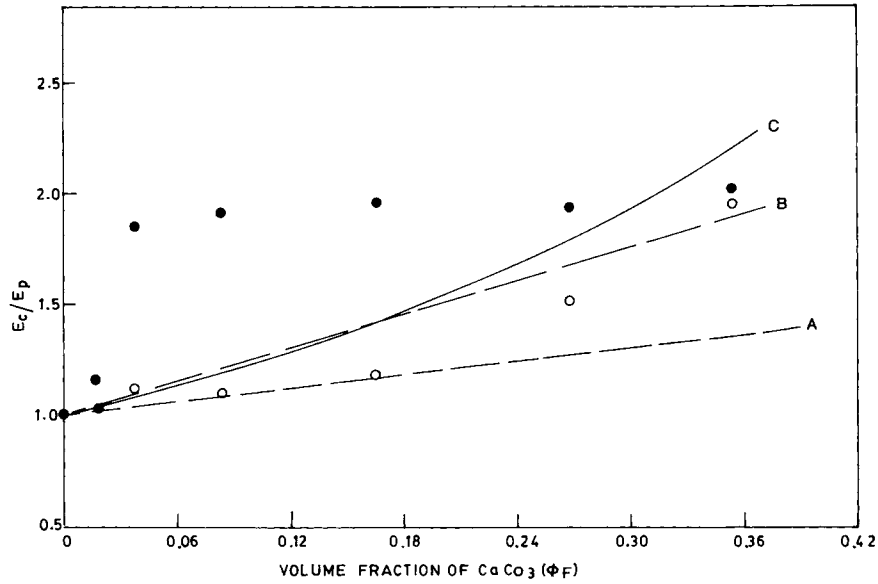


Figure 1 Plot of relative tensile modulus (E_c/E_p) of i-PP/CaCO₃ (○) and i-PP/CaCO₃/LICA-12 (●) composites against CaCO₃ volume fraction ϕ_F . Curves A, B, and C represent Einstein's equation without adhesion, Einstein's equation with adhesion, and modified Kerner's equation, respectively.

mers containing rigid particulate fillers even if the filler did not interact strongly with the matrix. Restriction in polymer molecular diffusion was reported²⁰ in the presence of solid particles due to an effective attraction potential between segments of the chain sequential to the repulsive potential that the polymer is subjected to when it approaches the solid particles. The increase in E_c/E_p at higher ϕ_F

(> 0.17) may not be due to better adhesion of CaCO₃ and i-PP. Such behavior may be a consequence of the balancing of the predicted increase in modulus due to the filler with the predicted decrease in elongation.¹⁶

Upon surface treatment, the modulus increases too rapidly after $\phi_F = 0.04$ to fit the models, indicating enhanced interaction of the filler and i-PP matrix,⁹ which may not be affected at low solid displacements. The modulus, however, levels off after

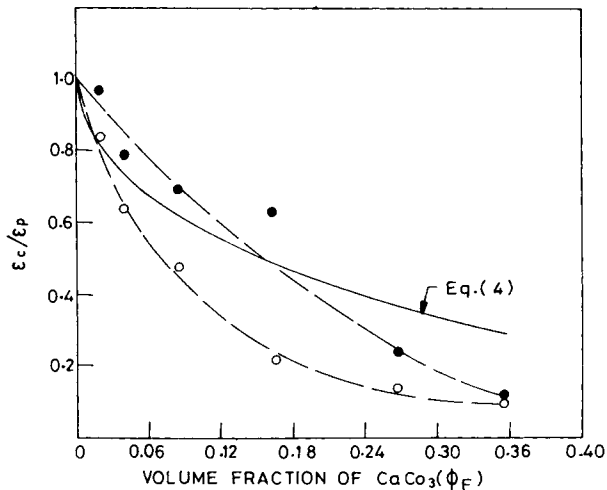


Figure 2 Relative strain-at-break (ϵ_c/ϵ_p) of i-PP/CaCO₃ (○) and i-PP/CaCO₃/LICA-12 (●) composites vs. ϕ_F . Dotted curves represent average of experimental data. The solid curve represents predicted behavior according to eq. (4).

