



UNIVERSITY OF TRENTO - Italy

Master of Science in Materials and Production Engineering

Lab Session 4

Polymer processing and analysis of products

Laboratory activity report
Course of Polymeric Materials Engineering

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Abstract

Two mixtures composed of 15% by weight of flame-retardant PP (black) and 85% of PPH-B-10-FB (white) were prepared. One mixture was subjected to compounding while the other was mixed manually before producing two samples with compression molding. the distribution of black PP in the white one is absolutely non-homogeneous, typical consequence of a manual mixing of pellets (without any homogenization mixing in between). Several samples produced by injection molding according to specific standards (ISO and ASTM) were analyzed and identified. This procedure was also useful for calculating the shrinkage to which some materials are subjected: it is clear that for reinforced materials, shrinkage is negligible due to the presence of glass fibers that give dimensional stability to the polymer; semi-crystalline polymers, on the other hand, exhibit higher shrinkage values than amorphous polymers. Lastly the diameter of six different filament samples have been measured in order to predict their mechanical properties in function of the draw ratio and the process parameters.

1 Introduction

The aim of this laboratory activity was to use different polymer processing techniques together with the analysis of the properties of some samples produced by the listed techniques.

2 Materials and methods

Two types of Polypropylene (PP) have been poured together in order to obtain a mixture with higher properties with respect to the matrix. For our purpose 15% in weight of flame retardant PP (PP HiRONIen V15 BLACK) pellet has been added to isotactic PP (PPH-B-10-FB). In Figure 1 is reported the technical datasheet of PPH-B-10-FB, while in Table 12 (Appendix) technical datasheet of PP HiRONIen V15 BLACK is reported. For compression molding a stainless steel plates with a frame of $12 \times 12 \text{ mm}^2$ has been filled with 34 g of the mixture composed by 27.22 g of isotactic PP and 6.68 g of flame retardant PP. For injection compounding 40 g of the mixture have been weighed. In this case the mixture was composed by 34.01 g of isotactic PP and 5.99 g of flame retardant PP.

Table III-1. Technical datasheet of the isotactic PP (PPH-B-10-FB).

| Sample | Test method | Value |
|---------------------------------|--------------------------------------|----------|
| MFI (g/10min) | ASTM D1238 (190 °C and 2.16 kg) | 12 ± 2 |
| Molecular weight distribution | | broad |
| Density (g/cm ³) | ASTM 1505 | 0.904 |
| Atacticity | Xylene solubles | 5 % max |
| Vicat softening point (°C) | ASTM D1525-A (9.81 N) | 154 |
| Heat deflection temperature | ASTM D648 (455 kPa) | 82 |
| Tensile strength at yield (MPa) | D638 (50 mm/min) | 35 |
| Elongation at yield (MPa) | D638 (50 mm/min) | 14 |
| Flexural modulus (MPa) | ASTM D790 (1.3 mm/min, 1% secant) | 1650 max |
| Rockwell hardness (R scale) | ASTM D785 | 111 |

Figure 1: Technical datasheet of PPH-B-10-FB

3 Experimental activity

3.1 Compression molding

Prepared amount of polypropylene mixture has been used for compression molding process. A press by Carver has been used, as illustrated in Figure 2.



Figure 2: Carver press for compression molding.

The material to be pressed is put between two stainless steel plates, one having a frame of $12 \times 12 \text{ mm}^2$ in order to produce a square plate of some mm of thickness. To avoid any adhesion with the plates, that are used to evenly distribute the pressure and to confine the melt (since the press is able to provide heat), two Mylar® foils have been put in between the steel and the material. The press has been set to produce a pressure of 8 tons, equivalent to 5.45 MPa, in the frame. The material has undergone an heat treatment under this pressure of 200°C for 10 minutes. After this, the press has been cooled with water circulating in a refrigerating circuit inside of it and the molded piece extracted. Produced plate is then visually analyzed and weighted in order to estimate weight losses.

