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A Rheological Approach to the Analysis of Plastication Influence on Fibers Breakage of LGF-filled Polypropylene

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Summary: Long glass fiber-filled polypropylene composites are widely used in industry because of their low cost and high performance. To investigate the rheological properties of such composites in the molten state an in-line slit-die rheometer was developed and mounted on an injection molding machine. The shear viscosity of filled PP determined by the in-line rheometer was found to strongly depend on the fiber length distribution. In particular, a linear correlation was determined between the viscosity at a constant temperature and shear rate and the average fiber length equation proposed by Huq and Azaiez. The developed model and the in-line rheometer were then used to assess the effects of the main plastication parameters (i.e. screw rotation speed and backpressure) on fibers damage. The experiments were carried out according to a central composite design and optimal plastication conditions were determined by means of the response surface method.

Keywords: degradation; fibers; poly(propylene); viscosity

Introduction

Long glass fiber-filled thermoplastics have higher rigidity and mechanical resistance when compared with the same polymers reinforced with short fibers. Moreover mechanical anisotropy can be intentionally designed as a result of the disposition of fibers along predetermined preferential directions. However, while short glass fiber-filled thermoplastics offer good performances and can be easily processed by traditional technologies, such as extrusion and injection molding, the length of long glass fibers are significantly degraded during the plastication process.[1] Composite mechanical properties such as modulus, strength and impact resistance can be dramatically affected by the retained fiber length, increasing rapidly above a critical length, which differs for each property[2–3] as it is shown in Figure 1. One key to discontinuous long fiber composite technology, therefore, is to retain the optimal fiber length throughout the plastication process.

In order to exploit the advantages of long fibers in injection molding the producers of these special compounds suggest to employ general purpose screws at very low rotation speed and backpressure to minimize the polymer shear rate.

The degradation of fibers length can be due to the single or combined effect of the following interactions[4]:

1. the fiber-fiber interaction, in which the abrasion at the points of contact between entangled fibers determines a high stress concentration that causes fiber breakage;
2. the interaction between fibers and the injection (screw and barrel) and feeding systems (nozzle, runners and gate);
3. the fiber-matrix interaction, where stress differences are due to different values of

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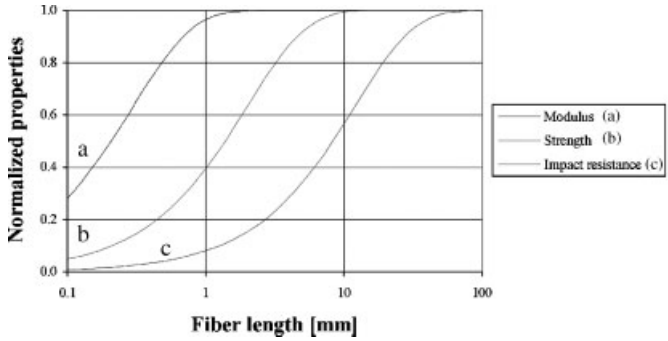

Figure 1.
Qualitative relation between the normalized mechanical properties and the fiber length of a glass fiber reinforced PP (fiber diameter = 10 μm).

viscosity which are in turn caused by the variable concentration of fibers. Moreover, during the plastication phase the matrix tends to cluster into particles with protruding fiber shares.

In general the process parameters that cause fiber length degradation are those that increase melt shear stress, namely:

- screw geometry,
- screw rotation speed,
- backpressure,
- melt temperature,
- maximum cavity pressure,
- packing pressure,
- geometry of both cavity and feeding system.

In particular among these factors, only those ones related to the plastication system (e.g. screw and nozzle geometry, screw rotation speed, backpressure and melt temperature) are considered within the scope of this paper.

The main objective of the paper is to determine the optimal plastication conditions for long glass fiber-filled polypropylene. This was accomplished by evaluating and minimizing the effects of the main plastication parameters on fiber damage according to a new rheological approach.

Experimental Part

The material used is a commercial grade of high impact polypropylene copolymer, selected for good low temperature performance, reinforced with 30% E-glass fibers which were initially 13 mm long. Since the characteristics of the material are closely related to the integrity of glass fibers, all the processing factors that involve fiber length degradation have to be carefully considered. The supplier of this material has therefore provided the processing advices reported in Table 1.

Table 1.
Process settings suggested by the supplier of the material.