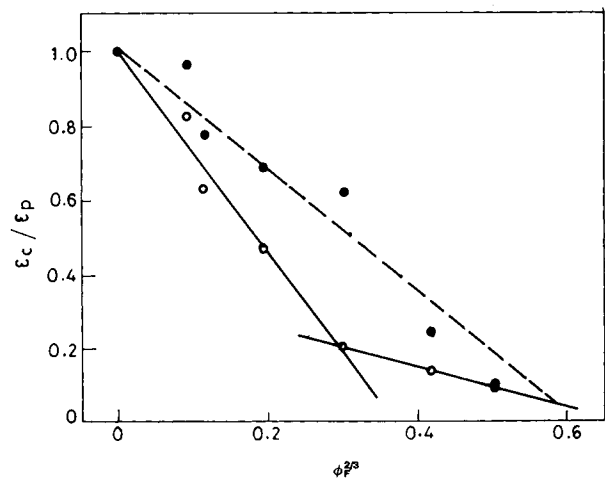


Figure 3 Variation of strain-at-break (ϵ_c/ϵ_p) of i-PP/CaCO₃ (○) and i-PP/CaCO₃/LICA-12 (●) composite against $\phi_F^{2/3}$.

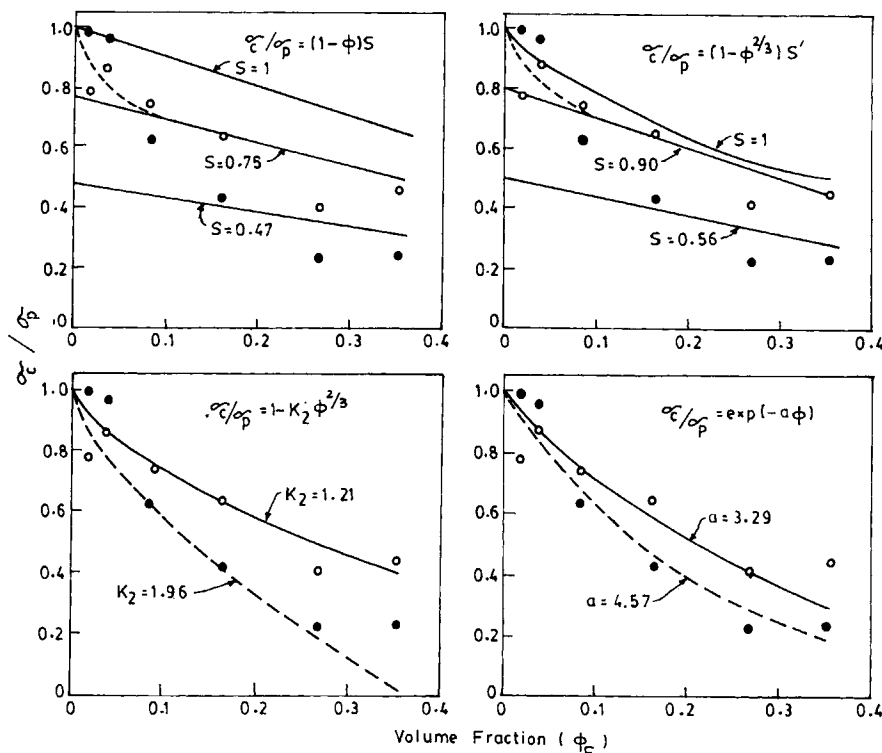


Figure 4 Comparison of experimental data with theoretical predictions for the composite composition dependence of relative tensile stress (σ_c/σ_p) of i-PP/CaCO₃ (O) i-PP/CaCO₃/LICA-12 (●) composites.

~ 4 vol % filler, possibly due to a balancing effect of the decrease in crystallinity sequential to the increase in the interaction of surface-treated CaCO₃ with i-PP with an increase in ϕ_F (Table I).

Breaking elongation exhibits a decrease with an increase in filler concentration in a manner shown in Figure 2. In the composites with untreated fillers, the decrease is quite rapid up to ~ 18% CaCO₃; beyond this point, the decrease is slow. With treated CaCO₃, the declining trend of elongation is maintained. The decrease is relatively rapid up to ~ 28% filler; the elongation values are, however, higher than in the former case. Nielsen's model¹³ [eq. (4)] for elongation with perfect adhesion

$$\epsilon_c/\epsilon_p = 1 - \phi_F^{1/3} \tag{4}$$

predicts higher values for ϵ_c/ϵ_p (ratio of breaking elongation of the composite and i-PP) than do the data with untreated CaCO₃. The values for treated CaCO₃-filled composites lie above the theoretical curve up to $\phi_F = 0.18$; values beyond lie below. The decrease in breaking elongation of i-PP in the presence of CaCO₃ indicates an interference by the filler

to mobility or deformability of i-PP. This interference is created through physical interaction and immobilization of the polymer matrix by imposing mechanical restraints. In the composites with surface-treated fillers, a plasticizing or lubricating type of behavior^{8,21} by the coupling agent is indicated that reduces the deformability of i-PP to a lesser extent.

