

Advanced Compounding: Extrusion of Polypropylene Nanocomposites Using the Melt Pump

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ABSTRACT: A melt pump was assembled into the compounding line to ensure both sufficient time for diffusion process of polymer chains into the silicate gallery and sufficient mechanical shear energy for exfoliation of clay layers. The melt pump in front of the open co-rotating twin-screw extruder controls the throughput rate and the residence time, whereas the screw speed and screw geometry in the extruder determine the mechanical shear energy applied on the compound. Due to melt pump employment, the melt in metering zone can be accumulated, which results in higher mixing efficiency. It was

found that using the melt pump leads to up to two times higher residence time and, consequently, higher level of material reinforcement as investigated by extensional rheology. Different melt pump adjustments, screw geometries, and screw speeds were tested and their effect on processing characteristics and material reinforcement was investigated. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1422–1428, 2009

Key words: polypropylene; organoclay; melt compounding; gear pump

INTRODUCTION

“Melt mixing” (compounding) is industrially the most attractive method for polymer nanocomposites preparation due to its technological simplicity (usage of common polymer processing machines in contrast to special equipment and procedures in chemical laboratories, which are required for “in situ” or “solution” method). Moreover, it is possible to use various matrix polymers (different molecular weights, grafting grades, copolymers, etc.) or even recycled polymer materials.^{1–5} The production efficiency of this method is considerably higher than other techniques employed for nanocomposites preparation (“melt mixing” proceeds in order of minutes, as compared to several hours for “in situ” and “solution” methods).^{6,7}

From the economical point of view, using the co-rotating twin-screw extruder as a continuous processing technology is industrially preferred to melt mixing in a discontinuous kneader. It is obvious that for the successful dispersion of silicate plates in polymer melt by continuous processing, the follow-

ing two requirements have to be fulfilled: sufficient high shear energy and enough long residence time.⁸ However, these two effects are opposite in the extrusion process. With higher shear forces (e.g., usage of kneading blocks generating higher shear rate or increase in screw speed), the residence time is shortened. To our knowledge, we presented for the first time⁹ both high shear rate and longer residence time that can be matched by implementing a melt pump in front of an open twin-screw extruder. The melt pump in extrusion technology is usually applied to reduce the pressure and throughput instability (melt pulsation) in the extruder. In the present study, the melt pump acts as an effective tool to control the residence time during compounding of polypropylene nanocomposites.

Only a few articles dealing with processing analysis of nanocomposites preparation in a twin-screw extruder have been published hitherto.^{10–19} The main goal was usually focused on variation in screw geometry, screw speed, or throughput rate. Wang et al.²⁰ studied dependency of compounding quality on feeding sequence and grafting grade of compatibilizer (MA grafting degree of 0.5 up to 4 wt %). Variation in feeding sequence (i.e., feeding of the premixed PP-g-MA and clay by a hopper and usage of side feeder for PP matrix) led only to a moderate increase in residence time. Drawbacks of this concept are reduced throughput rate and the necessity of premixing PP-g-MA with clay. In this article, a substantial prolongation of residence time is

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reported by using standard industrial feeding sequence without additional premixing. It is obvious that two-step compounding gives superior results as compared with that of one-step mixing.¹¹ Hence, successful preparation of nanocomposite masterbatch is essential to reach a delaminated system in the second processing step (dilution of masterbatch to final clay concentration). As the residence time is the dominant factor in production of nanocomposites in extruders,¹¹ the interest of this work is focused on the possibilities of melt pump application for polymer nanocomposites masterbatch preparation along with deeper analysis of processing conditions.

MATERIALS AND METHODS

Materials

The isotactic polypropylene (PP) homopolymer HC600TF (MFI 2.8 g/10 min; 230°C/2.16 kg) used for the preparation of nanocomposite masterbatches was supplied by Borealis (Linz, Austria). The used nanofiller (montmorillonite intercalated with dimethyl distearyl ammonium chloride) with commercial name Nanofil 5 was supplied by Süd-Chemie (Munich, Germany). The compatibilizer Scona TPPP 2112 FA (PP grafted with 1 wt % of maleic acid anhydride, PP-g-MA, MFI 14.8 g/10 min) was supplied by Kometra (Schkopau, Germany).

