MELT RHEOLOGICAL PROPERTIES OF TALC-FILLED ISOTACTIC POLYPROPYLENE COMPOSITES

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The melt rheological properties of talc-filled isotactic polypropylene have been studied at talc concentrations of 0−33.3 vol% and at 493 K. The composites followed a power law model in the shear stress−shear rate dependence and were shear thinning. The apparent melt viscosity increased whereas the melt elasticity parameter "first normal stress difference" decreased as the talc concentration increased. Surface modification of the talc by a coupling agent LICA 38 modified the rheological properties through bonding and/or a plasticizing/lubricating effect.

INTRODUCTION

Fillers and reinforcements constitute the bulk of the additives incorporated into polymers to modify their physical and mechanical properties, which find a wide spectrum off end use applications [1−6]. The properties that are reported to be enhanced are modulus, hardness, flexural strength, dimensional stability, heat distortion temperature, and the like, while trade offs in elongation, impact strength, etc., are achieved within tolerable limits. Lower material costs, accelerated

fabrication cycle, decreased rejects, and lesser molding shrinkage are also the advantages associated with the art of the filled polymer technology.

The interphase of these filled polymer systems plays a decisive role in modifying the composite properties [7−8]. Surface modified fillers ease the compounding and processing mainly by excluding the air gap and a sequential improvement in the wetting between the phases. The melt viscosity may increase or decrease depending on the filler shape and content whereas the melt elasticity parameter, "first normal stress difference" decreases with increase in the shear rate [1, 9−12]. This parameter could also decrease or increase depending on the shear rate and the filler-polymer interaction. In the isotactic polypropylene (i-PP)/CaCO$_3$ composites the melt viscosity increased with CaCO$_3$ content whereas the composites shear stress *vs*. shear rate dependence obeyed a power law behavior [1].

In this article the melt rheological properties of talc filled i-PP are reported. A piston-type capillary rheometer was used to generate the rheological parameters such as shear stress, shear rate, apparent melt viscosity, and the melt elasticity at talc concentrations of 0−33.3 vol% at 493 K. The effects of surface modification of the talc, with a titanate coupling agent LICA 38, on the rheological properties have also been examined.

EXPERIMENTAL

Materials

The isotactic polypropylene (i-PP) Koylene M0030 (MFI 10, density 0.9 gcm^{-3}), used in the work was obtained from M/S Indian Petrochemicals Corporation Ltd., Gujarat, India. A commercial grade talc (density 2.70 gcm^{-3}, average particle dia 0.43 μm) was obtained from local market. The titanate coupling agent employed for surface modification of the talc was neopentyl (diallyl) oxy, tri (dioctyl) pyrophosphato titanate, LICA 38 [7], obtained from M/S Kenrich Petrochemicals Inc., Bayonne, New Jersey, USA.

Talc Surface Modification

The talc was first slurried in moisture-free solution of the LICA 38 (0.4 wt% based on the weight of talc) in toluene. The slurry was stirred for 3 h using a magnetic stirrer. The coated filler was then heated for 8 h at 393 K in an air oven followed by vacuum heating at 383 K for 2 h to expel the toluene. The hydrophobicity acquired by the talc was

confirmed by floating test on water. While uncoated talc formed *lumps* and sank readily in water, the treated fillers dispersed on the surface of the water and floated. Similar method of surface modification of the filler was used in other works as well to obtain uniform coating of the coupling agent [13–14].

Compounding

The vacuum dried talc (both untreated and treated) and the i-PP were compounded on a two-roll mill (Richardson and Cruddas Ltd., Model -2–18×8 in) at $443 \pm 2\,\mathrm{K}$ for 10 min to form this primary sheets containing 0–33.3 vol% (ϕ_F%) (0–60 wt%) of the talc. Squares 1 cm in sides were cut from these sheets and fed to the rheometer for generation of results.

Measurements

The rheological properties of the i-PP/Talc systems were measured on an Instron capillary rheometer, model M.C.R. 1112, using a capillary die of $L/R = 67.20$ and applied wall shear stress range 40–400 kPa at a temperature 493 K.

RESULTS AND DISCUSSION

Shear stress (τ_w)–Shear Rate (γ_w) (Flow) Curves

The shear stress at the wall of the capillary rheometer, τ_w was evaluated using the following equation [15]:

$$\tau_w = \frac{F}{4A_p(L/D)}(P_a) \tag{1}$$

where F is the weight force (Kgf), A_p the area of plunger (cm^2), L and D the length (cm) and diameter (cm) of the capillary, respectively.