The decrease of elongation to lower values than of the Nielsen model [eq. (4)] hints upon a relationship of filler area fraction $\phi_F^{2/3}$ and elongation. Figure 3 shows a plot of ϵ_c/ϵ_p vs. $\phi_F^{2/3}$, which reveals that the elongation is very sensitive to filler area fraction, in particular up to $\phi_F^{2/3} = 0.3$, and the sensitivity is lowered on filler surface modification. Following the method described by Mitsubishi et al.,⁷ eq. (5) was derived to study the effect of filler-polymer interaction on elongation:

$$\epsilon_c/\epsilon_p = (1 - K_1\phi_F^{2/3}) \tag{5}$$

where K_1 is a constant value depending on filler size and the modification of fillers. Table II shows the values of K_1 obtained from eq. (5). The mean value of K_1 estimated for the untreated CaCO₃-filled sys-

Table I Values of Percent Crystallinity of i-PP Component in i-PP/CaCO₃ Composites Estimated from DSC Studies and X-ray Diffraction Measurements

Sample Composition (vol % filler)	% Crystallinity ^a	
	DSC method ^b (ΔH /g)	X-ray method
i-PP	62.2	67
i-PP/CaCO ₃ 1.89%	78.1 (63.6)	68 (55)
i-PP/CaCO ₃ 3.90%	71.6 (61.5)	65 (56)
i-PP/CaCO ₃ 8.37%	66.2 (53.2)	63 (51)
i-PP/CaCO ₃ 16.45%	54.2 (40.7)	59 (44)
i-PP/CaCO ₃ 26.78%	44.8 (30.3)	48 (33)
i-PP/CaCO ₃ 35.42%	40.4 (24.7)	43 (26)

^a Crystallinity (%) values in parentheses are for composites with surface-treated CaCO₃.

^b Heat of crystallization ΔH is proportional to crystallinity (%) (Ref. 10).

tem was 2.33, which was quite close to a reported value.⁷ The interaction parameter decreases for the surface-treated composites, revealing a plasticizing/lubricating effect of the coupling agent.²¹

An indication toward some degree of interaction between the filler and the polymer was evident in the modulus data. Surface treatment of the filler enhanced this interaction to a significant extent. The elongation data indicated hinderance to molecular mobility/deformability in untreated CaCO₃-filled composites (thus supporting the modulus increase data), while a plasticizing/lubricating type of effect was shown in the presence of a coupling agent. One problem in particulate-filled composites^{13,16} is poor stress transfer at the filler-polymer interface. Because of nonadherence of the filler to the polymer which may give rise to dewetting or cavitation coupled with breakdown of filler agglomerates, discontinuity is created in the structure. The filler particles cannot carry any load, making it a weak body. Stress concentrations will be created around the particles, reducing the composite strength further. For any significant contribution to mechanical and other properties by the dispersed

phase in a two-phase composite, two important requirements are (a) continuity in the structure and/or (b) interfacial adhesion. More insight into these aspects of the composites would be obtained from the analysis of the tensile strength data.

Analysis of Tensile Stress Data

To explore the generation of discontinuity and sequential weakness in the structure of these two-phase composites, the tensile yield stress data were analyzed using some of the most commonly used theoretical predictive models, the details of which are described elsewhere.^{22,23}

The following models were used:

$$\sigma_c / \sigma_p = (1 - \phi_F) S \quad (6)$$

$$\sigma_c / \sigma_p = (1 - \phi_F^{2/3}) S' \quad (7)$$

$$\sigma_c / \sigma_p = (1 - K_2 \phi_F^{2/3}) \quad (8)$$

$$\sigma_c / \sigma_p = \exp(-a\phi_F) \quad (9)$$

where σ_c and σ_p denote the tensile strength of the composite and matrix, respectively. These equations describe no adhesion type of structure and are based on the relationship of area fraction to volume fraction of the inclusions.^{24,25} In the first power-law relationship [eq. (5)], the parameter S was introduced in analogy to S' in eq. (6) to account for the weakness in the structure brought about by discontinuity in stress transfer and generation of stress concentration at the filler-polymer interface, as proposed by Nielsen.²⁶ The maximum value of S (or S') is unity for "no stress concentration effect"; the lower