Compounding process

For the compounding process, an intermeshing, corotating twin-screw extruder Theysohn TSK30/40D (Theysohn Extrusionstechnik, Korneuburg, Austria) using 10 barrel segments and a string die was employed. The PP and compatibilizer were fed upstream through the main hopper and the organoclay downstream at the 4th extruder barrel. All the

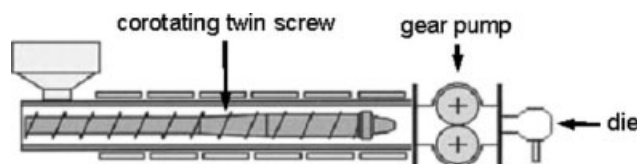


Figure 1 Scheme of setup for the compounding process.

components were fed by separately controlled gravimetric dosage units at an overall throughput rate of 10 kg/h. The screw geometry and speed were varied according to Table I to observe the influence of melt pump on compounding quality at different processing conditions. The Extrex SP gear pump was purchased from Maag Pump Systems Textron (Oberglatt, Switzerland). Three different melt pump adjustments were examined: (1) Δp negative, where the negative pressure difference between the outlet and inlet pressure of the melt pump has been set ($p_{\text{out}} - p_{\text{in}} = -100$ bar). In this way, a back pressure of polymer melt up to 9th extruder segment (approximately 30–40 cm before the melt pump) has been achieved. (2) Δp neutral, where the inlet and outlet pressure have been kept at the same level ($p_{\text{out}} - p_{\text{in}} = 0$ bar) and (3) Δp positive, with a positive pressure difference ($p_{\text{out}} - p_{\text{in}} = 5$ bar) was set. For a comparison, all the tested compounds were processed without the melt pump as well. The setup for the compounding process is schematically illustrated in Figure 1. Specifications of screw geometries (low and high shear configuration, indicated as G1 and G2, respectively) are described in Figures 2 and 3. The high shear configuration (G2) was assembled by insertion of kneading blocks with 90° discs arrangement in the 7th cylinder element and mixing screw elements into 9th cylinder element, as compared with G1 configuration. Extruder temperature profile has been set at 160–200°C from hopper up to die. The melt pump temperature was kept at 200°C. The values of residence time and extruder torque for different adjustments of the melt pump are plotted in Figures 4–7; the radial pressure profile in the extruder was monitored from 5th up to 10th segment (Figs. 8–11). The minimal residence time was measured by using a color masterbatch as the time between granulate insertion into the hopper and coloring of the outgoing molten string. The compatibilizer admixture related to organoclay content (20 wt %) was chosen in a ratio (Clay : Compatibilizer) of 1 : 1 according to our previous investigations.^{21–25}

Extensional melt rheology

We have already presented the advantages of polymer nanocomposites reinforcement assessment by melt strength evaluation using Rheotens

TABLE I
Indication of the Prepared Nanocomposites

Melt pump adjustment	Screw speed (rpm)	Geometry
Without melt pump	100	1
Δp negative		
Δp neutral		
Δp positive		
Without melt pump	75	1
Δp negative		
Δp neutral		
Δp positive		
Without melt pump	100	2
Δp negative		
Δp neutral		
Δp positive		
Without melt pump	75	2
Δp negative		
Δp neutral		
Δp positive		

