

Tensile Properties of Polypropylene/Kaolin Composites

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SYNOPSIS

Tensile properties of isotactic polypropylene filled with particulate kaolin fillers were evaluated in the composition range 0–60 wt % kaolin. Tensile modulus increased with filler concentration while breaking elongation and tensile strength decreased. The modulus increase was attributed to the restriction on the molecular mobility of the polymer imposed by kaolin particles. The decrease in elongation was also an effect of this restriction coupled with interference to stress transfer by the filler particles. Generation of discontinuity in the composite structure through formation of stress concentration points accounted for the tensile strength decrease. Morphology studies by SEM also indicated the introduction of stress concentration points by the presence of bare and nonadherent kaolin particles and their agglomerates with sharp edges in these composites.

INTRODUCTION

The scope of the application of polymeric materials has been widened by the incorporation of various additives into the polymer.^{1–5} These additives, when incorporated into a thermoplastic, modify certain properties such as modulus, tensile strength, moldability, etc., with an accompanying reduction in cost. Of all the additives used for thermoplastics, the bulk consists mainly of inorganic materials such as talc, CaCO₃, various silicates, glass beads, and glass fibers, etc. The influence of various particulate fillers on crystallinity, tensile strength and modulus, thermal conductivity, and melt rheology of polypropylene has been extensively studied.^{6–10} In general, the crystallinity is reduced upon incorporation of fillers. Modification of tensile properties depends on the polymer-filler combination, as well as on the interface of these two phase systems. While melt viscosity is also found to increase, melt elasticity decreases with increasing filler content. Decreases in melt elasticity add to the processing safety of the composites by increasing the critical shear stress for melt fracture, ensuring the smooth surface of the extrudates.

In the present study, the effect of the incorporation of kaolin in the mechanical properties of isotactic polypropylene (*PP*) has been reported. Tensile properties of *PP*/kaolin composites are studied at kaolin concentrations of 0 to 60 wt %. Various

theoretical models have been used to analyze the tensile data. State of dispersion of the filler in the polymer matrix has been analyzed by studying the morphology of the composites with the help of scanning electron microscopy.

EXPERIMENTAL

Material

Isotactic polypropylene (*PP*) Koylene M0030 (specific gravity 0.899, MFI 10) was obtained from Indian Petrochemicals Corporation, Ltd. The kaolin used was industrially pure kaolin of "Light" grade (specific gravity 2.57, particle size < 5 μm), supplied by Vivek Pharma, Bombay.

Preparation of the Composites

Kaolin was first dried in an air oven at a temperature 0403–413 K for 48 h, followed by vacuum drying at 353 K. The *PP* and kaolin were then homogenized on a two-roll mill at 433 ± 2 K for 10 min to prepare thin sheets of the composites containing 5, 15, 30, 50, and 60% by weight (1.8, 5.8, 12.9, 25.7, 34.2% by volume) of kaolin. Sheets of 1 mm and 3 mm thickness were then molded from several plies of these primary sheets in a compression mold at 513 ± 2 K and 200 MPa pressure on a compression press. Tensile specimens were machined from molded sheets 1 mm thick while impact specimens were cut from sheets 3 mm thick. Specimens from unfilled *PP* were also prepared under identical conditions of milling and molding in order to ensure an identical