Table II Values of the Parameter K_1 [eq. (5)] in i-PP/CaCO₃ Composites

CaCO ₃ vol %	Values of K_1	
	i-PP/CaCO ₃	i-PP/CaCO ₃ /LICA-12
0	—	—
1.89	2.344	0.452
3.90	3.216	1.877
8.37	2.749	1.621
16.45	2.672	1.232
26.78	2.073	1.841
35.42	1.809	1.789
Mean value	2.328	1.672

For data variation, the mean was estimated excluding the value at a certain point, e.g., for i-PP/CaCO₃ at $\phi_F = 3.90\%$ and for i-PP/CaCO₃/LICA 12 at $\phi_F = 1.89\%$.

the value, the "greater the stress concentration effect." The weight-age factor K_2 (i.e., coefficient of $\phi_F^{2/3}$) in eq. (7) takes into account the adhesion quality between the matrix and the inclusion²⁷; the lower the value, the better the adhesion. In the extreme case of poor adhesion with spherical inclusions, the weight-age factor assumes²⁴ a value of 1.21. The porosity model [eq. (8)] assumes inclusions to be equivalent to pores or voids in nonpolymeric materials such as metals and ceramics²⁸ as well as polymer blends²⁴ and composites.²⁹ The pores do not have any influential role on the composite mechanical properties due to nonadhesion at the interface boundary. The parameter a is related²⁴ to stress concentration; the higher the value, the higher the stress concentration.

Using suitable values of S , S' , K_2 and a at each individual CaCO_3 concentration, some degree of agreement can be obtained between the tensile stress data and the first and fractional power-law model, the Nicolais and Narkis model, and the porosity model [eqs. (6)–(9)] (Table III). Stress concentration values are seen to be less than unity accord-

ing to first and two-thirds power-law models, and greater than unity according to the Nicolais–Narkis model and the porosity model, both types indicating significant weakness or discontinuity in the structure. The values for i-PP/ CaCO_3 /LICA 12 composites had similar trends except at $\phi_F = 3.9\%$ for S and at $< 8.37\%$ for S' , where the values were close to unity.

Comparison of the experimental data with the theories are presented in Figure 4. The data with untreated CaCO_3 up to $\phi_F = 0.04$ lie within two theoretical lines corresponding to $S = 1$ and 0.75 in the first power-law relation [eq. (6)], whereas beyond this ϕ_F , the data fit reasonably well with the curve with $S = 0.75$. This indicates that the system changes over quickly from the state of no stress concentration to a state with some degree of stress concentration upon incorporation of CaCO_3 into i-PP. Similar behavior is also clearly indicated in Nielsen's model [eq. (7)], where the data at $\phi_F > 0.04$ show a good fit with the curve with $S' = 0.90$.

Nicolais and Narkis's model [eq. (8)] shows good agreement with these data with $K_2 = 1.197$, which is very close to 1.21 for no-adhesion with spherical fillers.²⁴ The K_2 value 1.197 is somewhat higher than the value reported by Mitsuishi et al.⁷ with particles 4.5 μm in diameter, which may be due to the difference in particle size and size distribution. Thus, it seems that adhesion between CaCO_3 and i-PP was absent, which, as stated before, is quite plausible due to the absence of any chemical interaction between the two phases. Similar results are reported³⁰ for other spherical particle-filled composites. This indicates that the interface in the composite is very weak and cannot sustain the load so that failure takes place at large deformations. The porosity model [eq. (9)] also exhibits a good fit with the data with $a = 3.29$ (Table III). As stated earlier, a higher value of a would indicate significant stress concentration in the composites.