The apparent shear rate, γ_a, was determined according to the following expression (19):

$$\gamma_a = \frac{2}{15}\frac{V_{xh}d_p^2}{D^3}(s^{-1}) \tag{2}$$

where V_{xh} is the crosshead speed (cm/sec), d_p the diameter of the plunger (0.928 cm), and D the diameter of the die (0.0759 cm). The apparent flow behavior indices n' were calculated from the slopes of linear plots of log τ_w vs. log γ_a (not shown), which were then employed

to estimate the true shear rate at the capillary wall, γ_w, by applying the Rabinowitsch correction [16–18]:

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

Finally, the apparent melt viscosity, η_{app}, was calculated using the following relation [16–18]:

$$\eta_{app} = \frac{\tau_w}{\gamma_w} (Pa.s) \tag{4}$$

Variations of $\log \tau_w$ against $\log \gamma_w$ in the i-PP/Talc and the i-PP/Talc/LICA 38 composites were linear in the range of shear rates $(300-9000 \, s^{-1})$ studied, Figures 1 and 2, respectively. This implies that the composite melts follow a power law behavior, similar to other related results [1,18]. The flow curve moves upward with increase in the ϕ_F. This means that at a constant shear rate the composite melts
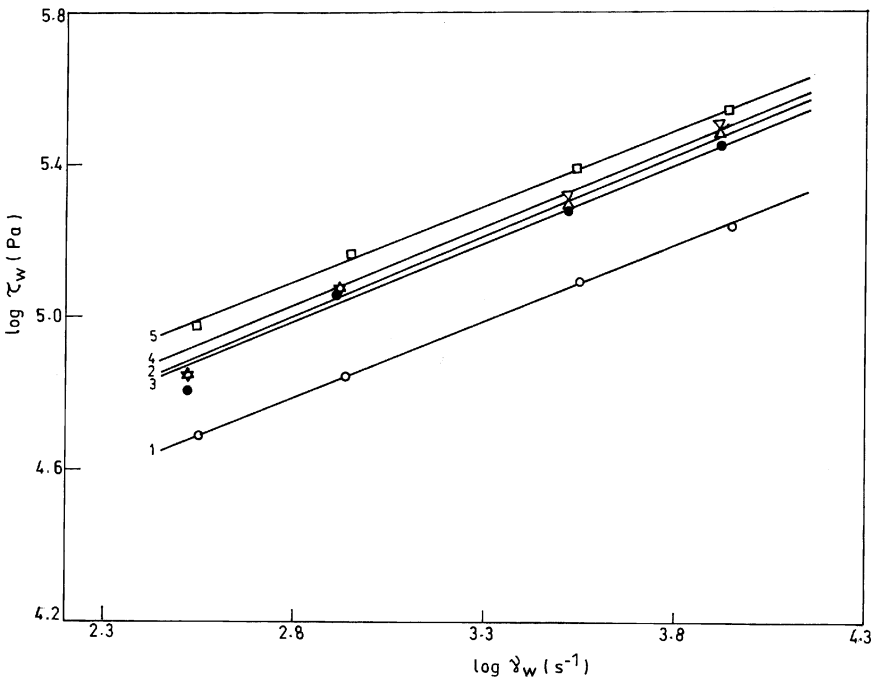

