

Effect of Wood Fibers on the Rheological Properties of i-PP/Wood Fiber Composites

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ABSTRACT: The effects of wood fibers on the melt rheological behavior of isotactic poly(propylene) (i-PP)/wood fiber (WF) composites have been studied at WF concentrations of 0–32.2 vol % at 493 K. Shear stress–shear rate variations obeyed a power law equation, and the composites exhibited shear thinning, which increased with filler content. At a low shear rate, the apparent melt viscosity increased, while melt elasticity, after an initial decrease, also increased with WF concentration. At a higher shear rate, after an initial

decrease, the melt viscosity showed an increase, as did melt elasticity, with increase in filler content. A titanate coupling agent, LICA 38, used to modify the wood fiber surface, modified these rheological parameters by functioning as a plasticizer/lubricant. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 644–650, 2004

Key words: isotactic; poly(propylene); composites; viscosity

INTRODUCTION

Various property-modifying additives have been incorporated in a commercially versatile polymer, isotactic polypropylene (i-PP), in order to suit a wide variety of applications at economical costs.^{1–14} Some of these additives are ethylene–propylene rubber,³ acrylonitrile–butadiene–styrene terpolymer,⁴ triblock copolymer styrene–ethylenebutylene–styrene,⁵ glass fibers and asbestos,¹ inorganic materials such as talc, kaolin, calcium carbonate, and metal powders.^{6–14} An inexpensive filler of organic origin, wood flour, has also found extensive use in plastic composites, causing beneficial properties such as decreased molding shrinkage, increased stiffness and creep resistance, while maintaining good overall mechanical properties.^{15–17}

Polymer–filler interactions play a significant role in governing the interparticle network and the rheological properties of these filled composites.¹⁸ The higher the adhesion between the matrix and the inclusion, the lower the tendency for the particles to cluster and the better the resulting dispersion. The adhesion or wettability between the phases can be enhanced by surface modification of the dispersed phase.^{14,18} Although the exact mechanism of function of these sur-

face-modifying agents is not well understood, it is generally agreed that the agents function by displacing air voids and water from the filler surface.^{14,18–22} In recent times, titanate based coupling agents have assumed importance in filled polymer applications.¹⁴

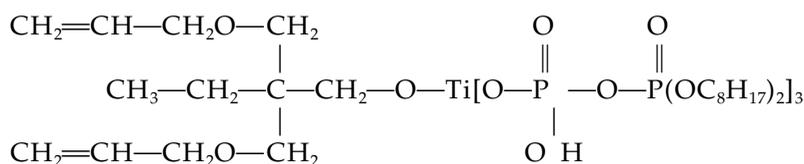
For this article, the melt rheological properties of wood fiber (WF) filled i-PP were studied at a range of 0–32.2 volume percent (ϕ_f) (0–70 phr) filler at 493 K. A piston-type capillary rheometer was employed to generate shear stress–shear rate data, apparent melt viscosity, and melt elasticity parameters. The effects of filler surface treatment with a titanate-coupling agent, LICA 38, on these rheological characteristics were also examined.

EXPERIMENTAL

Materials

Commercial i-PP, Koylene M 0030 (MFI 10, density 0.90 g/cm³), from M/S Indian Petrochemicals Corporation Ltd., Gujarat, India, was used. Wood flour (WF) from Kail Wood (botanical name – *Pinus Excelsa*)¹⁶ was sieved, and particles in the size range of 150–300 μm (density 1.326 g/cm³) were used. The wood was a mixed wood containing 4 to 5% sapwood and the rest heartwood. The particles were oven-dried at 363 K for 1.5 h to expel moisture prior to mixing with i-PP. A liquid neoalkoxy–organotitanate coupling agent, LICA 38, obtained from M/S Kenrich Petrochemicals, Inc., Bayonne, N.J., was employed for the surface treatment of wood fibers. LICA 38 is, chemically, neo-pentyl-(diallyl)-oxy-tri(dioctyl)-pyro-phosphato titanate.¹⁴

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Surface treatment of WF

A toluene solution of LICA 38 (0.4 g in 10 mL toluene) was mixed with 100 g of WF in a laboratory mixer (Sumet, Model 2 L) for 30 min following methods used by other researchers.^{23,24} The mixture was then dried in an air oven at 383 K for 3 h and stored in a sealed container.

