

Correlation between Rheotens measurements and reinforcement of polymer nanocomposites in the injection molding compounder

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Abstract. The evaluation of the effectiveness of reinforcement of polymers and polymer nanocomposites (PNCs), in particular the improvement of Young's modulus, is made by performing standardized tensile tests. Structural and morphological characterizations typically are investigated using expensive techniques like transmission electron microscopy (TEM), X-ray scattering and sometimes also rheological analyses (rotational rheometry). The objective of this study is to generate faster and economically advantageous data to verify the quality of the produced PNC-compound in an on-line measurement system. Subsequently injection molded parts are processed by using the Injection Molding Compounder (PNC-IMC) "by only one plasticizing process". In comparison to the conventional compounding process, where the compound has to be pelletized and fed into the injection molding machine for the second plasticizing process, injection molding compounding combines these two processing steps. This paper shows first results and problems with the implementation of the Rheotens equipment into the concept of the IMC. Different processing techniques and various processing conditions were compared and the occurring effects were detected both with tensile testing and extensional melt rheology. Both, the increase of the Young's modulus by using layered silicates as nanofillers is compared to the virgin polypropylene and the correlation of the level of melt strength with Rheotens measurements is shown. These results give a good overview on both the possibilities and the limitations of the material pre-tests by the use of extensional rheology in the concept of the IMC for producing PNCs. Further studies to enable a fast and efficient way of estimating the level of reinforcement in PNCs by means of rheotens measurements will be carried out towards industrial usability. Furthermore the verification of exfoliation and intercalation of the layered silicates in the polymer matrix using small angle X-ray scattering is planned.

Keywords: Injection molding compounding, polymer nanocomposites, layered silicates, extensional rheology

1. Introduction

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1.1. Polymer nanocomposites

Polymer nanocomposites represent that class of polymer materials, which are currently investigated with greatest interest. They consist of the base polymer and organic or inorganic fillers where at minimum one dimension of the length is in the nanometer range. These nanofillers are dispersed during processing in a way that the different layers have a distance of a few nanometers to each other. The special feature of nanofillers in comparison to conventional fillers is, that already low volume fractions (< 10 wt%) in the polymer matrix lead to remarkable property improvements. For example, mechanical, optical and electrical properties are positively influenced. The reason for this improvement is due to the fact that the magnitudes of the nanofillers and the macromolecules of the polymer matrix are similar and thus even at low filler content, the distance between the particles are in the nanometer range. Furthermore, nanofillers have large specific surfaces and thus allow a very good coupling to the polymer matrix. Another criterion which especially affects the tensile strength is the form factor (length-thickness-ratio). This factor is closely related to the specific surface [1].

1.2. Injection molding compounder

The injection-molding compounding process combines two processing steps: the material compounding, which normally takes place at the raw material manufacturer and the injection-molding process which usually is done at the injection molder. The final part is processed directly with only one plasticizing process, and the material used does not have to be granulated and plasticized again in the plasticizing unit of an injection-molding machine after the compounding step. The molten material exits the extruder and is directly fed into a melt accumulator and further into the injection unit. After the shot volume is reached, a conventional injection-molding process starts.