3.1.1 Compounding (internal mixer)

The process has been carried out with the instrument Thermo Haake Rheomix 600, where the polypropylene mixture undergoes a thermal treatment of 200°C for 10 minutes. Rotation speed has been set at 40 rpm.

The product obtained (Figure 3) by this process has then been subjected to compression molding, using the same parameters as Plate 1. Tangential speed of the compounder is estimated to 0.082 m/s.

3.1.2 Production of dumbbell specimens

After the analysis of the plate, this has been cut to obtain ISO 527-1BA shaped specimens, that are used in another laboratory activity.



Figure 3: Rheomix 600 after usage. Remains of polypropylene mixture are visible.

In Table 1 the main parameters used in the processes are reported.

Table 1: Summary of the main parameters used in the processes

| Process | Time (min) | Temperature (°C) | Pressure (MPa) | Rotational speed (rpm) |
|-----------------------|------------|------------------|----------------|------------------------|
| Compression molding 1 | 10 | 200 | 5.45 | — |
| Compounding | 10 | 200 | — | 40 |
| Compression molding 2 | 10 | 200 | 5.45 | — |

3.2 Injection molding: sample evaluation

Different specimens of unknown polymeric materials have been analysed and identified. They have been produced by injection molding according to specific standards (ISO and ASTM):

- ISO 10.0 × 4.0 × 172 (mm);
- ASTM 12.7 × 3.3 × 165 (mm);

In Table 2 the types of samples are divided by standard (ASTM and ISO).

Table 2: Materials used in sample evaluation

| ASTM dumbbell | ISO dumbbell |
|-------------------|--------------------------------------|
| ABS | POM bi-injected |
| COC | PA11 mono-injected |
| PP | PP-GF 30 (white) and PP-GF35 (black) |
| HDPE Eltex yellow | PA6-GF50 |
| PE/PP blend | |
| PA11 | |

Size of all specimens and the mold cavity have been measured through a caliper in order to evaluate the shrinkage after the process according to Equation 1.

$$\text{shrinkage} = \frac{\Delta x}{x_0} \quad (1)$$

Where Δx is the difference between the initial and final dimension (length, width and thickness) and x_0 is the initial dimension (length, width and thickness).

ASTM samples (with sprue and bar) have been weighted through the balance Mettler PM 4600 in order to compare the total weight and polymer density (taken from literature [1]).

3.3 Filament analysis

Different fibers provided by University of Trento (polypropylene, see Materials and Methods) have been analyzed: in particular the diameter of six different filament samples have been measured in order to predict their mechanical properties in function of the draw ratio and the process parameters. Diameters have been taken using micrometer. The filament linear density (titer, fineness) is calculated accordingly to the Equation 2.

$$t = \rho \cdot A \quad (2)$$

where t is the titer expressed in dtex, ρ is the density taken equal to 0.9 g/cm^3 and A is the cross-section of the fiber, considered as circular. Titer in denier is found multiplying t by a factor 0.9. The apparent draw ratio DR is calculated using Equation 3.

$$DR = \left(\frac{D_{max}}{D_{min}} \right)^2 \quad (3)$$

where D_{max} is the maximum diameter of the collected fibers while D_{min} is the minimum diameter. The fiber strength T_{as} (tenacity as spun) is measured in $\frac{\text{cN}}{\text{dtex}}$ and it's calculated accordingly to the Equation 4.

$$T_{as} = \frac{\sigma_Y}{100 \cdot \rho} \quad (4)$$

The tenacity after drawing T_{DR} is given by Equation 5.

$$T_{DR} = T_{as} \cdot DR \quad (5)$$

The tensile strength σ_b of the fibers is calculated accordingly to Equation 6.

$$\sigma_b = T_{DR} \cdot \rho \cdot 100 \quad (6)$$

where ρ is 0.9 g/cm^3 .

4 Results and discussion

4.1 Compression molding

The mold before and after pressing is reported in Figure 4.

