

## RHEOLOGY STUDY OF RICE HUSK ASH - POLYPROPYLENE COMPOSITE

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**RINGKASAN:** Sifat-sifat reologi yang terdapat pada komposit abu sekam padi-polipropilena telah dikaji dengan menggunakan 'Brabender slit capillary rheometer'. Tegasan ricih dan kelikatan ricih leburan meningkat dengan penambahan kandungan pengisi. Pengisi diolah dengan agen pengkupel berasaskan silina. Silina yang digunakan ialah Prosil 2020, sejenis agen pengkupel silina yang mengandungi peroksida bis(t-butyl peroksi) di-isopropil benzena. Peroksida tersebut menyebabkan pengguntingan rantai molikul polipropilena, mengurangkan tegasan ricih dan kelikatan ricih. Oleh itu pengisi dan agen pengkupel (kepekatan peroksida) mempunyai kesan yang bertentangan ke atas reologi leburan komposit. Untuk leburan yang mempunyai kandungan pengisi yang tinggi, kesan peroksida adalah lebih dominan. Kajian tork campuran dan indek keboleheleleran menyokong pengukuran reologi dengan teknik dai 'slit capillary'.

**ABSTRACT:** The rheological properties of rice husk ash-polypropylene composite was studied using a Brabender slit capillary rheometer. The melt shear stress and viscosity increased with filler content. The filler was subsequently treated with a silane-based coupling agent. The silane used was *Prosil 2020*, a proprietary silane coupling agent containing the peroxide bis(t-butyl peroxy)di-isopropyl benzene. The peroxide induces  $\beta$ -scission of the polypropylene molecular chains reducing the shear stress and viscosity. Hence, the filler and the coupling agent (peroxide concentration) have opposing effect on the rheology of the composite's melt. For high filler content melt, the peroxide effect is more prominent lowering the overall stress and viscosity. At higher shear rate, the effect of filler concentration is more dominant. Mixing torque and melt flow index studies support the rheology measurements by the slit die technique.

**KEYWORDS:** Polypropylene, rheology, rice husk ash, filler, composite, compounding, *Prosil*, coupling agent.

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## INTRODUCTION

Rheology studies on particulate-filled polypropylene using slit-dye technique have been described by many workers. Among the earliest work carried out in this field was one pioneered by Han, (1974) who studied the rheological properties of calcium carbonate-filled polypropylene melts. Han *et al.*, (1981) also investigated the effects of silane and titanate coupling agents on the rheological properties, processability and mechanical properties of glass and calcium carbonate-filled polypropylene. Subsequently, their following study investigated the effects of coupling agents on the rheological behaviour and processability of unfilled polypropylene melt (Han *et al.*, 1984). Investigations on the influence of molecular weight on the rheological properties of polypropylene were performed by Minoshima *et al.*, (1980) and Tzoganakis *et al.*, (1989). Bajaj *et al.*, (1989) and Goel, (1980) studied the rheological behaviour of talc-filled polypropylene while rheology of other polymer systems have been reported elsewhere (Dharia and Wolkowicz, 1992; Lee, 1981). An excellent review on the theories of filled thermoplastics was described by White, (1986).

Most of the rheology studies on the polymer systems were carried out using capillary rheometers while Han, (1974) used a Weissenberg rheogoniometer for measurements at low shear rate and a custom-designed slit-die rheometer for high shear rate applications. In this study, the rheological properties of Rice Husk Ash (RHA)-filled polypropylene are studied making use of a Brabender slit-die rheometer, similar to that devised by Han, (1974). The melt behaviour was also studied using a twin-rotor mixer and a melt flow indexer. The main interest of this study is to investigate the effect of incorporating RHA filler (untreated filler and treated by a silane-based coupling agent, *Prosil 2020*) to the rheological properties of polypropylene.

The RHA used in this study has about 95% silica with a mean particle size of 5  $\mu\text{m}$  and density of 2.2  $\text{g cm}^{-3}$ .

## MATERIALS AND METHODS

The rice husk ash used in this study was obtained from a rice mill. The RHA was ground to fine powder using a ball mill. The polypropylene used was Propelinas 600G (homopolymer) from Polypropylene (M) Sdn. Bhd. with a density and melt index specified as 0.9  $\text{g cm}^{-3}$  and 12 g per 10 min respectively. The coupling agent chosen was *Prosil 2020*, a proprietary material from Prosil Inc., containing a specific peroxide to generate free radicals that initiate reaction with the matrix material. The particle size distribution of the RHA was determined by a Horiba particle size analyser. Density of the particles were measured based on ISO 8962, with some modifications using a glass pycnometer (Fuad *et al.*, 1993).

