Rheological Properties of Calcium Silicate-Filled Isotactic Polypropylene

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ABSTRACT: The melt rheological behavior of calcium silicate-filled isotactic polypropylene, with filler volume contents of 0–17.8%, was determined at 493 K. The composites followed the power law in shear stress versus shear rate variations and were shear thinning. Initially, apparent melt viscosity decreased until a critical filler volume content of 8.5% was reached. However, on further increase in calcium silicate concentration, apparent melt viscosity increased. Melt elasticity also showed an initial decrease until 8.5% filler content was reached and then an increase beyond this filler content. Surface treatment of calcium silicate with a titanate coupling agent, LICA 38, modified the rheological properties because of the plasticizing/lubricating effect of LICA 38. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1511–1518, 2003

Key words: shear; composites; melt; viscosity

INTRODUCTION

Fillers and reinforcements have always played an important role in the modification of polymers to make the polymers suitable for a wide variety of end uses.[1–7] They afford a means of extending the available volume of polymers while improving many properties, which results in associated economic advantages, such as lower material cost, faster molding cycles arising out of increased thermal conductivity, fewer rejects due to warpage, etc. The full advantage of fillers is realized when their surfaces are modified with a suitable coupling agent.[2–8] Surface-treated fillers offer compounding and processing facilities by enhancing dispersion and in many cases decreasing melt viscosity. Boaira et al.[9] reported a decrease in melt viscosity of mica-filled polypropylene (PP) with increasing shear rate, and a significant reduction in viscosity of surface-treated mica. Han et al.,[10] in a study on the effect of various coupling agents on rheological properties and processibility of highly filled PP, showed that the effect on melt viscosity of filled systems is a function of the polymer–inclusion combination. In calcium carbonate/PP composites, the viscosity increased with filler concentration and the composites followed power law relations.[11]

Results of rheological studies on calcium silicate-filled isotactic polypropylene (i-PP) composites are reported. A piston-type capillary rheometer was used to generate rheological data (e.g., shear stress, shear rate, apparent melt viscosity, and melt elasticity) at calcium silicate ($CaSiO_3$) concentrations of 0–17.8 vol % and at 493 K. The effect of a titanate coupling agent (LICA 38, used for surface modification of the filler) on rheological parameters was also examined.

EXPERIMENTAL

Materials

Isotactic polypropylene (i-PP; Koylene M0030) of specific gravity 0.90 and melt flow index (MFI) 10 was obtained from M/s Indian Petrochemicals Corporation Ltd., Gujarat, India, and used as received. A commercial grade of calcium silicate ($CaSiO_3$), with density of 2.90 g cm^{-3} and average particle diameter of 10 μm, was supplied by M/s Burogoynne Bridges, Mumbai, India and was used as the filler. LICA 38, a liquid neoalkoxy organotitanate coupling agent supplied by M/s Kenrich Petrochemicals Ltd., Bayonne, NJ, was employed to surface treat the calcium silicate. The chemical formula of LICA 38 [neopentyl(diallyl)oxy,tri(dioctyl)pyrophosphato titanate] is shown in Scheme 1.[8]

Treatment of CaSiO₃ surface

LICA 38 (0.2 g, corresponding to 0.4 wt % on the basis of filler[8]) was dissolved in 10 mL of toluene. This solution was then mixed with 50 g of $CaSiO_3$ in a laboratory mixer (Sumeet, Model - 2L) at 3000 rpm for 30 min. The treated $CaSiO_3$ was then dried in an air oven at 383 K for ~5 h to expel toluene, and finally

CH₂=CH-CH₂-O-CH₂   O   O

CH₃-CH₂-C - CH₂-O-Ti - [O - P - O - P (OC₈H₁₇)₂]₃

CH₂=CH-CH₂-O-CH₂   OH
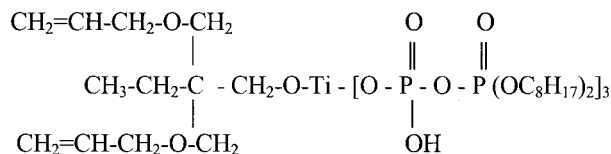
Scheme 1

stored in a sealed container. A similar procedure for filler surface treatment has been used in other works.[6,12–14]

The hydrophobicity of treated $CaSiO_3$ was measured qualitatively by the filler desorption test. When dropped on water in a beaker, the untreated $CaSiO_3$ remained as lumps and sank immediately to the bottom, whereas the treated powders spread on the water surface. This result showed that the surface of calcium silicate had been coated by the coupling agent.[15]

Mixing of ingredients

Calcium silicate (both unmodified and modified) was first vacuum dried and then compounded with i-PP at 438 ± 2 K on a two-roll mill (Richardson and Cruddas Ltd., Model - 218) for 10 min to prepare thin primary sheets containing $CaSiO_3$ at 0–17.8 vol % (ϕ_F %) or 0–70 phr. Filler concentration is expressed in volume % (ϕ_F %) and calculated from the ratio of the mass of the particle to that of the composite and densities of the components. Because the mixing was done on a tow-roll mill, no filler was assumed lost during compounding. The milled sheets were cut into squares, ~0.5 cm in size, which were fed into the rheometer for generation of data.