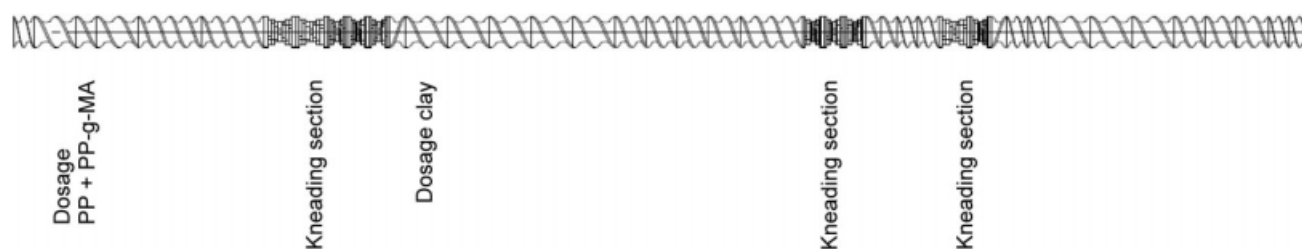


Figure 2 G1 screw configuration.

equipment.^{21–25} The main benefit of the Rheotens measurement consists in its simplicity without need of expensive scientific equipment and additional time for specimens preparation (primary granulate obtained from the extrusion process can be used). The principle of this measurement is illustrated in Figure 12. It is based on elongation of an extruded string by two or four rotating wheels connected with a force transducer. The rotation speed is linearly increased up to when the molten string breaks. The tensile force applied to the wheels along with the draw rate at break allows calculation of the melt strength (stress at break) according to

$$\sigma_b = F_b \times v_b / A_0 \times v_0 \quad (1)$$

where σ_b is the stress at break [Pa], F_b is the tensile force at break [N], v_b is the draw rate at break (mm/s), A_0 is the initial cross-section of molten string (at the die outlet) (m²), v_0 is the extrusion speed of molten string (piston speed) (mm/s).

In our work, the Rheotens 71.97 equipment (Göttfert, Buchen, Germany) in combination with a capillary rheometer was used. The following measuring conditions for capillary rheometer were set: cylinder diameter, 12 mm; die (length/diameter), 30/2 mm; temperature, 210°C; piston speed, 1.9 mm/s; shear rate, 273.6 s⁻¹. The Rheotens equipment was set by applying wheel acceleration of 60 mm/s² and gap between wheels of 0.6 mm.

To compare the melt strength level of different nanocomposites (revealing different magnitudes of v_b), the tensile force at a draw rate of 300 mm/s was chosen as a comparative value. The data were evaluated from at least three measurements for each sample with a measurement error of 2%.

RESULTS AND DISCUSSION

Advanced compounding using the melt pump

The effect of melt pump on processing characteristics during compounding at different screw geometries and speeds is plotted in Figures 4–11. It is obvious that the pressure profile as well as torque and residence time in the extruder are strongly affected by melt pump adjustments. According to the expectations, the highest effect of the melt pump on increase in residence time and extruder torque occurs by adjustment of melt pump to negative pressure difference; on the other hand, no significant differences between processing characteristics at neutral and positive melt pump operating modes were observed. As can be seen from Figures 4–7, values of residence time and average torque revealed the same trend, which has an important impact on the processing efficiency. The level of torque in the extruder gives information about level of shear forces applied during compounding. It can be clearly seen that both residence time as well as shear forces can be increased at the same time by use of the melt pump. The applied shear energy can be controlled by the screw speed and the residence time by adjustment of the melt pump. In this way, efficiency of dispersive as well as distributive mixing in continuous compounding can be substantially increased, depending on construction of twin-screw extruder and the melt pump. The main benefit of the melt pump consists in approximately two times higher residence time achievable. In this way, the diffusion process of intercalation and subsequent delamination of silicate platelets in the polymer matrix are substantially prolonged. The residence time

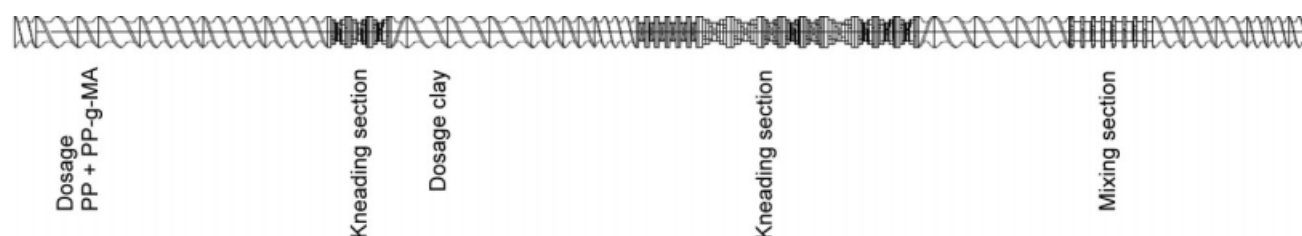


Figure 3 G2 screw configuration.