Composites with surface-treated CaCO_3 show better adhesion with the filler at low ϕ_F (Fig. 4). The data lie above the theoretical curve for no adhesion up to $\phi_F = 0.04$, beyond which the data lie below those with untreated filler. This may be due to a lubrication/plasticization effect by the coupling agent at the interface, similar to other studies.⁸ Because of scattering, the data did not show any meaningful fit with curves with average values of the parameters S and S' . Nevertheless, the individual data points beyond $\phi_F = 0.04$ exhibit an increased extent of stress concentration than did the composites with untreated CaCO_3 , according to eqs. (6) and (7) (Table III). In this range of the data, eqs. (8) and

Table III Values of Stress Concentration Parameters S [eq. (4)], S' [eq. (5)], a [eq. (7)], and Adhesion Property K_2 [eq. (6)] in i-PP/ CaCO_3 and i-PP/ CaCO_3 /LICA 12 Composites

CaCO_3 vol %	S	S'	K_2	a
0	—	—	—	—
1.89	0.799 (1.012)	0.864 (1.094)	3.047 (0.107)	12.890 (0.402)
3.90	0.904 (0.997)	0.982 (1.082)	1.142 (0.363)	3.614 (1.092)
8.37	0.809 (0.689)	0.917 (0.781)	1.351 (1.926)	3.575 (3.445)
16.45	0.769 (0.515)	0.918 (0.614)	1.190 (1.900)	2.686 (5.133)
26.78	0.565 (0.312)	0.707 (0.390)	1.413 (1.858)	3.300 (5.520)
35.42	0.692 (0.352)	0.903 (0.455)	1.105 (1.544)	2.274 (4.182)
Mean value	0.756 (0.467)	0.900 (0.560)	1.197 (1.957)	3.293 (4.570)

Because of data scatter, mean values were taken excluding some data points; for S at $\phi_F = 3.9\%$ and 26.78%; for K_2 at $\phi_F = 1.89\%$ and 26.78%; for a at $\phi_F = 1.89\%$ and 35.42%. Values in parentheses are for i-PP/ CaCO_3 /LICA-12 composites; the mean was taken for $\phi_F > 3.9\%$.

(9), however, show good fit with K_2 and α , being 1.96 and 4.57, respectively, implying a significant increase in stress concentration in the presence of the coupling agent. The value of interaction parameter ($K_2 = 1.96$) according to eq. (8) is seen to be higher than in the case of composites with unmodified CaCO₃ ($K_2 = 1.197$). A similar trend was also reported by Mitsuishi et al.⁷ despite the use of a different coupling agent.

Polypropylene is a hydrocarbon polymer with very low intermolecular interaction forces. The polymer chains, however, fit into the crystal structure. It is this crystallinity that imparts mechanical strength to the polymer. The presence of any inclusion such as filler, blending polymer, or any other additive interferes with the i-PP molecules fitting into the crystal structure, so that the strength properties may decrease. If, however, the loss in crystallinity is compensated for by an enhanced interaction of the polymer with the inclusion, the original strength of the former may be retained. Thus, the interface between the inclusion and i-PP plays a decisive role in determining the strength of the filled i-PP composites.¹⁶

In the CaCO₃-filled i-PP systems, the tensile strength and elongation decreased while tensile modulus showed an increase with filler concentration. Filler particles used were quite fine¹⁰ with an average diameter 5.5 μm , so that some degree of surface interaction with i-PP is a distinct possibility. Although the presence of CaCO₃ decreased the crystallinity of i-PP, as shown by X-ray diffraction and DSC studies (Table I), which in turn would decrease the strength properties, it is this physical interaction that should also be taken into account in determining the above properties. An increase was observed only in modulus values, which is a property determined at low solid displacement and which may not reveal microweaknesses in the structure, if any. However, this increased interaction was not enough to stop the decrease in tensile strength because this property is evaluated at large solid displacement, in which case any weakness in the structure will magnify the stress transfer reduction. Furthermore, formation of an increased quantity of amorphous i-PP in the presence of CaCO₃ will also reduce the tensile strength. Decrease in elongation is obviously due to increased rigidity in the presence of filler, which impedes the deformation of i-PP.

Upon treatment of the filler surface with LICA 12, the tensile modulus showed a dramatic increase due to the enhancement of polymer-filler interaction despite the decrease in crystallinity consequent to the enhanced interaction (Table I). Tensile strength

showed a large decrease due to this decrease in crystallinity, in particular, beyond $\phi_F = 0.04$. Furthermore, the plasticization type of function of the coupling agent also aids in the decrease in tensile strength. The slightly higher elongation values than of the untreated CaCO₃-filled composites are also attributed to the lubricating/plasticizing⁸ action of the coupling agent, as stated before.