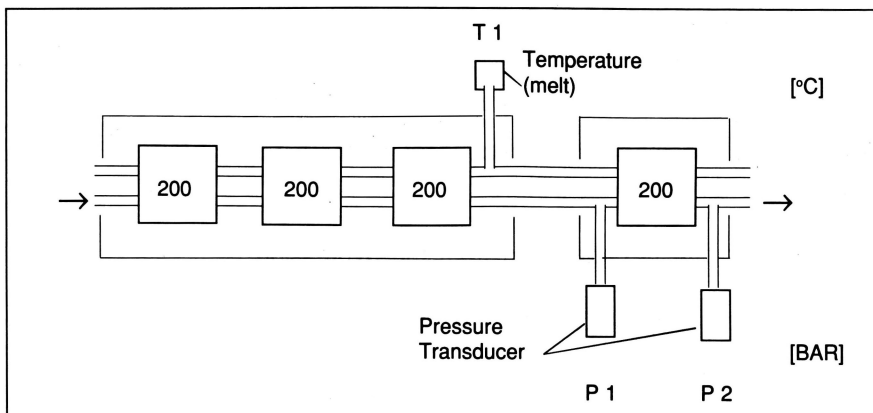
## Filler Treatment

The treatment level used for the *Prosil 2020* coupling agent was 1.5% by mass of the RHA filler. The coupling agent was diluted in ethanol to make up a 10% solution for better dispersion. The RHA filler was charged into a bench top tumbler mixer and the *Prosil* solution was added slowly over a period of 15 min to ensure uniform distribution of the coupling agent. After completion of the silane addition, the filler was continuously mixed for another 30 min. The treated filler was then dried at 100°C for at least 2 h.

## Compounding and Rheology Study

The untreated RHA and *Prosil*-treated RHA were compounded into polypropylene by means of a Berstoff twin-screw compounder with a constant temperature profile of 200°C, at 150 rpm. The compounds were extruded through a 4-strand rod die into a water bath, pulled and pelletized. The compounded samples were dried at 70°C for about 12 h prior to rheology study.

A Brabender rheometric slit capillary die was used for studying the rheological property of the filled polypropylene. The slit die (height 2 mm, width 20 mm, length 160 mm) was used in conjunction with a measuring extruder (brabender 19/25D with metering screw, 4:1) and the Plasticorder PL-2000-6 data processing system. Two pressure transducers (at 100 mm apart) and a thermocouple were employed for shear stress determination. Configuration of the set-up is as shown in Figure 1. The extrudates were cut off at regular intervals and weighed to get the mass extruded per min value which was then input into the extruder evaluation software. Based on the melt density (determined earlier by the Melt Flow Index technique), the volumetric output and thus the shear rate may be computed. Viscosity determination and Rabinowitsch correction applied to get the true shear rate were performed by the aid of the Brabender evaluation software.



**Figure 1.** Set-up configuration for the Brabender slit-die rheometer system

### **Brabender Mixing Study**

Mixing study was carried out using a Brabender W50E thermoplastics mixer. The untreated RHA filler, treated RHA filler, and polypropylene were mixed and weighed proportionally to prepare samples equivalent to 10, 20, 30, 40 and 50% filler loadings. Mixing was carried out at a mixer temperature of 180°C, rotor speed of 40 rpm, for a period of 5 min. A torque versus time curve was obtained for each sample.

### **Melt Flow Index (MFI) Test**

MFI of the composites were determined from the extruded granules according to ASTM D 1238 using a weight of 2.16 kg at a temperature of 230°C on a Zwick 4105.

## **RESULTS AND DISCUSSION**

### **Effect of Shear Rate on Shear Stress**

The true wall shear stress,  $\tau_w$  may be calculated from the expression:

$$\tau_w = Hp/2L \quad (1)$$

where;

H = height of the slit (of the die)

L = distance between the two pressure transducers

p = pressure difference between the two transducers

Knowing the dimensions of the die, expression (1) may be simplified to:

$$\tau_w = 0.01p \quad (2)$$

i.e. the shear stress measurement is dependent on the pressure drop between the two points along the length of the capillary.