Rheological studies

Rheological measurements were performed on a Rheograph-2001 (Göttfert, Germany) of cylindrical die with a diameter of 1 mm and a length/diameter (L/D) ratio of 30 at 493 K. The initial melting time of polymer was 2 min, and the comparison interval was 8 s. The instrument was set at constant speed/shear rate mode with eight piston speeds in the range 0.04–2.4 mm s⁻¹, which correspond to the shear rate range 40–6000 s⁻¹. Rheological parameters, apparent melt viscosity and melt elasticity, were calculated with the RABKOR program (version 9.6) in accordance with the instrument manual.[16,17]

RESULTS AND DISCUSSION

Shear stress–shear rate curves

The shear stress–shear rate dependence was determined at a constant temperature of 493 K and varying pressures. The apparent shear rates, γ_{app}, were estimated according to eq. 1:[18]

$$\gamma_{app} = \frac{4Q}{\pi R^3} \, (s^{-1}) \tag{1}$$

where R is the radius of the capillary die (cm) and Q is the volumetric flow rate (cm³/s). The volumetric flow rate Q is given by

$$Q = \frac{AS}{t} = AV \, (cm^3 \, s^{-1}) \tag{2}$$

where V is the piston speed (cm/s), A is the piston-free area (cm²), t is the time(s), and S is the piston path (cm). From the γ_{app} values, the wall shear rate values, γ_w, were calculated by applying the Rabinowitsch–Weissenberg correction:[19,20]

$$\gamma_w = \frac{3n' + 1}{4n'} \gamma_{app} \, (s^{-1}) \tag{3}$$

where n' is the flow behavior index obtained as the slope of log τ_w–log γ_{app} plots (not shown).

The apparent shear stress was calculated according to eq. 4:[16]

$$\tau_{w(app)} = \frac{PD}{4L} \times 30 \, (Pa) \tag{4}$$

where P is the pressure applied on the piston, L is the capillary length (cm), and D is the capillary diameter (cm). The wall shear stress τ_w was estimated by applying the Ryder–Bagley correction:[18,19]

$$\tau_w = \frac{P}{2(L/R + e)} \, (Pa) \tag{5}$$

where e is the negative of the slope of the P versus L/R plot in a range of shear rates.

The apparent melt viscosity (η_{app}) values were determined from the shear stress and shear rate data as follows:[19,20]