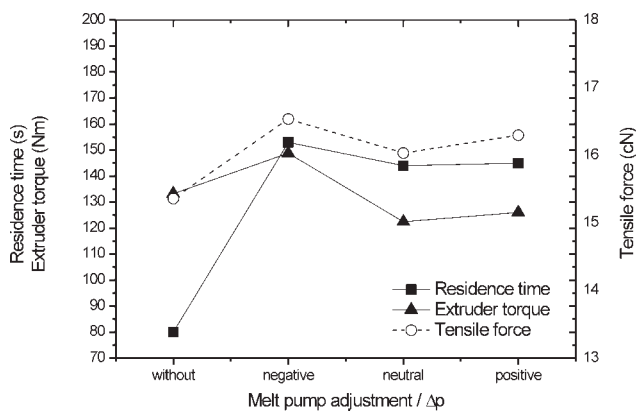


Figure 4 Residence time and extruder torque vs. tensile force (G1, 100 rpm).

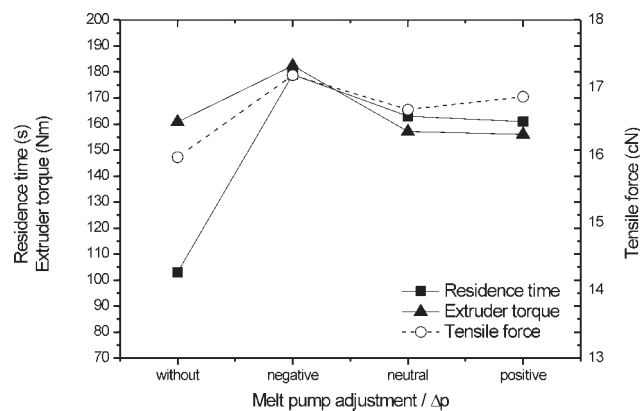


Figure 6 Residence time and extruder torque vs. tensile force (G2, 100 rpm).

is a dominant factor in production of satisfactory nanocomposites in extruders¹¹ so the implementation of melt pump into compounding process introduces an interesting and technologically accessible method of continuous compounding enhancement employable in the field of polymer composites and blends. It should be mentioned that maximal residence time achieved in this study was limited by melt pump construction and torque limitation in extruder. By the usage of larger processing equipment (allowing higher pressure in the melt pump and higher extruder torque), a further significant increase in residence time can be expected.

Evaluation of melt pump effect using extensional rheology

According to our previous investigations,^{9,21–25} the level of reinforcement in PP nanocomposites can be estimated by using extensional rheology with analysis of the melt strength. The silicate platelets form different levels of 3D physical network in the polymer matrix depending on their level of delamina-

tion.^{1–3} Higher delamination results in higher extent of physical network (higher material reinforcement) and therefore in an increase in melt strength. Different particle–particle and polymer–particle physical interactions result in variations in viscoelastic response. It is possible to use extensional rheometry to identify changes in the melt elongational behavior. Individual silicate platelets form a nanoscale network (cardhouse structure)²⁷ and raise the melt strength of the composite.