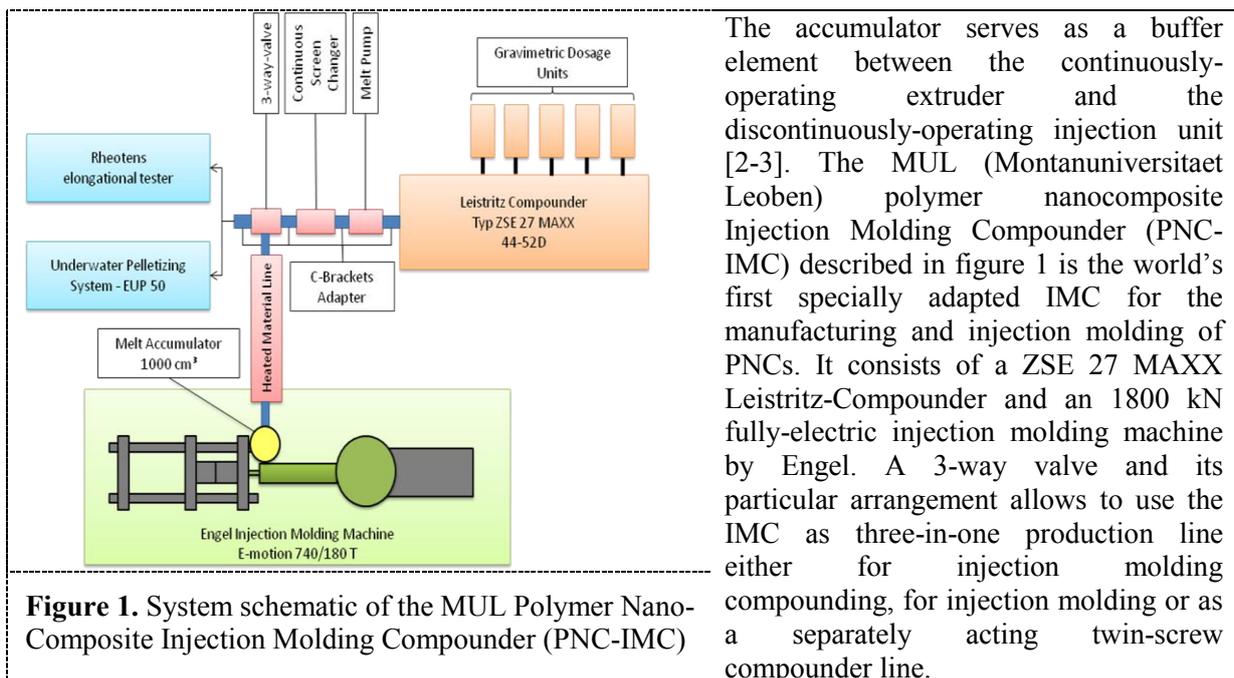


Figure 1. System schematic of the MUL Polymer Nano-Composite Injection Molding Compounder (PNC-IMC)

1.3. Extensional rheometry (Rheotens)

The drawability of polymer melts in many processes is of crucial importance. The elongational tester Rheotens allows determining the drawing force of a melt strand extruded through a round die as a function of the drawing speed. Based on the gained technical strain curves the polymer melt can be characterized [4-5].

The extrudate is pulled off from the upper draw down wheels, while the lower wheels are used to stabilize the strand. Both pairs of wheels are mounted on a weighing beam which is connected to a displacement transducer. Withdrawing of the melt strand forms a movement of the weighing beam which is detected by the transducer and converted into a pull-off force. It is important that at the beginning of the measurement, the exit speed of the strand corresponds to the drawing speed.

Therefore drawing speed is set by the wheel speed so that no force acts on the strand. During the measurement the drawing speed is constantly increased until the strand breaks. The pull-off force is recorded as a function of the drawing speed.

2. Materials and methods

2.1. Materials

An isotactic PP homopolymer Boremed DM55pharm (MFR 2.8 g/10 min; 230 °C/2.16 kg), supplied by Borealis, was used for the preparation of nanocomposites in combination with the nanofiller Nanofil 5 (montmorillonite intercalated with dimethyl distearyl ammonium chloride) and the compatibilizer Scona TPPP 2112 GA (PP grafted with 1.2 wt% of maleic acid anhydride, PP-g-MA, MFR 6 g/10 min; 190 °C/2.16 kg), supplied by Kometra.

2.2. Preparation of polypropylene nanocomposites

The preparation of PNC was carried out with the intermeshing, co-rotating twin-screw extruder of the PNC-IMC. As first step a compatibilizer/nanofiller masterbatch (MB) was manufactured using a standard screw configuration by feeding the compatibilizer through the main hopper and the nanofiller downstream at the 4th extruder barrel. The MB concentration was 50 wt% organoclay and 50 wt% compatibilizer.