Composite preparation

WF (both unmodified and surface-modified) was vacuum dried to 1–3% moisture content, and then mixed with i-PP at 438 ± 2 K on a two-roll mill (Richardson and Cruddas India Ltd., Model 218) for 15 min to prepare primary sheets with 0–32.2 vol % (0–70 phr) WF content. This range of WF vol. % is used in industry also. The milled sheets were cut into squares of ≈ 0.5 cm sides, which were fed into the rheometer for data generation.

Rheological studies

A Rheograph 2001 (Göttfert, Germany) having a cylindrical die with a diameter of 1 mm and a L/D ratio of 30, was used at 493 K. This temperature is used in industry to mold and extrude filled i-PP systems. The comparison interval was 8 s, with an initial melting time of 2 min. The instrument was set at a constant speed/shear rate mode. Eight piston speeds in the range of 0.04–2.4 mm/s, corresponding to a shear rate range of 40–6000 s^{-1} , were employed to generate the rheological data. Rheological parameters of melt viscosity and melt elasticity were calculated using the RABKOR program (version 9.3), following the instrument manual.^{25,26}

RESULTS AND DISCUSSION

Shear stress–shear rate curves

The shear stress–shear rate data were generated at varying pressures at a constant temperature of 493 K. The apparent shear rates, γ_{app} , were estimated using eq. (1):^{25,27}

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

where R is the radius of the capillary die (cm) and Q the volumetric flow rate (cm^3/s). The volumetric flow rate, Q , is given as eq. (2):

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

where V is the piston speed (cm/s), A the piston-free area (cm^2), t the time (s), and S the piston path (cm). Wall shear rate (γ_w) values were obtained from the γ_{app} data by applying the Rabinowitsch–Weissenberg correction, eq. (3):²⁷

$$\gamma_w = \frac{3n' + 1}{4n'} \gamma_{\text{app}} \quad (3)$$

where n' is the power-law flow index obtained as the slope of $\log \tau_w$ versus $\log \gamma_{\text{app}}$ plots (not shown).

The apparent shear stress $\tau_{w(\text{app})}$ was calculated using eq. (4):²⁵

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

where P is the pressure applied on the piston (Pa), L the capillary length (cm), and D the capillary diameter (cm).

The viscous drag that occurs in the entry region is independent of the length of the capillary and considered to increase the effective length of the die to account for this effective increase in length in terms of the die radius. The Ryder–Bagley correction was applied to estimate the true wall shear stress, τ_w .²⁷

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

where the end correction term, e , is the negative of the slope of the P versus L/R plot over a range of shear rates, and R is the radius of the die.

The apparent melt viscosity, η_{app} , was estimated as^{13,28}

$$\eta_{\text{app}} = \frac{\tau_w}{\gamma_w} \quad (6)$$

The variations of $\log \tau_w$ against $\log \gamma_w$ in the i-PP/WF and i-PP/LICA 38 composites at 493 K are

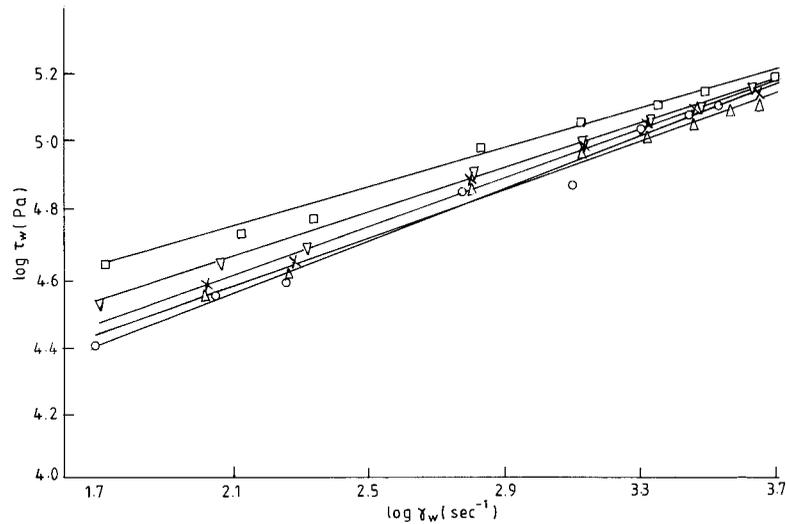


Figure 1 Log of shear stress (τ_w) vs. log of shear rate (γ_w) plots at 493 K for pure i-PP (\circ) and i-PP/WF composites: (Δ) i-PP/WF 9.2%, (\times) i-PP/WF 16.9%, (∇) i-PP/WF 25.3%, (\square) i-PP/WF 32.2%.