Impact Properties

The relative izod impact strength values (I_c/I_p) of i-PP/CaCO₃ composites are shown in Figure 5 as functions of ϕ_F . The strength increases with CaCO₃ content up to $\phi_F = 0.04$; the value then decreases, and at 35.4 vol % filler, the strength is lower than that of unfilled i-PP. The increase in impact strength at low ϕ_F may be attributed to the formation of smaller-sized crystallites, i.e., spherulites,¹⁰ as well as to capacity to absorb more energy by the increased portion of amorphous i-PP. A further increase in ϕ_F reduces the deformability of i-PP, reducing in turn the ductility in the skin area so that the composite tends to form a weak structure. Similar results were reported in mica-filled i-PP composites.³¹ Systems with surface-treated CaCO₃ also exhibit a similar trend; the impact values are, however, higher than are the untreated CaCO₃-filled compositions. This is once again attributed to the lubricating/plasticizing effect by the coupling agent, similar to other

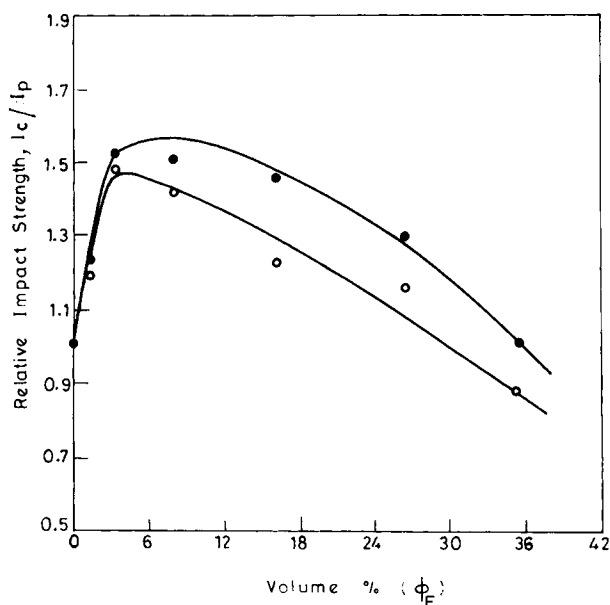


Figure 5 Variation of relative izod impact strength (I_c/I_p) or i-PP/CaCO₃ (○) and i-PP/CaCO₃/LICA-12 (●) against ϕ_F .