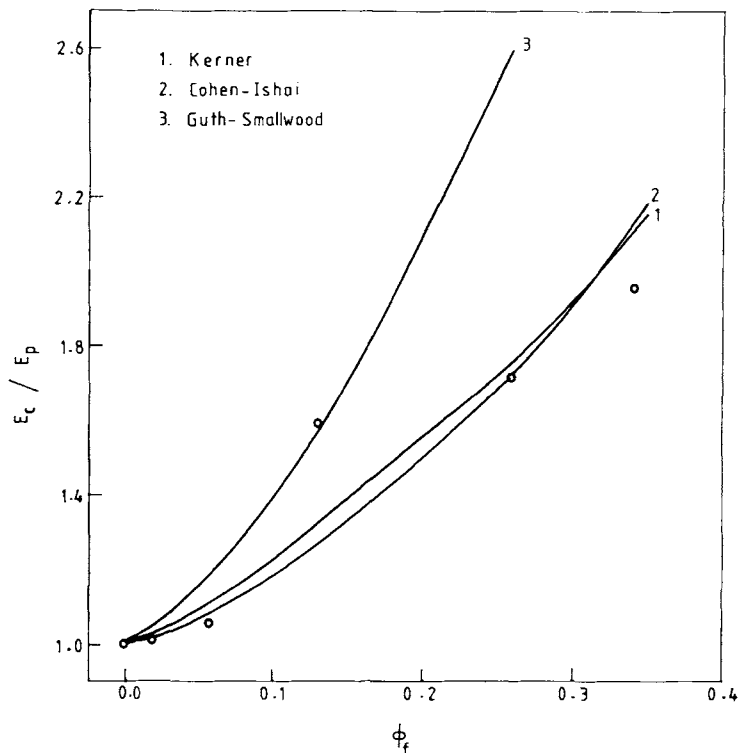


Figure 1 Comparison of variation of relative modulus data with theoretical predictions against volume fraction kaolin (ϕ_f): (1) Kerner's equation for perfect adhesion and a rigid filler, (2)Cohen-Ishai equation for spherical filler, (3) Guth-Smallwood equation.

thermal history for the composites and the unfilled polymer. It was further assumed that thermal degradation of the polymer, if any, occurring in the milling and molding cycles were identical in the composites and in the unfilled polymer samples.

Measurements

Tensile properties of the dumbbell shaped specimens were measured according to an ASTM D638-82 test procedure on an Instron (Model 1121) at an initial

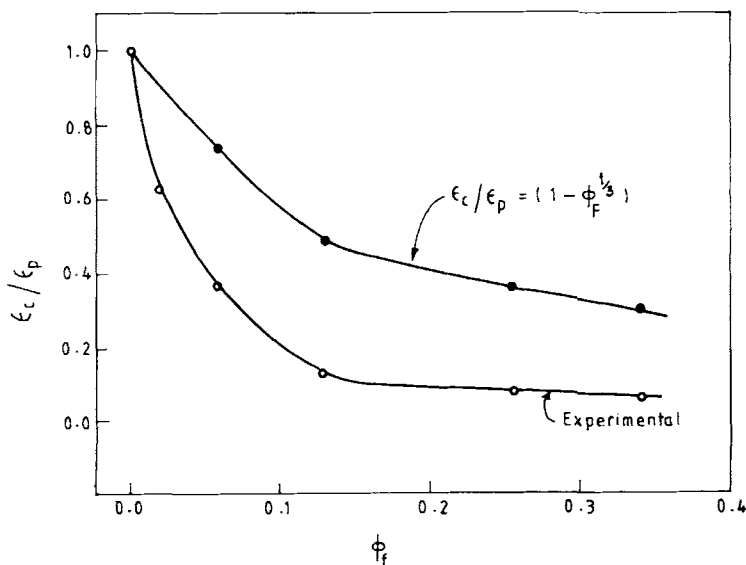


Figure 2 Comparison of Nielsen model [eq. (14)] (●) for relative elongation at break with experimental results (○) against ϕ_f .

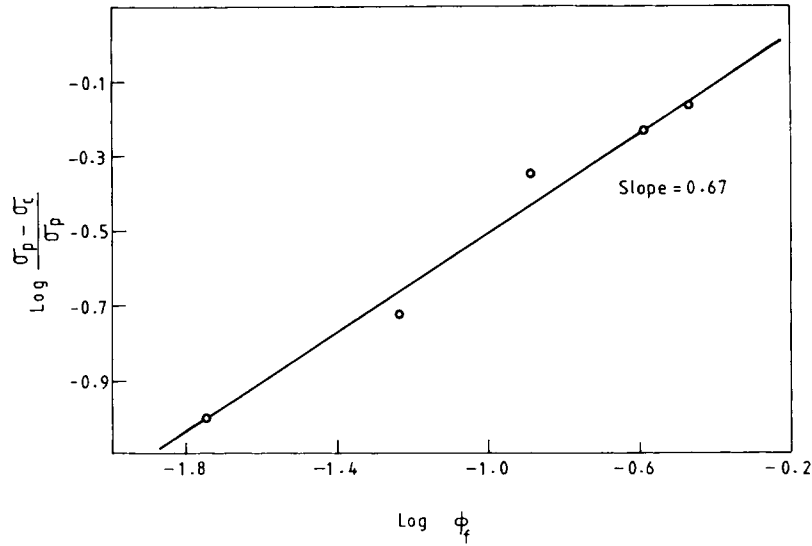


Figure 3 Variation of $\log (\sigma_p - \sigma_c) / \sigma_p$ as a function of $\log \phi_f$.