shown in Figures 1 and 2, respectively. The variation of data was within $\pm 2\%$. The plots were linear, implying that power law behavior was followed by the composite melts, similar to other systems.^{28,29} As WF concentration increased, the flow curves moved upward. This means that, at a constant shear rate, a system with high WF concentration shows higher shear stress than a composite with low WF content. Similar findings were reported earlier.^{28,29}

Table I shows the values of the power law behavior indices, n , of the power law relation [eq.(7)]:^{29,30}

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

determined as the slope of the $\log \tau_w$ versus $\log \gamma_w$ plots. The values of n were less than unity, implying

the pseudoplastic nature of the melts, as is common in thermoplastic systems.^{28,31,32} The n values decrease to an extent with increase in ϕ_F in i-PP/WF composites, which indicates that the pseudoplasticity increases with WF concentration. A similar trend is observed in the i-PP/WF/LICA 38 composite melts. At corresponding ϕ_F values, the magnitude of n varied inappreciably from those for the i-PP/WF systems.

Filled polymer systems exhibit a yield stress at low shear rates (e.g. 10^{-2} to 10^0 /s), particularly with very fine particles of diameter $< 0.5 \mu\text{m}$.^{18,33-36} The yield stress arises out of the formation of an interparticle network. In the present system, the high shear rate range ($40-6000 \text{ sec}^{-1}$) used in the study, combined with the use of large WF particles ($150-300 \mu\text{m}$), prevented the composites from exhibiting any yield

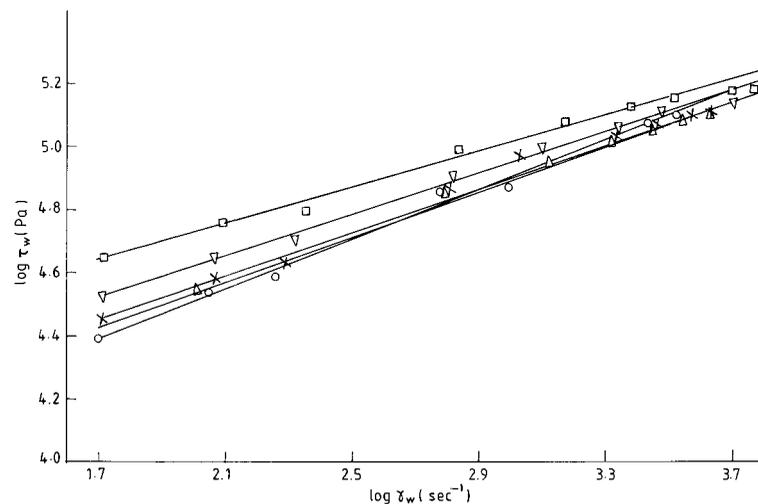


Figure 2 Variations of $\log \tau_w$ vs. $\log \gamma_w$ of pure i-PP (\circ) and i-PP/WF/LICA 38 composites at 493 K: (Δ) i-PP/WF 9.2%, (\times) i-PP/WF 16.9%, (∇) i-PP/WF 25.3%, (\square) i-PP/WF 32.2%.

TABLE I
Values of Power Law Index (n) for i-PP/WF and
i-PP/WF/LICA 38 Composites

ϕ_F (%)	n Values	
	i-PP/WF	i-PP/WF/LICA 38
0	0.379	0.379
9.2	0.362	0.358
16.9	0.360	0.346
25.3	0.333	0.330
32.2	0.292	0.328

value. Other filled polymer systems have also been reported to show an absence of yield stress.^{28,29,37,38}