The apparent shear rate is determined from the expression:

$$\gamma = 6Q/Bh^2 \quad (3)$$

where;

Q = volumetric flow rate

B = width of the slit

Again, the expression may be simplified to:

$$\gamma = 75Q \quad (4)$$

i.e. the shear rate is dependent on the amount of extrudate generated per unit time. Applying the Rabinowitsch correction to account for the non-Newtonian behaviour of the polymer melt, the true shear rate may be represented by:

$$\gamma = 75Q \left( \frac{2n + 1}{3n} \right) \quad (5)$$

where  $n$  is defined by

$$n = \frac{d \ln \tau_w}{d \ln 75Q} \quad (6)$$

and may be determined from the gradient of the  $\ln \tau_w$  versus  $\ln (75Q)$  plot.

The effect of shear rate on the shear stress of the neat and filled polypropylene is as shown in the logarithmic plot in Figure 2. It may be observed that over the range of shear rate investigated the melts follow the power law:

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

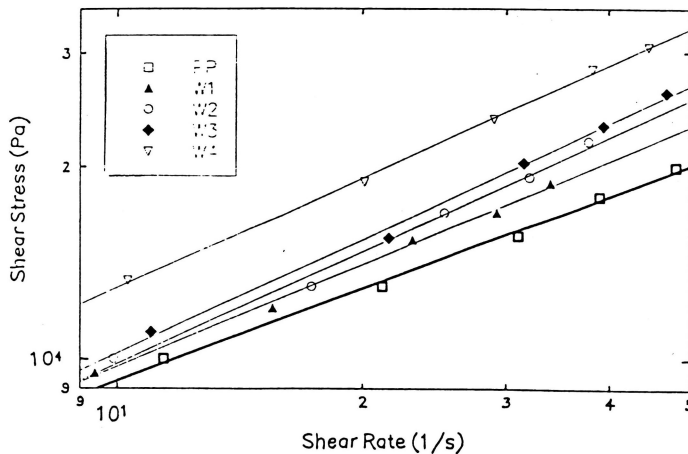
where;

$\tau_w$  = shear stress at the wall

$K$  = material consistency

$\gamma$  = shear rate at the wall

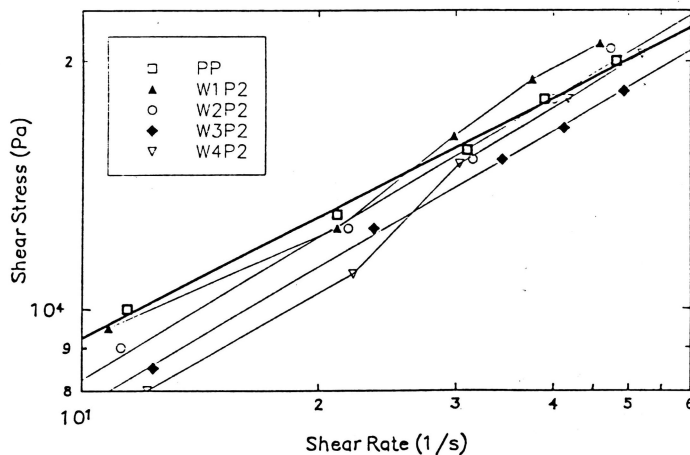
$n$  = flow index



**Figure 2.** Effect of shear rate on shear stress of RHA-filled polypropylene. W1, W2, W3 and W4 represent 10, 20, 30 and 40% filler contents respectively

It is observed that the shear stress increases with shear rate. As the filler content increases, the shear stress also increases accordingly, i.e. at a fixed shear rate the melt having higher filler content exhibits higher shear stress (Figure 2). The increase in shear stress may be attributed to the non-viscous behaviour (extremely high viscosity) of the filler particle. Addition of such fillers inevitably increases the overall viscosity of the melt and thus higher stress will be encountered during the extrusion process. This is in line with subsequent observation (during the Brabender mixing study) that incorporation of higher filler loadings increases the mixing torque. Han, (1974) and Bajaj *et al.*, (1989) reported similar findings in their studies on CaCO<sub>3</sub> and talc-filled polypropylene systems, respectively.