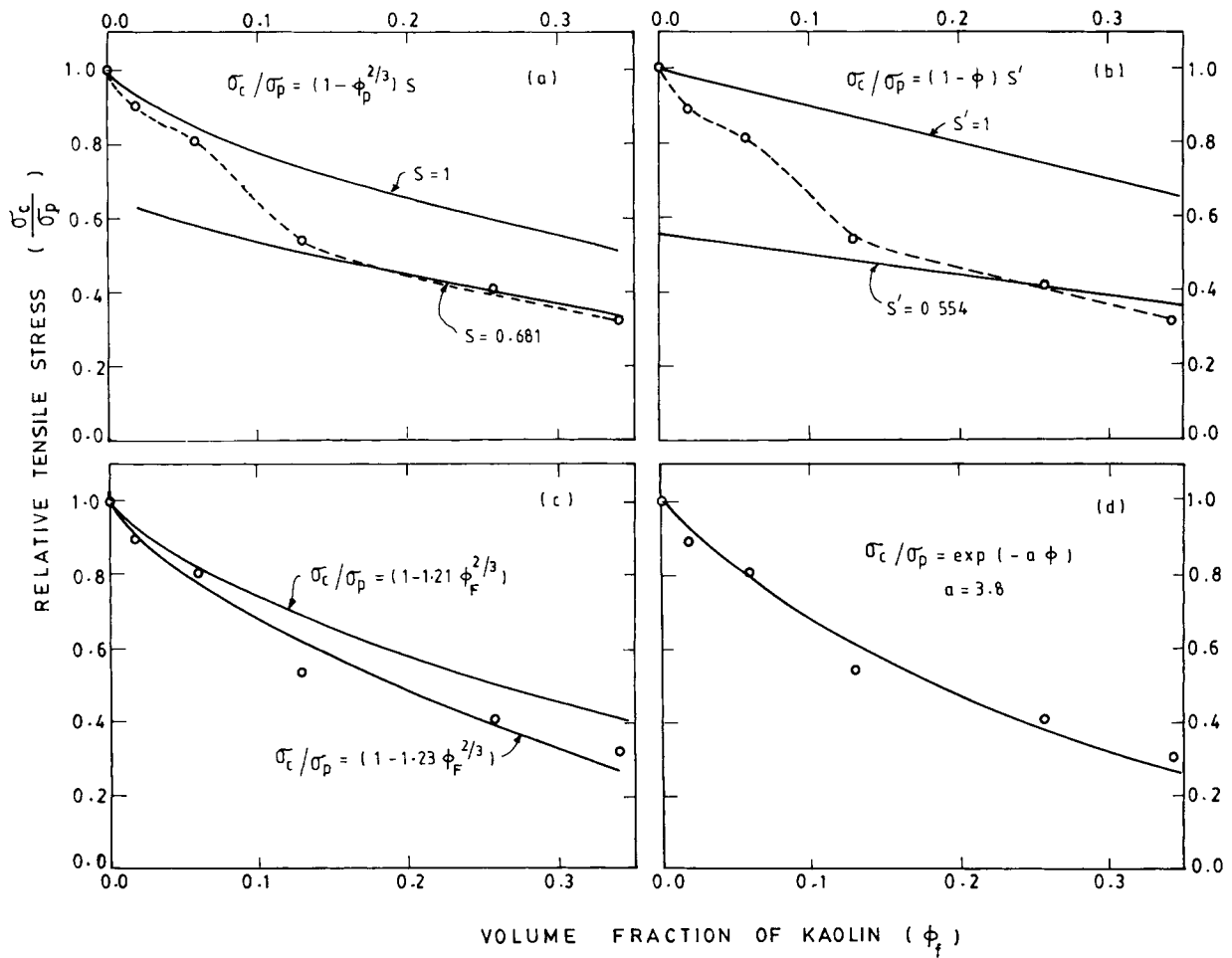


Figure 4 Comparison of experimental data with various theoretical predictions for the composite composition dependence of tensile breaking strength for PP/kaolin composites.

crosshead separation of 5 cm and crosshead speed 20 mm/min. Tensile tests were performed at ambient temperature of 303 ± 2 K.