FIGURE 1 Log shear stress (τ_w)–log shear rate (γ_w) plots in the i-PP/Talc composites at 493 K: (0) i-PP; (Δ) i-PP/Talc 7.7%; ($\bullet$) i-PP/Talc 15.2% (∇) i-PP/Talc 25% ($\square$) i-PP/Talc 33.3%. Two data points of older work are represented by the star of David symbol.
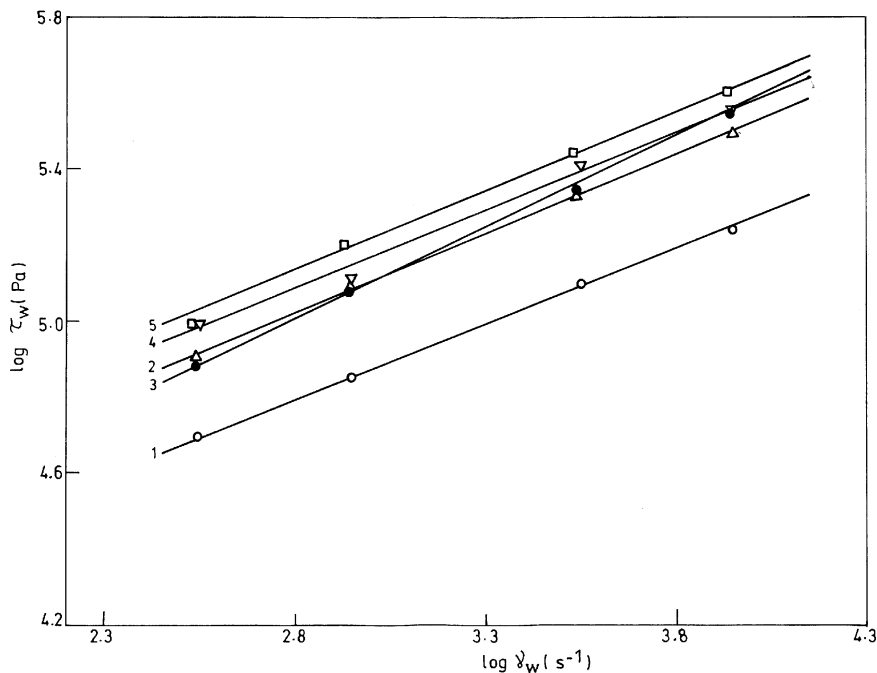
FIGURE 2 Variations of log τ_w vs log γ_w in the i-PP/Talc/LICA 38 composites at 493 K. Descriptions of the curves are as in Figure 1.

exhibit higher shear stress with increase in the talc concentration (vol%).

Table 1 exhibits the values of the power law behavior indices, n, of the power law expression [Eq. 5]:

$$\tau_w = K \, \gamma_w^n \tag{5}$$

determined as the slopes of the plots of log τ_w vs. log γ_w. The n values were less than unity, 0.41 ± 0.01 for the i-PP/Talc systems and 0.44 ± 0.04 for the i-PP/Talc/LICA 38 composites. This means that the composites were pseudoplastic, as shown by thermoplastic systems [18–19].

Some previous works with very fine particle filled polymers showed yield stress at low shear rates, viz 10^{-2} to 10^0 s^{-1}, due to interparticulate interactions [2, 20–22]. The filler particles in these studies were <0.5 μm in diameter. In the present study the average diameter of the talc particles was 0.43 μm. Although interparticulate interaction is expected through surface hydroxyl groups [5], no yield stress was exhibited by either the i-PP/Talc or the i-PP/Talc/LICA 38 systems.

TABLE 1 Values of the Power Law Flow Indices n in the i-PP/Talc and the i-PP/Talc/LICA 38 Composites

	n value	
ϕ_F (%)	i-PP/Talc	i-PP/Talc/LICA 38
0	0.40	0.40
7.7	0.42	0.42
15.2	0.42	0.48
25.0	0.42	0.41
33.3	0.40	0.42

This may be attributed to the high values of the γ_w (viz, $300-9000\,\mathrm{s}^{-1}$) used for the measurements. Other filled polymer compositions also reported the absence of yield stress [1, 8, 23, 24].

Apparent Melt Viscosity (η_{app})

The variations of the apparent melt viscosity, (η_{app}), with the γ_w in the i-PP/Talc and the i-PP/Talc/LICA 38 composites are presented in Figures 3 and 4, respectively. The η_{app} values were of similar order with the i-PP filled with wood flour [18] and kaolin [11] whereas the data were lower than another filled i-PP composite [1] by $\sim$1 order of magnitude. This may be due to the different grades of i-PP used for the studies.

It may be noted from Figures 3 and 4 that the apparent viscosity decreases with increasing shear rate in both the i-PP/Talc and the i-PP/Talc/LICA 38 composites. This implies that as with the nonfilled i-PP, its composites with the talc powers are also shear thinning. At any fixed γ_W value, the melt viscosity increased with the concentration of the talc particles, compared to the non-filled i-PP.