Application of the silane coupling agent containing a peroxide generator to the RHA filler, results in marked changes in the rheological behaviour of the melt (Figure 3). Overall, there is a drastic drop in shear stress when compared to the filled melt without any coupling agent. The shear stress of most of the composite melts is even lower than the that of neat polypropylene particularly at lower shear rate indicating the peroxide effect overwhelming the filler effect. The decrease in the stress is thought to result from degradation of the polypropylene molecular chains due to free radical attack generated by the peroxide. The degradation results in lowering of the molecular weights of the polypropylene matrix and consequently easing the flow of the melt. Tzoganakis *et al.*, (1989) produced nine different molecular weight polypropylenes by controlled peroxide degradation and showed similar effect of decreasing shear stress with lowering of molecular weight.



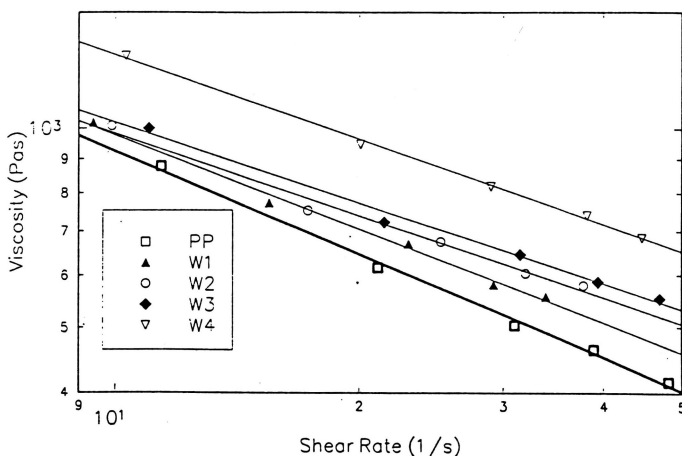
**Figure 3.** Effect of shear rate on shear stress of RHA-filled polypropylene treated with 1.5% silane (Prosil 2020) coupling agent. W1P2, W2P2, W3P2 and W4P2 represent 10, 20, 30 and 40% filler contents respectively

For low filler content samples (e.g. at 10% filler loading) undergoing higher shear rate, the shear stress seems to be greater than that of the neat polypropylene. This is probably due to the lower peroxide concentration in the polypropylene melt resulting in lower degree of degradation and thus the filler content seems to exert greater influence on the shear stress than the degradation effect. At higher loadings, the higher concentration of the peroxide results in higher degree of chain scissions resulting in greater fall of the shear stress values at all shear rates evaluated.

The peroxide used in *Prosil 2020* is bis(t-butyl peroxy)di-isopropyl benzene with a 10 h half life at 122°C. Work on grafting of polypropylene employing various organic peroxides have been described by Callais and Kazmierczak, (1990).

### Effect of Filler Loading on Viscosity

As expected, addition of RHA filler to the polypropylene matrix increases the melt viscosity, as shown in Figure 4. The viscosity increases steadily with filler loading; at 40% filler loading the increase was most substantial, parallel to that observed in the previous shear stress versus shear rate curve. The increase in viscosity with respect to filler concentration is similar to those reported of mica/polypropylene and  $\text{CaCO}_3$  polypropylene (Han, 1974) systems. Incorporation of filler is thought to hamper the matrix intermolecular motion, reducing molecular mobility and thus increasing viscosity of the melt. Goel, (1980), however, reported that the viscosity of a 40% talc-filled polypropylene is independent of filler concentration.

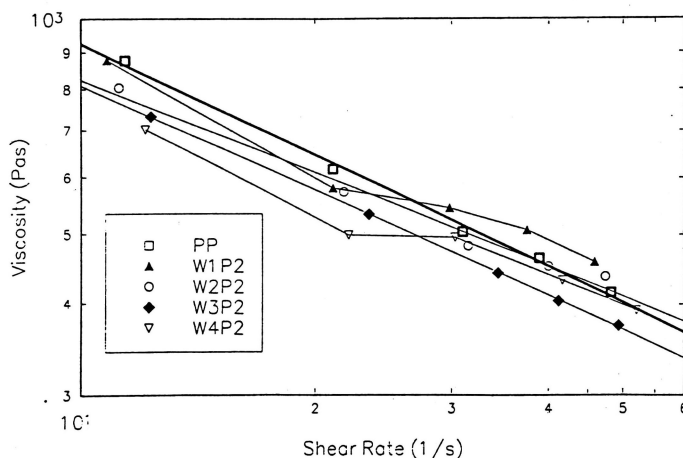


**Figure 4.** Effect of shear rate on viscosity of RHA-filled polypropylene. W1, W2, W3 and W4 represent 10, 20, 30 and 40% filler contents respectively

According to Folkes, (1982) at very high shear rate, typically at  $10^4$  and  $10^5 \text{ sec}^{-1}$ , the viscosity of neat and glass-filled polypropylene converged to a very similar value indicating that only at high shear rate, the viscosity is independent of filler content. A similar trend was observed by Minoshima *et al.*, (1980) for a series of neat polypropylene melts of varying molecular weight. Since the shear rate evaluated here is well below the above range, this effect was not observed in our system.