The level of melt strength, manifested itself by magnitude of tensile force detected at a draw rate of 300 mm/s, is plotted in Figure 13. Nanocomposite systems prepared with the usage of melt pump possess considerably higher levels of melt strength (higher value of tensile force) as those processed without the melt pump. However, at the Δp neutral melt pump operating mode a deterioration in elongational properties occurred. This phenomenon can be assigned to differences in residence time and shear rate applied by the melt pump. At the Δp maximal mode, the residence time was substantially prolonged (Figs. 4–7) and, consequently, diffusion of

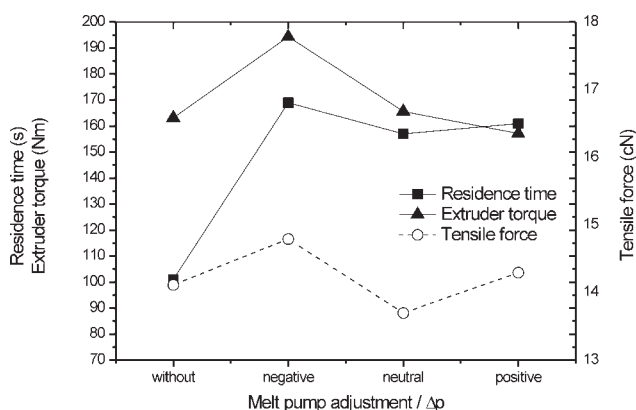


Figure 5 Residence time and extruder torque vs. tensile force (G1, 75 rpm).

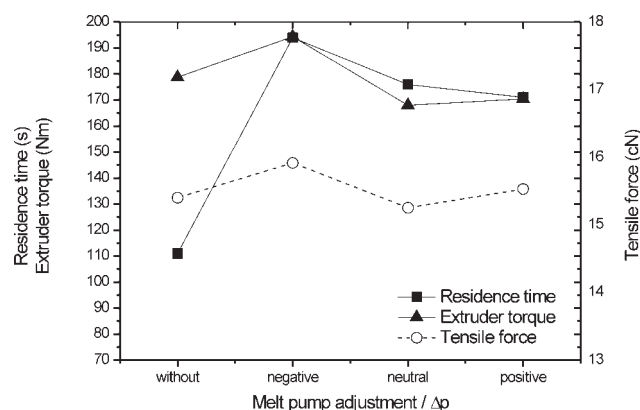


Figure 7 Residence time and extruder torque vs. tensile force (G2, 75 rpm).

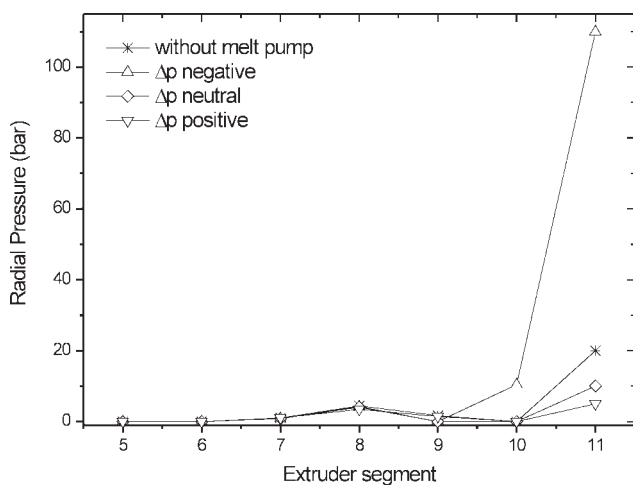


Figure 8 Pressure profile during compounding (G1, 100 rpm, 11 = melt pump inlet).

polymer chains into the silicate interlayer gallery was favored. At the Δp positive mode, the increase in residence time was not so high as in Δp maximal mode, but the outlet pressure in the melt pump was approximately two times higher than the inlet pressure, resulting in additional “melt stretching” inside the melt pump. This additional melt elongation could support higher material reinforcement due to higher orientation of silicate platelets in the flow direction. Subsequently, higher magnitude of melt strength as in the system applying Δp neutral melt pump mode could be reached.