Figure 5 exhibits variations of the η_{app} vs. the filler volume percent, ϕ_F(%), in the i-PP/Talc composites at a fixed γ_w value 1995.3 (s^{-1}) and at 493 K. The melt viscosity increases by $\sim 67-100\%$ as the talc concentration is increased from 0 to 33.3%. The polymer flow is substantially influenced by the particle shape and aggregation in the filled polymer systems. The composites filled with acicular and associated particles are more resistant to flow than those filled with spherical or regularly shaped particles [1, 25]. In the present work the talc particles were acicular with average particle diameter $\sim 0.43\,\mu m$ (3). The silicate type particles exhibit interparticle interactions, which may introduce discontinuity and obstructions to the flow of the polymer [5,18]. The increase in the melt viscosity may be attributed to this obstruction to flow by the talc particles.
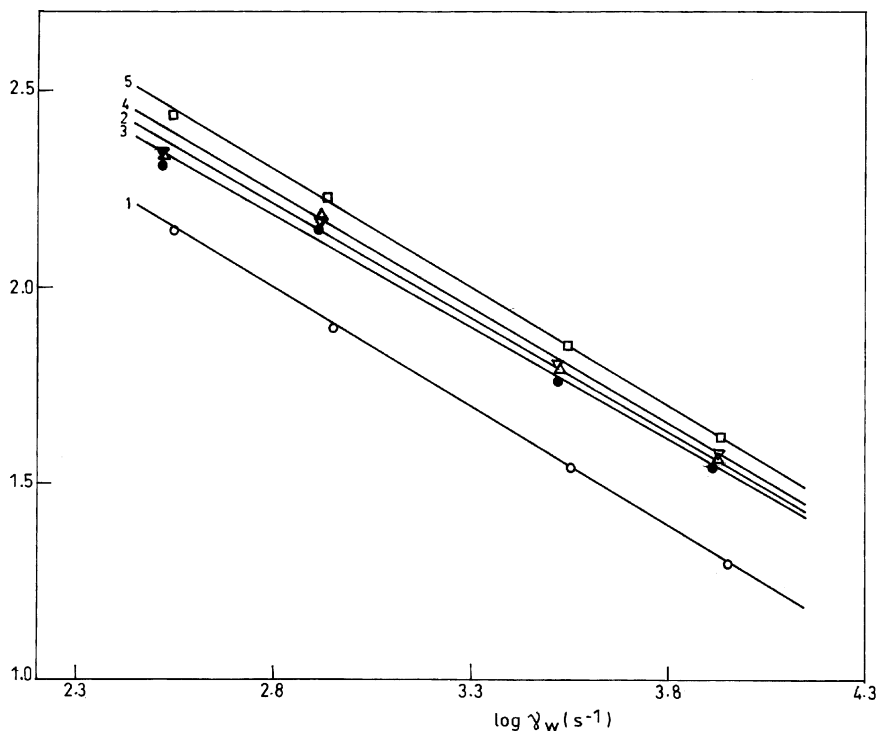
FIGURE 3 Plots of the log (apparent melt viscosity, η_{app}) against log γ_w in the i-PP/Talc composites at 493 K. Descriptions of the curves are as in Figure 1.

In the i-PP/Talc/LICA 38 systems, quite similar variations of the η_{app} vs. $\phi_F(\%)$ were observed, Figure 5. The η_{app} increased by ~69−119% as the content of the talc particles increased from 0 to 33.3%. At a corresponding value of ϕ_F, the η_{app} data were higher than those of the previous composites by ~9−14%, depending on the ϕ_F. This indicates a higher extent of obstruction of the melt flow, possibly arising out of an enhanced bonding between the i-PP and the talc powders, as was also observed in the tensile modulus data of the i-PP/Talc composites [3]. Thus, although the surface modifier would smoothen the talc particle surfaces, expelling the water of hydration and the air bubbles, as well as a plasticizing/lubricating type of function was exhibited by the modifier, as in other composites [3, 10, 26], it seems that the polymer-filler interactions take prominence during the melt flow of the i-PP/Talc/LICA 38 composites. Similar results were noted in kaolin filled i-PP too [11].
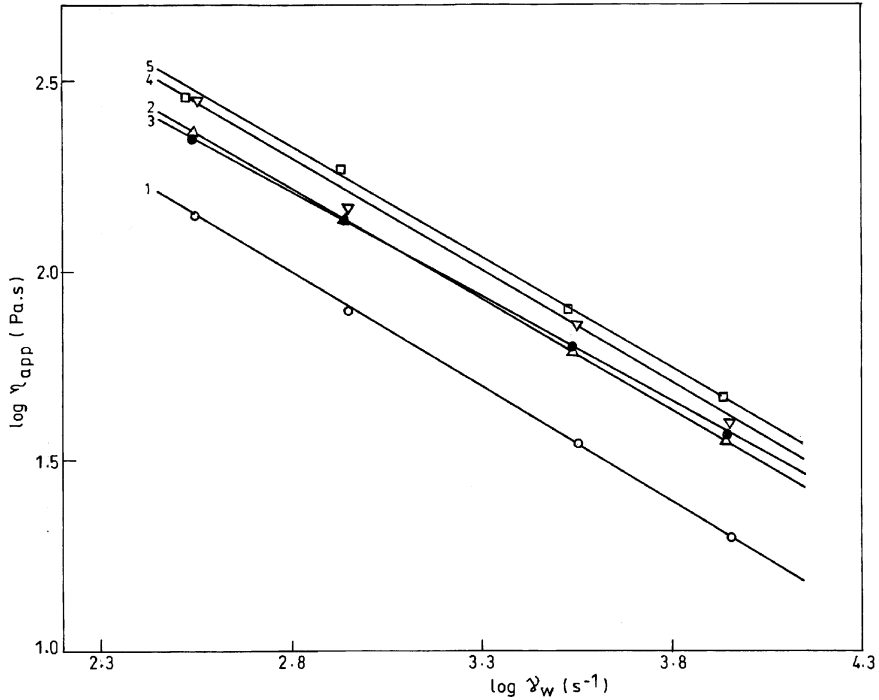
FIGURE 4 Log η_{app} − log γ_w variations in the i-PP/Talc/LICA 38 composites at 493 K. Descriptions of the curves are as in Figure 1.

