

The Influence of Nanoparticles on Rheological Properties of Polypropylene

Piia Peltola, Elina Välipakka, Seppo Syrjälä and Kalle Hanhi

Tampere University of Technology, Laboratory of Plastics and Elastomer Technology

P.O. Box 589, 33101 Tampere, Finland

ABSTRACT

In this study polypropylene (PP), maleic anhydride-grafted polypropylene (PPgMA) and organically modified montmorillonite clay were melt compounded in a twin-screw-extruder. The main objective was to study the effect of nanofillers on rheological behaviour of the materials. The rheological characterization was carried out by using rotational and capillary rheometry.

INTRODUCTION

Over the last two decades the nanocomposites have generated a lot of interest among scientists and industry. Engineered thermoplastic polymers form a wide and continuously growing market as they have very favourable properties. Polypropylene is one of the most widely used polymers showing an attractive combination of low cost, low weight, and extraordinary versatility in terms of properties and applications. By adding nanosized particles into the polymer matrix it is possible to enhance material properties such as mechanical, thermal and gas barrier properties even at a relatively low particle content (1-5 w-%). The enhanced properties of nanocomposite material have their origin at the high surface area of nanoscale particles [1-2].

Processing of polymer nanocomposites by melt compounding has found to be a very demanding and challenging task. It seems that among the parameters affecting compounding behaviour (temperature, shear rate, screw speed and screw configuration)

the rheological properties of matrix polymer have large effect on the degree of dispersion and exfoliation of organoclays that are very essential to nanocomposite properties [3-6]. Rheological properties play also important role when processing polymer products by means of extrusion and injection molding. Previous rheological studies of nanocomposites have shown that at high shear rates nanocomposites demonstrate greater shear thinning tendency than pure polypropylene because of preferential orientation of organoclay layers [7-8].

In case of polypropylene, it is necessary to use compatibilizers to obtain a good intercalation effect and adhesion between the nonpolar polypropylene and the hydrophilic organoclay. Maleic anhydride grafted polypropylene (PPgMA) is one of the most commonly used compatibilizers. It must be emphasized that too low PPgMA content cannot enhance the compatibility greatly, while too high maleic anhydride content may lead to deterioration of the nanocomposite properties due to the low molecular weight of PPgMA. Therefore the most typically used proportion of PPgMA to clay seems to be 3:1 [9-11]. When using compatibilizers one must make a distinction between the properties achieved by using nanofillers to those of neat polypropylene.

In this study the PP, montmorillonite and compatibilizer were melt compounded with twin-screw-extruder. The rheological properties of the compounds were examined by using rotational and capillary rheometry.

Table 1. Physical properties of materials

Trade name	Density [g/cm ³]	Softening point [°C]	MFR g/10 min
PP HF700SA	0.908	153	21
Licomont AR 504	0.89-0.93	154-158	-
Nanomer 1.44P	1.7	-	-

EXPERIMENTAL

Materials

The isotactic polypropylene homopolymer (HF700SA) of injection grade provided by Borealis was used as base-polymer. The compatibilizer used in this study was maleic anhydride modified polypropylene (Licomont® AR 504) provided by Clariant. Nanomer® 1.44P was supplied by Nanocor. This surface modified montmorillonite clay is especially intended for use with polypropylene. All the materials used in this study are commercially available and the physical properties of the base polymer, compatibilizer and organoclay are summarized in Table 1.

Melt compounding

The polypropylene (PP) nanoclay composites were compounded by using co-rotating twin-screw-extruder ZSK 25 by Werner and Pfleiderer. Barrel temperatures were from feeding to die respectively (170, 170, 170, 180, 180, 180, 185 °C). Three different screw speeds were used i.e. 200, 500, 1000 rpm. The materials were dried at 80 °C for 6 h before melt processing. The PP granules, PPgMA and clay were metered

independently in the required proportions by using gravimetric dosing units.

The concentration of 5 w-% of nanoclay and 9 w-% of PPgMA were compounded to polypropylene. Neat PP and PP+PPgMA were also extruded in order to see the effect of the processing on material properties. Prepared compounds are presented in the Table 2.

Rheological characterization

The rheological measurements were carried out by using capillary (Göttfert Rheograph 6000) and rotational rheometer (Physica MCR 301). Before the measurements all samples were dried at 80 °C in an oven for 3 h in order to prevent moisture induced degradation phenomena.

The samples for rotational rheometry measurements were prepared by compression molding the melt blended granules with a hydraulic press (200 bar, 180 °C and 2 min) into thin disks (diameter 25 mm and thickness 1 mm). The rotational rheometry experiments with a parallel-plate geometry (diameter 25 mm, gap of 1 mm) were carried out in order to obtain low shear rate range data from 0.001 to 1 s⁻¹ at 200 °C.