Impact fractured surfaces of the composites were studied by a Cambridge stereoscan (Model S4-10) electron microscope.

RESULTS AND DISCUSSION

Tensile parameters were estimated from the stress-strain curves and are presented in Figures 1–4 as the plots of the ratio of the property of the composite (subscript *c*) to that of the unfilled *PP* (subscript *p*) vs. volume fraction ϕ_f of the filler.

Figure 1 presents the variation of relative tensile moduli of the composites, E_c/E_p , against filler volume fraction ϕ_f . The elastic modulus increases with increasing filler content. The modulus values were also compared with some of the theoretical predictions in Figure 1. Curve 1 is the plot of the Kerner equation.^{11,12}

$$\frac{E_c}{E_p} = 1 + \frac{15(1 - \gamma_p)}{8 - 10\gamma_p} \frac{\phi_f}{1 - \phi_f} \quad (1)$$

where $\gamma_p = 0.35$ is the Poisson ratio of *PP*. Curve 2 is the plot of the Cohen–Ishai equation¹³ for rigid and spherical fillers:

$$\frac{E_c}{E_p} = 1 + \frac{\phi_f}{1 - \phi_f^{1/3}} \quad (2)$$

The Guth–Smallwood equation¹⁴ for filled polymer composites is shown as curve 3:

$$\frac{E_c}{E_p} = 1 + 2.5\phi_f + 14.1\phi_f^2 \quad (3)$$

Both eqs. (1) and (2) fit reasonably well with the experimental results, while the Guth–Smallwood model, curve 3, showed higher values. These results tend to indicate that incorporation of kaolin increases the rigidity of *PP* through the restriction in the mobility of the polymer molecules.

Relative elongation at break (ϵ_c/ϵ_p) decreases to a significant extent with the increase in kaolin content, as shown in Figure 2, the decrease being quite pronounced at lower filler content (i.e., up to $\phi_f = 0.13$ or 30 wt %) and only marginal thereafter. Nielsen's simple model¹⁵ for relative elongation at break for perfect adhesion [eq. (4)] predicts higher values for ϵ_c/ϵ_p than the experimental results.

$$\frac{\epsilon_c}{\epsilon_p} = 1 - \phi_f^{1/3} \quad (4)$$

From the above results it is apparent that the presence of kaolin particles interferes with stress transfer, in particular in the absence of any specific adhesion between *PP* and kaolin. This interference is due to the generation of discontinuity in the polymer matrix resulting in the early failure of the composites at small deformations. It is well known that for any significant contribution in mechanical and other properties by the dispersed phase in a two-phase composite, two factors of importance are continuity in the structure and/or interfacial adhesion.

The modulus data do not correctly reflect the weakness, if any, in the structure since weakness is a property determined at low solid displacement or low deformations. On the other hand, tensile breaking strength and elongation at break are properties that are estimated at large deformations. These properties, therefore, reflect weakness in the structure more correctly. Some indication of the generation of weak structure was obtained through the observation of the reduction in the breaking elongation upon incorporation of kaolin into *PP*. A more detailed insight into this aspect is attempted in the analyses of the tensile breaking strength data, which follow.

Analysis of Tensile Strength Data

The tensile breaking strength data of the composites were analyzed using some theoretical models in order to understand the generation of discontinuity or weakness in the structure of these two-phase systems. A comprehensive review is available.¹⁶

Based upon the relationship of area fraction to volume fraction of the inclusions,^{17,18} the dependence on composition of the mechanical properties of the two phase composites are commonly expressed by the first power law [eq. (5)] and two-thirds power law [eq. (6)] relationships:

$$\sigma_c/\sigma_p = (1 - \phi_f) \quad (5)$$

$$\sigma_c/\sigma_p = (1 - \phi_f^{2/3}) \quad (6)$$

where σ_c and σ_p denote the given mechanical properties (i.e., tensile strength) of the composite and the matrix, respectively. The weakness in the structure, caused by discontinuity in stress transfer or stress concentration at the narrow portions of the matrix at the interface of the dispersed phase and the matrix, is manifested in the deformation and ultimate failure of the body. This can be accounted for by proper modifications of these power law equations. Nielsen¹⁵ used a parameter *S* [eq. (7)], while Nicolais and Narkis¹⁹ used a weightage factor of 1.21 [eq. (8)] in the two-thirds power law expressions:

Table I Values of Stress Concentration Parameters S [eq. (7)] and S' [eq. (10)]

Composite Composition wt % Kaolin	ϕ_f	S	S'
0	0	—	—
5	0.018	0.966	0.916
15	0.058	0.952	0.859
30	0.129	0.727	0.622
50	0.257	0.693	0.556
60	0.342	0.622	0.483
Mean Value ^a		0.681	0.553

^a Mean taken for the last three values, that is, for composites with kaolin content > 15 wt %.

$$\sigma_c/\sigma_p = (1 - \phi_f)S \quad (7)$$

$$\sigma_c/\sigma_p = (1 - 1.21\phi_f^{2/3}) \quad (8)$$

Both eqs. (7) and (8) describe poor adhesion type structure. The maximum value of the parameter S in eq. (7) is unity for "no stress concentration effect," which is valid for nonfilled polymer. The lower the value of S the greater the stress concentration effect or poorer the adhesion, valid for filled polymer composites or blends. The weightage factor (i.e., the coefficient of $\phi_f^{2/3}$) in eq. (8) is believed to be dependent on the adhesion quality between the matrix and the inclusion.¹⁹ The lower the value the better the adhesion. The value 1.21 of the weightage factor is stated¹⁷ to be valid for the extreme case of poor adhesion with spherical inclusions.

A two parameter expression of the first power law [eq. (9)] was suggested by Piggott and Leidner,¹⁸

$$\sigma_c/\sigma_p = (A - B\phi_f) \quad (9)$$

where the parameter A accounts for the weakening of the structure due to stress concentration effect, and the parameter B accounts for the volume fraction proportionality of the strength. One weakness of eq. (9) is that the parameter A should never have a value other than unity, which represents the non-filled polymer with no inclusion. A modified form of eq. (9) may thus be written as

$$\sigma_c/\sigma_p = (1 - \phi_f)S' \quad (10)$$

where the stress concentration term has been used in a manner analogous to that suggested by Nielsen.¹⁵ Here, S' can assume its maximum value unity for the case of "no stress concentration effect," while any lower value will mean "greater stress concentration effect."

In a poor adhesion type composite, the filler may also be considered analogous to pores or voids²⁰ that

do not have any influential role on the mechanical properties of the composites due to nonadhesion at the interphase boundary. In such a system, the specific change in the tensile strength is directly proportional to the porosity P (or volume fraction ϕ_f of the inclusion) so that

$$-d\sigma/\sigma = a\phi_f \quad (11)$$

where a is the constant of proportionality. This yields, for the two phase polymer-filled system,

$$\sigma_c/\sigma_p = \exp(-a\phi_f) \quad (12)$$

The parameter a is suggested¹⁷ to be related to stress concentration; the higher the stress concentration the higher the value of a .

A plot of $\log[(\sigma_p - \sigma_c)/\sigma_p]$ vs. $\log \phi_f$ from these tensile strength data is presented in Figure 3 to determine the suitability of first power or two-thirds power law to the *PP*/kaolin system. From the slope of this curve, the value of the power law exponent can be determined according to eqs. (5) and (6). It may be noted that the slope corresponded with the two-thirds power law (the value being 0.67) over the entire range of filler volume concentrations. Some authors have reported better applicability of the first power law than the fractional power laws in the analysis of the strength²¹ and yield stress^{22,23} of composites. Other workers have observed the suitability of the fractional power law in filled polymer composites.^{7,24,25} The difference in the suitability of power-law models in these examples may be attributed, at least in part, to the variation in the degree of dispersion of the filler phase in the polymer matrix. In *PP*/kaolin composites, the applicability of the fractional power-law model indicates a dependence of the tensile strength on the area fraction of the filler phase, which governs the interaction or adhesion parameters between the two phases. The present analysis may, however, be further modified by the consideration of the stress concentration parameters described in eqs. (7)–(11).