Melt Elasticity

The melt elasticity parameters, the extrudate swell ratio, and the first normal stress difference, of the i-PP/Talc and the i-PP/Tals/LICA 38 composites, were determined at 493 K. The extrudate swell ratio is expressed as:

$$\text{Extuadate swell ratio} = \frac{D_e}{D_d} \tag{6}$$

where D_e is the diameter of the extrudate measured when the extrudate emerges from the die and D_d the diameter of the die. Using the value of the extrudate swell ratio at each shear rate, the first normal stress difference $(\tau_{11} - \tau_{22})$ (Pa), was computed according to the Tanner' equation [27]:

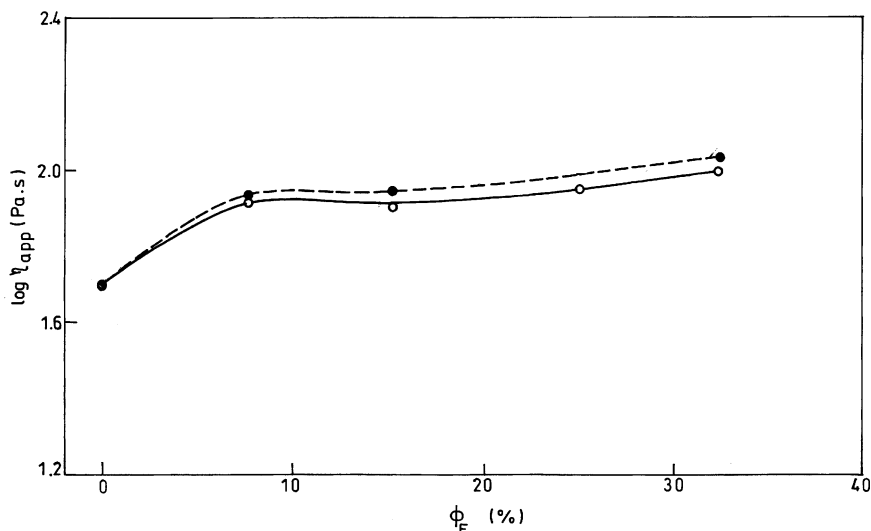$$\tau_{11} - \tau_{22} = 2\tau_w [2\left(\frac{D_e}{D_d}\right)^6 - 2]^{1/2} \tag{7}$$

FIGURE 5 Plot of the log η_{app} against ϕ_F (%) at 493 K at a fixed γ_w value of 1995.3 (s^{-1}) in (○) i-PP/Talc and (●) i-PP/Talc/LICA 38 composites.

The $\tau_{11} - \tau_{22}$ values in this work were of similar magnitude to the i-PP filled with kaolin and wood flour particles [11,18] and $\sim$1 order of magnitude higher than another i-PP system [1].