Correlation of power-law index (n) with ϕ_F

Since increase in ϕ_F produced a systematic decrease in the power law flow index, n , of these composites, an attempt was made to establish a correlation, if any, between the two parameters. Regression analysis was performed on the variables, and a value of 0.7-0.9 for the correlation coefficient (r^2) was considered to represent a linear correlation in light of the data scatter in such experimental work. The following correlation [eq. (8)] was found to describe the parameters:

$$n_c/n_p = 1 - X\phi_F \quad (8)$$

where n_c is the n value of the composite and n_p is the n value of i-PP. The parameter X , known as the coefficient of pseudoplasticity, describes the ability of the dispersed phase WF to bring about a change in the flow pattern of the melts in a capillary at 493 K. The values of the parameter X and the coefficient of correlation r^2 for the composites are shown in Table II, while their correlations are presented in Figure 3. The filler, WF, is quite capable of introducing pseudoplasticity into the polymer. The coupling agent, LICA 38, decreases the pseudoplasticity index marginally (i.e., increases the pseudoplasticity possibly through a plasticizing/lubricating function).^{9,39}

Apparent melt viscosity (η_{app})

Figures 4 and 5 present the variations of apparent melt viscosity, η_{app} , of the i-PP/WF and i-PP/WF/LICA 38

TABLE II
Values of Pseudoplasticity Coefficient (X) and
Correlation Coefficient (r^2) for i-PP/WF and
i-PP/WF/LICA 38 Composites

Composite System	X	r^2
i-PP/WF	0.021	0.911
i-PP/WF/LICA 38	0.004	0.963

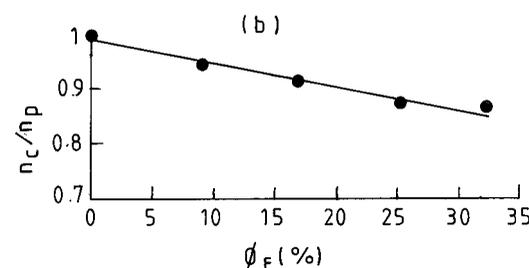
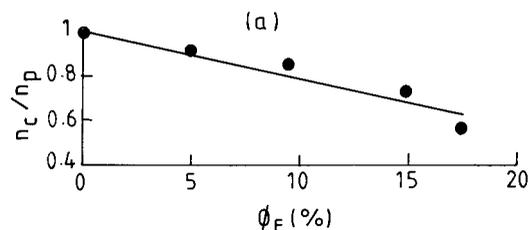


Figure 3 Plot of ratio of power law flow index of the composite n_c to that of i-PP n_p , against ϕ_F in: (a) i-PP/WF and (b) i-PP/WF/LICA 38 systems.

composites against γ_w . The η_{app} values of these composites were slightly higher than those of a similar system,²⁸ while the data were about one order lower than those for an inorganic filler containing i-PP system.^{29,30} This may be due to the use of different grades of i-PP in the works.

It may be seen from Figures 4 and 5 that η_{app} decreases with increasing γ_w in both types of composite, implying that, like i-PP, the WF-filled composites are shear-thinning. At a given γ_w value, the apparent viscosity increases with WF volume percent, ϕ_F (%). The η_{app} versus γ_w plots, however, tend to converge at very high γ_w values. At and above γ_w values of approximately 4500 (s^{-1}), the η_{app} is not affected by the presence of WF and/or LICA 38. This phenomenon has some advantage for the processing of these composites, which implies that, even with such high loading of particulate filler, the systems are processable through high-shear techniques (e.g. injection molding).^{27,30,40}

Variations of η_{app} versus ϕ_F at two fixed γ_w values of 126 s^{-1} and 1995 s^{-1} are presented in Figure 6. In the i-PP/WF composites with γ_w of 126 s^{-1} , η_{app} increased by 7–60% compared to i-PP, as ϕ_F increased from zero to 32.2 vol %. The presence of WF introduces mechanical restraints into the system, the extent