Process setting	Suggested value
Feed section temperature	220–240 °C
Melt temperature	240–270 °C
Mold temperature	60–100 °C
Injection speed	Slow, 20–30 mm/s
Injection pressure	300–600 bar
Screw rotation speed	30–150 rpm, circumferential speed max. 0.25 m/s
Backpressure	As low as possible, 0–10%
Holding pressure	50–70% of the injection pressure
Holding time	As long as practical
Drying	Not necessary

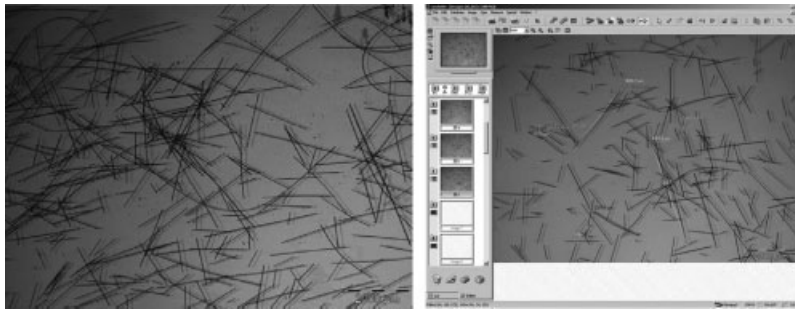

Figure 2.
Images of the processed fibers as observed using optical microscopy and analyzed by the image software.

After processing, fibers were freed from the polypropylene matrix by pyrolysis, i.e. by placing the specimens in a furnace at a temperature of about 500–600 °C for 1 to 5 hours in order to burn all the matrix. The residual fibers were dispersed in water by means of ultrasounds and subsequently dried. Figure 2 shows an image of the fibers obtained with this technique as observed under the microscope. To generate this sort of pictures, fibers were disposed on a glass slide and images were captured using a CCD camera coupled to an Olympus SZX12 optical microscope. A commercial image analysis software was used to measure the fibers length.

In order to evaluate the plastication influence on polymer rheology a slit-die rheometer was developed. The design of this apparatus aimed at replicating, during the test, the same plastication conditions of the injection molding process, i.e. the same thermo-mechanical history. An injection molding machine (IMM) was used as an integrated subsystem of the new tool. In particular, the IMM melts the polymer and generates the flow rates to obtain the desired shear rates in the slit die. The practical implementation of the ideas above described presented some difficulties. The most critical aspect tackled was the accurate measurement of flow rate through the slit die. In fact, the plastication subsystem of an IMM is not designed to accurately measure the volumetric flow rate. This is mainly due to the following factors:

– The standard measurement resolution of the screw displacement velocity is only 0.1 mm/s. For a screw diameter of 40 mm, this means an insufficient resolution of 125.6 mm^3/s.
– There is a back-flow at the tip of the screw due to the non perfect seal of the non–return valve.

To solve these weak points, a piston/cylinder system, connected to the end of the slit die and instrumented with a position sensor, was implemented.[5]

The layout and the structure of the rheometer, reported in Figure 3, are based on the functional characteristics required by the instruments:

– to analyze the material coming from the press injection unit,
– to be easily cleaned, and in general practical to use.

The first requirement was satisfied by placing the rheometer in the same location where molds usually are located. In order to create an instrument which is easy to clean, a simple configuration of the melt flow channels has been thought. Globally, the instrument has been divided into two subsystems:

1. the slit die connected to the fixed plate of the press,
2. the flow rate measurement subsystem.

The in-line rheometer was installed on an all-electric IMM ENGEL e-motion 440/100 equipped with a standard 40 mm screw.