$$\eta_{app} = \frac{\tau_w}{\gamma_w} \, (Pa \cdot s) \tag{6}$$

Variations of log τ_W with log γ_w in i-PP/CaSiO₃ and i-PP/CaSiO₃/LICA 38 composites at 493 K are shown in Figures 1 and 2, respectively. The plots are linear in the shear rate range studied (40–6000 s⁻¹), which implies that the melts obeyed power law behavior like other filled i-PP systems.[4,21,22] The flow curve moved downward compared with i-PP content until ϕ_F reached 8.5% in both systems. Thus, the system showed lower shear stress at low contents of $CaSiO_3$, up to 8.5 vol %, and at a constant shear rate. In contrast, at higher contents of $CaSiO_3$, the composites
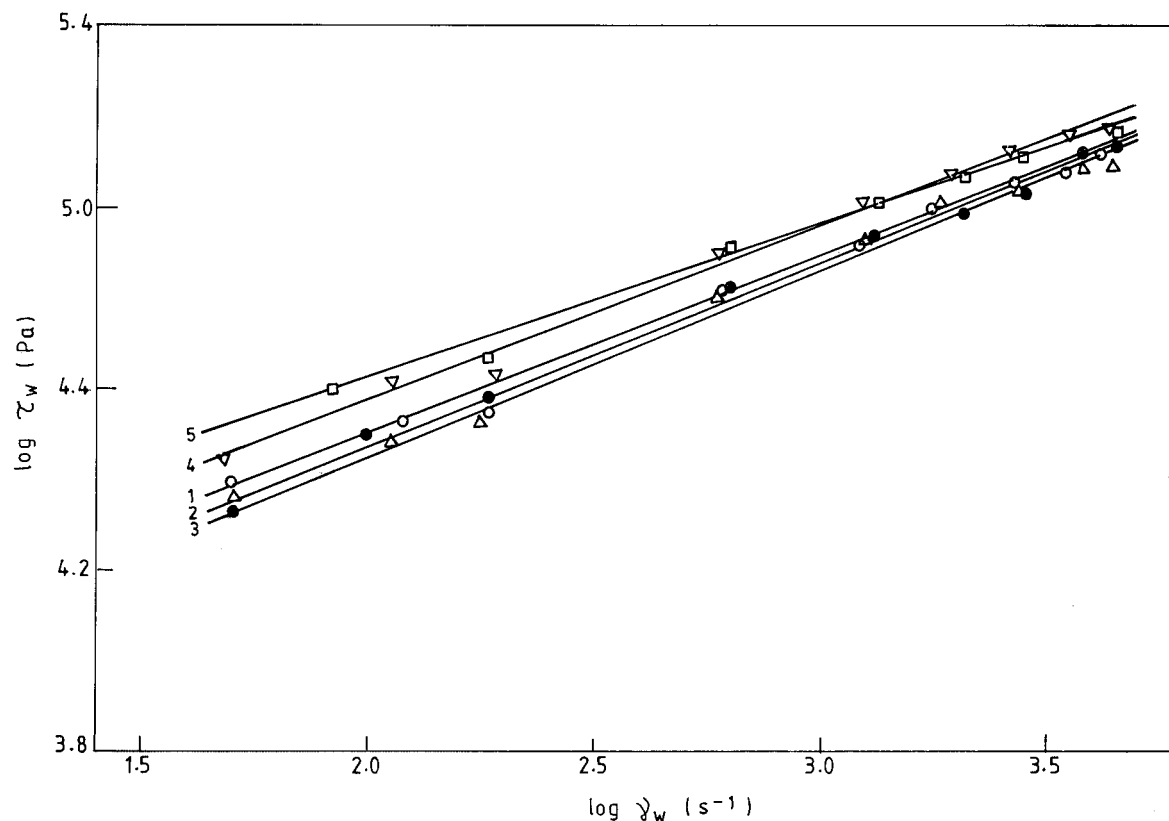
Figure 1 Plots of log shear stress (τ_w) versus log shear rate (γ_W) of i-PP/CaSiO$_3$ composites at 493 K: (○) i-PP; (△) i-PP/CaSiO$_3$, 4.4%; (●) i-PP/CaSiO$_3$, 8.5%; (▽) i-PP/CaSiO$_3$, 13.4%; (□) i-PP/CaSiO$_3$, 17.4%.

registered higher shear stresses. Han reported an increase in shear stress with CaCO$_3$ content at a fixed rate of shear in i-PP/CaCO$_3$ composites.[4] Similar results were also observed in i-PP/WF systems.[21] On the other hand, in kaolin-filled i-PP composites, the shear stress at first decreased with an increase in ϕ_F and, with further increase in the filler content, the shear stress increased again.[22] A flow-favoring orientation of platy CaSiO$_3$ seems to lower the shear stress at low ϕ_F in these CaSiO$_3$-filled composites, which is similar to the behavior noted in i-PP/kaolin composites.[22]

Power law flow indices (n) of the power law relation shown in eq. 7 were determined from the slopes of the linear variations of log τ_w–log γ_w (Table I):

$$\tau_w = K\gamma_w^n \qquad (7)$$

The n values were all less than unity, indicating the pseudoplastic nature of these composite melts that is common to thermoplastic composites/blend systems.[21–23] The values of n increased with ϕ_F up to 8.5%, indicating a decrease in pseudoplasticity. In contrast, beyond this ϕ_F, the value of n either remained the same or decreased to varying extents depending on the system.

Polymer composites containing very fine particles (viz. particle diameter of <0.5 μm) exhibit yield stress at low γ_w values of 10^{-2}–10^0 s^{-1} due to strong interparticulate interactions.[24–27] However, in the i-PP/CaSiO$_3$ systems, no such yield stress was observed. Although particle interaction in these flake-type silicate materials is a possibility, the absence of yield stress may be due to the high range of γ_w values (40–6000 s^{-1}) employed for the rheological measurements. In other filled polymer systems, yield stresses were not reported.[4,21,28,29]

Apparent melt viscosity (η_{app})

Variations of apparent melt viscosity (η_{app}) versus γ_W in the i-PP/CaSiO$_3$ and i-PP/CaSiO$_3$/LICA 38 composites are presented in Figures 3 and 4. The η_{app} values in these systems are of similar order to those of i-PP composites[21,22,30] and lower than those of other similar composites[4,10] of i-PP by ~1 order of magnitude. These results may be because of the different grades of i-PP employed for the studies cited.