Variations of the $\tau_{11} - \tau_{22}$ vs. γ_w for the i-PP/Talc and the i-PP/Talc/LICA 38 composites are presented in Figures 6 and 7, respectively. It is apparent that the first normal stress difference increased with the shear rate. This is quite expected because on emergence from the die the stored elastic energy is released and causes the polymer swell. At higher shear rates the extent of elastic energy stored and subsequently released will be greater. In the filled polymeric systems the extrudate swell decreases, which in turn decreases the $\tau_{11} - \tau_{22}$ value with the addition of the fillers, as compared to the non-filled polymer. At a fixed shear rate the $\tau_{11} - \tau_{22}$ decreases with increase in the talc concentration (Figures 6 and 7).

Figure 8 exhibits the variation of the $\tau_{11} - \tau_{22}$ as function of ϕ_F at a constant γ_w value 1995.3 (s^{-1}) and at 493 K for the i-PP/Talc and the i-PP/Talc/LICA 38 composites. The melt elasticity decreased with the increase in the talc content, the decrease was marginal in the regions beyond $\phi_F = 7\%$ in both types of composites. In the i-PP/Talc system the total drop in the $\tau_{11} - \tau_{22}$ was 92−98% based on the value of the non-filled i-PP depending on the ϕ_F. It has been
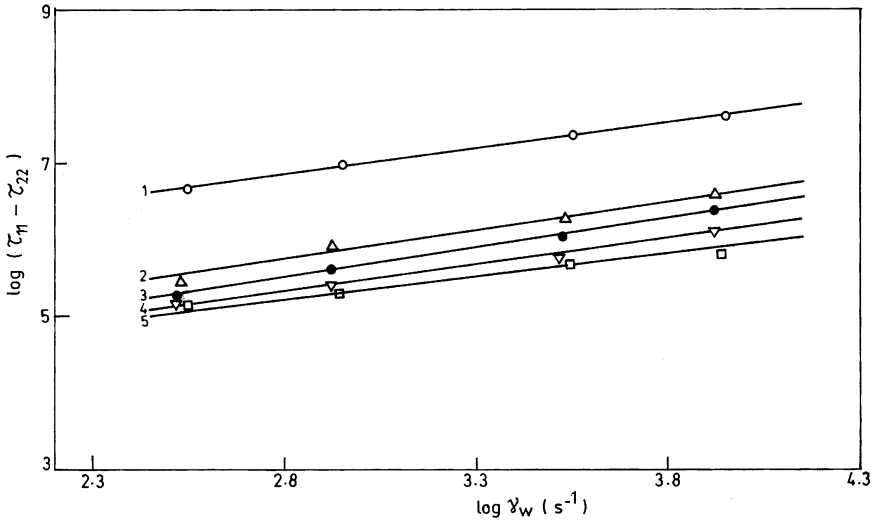
FIGURE 6 Variation of the log (first normal stress difference, $\tau_{11} - \tau_{22}$) against log γ_w at 493 K in the i-PP/Talc composites. Descriptions of the curves are as in Figure 1.
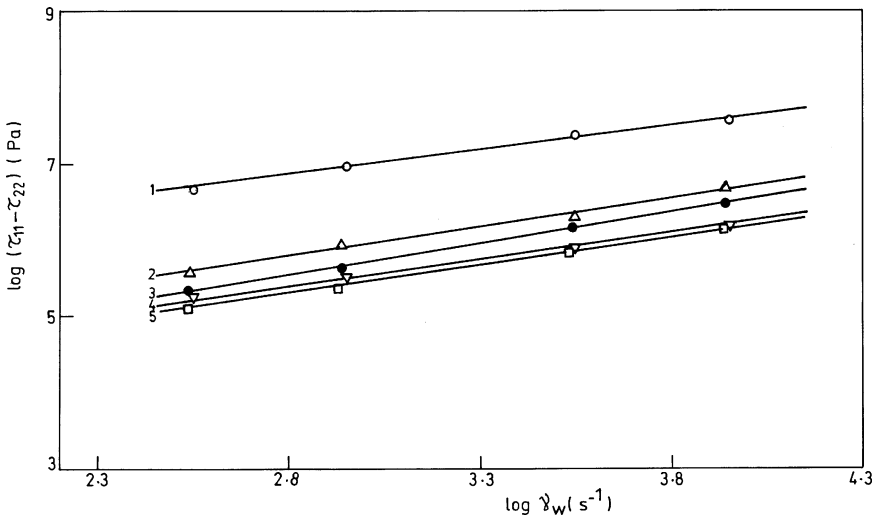