By using suitable values of S or S' (Table I) at each individual composite composition, some degree of agreement can be achieved between the tensile strength data and both the first power and the fractional power law models [eqs. (7)–(12)]. The values of stress concentrations are all less than unity, indicating the significant extent of stress concentration that causes discontinuity in the structure of the composites.

Figure 4 compares experimental data to the theoretical expressions for tensile stress. Nielsen's model [eq. (7)] in Figure 4(a) exhibited good agreement

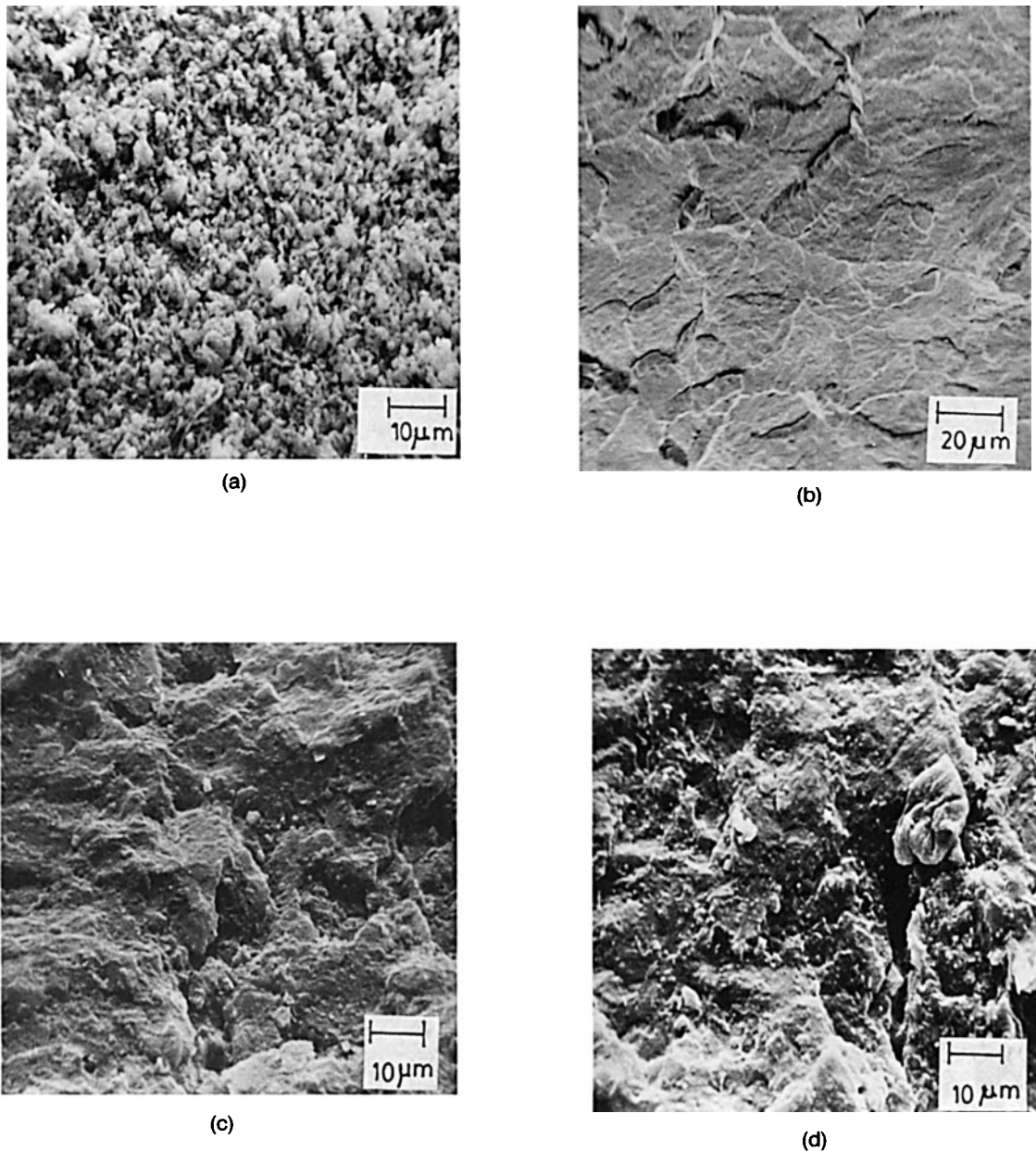


Figure 5 Scanning Electron Micrographs of kaolin particles (a) and fractured surfaces of PP/kaolin composites of varying composition (wt % kaolin): (b) 0, (c) 5, (d) 15, (e) 30, (f) 50, (g) 60.