The apparent viscosity decreased quite sharply with increasing γ_W in both i-PP/CaSiO$_3$ and i-PP/CaSiO$_3$/LICA 38 composites (see Figures 3 and 4). This result implies a shear-thinning behavior of the composites like that seen with nonfilled i-PP. At a constant value of γ_W, the η_{app} decreased until ϕ_F reached 8.5%, and then increased with further increases in ϕ_F. The η_{app}

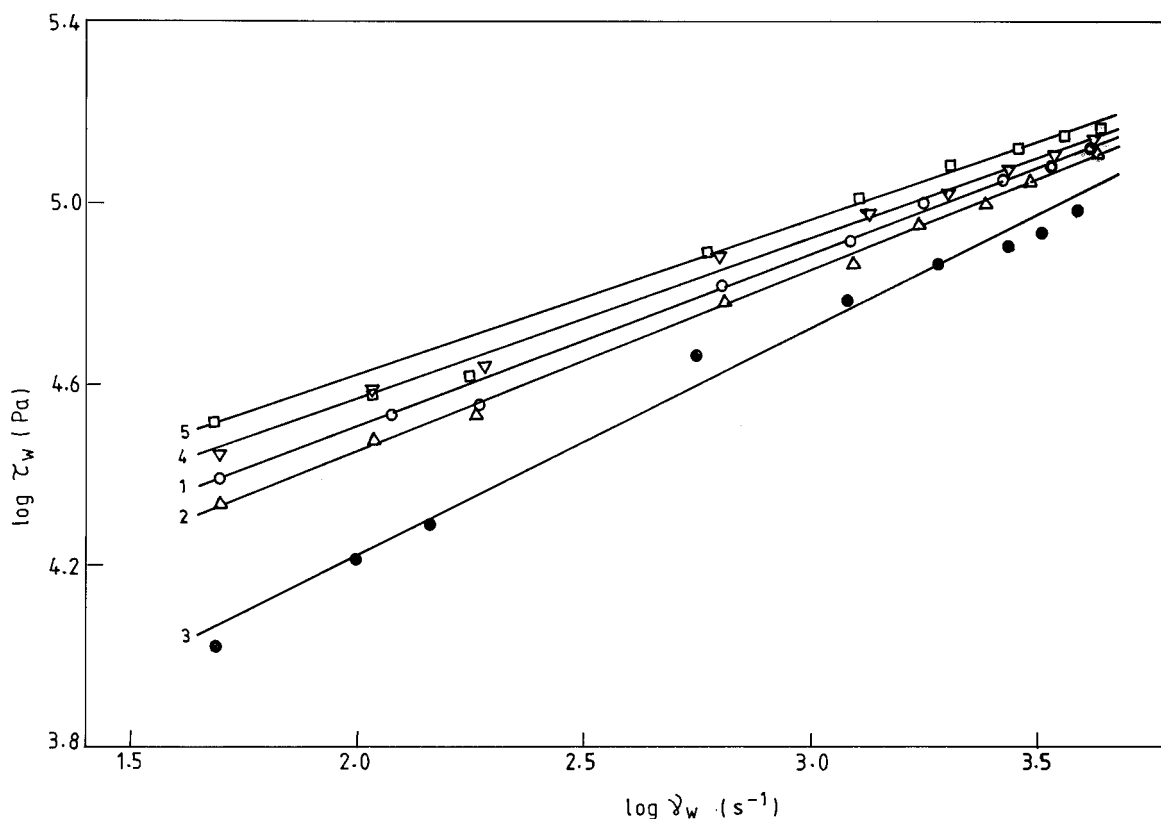**Figure 2**   Log τ_w–log γ_W variations in i-PP/CaSiO$_3$/LICA 38 composites at 493 K. Key to symbols is given in Figure 1.

versus γ_W plots exhibited a converging trend at higher γ_W values. However, at values of $\gamma_W > 5000$ s^{-1}, the effects of CaSiO$_3$ and/or LICA 38 on shear viscosity of i-PP decreased significantly, which is similar to results reported in the literature.[21,22]

Variation in the η_{app} of i-PP/CaSiO$_3$ composites versus ϕ_F at a fixed γ_W value of 631 s^{-1} and at 493 K are presented in Figure 5. The viscosity showed an initial decrease to a minimum at ϕ_F of 8.5%. This decrease is 14% compared with that of i-PP. With further increases in ϕ_F, the value of η_{app} increased by ~16–19% depending on the value of ϕ_F. Calcium silicate particles were acicular, with substantial particle–particle interactions through surface groups, which makes the polymer melt thixotropic.[15,31] It seems that at ϕ_F values up to 8.5%, the particle–particle network

was ruptured by shear forces, disposing the flaky particles in a flow-favoring orientation and thereby decreasing the melt viscosity. With a further increase in ϕ_F, the network formation was restored, at least in part, which created discontinuity in the process of increasing the melt viscosity. Thus, particle orientation predominates at low ϕ_F values (up to 8.5%), whereas a particle network assumes dominance at higher particle concentrations.[9]