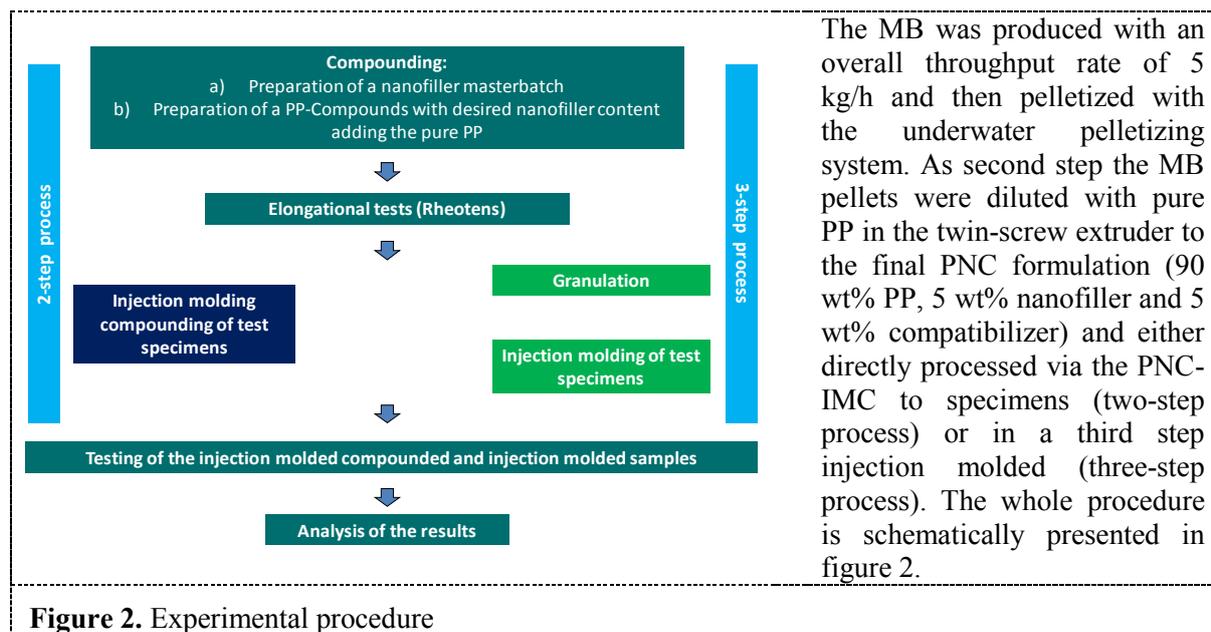


Figure 2. Experimental procedure

For compounding, injection molding compounding and the Rheotens tests according to a Shainin DoE four process parameters were identified. Their different values are listed in table 1.

Table 1. Process parameters and their different values for the compounding of the PNCs.

	Value -1	Value +1
Screw speed (ss) [rpm]	50	200
Screw geometry (sg)	standard	optimized
Temperature profile extruder (T) [°C]	180-190-200-200-...	210-220-230-230-...
Screen changer mesh (sc)	no	yes

2.3. Determination of the mechanical properties (tensile test)

The tensile specimens according to ISO 3167 (multipurpose specimens type A) for the investigation of the mechanical properties were produced both with the two-step PNC-IMC process and with the three-step process using the injection molding machine of the PNC-IMC.

A Zwick Z250 universal tensile testing machine was used to carry out the tensile tests according to ISO 527. All tests were done at standardized conditions ($23 \pm 2^\circ\text{C}/50 \pm 5\%$ r.H.). For evaluation the Young's modulus E_t , tensile strength σ_M and strain at break ε_B were determined (according to ISO 527).

2.4. Determination of the melt strength (elongational test - Rheotens)

For all four process parameters (see table 2) two factor levels (low -1 and high +1) were used. At first one series with the pure PP and all four process parameters at factor -1 were processed. Then the nanofiller reinforced material was examined by the same factor settings (all -1). The remaining series of each material group were produced by changing one factor at a time to the high level +1 and setting it back to the low level -1 (see table 2). The purpose of these series was to compare the elongational tests with the tensile tests and to compare the results within the series. It is important to mention that these elongational tests were made at a throughput rate of 1 kg/h due to the fact that at higher throughput rates the extruded strands did not break in the Rheotens test. Therefore the elongational test results cannot be compared exactly with the tensile tests.

Table 2. Overview of the elongational tests settings at a throughput rate of 1 kg/h.

Series	Material	Settings	Temperature die	Wheel gap		Starting speed wheels
				upper	lower	
[/]	[/]	[/]	[°C]	[/]	[/]	[mm/s]
1		pure, all -1				55
2		filled, all -1				65
3	DM55	filled, ss +1	210	0.85	1.3	80
4		filled, sg +1				80
5		filled, t +1				80
6		filled, sc +1				65

In all experimental series, grooved wheels were used and the drawing acceleration was 60 mm/sec^2 . Further the same die with a diameter of 2 mm and a length of 40 mm was used for all measurements maintaining the die temperature of 210°C . The starting speed of the draw down wheels had to be varied due to flow inhomogeneity in order to be able to ensure a pull-off force of zero at the beginning of each measurement.