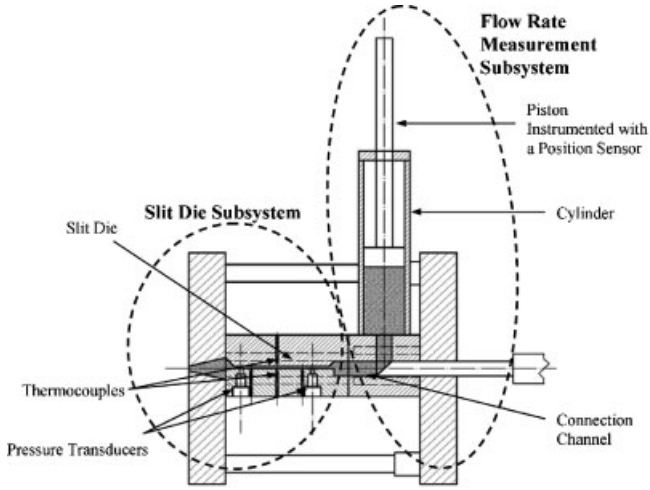

Figure 3.
Scheme of the in-line rheometer

A Rheological Approach to the Measurement of Fiber Breakage

The standard method for the measurement of fibers length, as it is described in the previous section, is time consuming and expensive and therefore it can be unsuitable for large experimental campaigns. In order to overcome these drawbacks, in this paper a new approach is proposed. According to this method, the average fibers length is indirectly evaluated by measuring the viscosity of the plasticated polymer by means of the in-line rheometer. This approach is based on the experimental observation that during the injection phase high values of viscosity at low shear rates are due to a certain extent to the resistance to alignment that fibers enforce by mutually interacting, which is strongly related to fibers length. A model that correlates the polymer viscosity, as measured by an in-line rheometer, with the average fibers length could be used to simplify the analysis of the plastication influence on fibers breakage. The first part of this work was therefore committed to the development of such a model.

In order to collect statistical data about the relationship between viscosity and average fibers length, they were both varied by conducting experiments at different plastication settings. Since both injection speed and melt temperature strongly influence the viscosity of the polymeric matrix, they were maintained constant during the experiments. Screw rotation speed and backpressure were varied according to a full factorial DOE plan with two factors on two levels (Table 2) and three replications per treatment.

The tests were carried out randomly at various shear rates in order to create the entire curves of apparent viscosity as they are shown in Figure 4. From this graph it is evident that the larger variations of viscosity at different processing conditions are registered for the lowest shear rates. Therefore, the values of apparent viscosity considered in the analysis were those measured at the minimum shear rate achievable with the available IMM and in-line rheometer, i.e. 345 s^{-1}, as reported in Table 3.

The principal methods of statistical analysis employed were main effects plots and analysis of variance (ANOVA). The ANOVA was conducted using MINITAB® software. The main effects plots (Figure 5)

Table 2.
Factors and levels of the experimental plan.

Level	Low	High
Screw rotation speed [m/min]	5	36
Backpressure [bar]	50	150

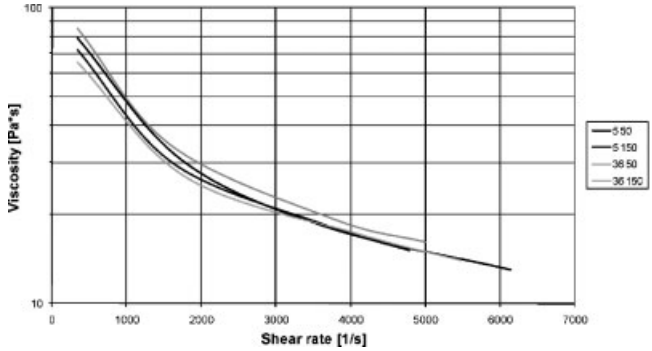

Figure 4.
Apparent viscosity curves for various conditions of plastication.

Table 3.
Experimental array for the viscosity measurements.

Run Order	1	2	3	4	5	6
Screw speed [m/min]	5	36	5	5	36	36
Backpressure [bar]	150	50	150	50	50	150
Viscosity [Pa*s]	73.98	84.81	69.18	80.40	82.84	66.37
Run Order	7	8	9	10	11	12
Screw speed [m/min]	36	5	36	5	5	36
Backpressure [bar]	50	150	150	50	50	150
Viscosity [Pa*s]	87.90	72.78	65.28	78.90	77.17	64.39

reveal the relative magnitude and direction of the effects of individual plastication parameters.[6]

In this preliminary analysis the main effect of the screw rotation speed seems to be negligible. Therefore, only the backpressure will be used to vary the viscosity and consequently the length of fibers. The screw rotation speed was kept constant at a value of 24 m/min while the backpressure was varied from 50 to 200 bars in 9 steps. The viscosity values for these tests are reported in Table 4.