With surface treatment of CaSiO$_3$, the η_{app} versus γ_W plot exhibited a similar pattern to that of the i-PP/CaSiO$_3$ system. However, the η_{app} data were lower than those for the corresponding untreated filler contents (Figure 5). At $\phi_F = 8.5\%$, the minimum was more pronounced. It has been observed, in studies of the solid-state properties of i-PP/CaSiO$_3$/LICA 38 composites, that LICA 38 smoothens the particle surfaces, and its long alkyl moiety exhibits a plasticizing/lubricating type of function[15] similar to that noted in studies of other composites.[6,10,32] It appears that this plasticizing/lubricating function is also operative under the melt flow conditions that decrease the η_{app} values to a certain extent.

Melt elasticity

Because of the viscoelasticity of the polymeric materials, melt elasticity is manifested in terms of normal

TABLE I
Power Law Index (n) Data of i-PP/CaSiO$_3$ and
i-PP/CaSiO$_3$/LICA 38 Composites

	Values of n	
Vol %	i-PP/CaSiO$_3$	i-PP/CaSiO$_3$/LICA 38
0	0.39	0.39
4.4	0.41	0.40
8.5	0.42	0.49
13.4	0.39	0.36
17.8	0.34	0.35
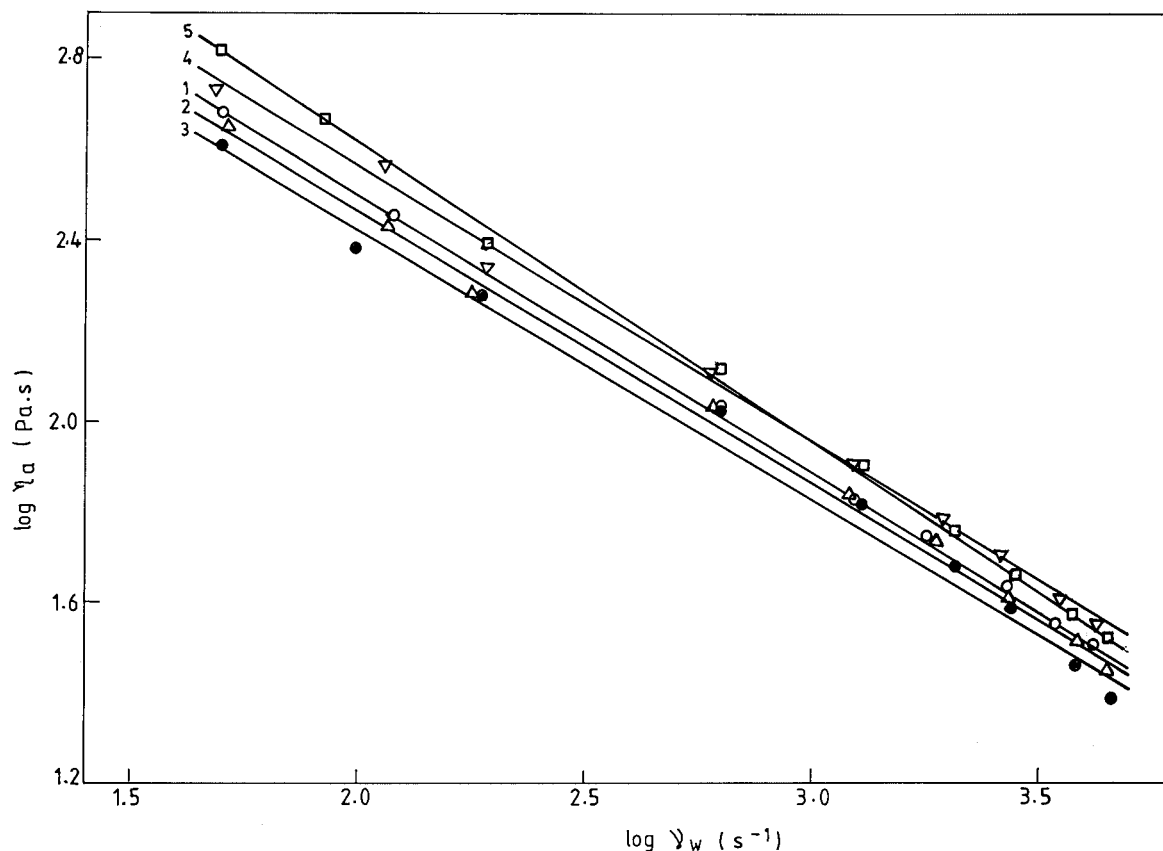
Figure 3 Variations of log η_{app} (apparent melt viscosity) versus log γ_W in i-PP/CaSiO₃ composites at 493 K. Key to symbols is given in Figure 1.