The higher shear rate measurements

Table 2. Compounded materials

Compound	PP [w-%]	Clay [w-%]	PPgMA [w-%]	Screw speed [rpm]
1	100	-	-	-
2	100	-	-	200
3	100	-	-	500
4	100	-	-	1000
5	91	-	9	200
6	91	-	9	500
7	91	-	9	1000
8	86	5	9	200
9	86	5	9	500
10	86	5	9	1000

were performed by using capillary rheometer over the shear rate range from 10 to 5000 s^{-1} at 200 °C. A capillary aspect ratio equal to 20 was used in all cases.

Thermal gravimetric analysis

The thermal gravimetric analyzer (Perkin Elmer gravimetric analyzer TGA6) was used to evaluate the thermal stability of composites and to verify the nanoclay concentration. The tests were performed in the standard mode under nitrogen atmosphere at temperature range from 50 to 500 °C at heating speed 20 °C/min.

RESULTS AND DISCUSSION

TGA

TGA was used to evaluate the nanoclay concentration of the compounds. The aim was to verify the stability of the gravimetric feeding system. Also the thermal degradation of the compound could be examined.

The desired nanoclay concentration in the final compound was 5 w-%. As can be observed from the Fig. 1, the desired concentration was reached and the deviation was small. The measured nanoclay content is shown in Table 3. Degradation of the PP occurs between 300-450 °C.

Table 3. Clay concentration of the samples

Compound	Clay content [w-%]
PP+Clay5+PPgMA (200)	4.67
PP+Clay5+PPgMA (500)	4.61
PP+Clay5+PPgMA (1000)	4.90

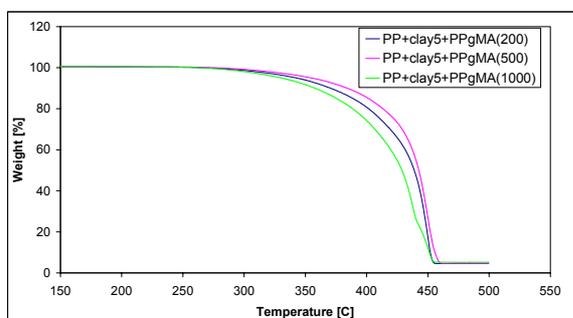


Figure 1. TGA results

Rheological properties

In the rotational rheometry of elastic melts with parallel-plate or cone-and-plate geometries the primary source of error is the flow irregularity, called edge fracture. In some studies it has been evaluated that the visible edge fracture would occur at 1 s^{-1} [12]. Therefore, in this paper the rotational rheometer results are limited to cover range from 0,001 to 1 s^{-1} .

In this study the rheological properties of the PP based nanoclay compounds were evaluated by using rotational and capillary rheometry. The assumption was that the measured data from both rheometers should be possible to combine.

Fig. 2 illustrates that the viscosity curves of neat PP continue smoothly. The same phenomena can be detected from the Fig. 3 where the data from PP+PPgMA is presented. As expected, the viscosity of PP+PPgMA is slightly lower than that of pure PP due to smaller molecular weight of PPgMA. However, the capillary data in the case of PP+Clay5+PPgMA was higher than expected by extrapolating the data obtained from rotational rheometer. This phenomenon is detected only in case of PP+Clay5+PPgMA compounds (Fig. 4) and it could be due to the thermal degradation. On the other hand, Gu et al. found almost the same type of behaviour in their research [7]. At low shear rates the viscosity of nanocomposite is ten times higher than neat PP and PP+PPgMA. This is commonly known phenomena when using fillers. The viscosity curve of neat PP shows a clear zero viscosity but the nanocomposite displays more significant shear thinning behaviour at low shear rates. The viscosity of nanocomposites intersects the viscosity of PP at 1 s^{-1} and after that the viscosities of nanocomposites are comparable with or even lower than those of neat PP. The viscosity data for all materials is plotted in Fig. 5.

One purpose of this study was to find out how the processing (screw speed) influences the rheological properties. There is no remarkable decrease in viscosities when dif-

ferent screw speeds were used as shown in the Fig. 2-5.