3. Results and Discussion

3.1. Tensile tests

Each experimental series consisted of two tensile test series. On the one hand specimens were produced by means of injection molding compounding (IMC) and on the other hand by conventional injection molding (IM). 15 test specimens were tested and the arithmetic averages \bar{x} as well as the standard deviations σ are listed in table 3.

Table 3 shows high scattering of elongation at break for PP DM55. As compared to pure PP DM55 the average increase of all compounded materials shows approx. 25% increase in Young's modulus. The tensile strength and the elongation at break increased by approx. 10 % compared to the unfilled

material. The highest increase was found for both IMC and conventional IM process at a high screw speed.

Table 3. Arithmetic average (\bar{x}) and standard deviation (σ) for the tensile tests with PP DM55

		Young's modulus		Tensile strength		Elongation at break	
		[MPa]		[MPa]		[%]	
		\bar{x}	σ	\bar{x}	σ	\bar{x}	σ
pure, all -1	IMC	1678	46	35.7	0.3	55	18
	IM	1668	66	35.8	0.4	32	13
filled, all -1	IMC	2155	28	38.8	0.2	58	11
	IM	2137	29	39.0	0.2	74	17
filled, ss +1	IMC	2201	22	39.0	0.2	76	24
	IM	2155	26	39.0	0.2	118	41
filled, sg +1	IMC	2121	23	38.6	0.2	51	25
	IM	2135	21	38.9	0.3	66	10
filled, t +1	IMC	2105	26	38.5	0.2	68	19
	IM	2089	33	38.5	0.3	68	9
filled, sc +1	IMC	2065	102	38.9	0.3	53	21
	IM	2146	54	39.2	0.3	59	16

To verify these results statistically, an analysis of variance (ANOVA) was made. ANOVA is a collection of statistical models used to analyze the differences between means of groups of results and their associated process variants and process parameters. Three important values which indicate the significance of a result will be shown. The first one is the F-value which examines the likelihood of a difference between two different observations (the higher the better). In order to use the F-value for statements about the processing influence, the values of 5 groups and 15 measured values ($F_{4,10}$ -distribution) must be looked up in the so-called Fisher-table. The F-value is 3.48 which means that each value greater than 3.48 suggests significance. The second one is the post hoc Tukey range test, which compares every group mean with every other group mean to reveal if a difference is significant. The third one is the coefficient of determination R^2 . The confidence levels of all analyses with ANOVA were set to 95%, which corresponds to an α -value of 0.05 (see table 4).

Table 4. Overview of the significance of the processing parameters on Young's modulus, tensile strength and elongation at break for PP DM55

	F-value			Tukey test			R^2		
	[/]			[/]			[%]		
	Y	σ_m	ϵ_b	Y	σ_m	ϵ_b	Y	σ_m	ϵ_b
filled, all -1	14.16	18.24	14.05	AB	AB	B	28.37	33.78	28.21
filled, ss +1				A	A	A			
filled, sg +1				BC	B	B			
filled, t +1				C	C	B			
filled, sc +1				C	A	B			

Considering the significance analysis of processing parameters in table 4, it turns out that like already assumed significance is visible. The Tukey method is a method of multiple comparisons. If

identical letters are assigned to different groups, the corresponding mean values with a defined likelihood do not differ significantly. If two groups do not have letters in common, there is a significant difference in the mean values. Looking at the individual parameters of the Tukey method it is obvious that two blocks can be arranged in which no significance difference occurs (AB/A/BC/C/C and AB/A/B/C/A). However these blocks are different for Young's modulus and tensile strength although one would rather expect a consistent trend. In addition, the coefficients of determination have only a maximum of around 30 % indicating that 70 % of the variation is caused by other factors than those listed.

3.2. Elongational tests

In order to compare the results of the elongational tests the average curves of each series were used. Since the average value curves of the various series have different starting speeds and therefore also the draw down force is different, the curves were shifted to a start speed of 70 mm/s. This means all average curves have a drawn down speed of 70 mm/s at a pull-off force of 0 N. A representative value for each curve was determined. In this case the pull-off force at a draw down speed of 400 mm/s was chosen. The average curves are represented in figure 3 with their characteristic values marked with a red vertical line at 400 mm/s.