Processing at higher screw speed resulted in the higher reinforcement of polymer matrix. The higher screw speed generates higher shear rate and, subsequently, facilitates clay dispersion during compounding. The high shear screw geometry possesses significantly higher radial pressure along the screws,

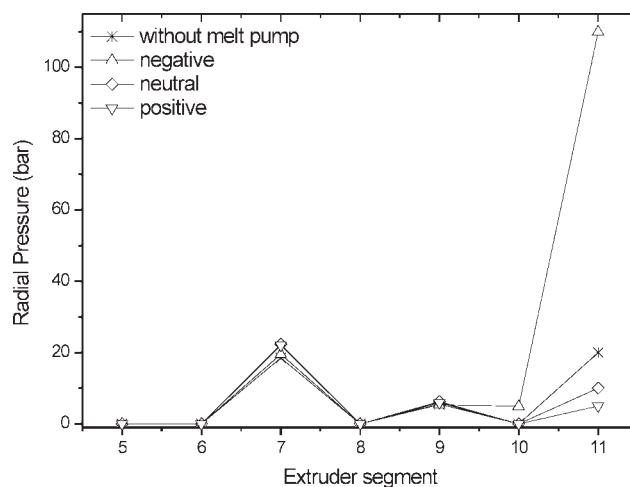


Figure 10 Pressure profile during compounding (G2, 100 rpm, 11 = melt pump inlet).

considerably higher average torque and residence time, as compared to the low-shear configuration (Figs. 4–11). The significant increase in radial pressure in the 9th cylinder element at G2 configuration was caused by the insertion of mixing screw elements into appropriate screw position. Similarly, employment of kneading blocks with 90° discs arrangement resulted in substantial pressure increase in the 7th cylinder element (Figs. 2, 3, and 8–11) as compared with G1 configuration. Generally, kneading blocks with 90° discs arrangement (as compared to other angles) enable the highest efficiency of dispersive mixing and facilitate delamination of silicate layers during compounding.

It can be clearly seen that the level of attainable material reinforcement is generally proportional to the residence time and torque in the extruder (Figs. 4–7). Therefore, the extent of reinforcement in the

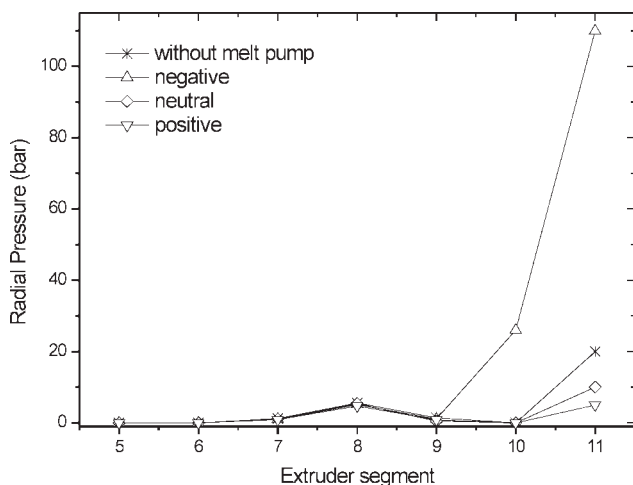


Figure 9 Pressure profile during compounding (G1, 75 rpm, 11 = melt pump inlet).

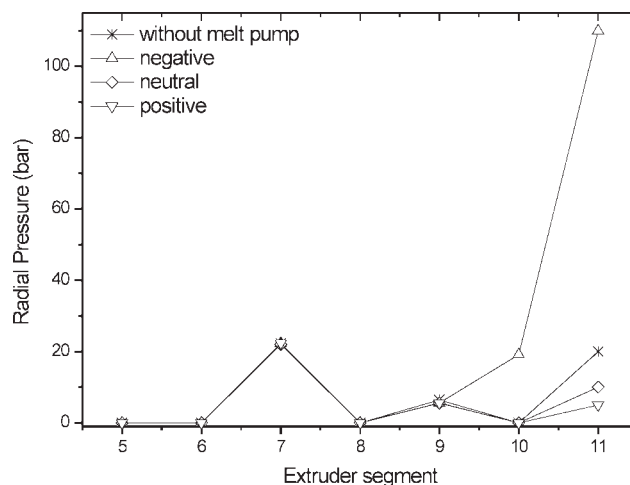


Figure 11 Pressure profile during compounding (G2, 75 rpm, 11 = melt pump inlet).