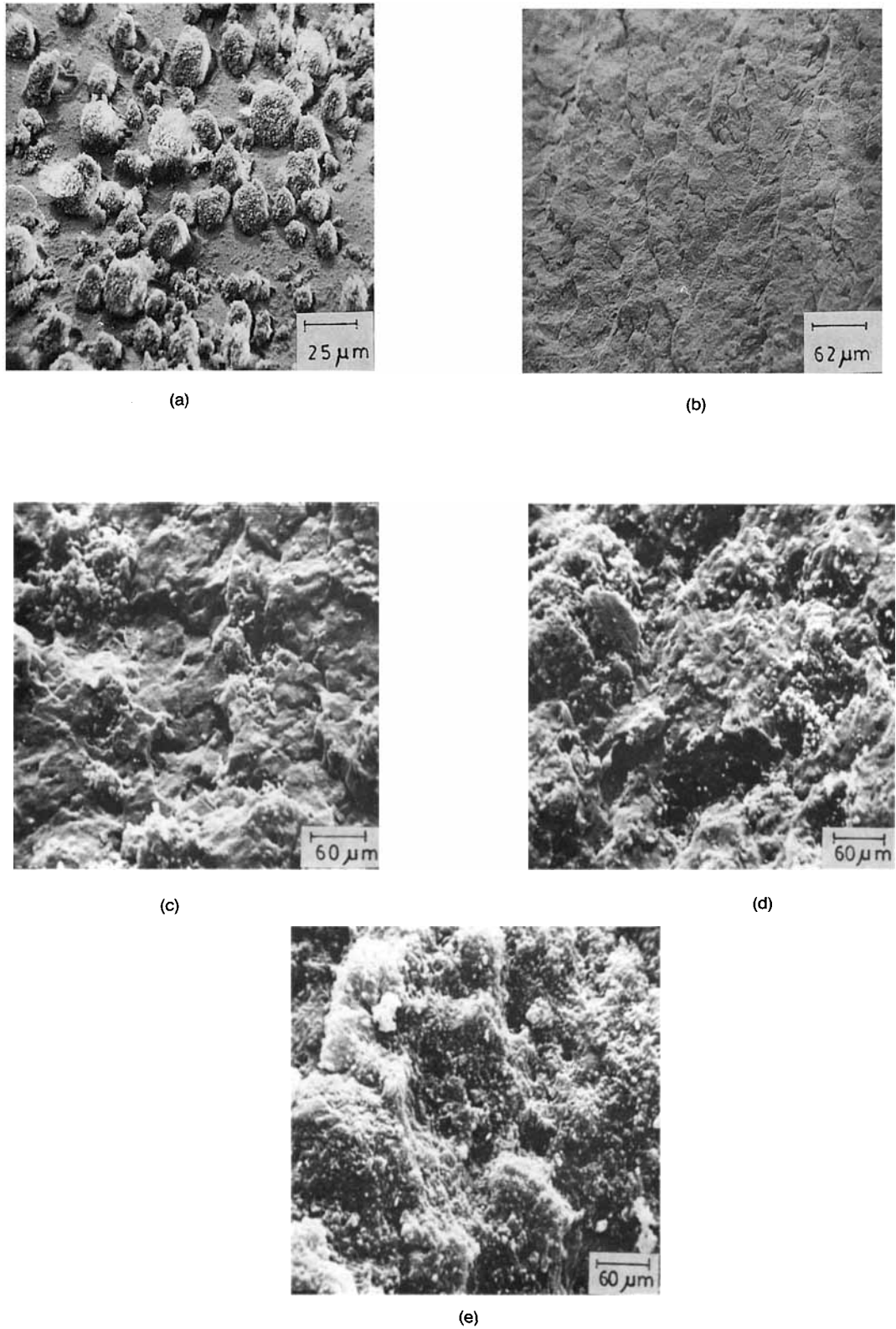


Figure 6 Scanning electron micrographs of CaCO_3 particles (a) and fractured surfaces of i-PP (b) and i-PP/ CaCO_3 composites of varying ϕ_F : (c) 0.04; (d) 0.16; and (e) 0.35. The micrographs of i-PP/ CaCO_3 /LICA-12 composites at corresponding CaCO_3 levels are presented in (f), (g), and (h), respectively.