stresses. First normal stress difference $(\tau_{11} - \tau_{22})$ in these systems is calculated from a mirror relationship between normal stress coefficient and viscosity.[16,17] It has been reported that a mirror relationship exists between (i) viscosity function $\eta(\gamma_w)$ and stress viscosity $\eta_0(t)$, and (ii) steady normal stress coefficient $\theta(\gamma_w)$ at a shear rate γ_w and normal stress coefficient θ_0 at small shear rates at a time t, if γ_w is equal to a constant k divided by the time t.[16,17] These mirror relationships for a viscoelastic fluid are shown in eq. 8 for the viscosity function and eqs. 9 and 10 for the normal stress coefficient:

$$\eta(\gamma_w = 1/t) = \eta_0(t) \tag{8}$$

$$\theta(\gamma_w) = (\tau_{11} - \tau_{22})(\gamma_w)/\gamma_w{}^2 \tag{9}$$

$$\theta(\gamma_w = k/t) = \theta_0(t) \; 2 \leq k \leq 3 \tag{10}$$

The normal stress coefficient $\theta(\gamma_w)$ can be calculated with the viscosity function $\eta(t)$ with eq. 11:

$$\theta(\gamma_w) = 2\sum_i(\eta_i/\gamma_{wi})[1 - (1$$

$$+ k\,\gamma_{wi}/\gamma_w)\exp(-k\gamma_{wi}/\gamma_w)] \tag{11}$$

In turn, $\tau_{11} - \tau_{22}$ can be estimated using eq. 9.[16,17]

Melt elasticity parameters $\tau_{11} - \tau_{22}$ were plotted as function of shear rate for the various ϕ_F (%) values (curves not furnished). At a constant shear rate of 631 s⁻¹ and 493 K, the variations of $\tau_{11} - \tau_{22}$ data were plotted against ϕ_F (%) in Figure 6. The $\tau_{11} - \tau_{22}$ data were of the similar order as those for some i-PP composites[4,30] and ~1 order of magnitude lower than those of other i-PP systems.[21,22] In the i-PP/CaSiO₃ systems, the melt elasticity showed an initial decrease to a minimum at $\phi_F = 8.5\%$, with the total decrease being ~5–60%, depending on ϕ_F, compared with i-PP. It was noted in the previous section that reason for the apparent initial melt viscosity decrease (until ϕ_F reaches 8.5%) was possibly the break down of particle networks and a flow-favorable orientation of the flaky CaSiO₃ particles. It may be possible that this orientation is disturbed immediately after the melt emerges from the die and the particles are quickly disoriented, thereby restricting the elastic energy recovery of the melt that decreases the elasticity. On further increase in ϕ_F, the elasticity increased by 44–47% compared with i-PP. At these ϕ_F values, particle networks may be formed again and the polymer may be squeezed out
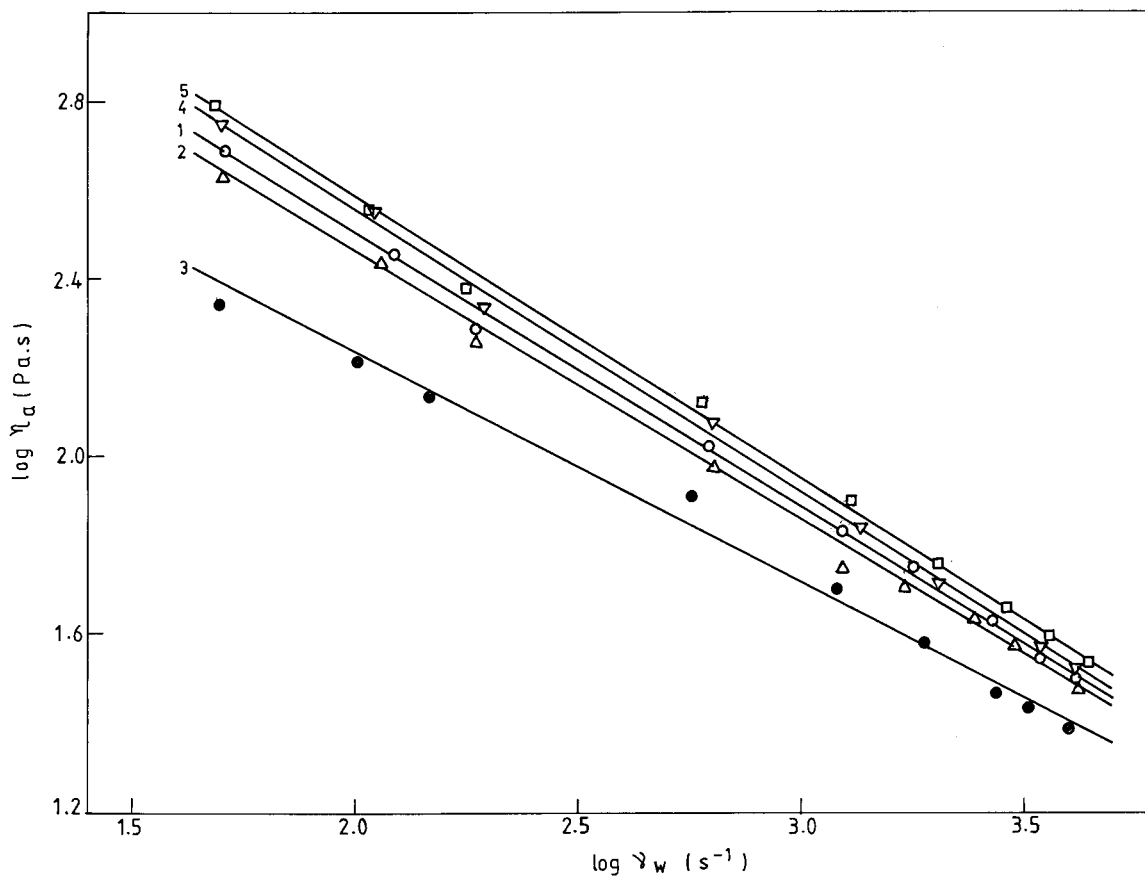
Figure 4 Log η_{app} plots in i-pp/CaSiO$_3$/LICA 38 composites at 493 K. Key to symbols is given in Figure 1.