FIGURE 7 Log $(\tau_{11} - \tau_{22})$–log γ_w plots at 493 K in the i-PP/Talc/LICA 38 composites. Description of the curves are as in Figure 1.
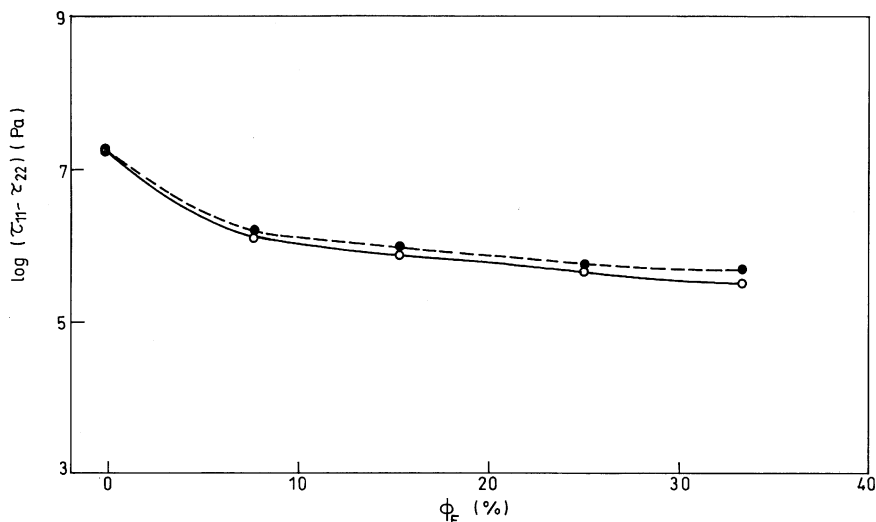
FIGURE 8 Plots of the $\log(\tau_{11} - \tau_{22})$ vs. ϕ_F (%) at 493 K at a constant γ_w value of 1995.3 (s^{-1}) in ($\circ$) i-PP/Talc and ($\bullet$) i-PP/Talc/LICA 38 composites.

reported that the presence of fillers hinders the elastic energy recovery decreasing the $\tau_{11} - \tau_{22}$ value. The effect becomes more prominent at high ϕ_F values [28,29]. In the i-PP/Talc composites it has been pointed out that the filler particles create discontinuity in the polymer and thus obstruct its flow, increasing the melt viscosity. This obstruction to flow could still persist after the melt emerges from the die so that the elastic energy recovery is hindered, which decreases the melt elasticity in these composites. The elastic energy recovery becomes increasingly restricted as the concentration of the talc increases. This observation is in good agreement with other results [1,10,18,21,28–29]. A decrease in the melt elasticity in the presence of the talc particles ensures processing safety through extrusion by increasing the critical shear stress for the melt fracture so that the extrudates of the composites would possess smooth surfaces.

In the presence of the coupling agent LICA 38, quite smiliar decreases in the $\tau_{11} - \tau_{22}$ values were observed as with i-PP/Talc systems. The values were marginally higher than those without the coupling agent at corresponding ϕ_F levels, however. This may be due to an enhanced elastic energy recovery of the polymer aided through a plasticizing/lubricating type of function by the coupling agent, which may partially restore matrix continuity [3,26].

CONCLUSIONS

The variation of the shear stress vs. shear rate data in i-PP/Talc composites exhibit, power law behavior in the shear rate range $300-9000$ (s^{-1}) at a talc concentrations of $0-33.3$ vol% and at a temperature 493 K. The power law index varied between 0.41 ± 0.01, indicating a prseudoplastic nature of the composites. The apparent melt viscosity of the composites decreased with increasing shear rate, implying that the systems were shear thinning. The apparent melt viscosity increased with talc concentration due to an increased extent of obstruction imposed by the talc particles on the polymer flow. The melt elasticity decreased with increasing talc content due to the filler's obstruction to the polymer's elastic recovery. The latter increased with the filler content.

In the presence of a filler surface modifier, LICA 38, the composites showed similar rheological properties. The power law model was followed with n values in the 0.44 ± 0.04 range. Variations of the apparent melt viscosity and the melt elasticity with the ϕ_F also were similar to those in the previous systems; the coupling agent, however, modified these variations through enhancing talc$-$i-PP bonding this was manifested in the viscosity vs. ϕ_F variations and through a plasticizing/lubricating function in the elasticity$-\phi_F$ dependence.

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