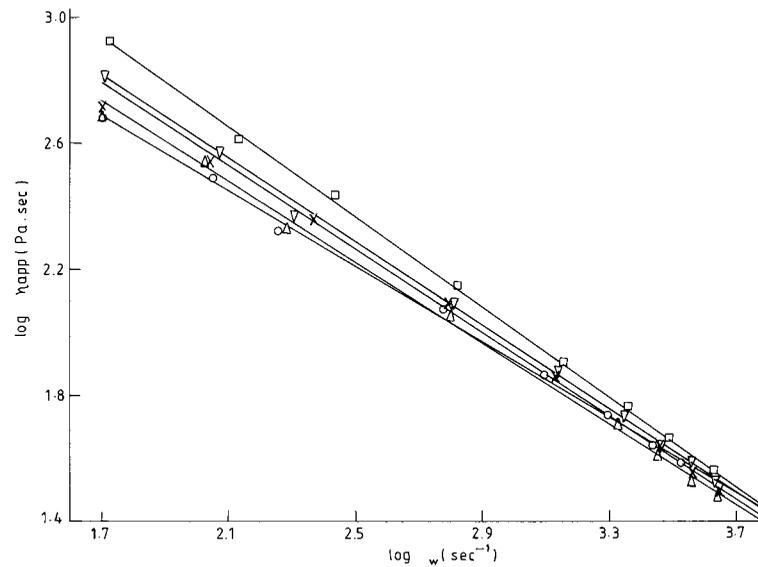


Figure 4 Log of apparent melt viscosity (η_{app}) vs. $\log \dot{\gamma}_w$ plots in i-PP/WF composites at 493 K: (○) pure i-PP, (Δ) i-PP/WF 9.2%, (X) i-PP/WF 16.9%, (∇) i-PP/WF 25.3%, (□) i-PP/WF 32.2%.

of which increases with ϕ_F .⁹ Melt viscosity increase may be attributed to this increased mechanical restraint, which in turn obstructs melt flow by the porous and irregularly shaped WF particles,²⁸ particularly at the low shear rate of 126 s^{-1} . At a higher shear rate of 1995 s^{-1} , η_{app} shows a marginal decrease up to a ϕ_F value of 9.2%; the value then increases by 1–18% compared to that of i-PP. The lesser increase in η_{app} at $\phi_F > 9.2\%$ implies that the obstruction to flow is in part overcome by a high rate of shear deformation, which may orient the soft WF particles, facilitating melt flow.

A similar dependence of η_{app} on ϕ_F was noted in the i-PP/WF/LICA 38 composites; the viscosity data were either similar or marginally lower than those for the i-PP/WF systems, however. This may be attributed to the lubricating/plasticizing function of the coupling agent, as was also observed in the solid-state properties of the composites. Plasticizing/lubricating functions of coupling agents were also reported in other works involving surface treated filler containing systems.^{9,10,39,41} The coupling agent smoothes the WF surface to a certain extent, decreasing their resistance to polymer melt flow.

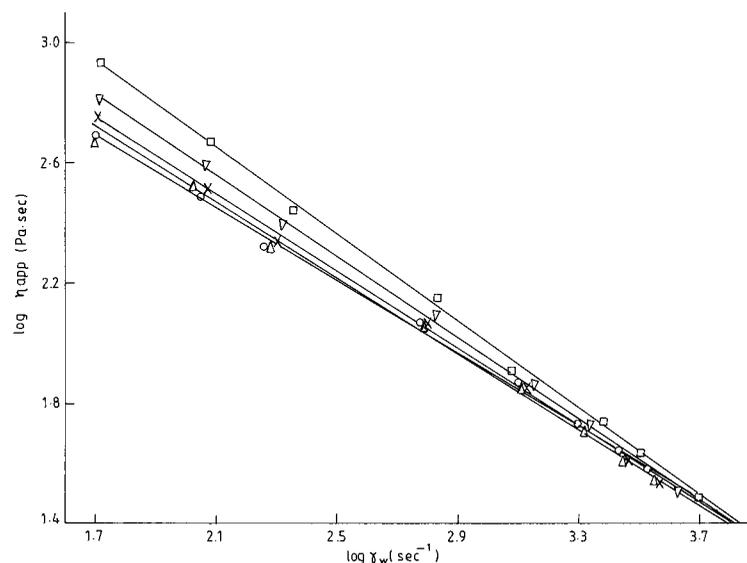


Figure 5 Variations of $\log \eta_{app}$ vs. $\log \dot{\gamma}_w$ in i-PP/WF/LICA 38 composites at 493 K: (○) pure i-PP, (Δ) i-PP/WF 9.2%, (X) i-PP/WF 16.9%, (∇) i-PP/WF 25.3%, (□) i-PP/WF 32.2%.