onto the surface. These conditions would partially restore matrix continuity after the melt emerges from the die, so elastic energy recovery would be facilitated. This recovery would, in turn, increase the melt elasticity. Such behavior was observed for i-PP/WF composites also.[30]
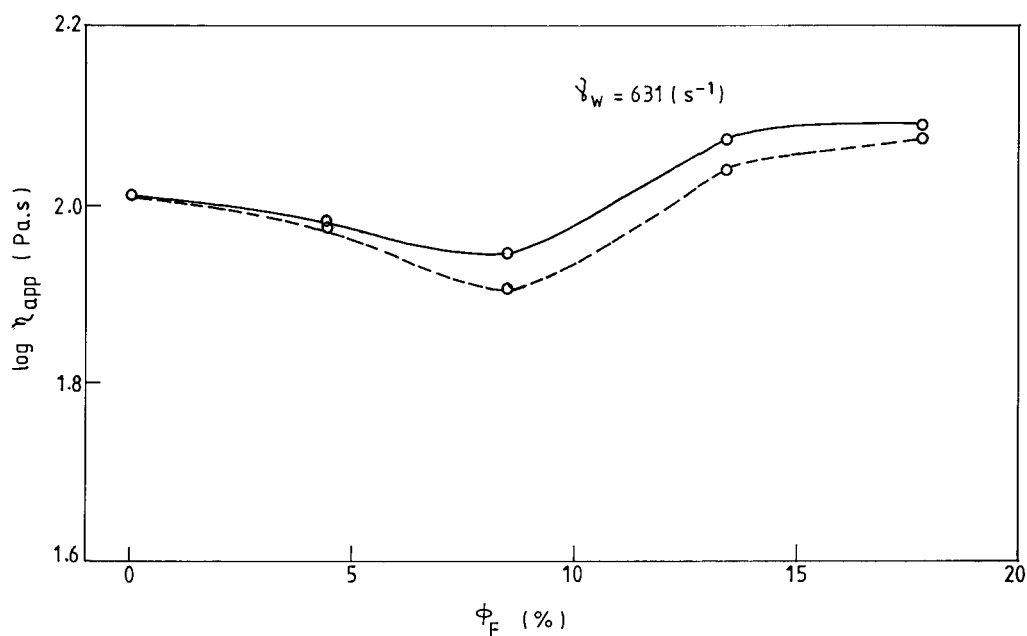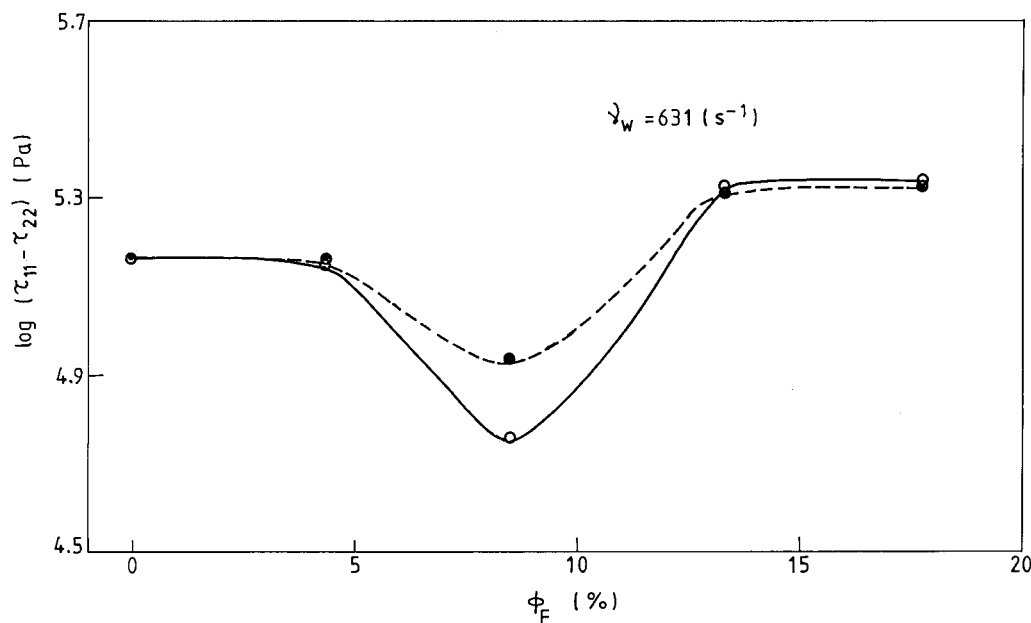