at higher volume fraction fillers ($\phi_f > 0.06$), with the S value 0.681, which is the mean of the composites with more than 15 wt % kaolin (Table I). At lower filler concentrations the experimental data were lower than, but close to, the theoretical curve, with $S = 1$. This indicates that the system changes over from the state of “lower stress concentration effect” to a system of significant stress concentration effect” upon the increase in the kaolin concentration beyond 15 wt %.

With the first power law expression [eq. (10)], the data beyond 15 wt % filler also shows a close fit

with the theoretical curve [Fig. 4(b)], with S' values of 0.554, which is the mean of the values with more than 15 wt % kaolin (Table I). Comparison of the data at lower ϕ_f , with the theoretical curve $S' = 1$ meaning no stress concentration, gives S' values close to 1, implying that according to this model also the system changes from the state of low “stress concentration effect” to “appreciable stress concentration effect” beyond a kaolin content of 15 wt %.

The expression of Nicolais and Narkis [eq. (8)] predicts marginally higher tensile strength values than the experimental data [Fig. 4(c)]. It is further

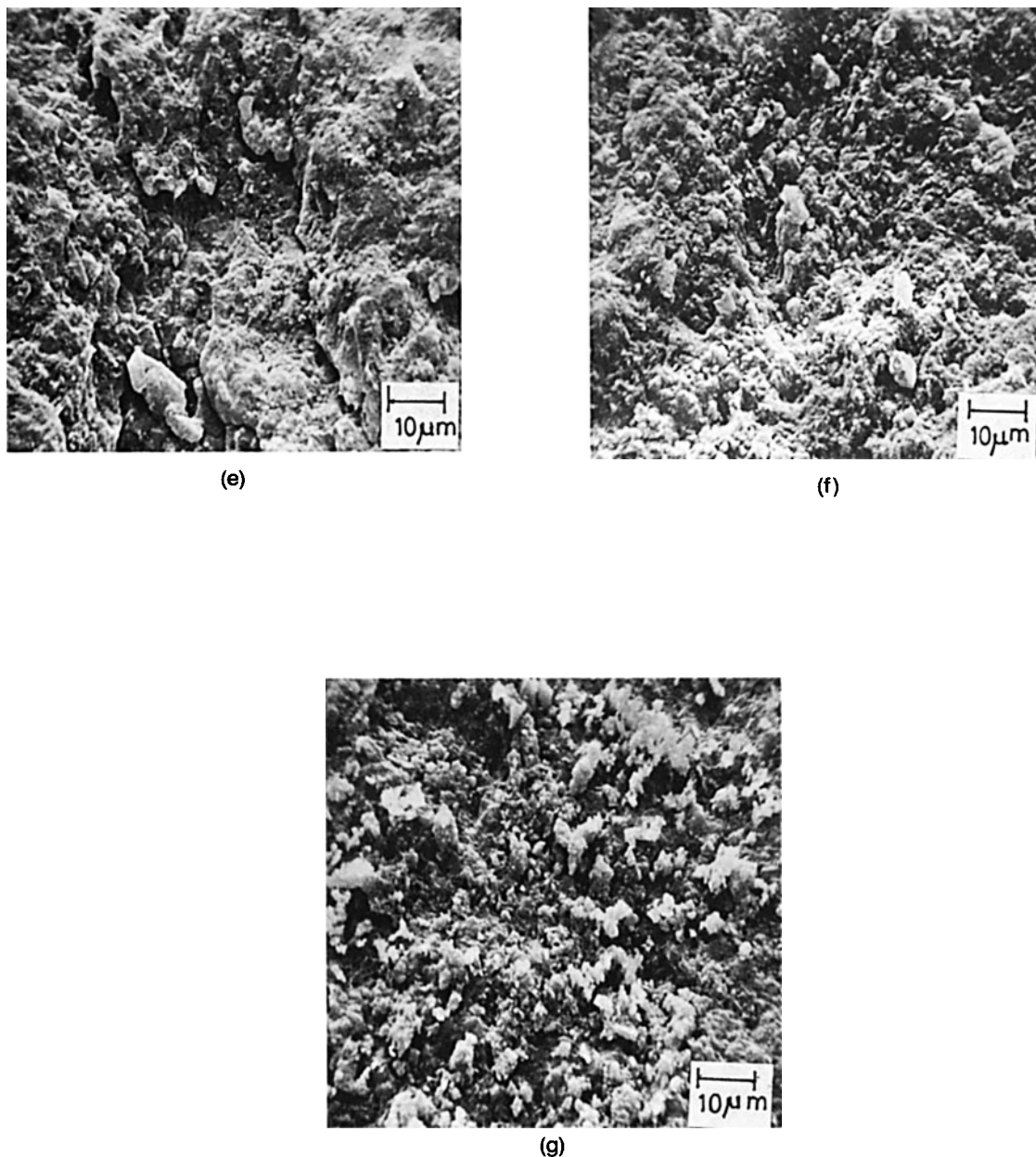


Figure 5 (continued from the previous page)

noted that a slight adjustment in the value of the coefficient of the term $\phi_f^{2/3}$ (i.e., using 1.23 in place of 1.21) gives a closer fit to the experimental data. This may be attributed to the slight deviation of the system from two-thirds power law, or to the non-spherical shape of the kaolin particles, or both.

Finally, the experimental data showed close agreement with the curve of porosity model [eq. (11), Fig. 4(d)], with the value of the parameter $a = 3.8$. The agreement was close over the entire range of kaolin concentration studied. It has already been mentioned that the higher the value of a , the greater the extent of stress concentration. Similar results

were reported by Gupta and Purwar¹⁶ in the study of *PP* based blends.

Thus, the analysis of tensile stress data using these models showed the occurrence of significant stress concentration in the structure due to the incorporation of kaolin filler into *PP*.

Fracture Surface Morphology

Scanning electron micrographs of the impact fractured surfaces of the composites are shown in Figure 5. These micrographs indicate a degree of roughness as compared to nonfilled *PP*, the roughness in-