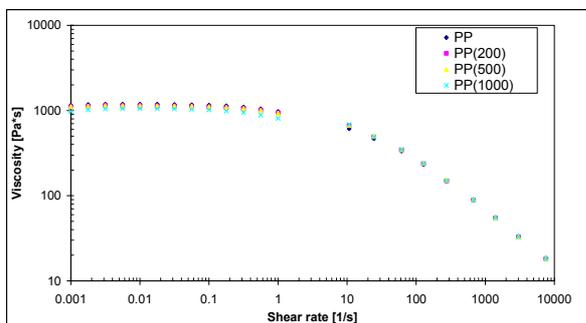


Figure 2. The viscosity data of neat PP

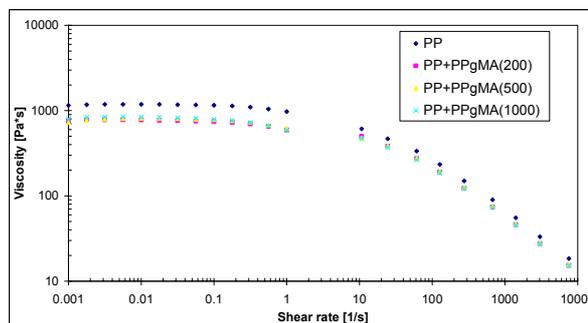


Figure 3. The viscosity data of PP+PPgMA

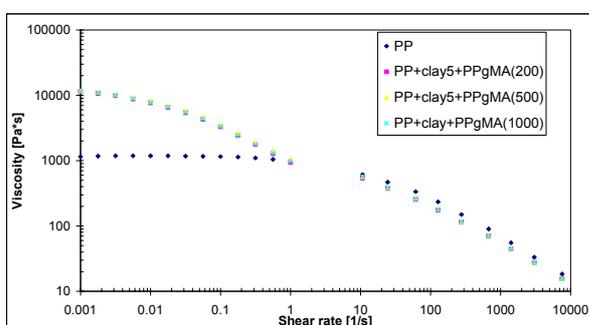


Figure 4. The viscosity data of PP+Clay5+PPgMA

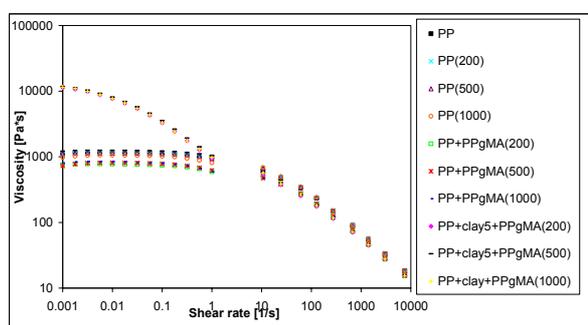


Figure 5. The viscosity data of compounds

CONCLUSIONS

Polypropylene montmorillonite clay nanocomposites were melt compounded by using twin-screw-extruder. Different screw speeds were applied (200, 500, 1000 rpm). The viscosities of the compounds were measured with both rotational and capillary rheometers. The different screw speeds had only a slight influence on rheological properties of compounded materials. But nanocomposites revealed stronger shear thinning effect with low shear rates. At the shear rate 1 s^{-1} the viscosities of nanocomposites intersects the viscosities of PP and PP+PPgMA. This phenomena shows that the nanocomposites might be easier to process due to decrease of viscosity.

ACKNOWLEDGEMENTS

We would like to give our sincere thanks to professor Seppo Syrjälä for his good advice. We are also grateful to Nanocor for providing nanoclays.

REFERENCES

1. Sinha Ray, S., and Okamoto, M. (2003), "Polymer/layered silicate nanocomposites: a review from preparation to processing", *Prog. Polym. Sci.*, 28, 1539-1641.
2. Thostenson, E.T., Li, C., and Chou, T. (2005), "Nanocomposites in context", *Composites Science and Technology*, 65, 491-516.

3. Incarnato, L., Scarfato, P., Scatteia, L., and Acierno, D. (2004), "Rheological behavior of new melt compounded copolyamide nanocomposites", *Polymer*, 45, 3487-3496.
4. Huan, H., Huan, Y., and Chuan, Y. (2003), "Microstructure changes of a polypropylene/montmorillonite nanocomposite in a single screw extruder", *Journal of Materials Science Letters*, 22, 1547-1549.
5. Krishnamoorti, R., and Yurekli, K. (2001), "Rheology of polymer layered silicate nanocomposites", *Current Opinion in Colloid & Interface Science*, 6, 464-470.
6. Wagener, R., and Reisinger, T. (2003), "A rheological method to compare the degree of exfoliation of nanocomposites", *Polymer*, 44, 7513-7518.
7. Gu, S., Ren, J., and Wang, Q. (2004), "Rheology of Poly(propylene)/Clay Nanocomposites", *Journal of Applied Polymer Science*, 91, 2427-2434.
8. Wagener, R., and Reisinger, T. (2003), "A rheological method to compare the degree of exfoliation of nanocomposites", *Polymer*, 44, 7513-7518.
9. Wang, Y., Chen, F., Li, Y., and Wu, K. (2004), "Melt processing of polypropylene/clay nanocomposites modified with maleated polypropylene compatibilizers", *Composites: Part B*, 35, 111-124.
10. Xu, W., Liang, G., Wang, W., Tang, S., He, P., and Pan, W. (2003), "PP-PP-g-MAH-Org-MMT Nanocomposites. I. Intercalation Behavior and Microstructure", *Journal of Applied Polymer Science*, 88, 3225-3231.
11. Ding, C., Jia, D., He, H., Guo, B., and Hong, H. (2005), "How organomontmorillonite truly affects the structure and properties of polypropylene", *Polymer Testing*, 24, 94-100.
12. Dealy, J., and Wissbrun, K. (1995), "Melt rheology and its role in plastics processing", *Chapman & Hall*, 280-281.