Figure 5 Plot of log η_{app} versus ϕ_F (%) at 493 K at a fixed γ_W value of 631 s^{-1} in (○) i-PP/CaSiO$_3$ and (●) i-PP/CaSiO$_3$/LICA 38 composites.

Figure 6 Log ($\tau_{11} - \tau_{22}$) versus ϕ_F (%) plotted at 493 K at a constant γ_W value of 631 s^{-1} in (○) i-PP/CaSiO$_3$ and (●) i-PP/CaSiO$_3$/LICA 38 composites.

In the presence of LICA 38, a quite similar melt elasticity variation was observed. Up to ϕ_F of 8.5% the data decreased by ~2–41%, showing a minimum at ϕ_F = 8.5%. The data were, however, slightly higher than those in the previous composites, possibly because of a lubricating/plasticizing function of LICA 38 that allows a marginal increase or recovery of elastic energy. At ϕ_F > 8.5% the melt elasticity increased again by 38–41%, compared with i-PP, due to squeezing out of i-PP onto the surface and sequential ease of elastic recovery. At these filler concentrations, the lubricating/plasticizing effect of the coupling agent does not seem to be apparent, the data being marginally lower than those at corresponding ϕ_F values in i-PP/CaSiO$_3$ systems. However, some of the surface groups are probably blocked by LICA 38, so that particle–particle interaction is marginally lowered, which in turn decreases the elastic energy recovery compared with i-PP/CaSiO$_3$ composites.

CONCLUSIONS

i-PP/CaSiO$_3$ composites exhibited power law behavior in shear stress–shear rate variations in the shear rate range 40–6000 s^{-1} at CaSiO$_3$ contents of 0–17.8 vol % and at 493 K. The power law indices varied in the range 0.38 ± 0.04, implying a shear-thinning characteristic of the melt. Apparent melt viscosity showed an initial decrease until ϕ_F reached 8.5% due to orientation of acicular CaSiO$_3$ particles in a flow-favoring direction, which was subsequent to the rupture of particle–particle network in the presence of shearing stresses. At ϕ_F > 8.5 vol %, the viscosity increased as

a result of obstruction to melt flow by the reformation of the particle network. Initially, the normal stress difference decreased until a CaSiO$_3$ content of 8.5 vol % was reached because of quick disposal of flaky filler particles in a flow-restrictive orientation as the melt emerged from the die, which decreased the elastic energy recovery. However, at ϕ_F > 8.5 %, the elasticity increased because of the squeezing out of the polymer towards the surface, which restored matrix continuity, at least in part, and facilitated elastic recovery.

Quite similar rheological behavior was shown by i-PP/CaSiO$_3$/LICA 38 composites. Power law behavior was exhibited, with n values of 0.42 ± 0.07. Dependence of η_{app} and $\tau_{11} - \tau_{22}$ on ϕ_F was similar to that of i-PP/CaSiO$_3$ composites. However, the titanate coupling agent modified these data by its lubricating/plasticizing effect and/or by blocking the surface groups of CaSiO$_3$.

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