### Effect of Coupling Agent on Melt Viscosity

Pretreatment of the RHA filler with the *Prosil 2020* coupling agent reduces the viscosity of the melt as shown in Figure 5. This general observation is in agreement with the previous work of Han *et al.*, (1981) on polypropylene- $\text{CaCO}_3$  (50 wt percent) composite treated with two types of silanes and a titanate coupling agents. Bajaj *et al.*, (1989) noted a similar effect with the titanate coated mica-filled polypropylene system. Although the RHA-filled polypropylene melt does show the familiar trend of decreasing viscosity upon addition of filler, the pattern of changes is not the same to any of the above systems. Incorporation of the treated RHA filler reduces the melt viscosity drastically such that the viscosity of most of the composite melts are even lower than that of the neat polypropylene. As the filler concentration increases, the viscosity decreases further - the most filled materials have the lowest viscosity. This is apparent particularly, at lower shear stress levels.



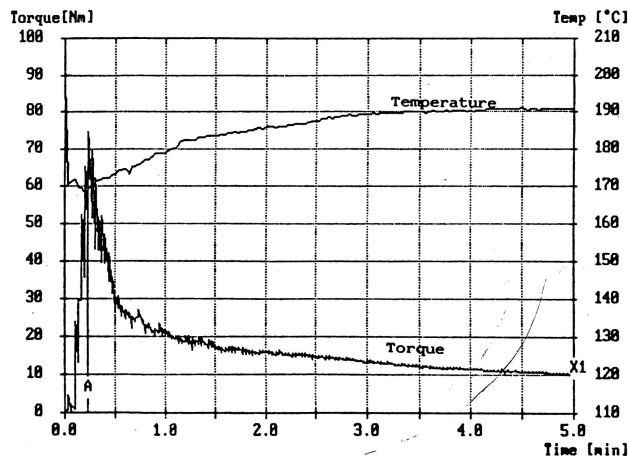
**Figure 5.** Effect of shear rate on viscosity of RHA-filled polypropylene treated with 1.5% silane (*Prosil 2020*) coupling agent. W1P2, W2P2, W3P2 and W4P2 represent 10, 20, 30 and 40% filler contents respectively



At low shear rate, the degree of viscosity reduction is greater with higher filler content, because higher filler loadings mean higher peroxide content originating from the coupling agent. Consequently, higher degree of molecular chain scissions is expected. At higher shear rates, however, the same trend is not observed. Here, the filler loading effect, i.e. higher viscosity with higher filler contents, seems to outweigh the effect of the coupling agent.

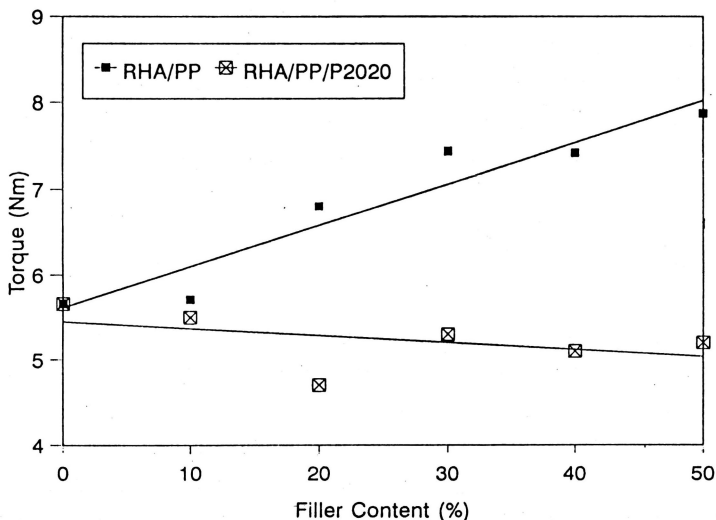
### Mixing Torque Study

Torque versus time curves were obtained for polypropylene and composites having various filler loadings. Torque values after a 5-min mixing time of the mixture were recorded by the mixer evaluation software. A typical curve is as shown in Figure 6. The peak torque is due to charging of sample; being cold and unmelted; the mixing torque is very high. Gradually as polypropylene begins to melt, the torque decreases and stabilizes after approximately five mins. For comparison purposes, the torque after three mins from the peak was taken as the value of interest.