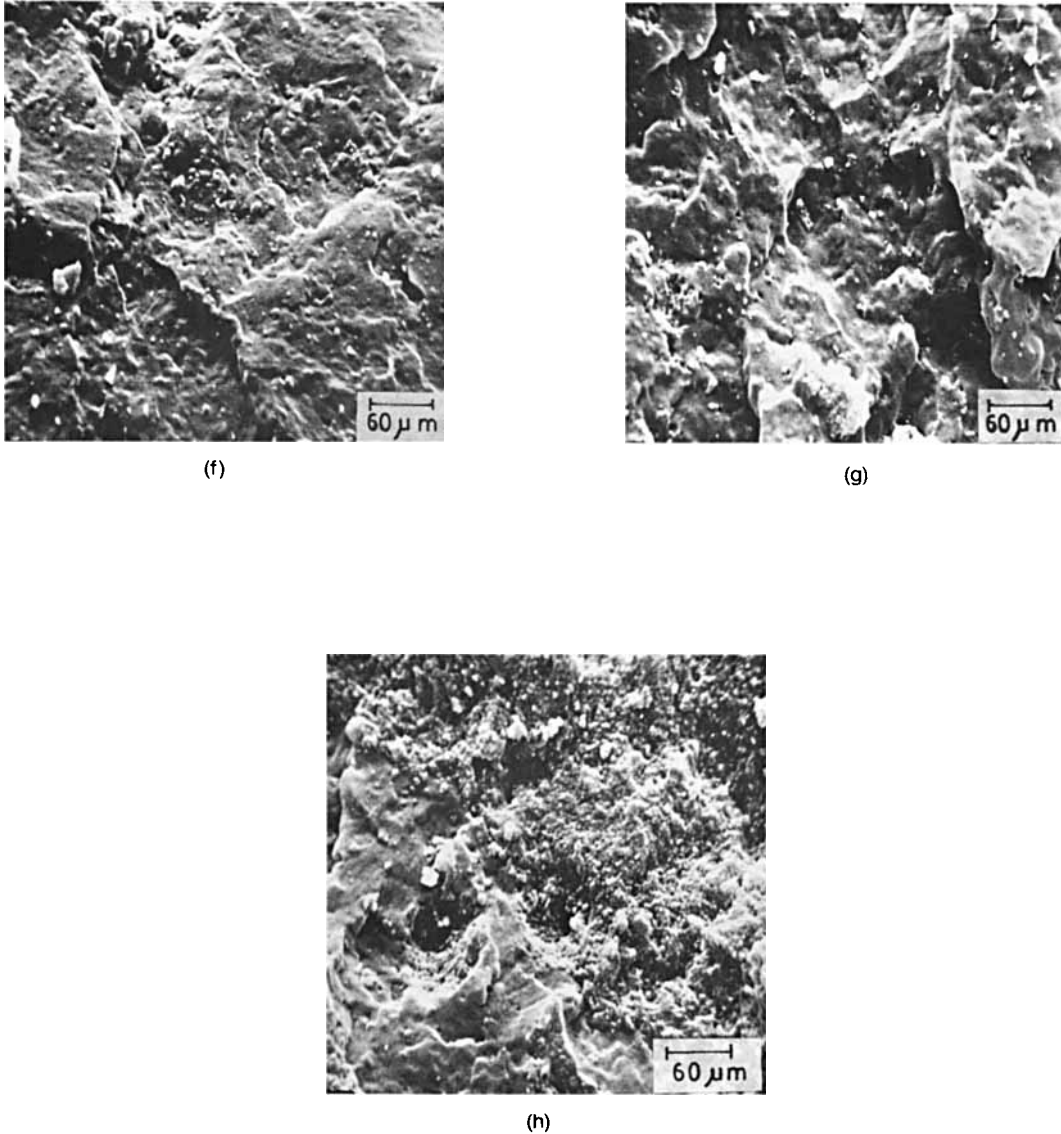


Figure 6 (continued from previous page)

reports,^{8,21} coupled with the formation of stress concentration points at higher CaCO₃ levels.

State of Dispersion

Scanning electron microscopic studies of the CaCO₃ particles and cryogenically fractured surfaces of i-PP/CaCO₃ composites are presented in Figure 6(a)–(h). The composites with untreated CaCO₃ show poor dispersion of the filler in the i-PP matrix. This may be ascribed to the crystalline nature of the polymer and agglomeration tendency of the fine CaCO₃ particles similar to other reports.³² The composites appear to be nonuniform with random fracture and uneven voids. The CaCO₃ particles ag-

glomerate to larger shapes, and a very small quantity of polymer residue is adhering to the filler surface. Better dispersion with a low degree of agglomeration of the filler was observed with surface-treated CaCO₃-filled composites [Fig. 6(f)–(h)]. The fracture surface appears to be uniform with an oriented fracture, which indicates an increased degree of deformation and fewer voids. Phase separation between the filler particles and the matrix is less distinct. The polymer shows uniform adherence with filler particles that is more distinct at lower filler levels, i.e., ϕ_F up to 0.16. This adhesion, which is indicative of improved interaction between the filler and i-PP, is responsible for altering the crystallization behavior⁸ of i-PP, which is manifested in

lowering the percent crystallinity of i-PP in the composites with treated CaCO₃ as compared to the composites with untreated filler.¹⁰

CONCLUSION

This study clearly demonstrates that incorporation of CaCO₃ greatly modifies the mechanical properties and morphology of i-PP. Tensile strength and breaking elongation decrease while modulus increases with filler content. Izod impact strength at first increases, showing a maximum at $\phi_F = 0.04$; the value then decreases with a further increase in ϕ_F , remaining higher than in the unfilled i-PP except at 35.4 vol % filler, where the value is less than in the unfilled i-PP. This indicates that CaCO₃ can be a very useful filler for i-PP even at very higher volume percent. The composites undergo a change from the state of continuous structure (zero stress concentration) to a state of discontinuous structure (with generation of stress concentration) at a critical filler 4 vol %.

Surface treatment of CaCO₃ with a titanate coupling agent LICA 12 modifies further the composite properties. It increases interaction of CaCO₃ with i-PP, causing increased amorphization of i-PP. Tensile modulus shows a rapid increase up to $\phi_F = 0.04$ due to this enhanced interaction. Tensile strength shows a negligible decrease at this ϕ_F ; the value, however, decreases below those of untreated CaCO₃-filled composites, with a further increase in ϕ_F due to increased amorphization of i-PP coupled with a lubricating/plasticizing effect of the coupling agent. Tensile strain and izod impact strength showed a similar trend as before, but the values were higher. This is also attributed to the lubricating/plasticizing effect by the coupling agent. SEM studies indicated better dispersion and decreased agglomeration of the filler upon treatment with LICA 12.

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