The 9 samples processed were then analyzed to determine the fiber length distribution for each test and therefore

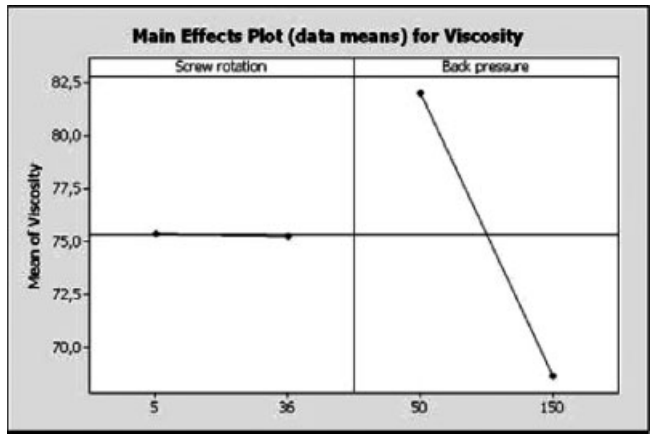

Figure 5.
Effects plot for the viscosity measurements.

Table 4.
Apparent viscosity measured at various values of backpressure.

Run Order	1	2	3	4	5	6	7	8	9
Viscosity [Pa*s]	77.88	72.54	74.24	77.67	66.46	65.71	62.98	57.90	55.42

for each value of viscosity. In order to improve the accuracy of the results a total of 800 to 1000 fibers per sample were counted.

Even though a full-length distribution is necessary to quantify the frequency of a fiber of given length present in the polymer, a single length characteristic should ideally be used to characterize and quantify the effect of the fibers length on viscosity. Bulk properties based on different length averages have been widely used to determine an effective average length of fibers. They are the number-averaged length, weight-averaged length and Z-averaged length defined respectively as[7–9]:

$$L_n = \frac{\sum L_i N_i}{\sum N_i} \quad (1)$$

$$L_w = \frac{\sum L_i^2 N_i}{\sum L_i N_i} \quad (2)$$

$$L_z = \frac{\sum L_i^3 N_i}{\sum L_i^2 N_i} \quad (3)$$

where N_i is the number of fibers of length L_i.

As far as our experiments are concerned, these three averages are likely to have a very weak correlation with the viscosity values measured at low shear rates because they assign the same importance to all the lengths, even though experimental evidence shows that the longer the fiber the higher its contribution to the viscosity. A new model-based averaging method has been recently proposed by Huq and Azaiez.[10] It is based on a mathematical model used for the determination of the contribution of fibers on the total stress and it is defined as:

$$L_{\text{mod-avg}} = \sqrt{\frac{\sum N_i L_i^3}{\sum N_i L_i}} \quad (4)$$

The viscosity values for the 9 tests are reported in Table 5 together with the number-averaged length and the average length according to Huq and Azaiez.

As it can be seen in the diagram of Figure 6, number-averaged length fails to accurately describe the effects of the various fiber lengths on the melt viscosity. The best fitting was obtained with a power law, achieving a coefficient of determination (R^2) of 86.6%. The coefficient of determination indicates how much variation in the dependent variable is explained by the model. The higher the R^2, the better the model fits the data.

Instead, the average lengths calculated according to Huq and Azaiez showed a very good correlation with the viscosity measures (Figure 7). The best fitting was obtained with the following linear equation:

$$L_{\text{avg-mod}} = 131.89\eta - 6939.3 \quad (5)$$

achieving a coefficient of determination of 95.8%.

Analysis of Plastication Influence on Fiber Breakage

By means of the model developed in the previous section, fiber length degradation can be calculated in terms of average length reduction by in-line measuring the melt viscosity. The developed model and the

Table 5.
Apparent viscosity measures compared to the number-averaged length and the average length according to Huq and Azaiez.

Run Order	Viscosity Pa*s]	L_n [μm]	$L_{\text{mod-avg}}$ [μm]
1	77.88	1722.81	3285.28
2	72.54	1098.14	2636.18
3	74.25	917.69	2588.18
4	77.67	1286.59	3339.48
5	66.47	1050.31	2357.06
6	65.72	964.39	1766.76
7	62.98	613.18	1301.93
8	57.90	325.67	456.06
9	55.42	269.78	378.77

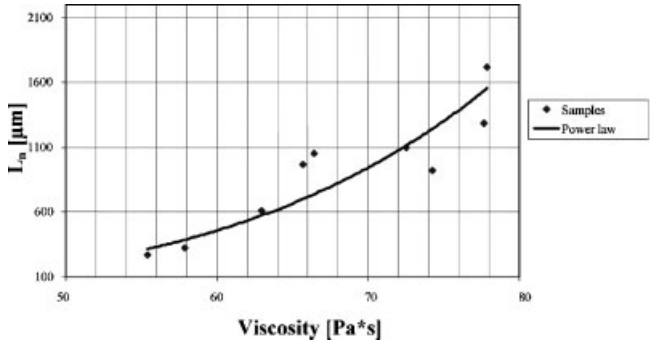

Figure 6.
Correlation between the viscosity measures and the number-averaged lengths.