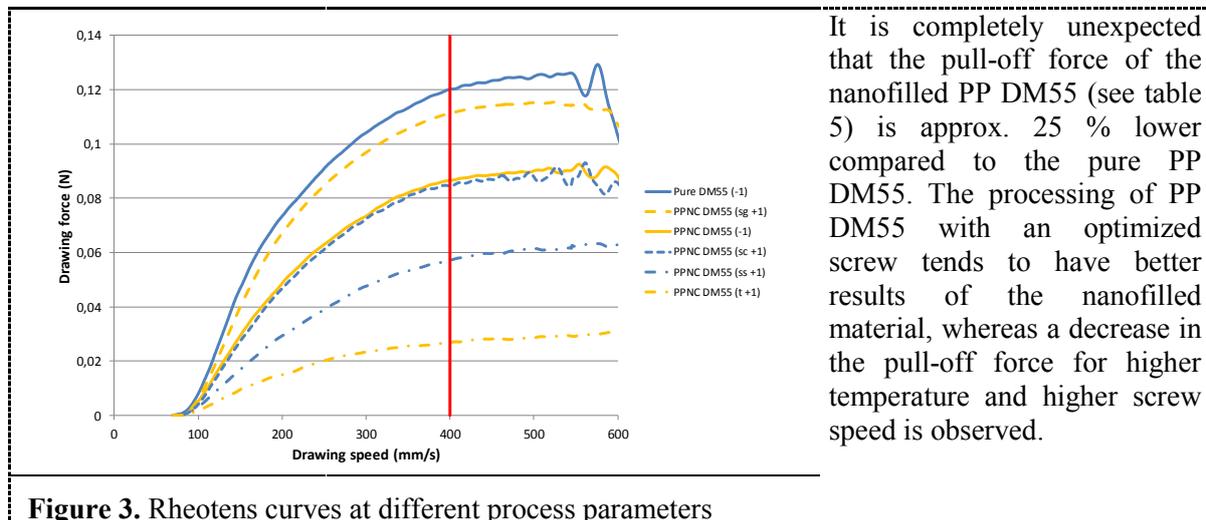


Figure 3. Rheotens curves at different process parameters

Table 5. Pull-off force (n) at an drawing speed of 400 m/s.

Process parameters	PP DM55
pure, all -1	0.12 ± 0.01
filled, all -1	0.09 ± 0.01
filled, ss +1	0.06 ± 0.02
filled, sg +1	0.11 ± 0.01
filled, t +1	0.03 ± 0.01
filled, sc +1	0.09 ± 0.01

3.3. Comparison tensile tests and elongational tests

Elongational tests and tensile tests were performed to get an overview of the trends and the possible correlation between these test methods. Since the trends of the tensile strength results are very similar to the Young's modulus results and the results of elongation at break scattered strongly, only the Young's modulus values are shown in Figure 4.