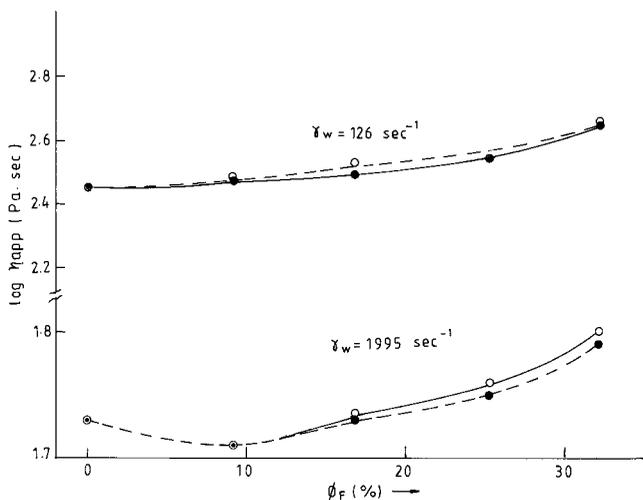


Figure 6 Plot of $\log \eta_{app}$ as functions of ϕ_F at 493 K at two fixed γ_w values of 126 s^{-1} and 1995 s^{-1} in (○) i-PP/WF and (●) i-PP/WF/LICA 38 composites.

Melt elasticity

Viscoelastic polymeric materials exhibit melt elasticity in the form of normal stresses. The first normal stress difference ($\tau_{11} - \tau_{22}$) in polymeric systems is evaluated from a mirror relationship between normal stress coefficient and viscosity.^{25,26} A mirror relationship exists between (i) the viscosity function $\eta(\gamma_w)$ and the stress viscosity $\eta_o(t)$, and (ii) the steady normal stress coefficient $\theta(\gamma_w)$ at a shear rate γ_w and the normal stress coefficient θ_o at small shear rates at a time t , if γ_w is equal to a constant k divided by the time t .^{25,26} These relationships for a viscoelastic fluid are described below:

Viscosity function

$$\eta(\gamma_w = 1/t) = \eta_o(t) \quad (9)$$

Normal stress coefficient

$$\theta(\gamma_w) = (\tau_{11} - \tau_{22})(\gamma_w) / \gamma_w^2 \quad (10)$$

$$\theta(\gamma_w = k/t) = \theta_o(t) \quad 2 \leq k \leq 3 \quad (11)$$

The normal stress coefficient, $\theta(\gamma_w)$, can be determined from the viscosity function, $\eta(t)$, according to eq. (12):

$$\theta(\gamma_w) = 2 \sum_i (\eta_i / \gamma_{wi}) [1 + (1 - k\gamma_{wi} / \gamma_w) \exp(-k\gamma_{wi} / \gamma_w)] \quad (12)$$

and subsequently $\tau_{11} - \tau_{22}$ can be calculated by employing eq. (10).^{25,26}

Melt elasticity data, $\tau_{11} - \tau_{22}$, were plotted against γ_w for the various ϕ_F (%) values (plots not shown) and at two fixed γ_w values (126 s^{-1} and 1995 s^{-1}) at 493 K. The dependence of $\tau_{11} - \tau_{22}$ on ϕ_F (%) is shown in Figure 7. The values of $\tau_{11} - \tau_{22}$ are about one order lower than those found in a similar system²⁸ and of nearly equal order to values for i-PP/inorganic filler composites.^{29,39} In the i-PP/WF systems at a low shear rate of 126 s^{-1} , the elasticity initially decreases up to a ϕ_F value of 9.2%; the value then increases with ϕ_F , the total increase being ≈ 7 –105% compared to i-PP. At a higher γ_w value of 1995 s^{-1} the melt elasticity increases by 6–32%. It was noted in the previous section that at a γ_w value of 126 s^{-1} and a ϕ_F value up to 9.2%,