in-line rheometer were in fact used to assess the effects of the main plastication parameters (i.e. screw rotation speed and backpressure) on fibers damage and to determine the optimal process conditions. The experiments were carried out according to a Central Composite Design (CCD) and optimal plastication conditions were determined by means of the Response Surface Method (RSM).[6]

A CCD with two factors consists of:

- 4 factorial points at $(-1, -1)$, $(-1, +1)$, $(+1, -1)$ and $(+1, +1)$, that may serve in a preliminary stage to fit a first-order (linear) model;
- 1 central point at (0,0), that provides evidence regarding the importance of a second-order contribution or curvature;
- 4 axial points at $(+\alpha, 0)$, $(-\alpha, 0)$, $(0, +\alpha)$ and $(0, -\alpha)$, that allow for efficient estimation of the quadratic terms in a second-order model.

The position of the axial points in a central composite design is denoted by α. In this case a value of $\alpha = 1$ was chosen since the factorial points were set at the extreme feasible values that the factors could assume.

As it can be deduced by the analysis of the CCD plan reported in Table 6, experimental tests were replicated 3 times both in the 4 nodal points and in the 4 axial points. In the central point 5 treatments were performed with 3 replications for a total of 15 runs. For each run the values of the measured viscosity and the average fibers length, as calculated by means of Equation 5, are shown in Table 6.

The RSM was then used to examine the relationship between the response variable

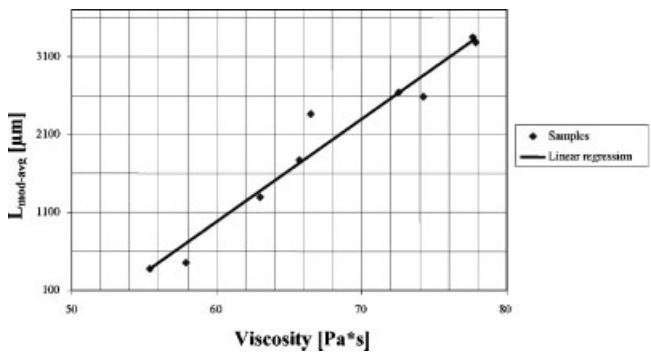

Figure 7.
Correlation between the viscosity measures and the average lengths according to Huq and Azaiez.

Table 6.
Central composite design plan.

Run Order	Screw speed [m/min]	Backpressure [bar]	Viscosity [Pa*s]	Length [μm]
1	6	120	63.34	1414.57
2	21	120	67.24	1929.49
3	36	190	53.19	75.97
4	6	190	53.66	138.10
5	21	120	65.99	1765.15
6	36	120	65.52	1701.84
7	21	120	67.02	1900.20
8	6	190	54.47	244.75
9	21	120	65.36	1680.98
10	36	190	56.52	514.56
11	21	190	55.86	428.27
12	21	190	57.90	697.29
13	21	120	65.44	1691.15
14	21	120	68.19	2053.91
15	6	50	70.06	2301.77
16	21	50	69.24	2192.51
17	6	190	57.04	583.66
18	6	120	62.98	1367.71
19	21	120	67.92	2018.19
20	21	120	66.01	1766.47
21	6	50	72.03	2561.16
22	21	120	66.46	1826.79
23	36	120	65.43	1690.21
24	36	50	71.43	2480.99
25	21	120	65.72	1728.11
26	21	120	62.98	1367.71
27	21	120	65.28	1670.78
28	36	120	65.54	1704.49
29	36	50	71.42	2480.99
30	6	50	71.34	2469.81
31	36	50	73.39	2740.57
32	21	50	70.33	2336.72
33	21	120	66.37	1814.75
34	21	50	69.03	2164.91
35	21	190	55.42	370.11
36	6	120	57.10	592.19
37	21	120	64.39	1553.89
38	36	190	60.41	1028.83
39	21	120	65.28	1670.78