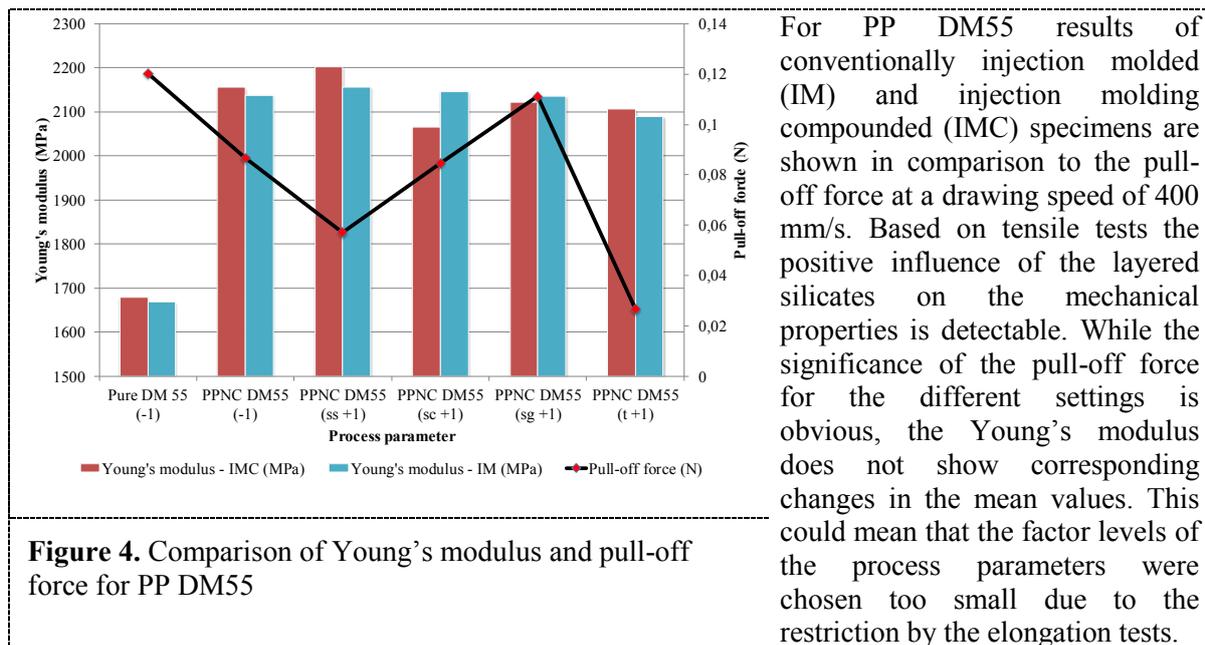


Figure 4. Comparison of Young's modulus and pull-off force for PP DM55

Thus a comparison between the elongational test results and the Young's modulus values seems to be questionable. Furthermore figure 4 shows an opposite trend of pull-off force and Young's modulus (usually the pull-off force decreases with increasing Young's modulus and vice versa). A possible reason for this effect is the considerable lower throughput rate (1 kg/h) which had to be implemented for performing the Rheotens elongational tests, while the production of the test specimens had been carried out with a throughput rate of 5kg/h.

4. Conclusion

The aim of this study was to find a correlation between elongational test measurements (Rheotens) and layered silicate reinforcement of polymer nanocomposites for the injection molding compounding process. Another objective was to determine, if the variation of selected process parameters during compounding, which results in different mechanical properties, is detectable by using the Rheotens elongational tests.

The preparation of the polymer nanocomposites had been carried out with the intermeshing, co-rotating twin-screw extruder of the PNC-IMC. At first a masterbatch (50 wt% organoclay and 50 wt% compatibilizer) was manufactured with the standard screw configuration at an overall throughput rate of 5 kg/h and subsequently pelletized with the underwater pelletizing system. In the second step the masterbatch pellets were diluted with pure PP DM55 in the twin-screw extruder. The final formulation of the compounded PNCs was constant at 90 wt% polypropylene, 5 wt% nanofiller and 5 wt% compatibilizer. The tensile bars for the investigation of the mechanical properties were produced both, with the two-step PNC-IMC process and the three-step process using the injection molding machine of the PNC-IMC. The calculated pull-off forces of the elongational tests (throughput rate 1 kg/h) and the values of the tensile tests (throughput rate 5 kg/h) were compared. It was found that the Young's modulus and the tensile strength often showed no significant changes. Although there were significant differences in the pull-off forces, changes in the process parameters could not be detected by using Rheotens elongational tests.

The comparison of the pull-off forces and tensile test results with pure and reinforced PP showed an unexpected trend. While the Young's modulus of the filled material was significantly higher, the PP DM55 showed lower pull-off forces when nanofilled. This shows, that no correlation could be found between the pull-off forces and the tensile test values under varying processing conditions.

In conclusion, it is crucial to say that the used concept of elongational tests for monitoring material property changes were feasible only for very low throughput rates. I must be pointed out again, that the elongational tests could only be performed at a throughput rate of 1 kg/h, depending on limitations of the Rheotens tester, while compounding was carried out at a throughput rate of 5 kg/h.

Furthermore, even for extremely careful experimental work, slightly different experimental settings (draw down wheel, weighing beam) can influence the results. These factors strongly restrict the applicability of the presented on-line extensional test in the laboratory and industrial application.

Encouraging approaches for the on-line determination of the melt quality would be either the use of a by-pass elongational testing equipment, which would enable measurements independent of the throughput rate, or a FT-NIR measurement system.

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