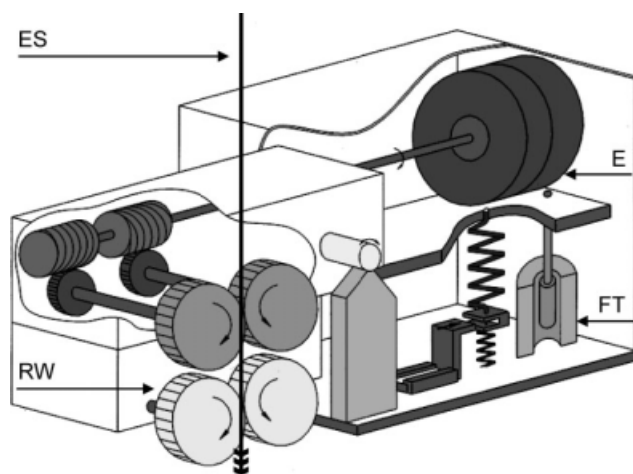


Figure 12 Principle of Rheotens measurement (ES = extruded string, RW = rotating wheels, E = engine, FT = force transducer).²⁶

nanocomposites investigated is dependent on both residence time as well as shear energy simultaneously within all melt pump operating modes. The described method to increase both shear rate as well as residence time simultaneously can be applied for different-scale processing machines and in this way transfer current know-how in the field of polymer nanocomposites from basic to applied research. Comparing the relevance of screw speed and geometry with regard to material enhancement, the higher screw speed using the low-shear configuration is preferable to lower screw speed with high-shear geometry (Fig. 13). That means, within the screw speeds and configurations tested, that higher screw speed is more important than increasing amount of kneading blocks to achieve higher shear rate and, consequently, maximal improvement in material properties. This relation will be further investigated

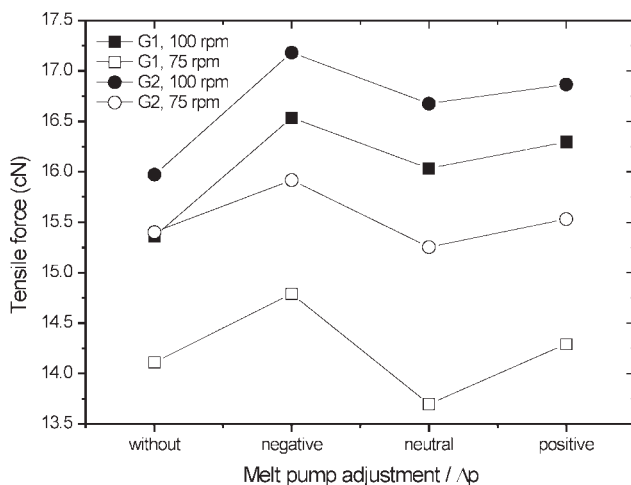


Figure 13 Melt strength level comparison of nanocomposite masterbatches.

to be confirmed applying broader range of screw speeds and geometries.

CONCLUSION

Advanced compounding by using a co-rotating twin-screw extruder in a combination with the melt pump has been presented. This configuration makes it possible to apply high shear forces and long residence time simultaneously within a continuous processing technique. It was shown that assembling the melt pump in front of an open compounder prolonged the residence time nearly two times, applying a negative pressure difference of -100 bar in the melt pump. This additional melt shearing led to a significant increase in material reinforcement, investigated by extensional rheology. Higher shear screw geometry and screw speed led to higher melt reinforcement as compared to lower shear screw configuration and screw speed, respectively. By use of a larger scale melt pump allowing higher pressure difference, a further increase in the residence time can be assumed. Generally, the mentioned technique of advanced compounding can be employed in the field of polymer composites and blends, where sufficient shear energy together with long enough residence time is required.

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