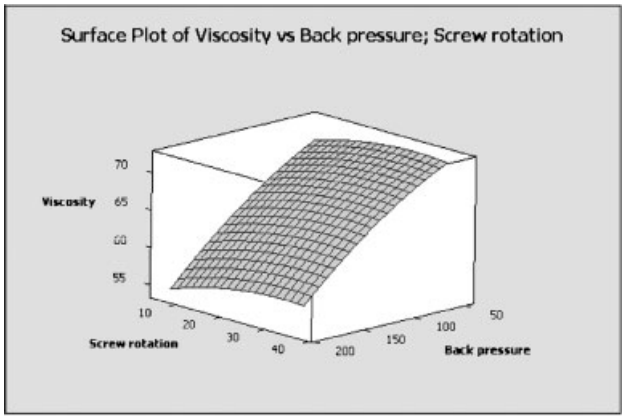

Figure 8.
Response surface for viscosity.

Table 7.
Coefficients of regression for the viscosity surface.

Term	Coefficient	Value
Constant	β_0	65.5032
Screw rotation	β_1	1.1562
Back pressure	β_2	−7.4338
Screw rotation*Screw rotation	β_3	−0.9968
Back pressure*Back pressure	β_4	−1.3521
Screw rotation*Back pressure	β_5	0.1788

viscosity, which is in turn related to the average fibers length through Equation 5, and the two experimental factors, viz. screw rotation speed and backpressure. As a result of the performed tests the response surface shown in Figure 8 was designed by fitting the experimental data with the following second-order model:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_1^2 + \beta_4 x_2^2 + \beta_5 x_1 x_2 \quad (6)$$

where β_i are the regression coefficients reported in Table 7.

Experimental data are fitted by the second-order model with a coefficient of determination of 88.9%. Optimal plastication conditions that maximize viscosity were found in correspondence to a backpressure of 50 bars and a screw rotation speed of 28.34 m/min. The maximum viscosity value is 71.72 Pa*s, which is in turn related to a maximum average fibers length of 2519 μm.

Conclusion

In this paper, the influence of plastication parameters on fiber damage in the injection molding of long glass fiber-filled polypropylene has been investigated. This analysis was carried out by means of an especially developed in-line rheometer, which was installed on an injection molding machine. The design of the experimental apparatus was aimed at replicating, during the test, the same plastication conditions (the same thermo-mechanical history) of the injection molding process and, in particular for this analysis, the effect of fibers length degradation on viscosity. The standard method for the measurement of fibers length is time consuming and expensive because it requires pyrolysis, ultrasound dispersion and drying to free the fibers from the polypropylene matrix. A model that correlates the polymer viscosity, as measured by an in-line rheometer, with the average fibers length was experimentally developed and proposed to simplify the analysis of the plastication influence on fibers breakage. This approach is based on the experimental observation that during the injection phase high values of viscosity at low shear rates are due to a certain extent to the resistance to alignment that fibers enforce by mutually interacting, which is strongly related to fibers length. The model correlates the apparent viscosity at constant temperature and shear rate with the average length proposed by Huq and Azaiez.[10]

The proposed model and the in-line rheometer were then used to assess the effects of the main plastication parameters on fibers damage and to determine the optimal plastication conditions according respectively to a Central Composite Design and the Response Surface Method. As expected, the analysis of experimental data showed a significant degradation of fibers length: although the initial fiber length is about 13 mm, the retained fiber length after the plastication process is about 2 to 3 mm in the best conditions. Experimental data were fitted by the second-order model with a coefficient of determination of 88.9%. Optimal plastication conditions that maximize viscosity were found in correspondence to a backpressure of 50 bars and a screw rotation speed of 28.34 m/min. The maximum viscosity value is 71.72 Pa*s, which is in turn related to a maximum average fibers length of 2519 μm. The optimal value determined for the backpressure matches with that one suggested by the supplier of the material. The only drawback in further lowering the backpressure is that air could be entrapped in the melt during the plastication

compromising the quality of the molding. While the suggested maximum limit for the screw rotation speed is about 15 m/min, experimental data showed that the optimal value is much higher (28.34 m/min). A lower backpressure associated with a higher screw rotation speed seem to increase the reinforcement length as reported also in another experimental work.[11]

Further improvement of the reduction of fiber degradation during the plastication process could be achieved by modifying the screw and non-return valve designs to decrease the melt shear stresses within the plastication system. Such a result would be obtained with a lower compression ratio of the screw, a longer melting zone and larger melt channels for the non-return valve and for the nozzle.

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