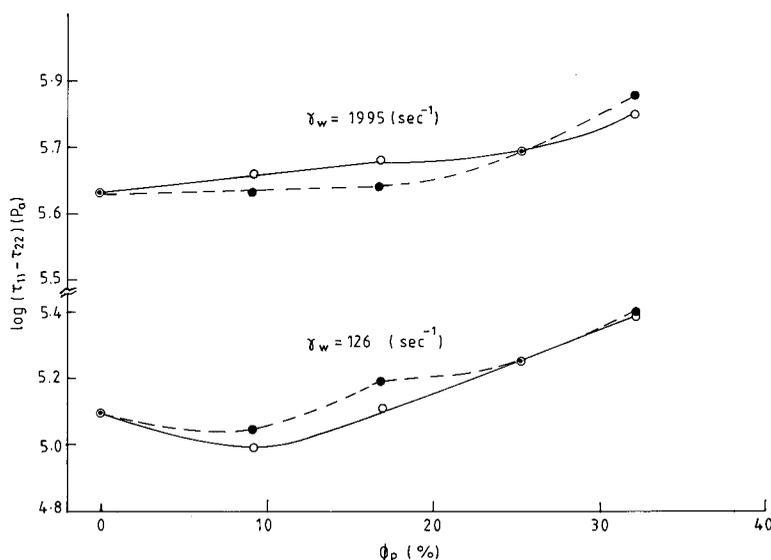


Figure 7 Variations of $\log(\tau_{11} - \tau_{22})$ vs. ϕ_F at 493 K at two constant γ_w values of 126 s^{-1} and 1995 s^{-1} in (○) i-PP/WF and (●) i-PP/WF/LICA 38 composites.

the WF particles created mechanical restraint in the melt flow of i-PP, increasing the viscosity. This restraint may cause discontinuity, which in turn may resist stress transfer for elastic energy recovery.²⁸ In addition, porous and soft WF particles may undergo distortion, absorbing some energy from the elastic deformation or recovery stresses, and in the process decreasing melt elasticity up to a ϕ_F value of 9.2%. However, in the presence of an increased concentration of WF, the enhanced discontinuity may result in the squeezing out of the polymer to the surface, particularly due to the non-interaction of WF with non-polar i-PP, which creates continuity on the surface that is retained even when the melt emerges from the die. This facilitates elastic energy recovery, increasing the melt elasticity. The increase in $\tau_{11} - \tau_{22}$ is relatively less at higher shear rate of 1995 s^{-1} which may be attributed to the partial disturbance of the matrix continuity on the skin of the samples.

In the presence of the coupling agent, LICA 38, similar behavior of melt elasticity was observed. At low shear rate ($\gamma_w = 126 \text{ s}^{-1}$), the elastic recovery was facilitated to a degree through the plasticization/lubrication effect of LICA 38,^{9,39} the $\tau_{11} - \tau_{22}$ values being marginally higher than in the i-PP/WF systems, particularly at a ϕ_F range of 9.2–16.9%. The data at high γ_w value (1995 s^{-1}) were either slightly less or marginally greater than in i-PP/WF composites, which implies that the elastic energy recovery is not sensitive to the presence of LICA 38, likely due to the large extent of shear deformation.

CONCLUSIONS

A power law model between shear stress and shear rate was followed by i-PP/WF composites at WF concentrations of 0–32.2 vol % at a range of shear rates ($50\text{--}6000 \text{ s}^{-1}$) at 493 K. The power law flow index, n , varied from 0.38 to 0.29, implying the pseudoplastic (shear thinning) nature of the melts. With increase in WF concentration, the value of n decreases. The apparent melt viscosity decreased with increasing γ_w values and in general increased with WF content except up to ϕ_F of 9.2% at γ_w of 1995 s^{-1} , which may be due to the shear induced orientation of WF particles facilitating melt flow. The melt elasticity parameter first normal stress difference also increased with WF concentration except up to ϕ_F of 9.2% at γ_w of 126 s^{-1} , which may be attributed to the resistance to elastic recovery by WF creating discontinuity in i-PP and/or absorbing some elastic energy.

Similar rheological behavior was shown by the composites in the presence of a titanate coupling agent, LICA 38. The composites obeyed power law behavior, and n values varied from 0.38 to 0.33. The decrease of n values with increase in ϕ_F was marginally less, how-

ever. Variations of melt viscosity and elasticity with γ_w and ϕ_F , respectively, were also similar to those of i-PP/WF systems. The coupling agent influenced these variations marginally through a plasticizing/lubricating effect.

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