creasing with an increase in kaolin content, in particular beyond 15 wt % kaolin. At these high filler loadings the filler particles are almost bare with very little polymer adhering to these particles. The distribution of kaolin particles is quite random throughout the matrix. Some filler agglomerates are also found in the micrographs. While kaolin particles are platelets of an average size of 2–3 μm , these agglomerates are, on the average, double the primary particles having sizes of 5–6 μm . It is therefore quite possible that kaolin particles and agglomerates with sharp corners are points of stress concentration causing discontinuity in the structure. These SEM studies, therefore, support the observation on the basis of stress concentration parameters S or S' [eqs. (7) and (10)] of the transition from low stress concentration effect (i.e., continuous structure) to high stress concentration effect (i.e., discontinuous or weak structure). At lower kaolin content the number of bare kaolin particles with sharp boundaries are small so that the system showed lower stress concentration. On the other hand, at kaolin content, more than 15 wt % the number of nonadherent bare kaolin particles with sharp corners are large, which may cause significant stress concentration effect. Greater stress concentration in the presence of larger size inclusions were reported by various authors.^{16–18,21} These authors also observed lower stress concentration for rounded or spherical inclusions than the inclusions of irregular shapes or with sharp corners.

CONCLUSIONS

Incorporation of kaolin particles increases the tensile modulus and reduces the tensile strength and elongation-at-break of *PP*. The modulus increase curve showed good agreement with the Kerner and Cohen–Ishai models, while elongation values were lower than Nielsen's prediction curve. Tensile strength decrease curve showed good fit with the porosity model, and upon adjustment of parameter, with Nicolais–Narkis model. The models with stress concentration terms did not describe the data satisfactorily over the whole range of filler concentration studied.

The system undergoes a transition from state of zero or low stress concentration effect (continuous structure) to a state of significant stress concentration effect (discontinuous structure). The stress concentration effect is increased with the increase

in the number of nonadherent kaolin particles with sharp boundaries.

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