**Figure 6.** A typical Brabender mixing curve for the RHA/polypropylene composite melt

As the filler content increases, the mixing torque of the untreated RHA melt rises steadily as shown in Figure 7. As the fine filler particles get into the polypropylene matrix, the mobility of the macromolecular chains of the polymer is reduced, thus offering more resistance (torque) to flow. In actual practice, dispersion of fillers in a polymer matrix is not perfect. Similarly, as in the case of most fillers, the RHA particles are probably not dispersed very well too. The fine RHA particles tend to combine together to form bonded aggregates which in turn may unite to form larger structures known as agglomerates (Ess and Hornsby, 1987).



**Figure 7.** Effect of Prosil 2020 coupling agent on the mixing torque of RHA-filled polypropylene

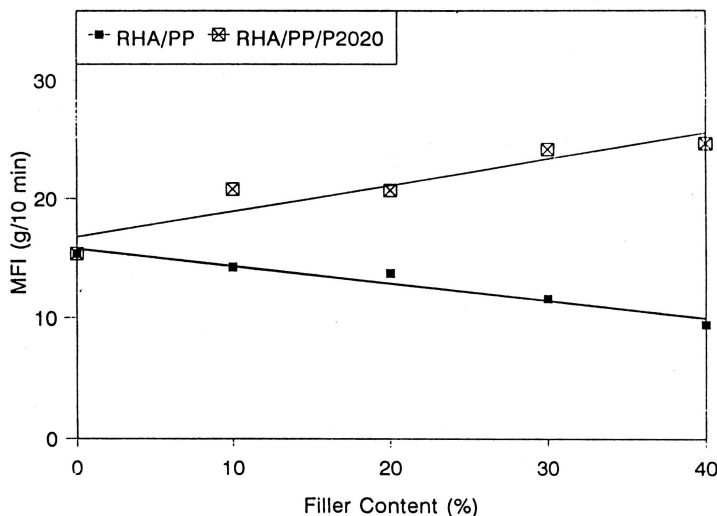
Addition of *Prosil 2020* coupling agent on the other hand, decreases the torque considerably for the RHA composite melts when compared to those without any coupling agent. The decrease is very obvious such that the mixing torque actually decreases with increasing filler contents. Lower torque means easier mixing and this may be brought about as indicated earlier, by the degradation of the polypropylene matrix (due to the peroxide attack). At higher filler contents, greater amount of free radicals are available, hence greater degree of degradation is expected resulting in remarkable lowering of the mixing torque.

### Melt Flow Index (MFI)

As filler content increases, the MFI value for the untreated RHA-polypropylene melt decreases as shown in Figure 8. This is an expected event, as addition of fillers to the polypropylene restricts molecular motion thus imposing extra resistance to flow. This trend is reflected in the earlier torque and rheology studies where increasing filler content results in higher torque and higher viscosity respectively.

Addition of the *Prosil 2020* coupling agent causes a marked increase in melt index of the RHA composite melt. As MFI values usually give good indication of the molecular weight of the material, the increasing MFI values of the *Prosil*-treated RHA melt may indicate lowering of the molecular weight with increasing filler concentration. The lowering of the molecular weights is believed to have been the result of peroxide-initiated degradation of the polypropylene matrix. Again this trend is in agreement with the observation of the torque study where the

torque of the Prosil-treated RHA composites decrease with filler loadings. Higher MFI values means easier flow of materials, i.e. lower viscosity melts. Thus, they support earlier observation in the rheology study where higher filler loadings were observed to result in lowering of the viscosity of the composite melt.



**Figure 8.** Effect of Prosil 2020 coupling agent on the MFI of RHA-filled polypropylene

## CONCLUSIONS

The viscous properties of RHA-filled polypropylene with and without coupling agent was investigated using Brabender slit-die rheometer. The shear stress and melt viscosity increases with filler concentration. When the RHA was pre-treated with a peroxide containing silane coupling agent, the viscosity decreases. The degree of viscosity reduction increases with filler, i.e. peroxide concentration. Drop in viscosity is attributed to the peroxide-induced degradation of the polypropylene matrix. Results from the Brabender mixing torque and the MFI studies corroborate the rheological properties investigated using the slit-die technique.

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