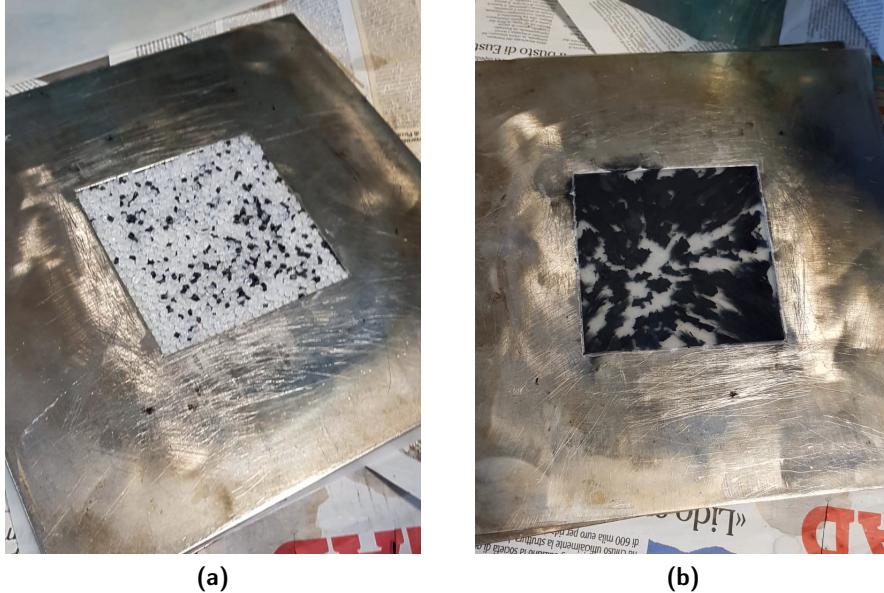


Figure 4: Mold (a) before and (b) after compression.

The produced plate after manual mixing is illustrated in Figure 5.



Figure 5: Plate produced in compression molding.

As it can be easily noted, the distribution of black PP in the white one is absolutely non-homogeneous, typical consequence of a manual mixing of the pellets (without any homogenization mixing in between). The other evident property of the pressed plate is the flash of melt outside of the mold: this is due to the too high amount of polymer inserted in the mold. The weights of the product before and after compression are reported in Table 3.

Table 3: Mass of the sample before and after pressing.

| Mixture mass (g) | Plate mass (g) | Variation (%) |
|------------------|----------------|---------------|
| 34.00 | 32.50 | -4.41 |

4.1.1 Compounding (Internal Mixer)

A comparison between plates after compression molding is reported in Figure 6.

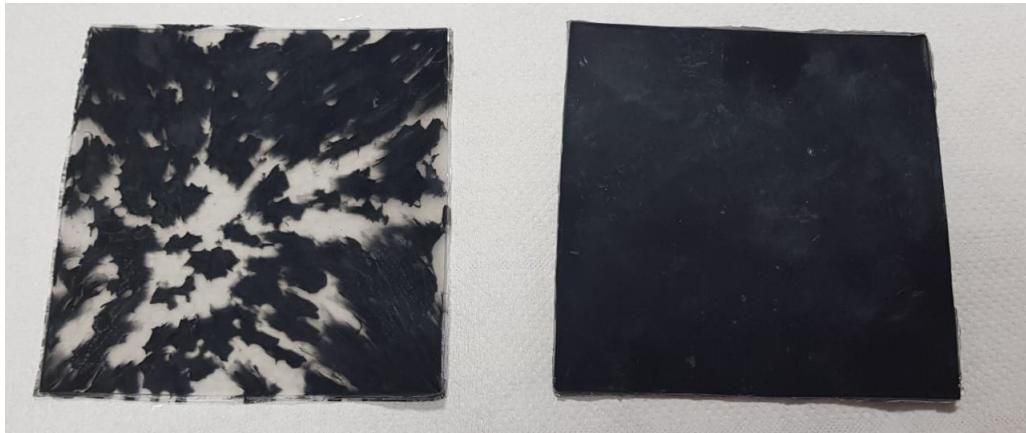


Figure 6: Compressed plates: plate 1 (from pellets) at left and plate 2 (from compounding) at right.

It can be seen that subjecting the sample to compounding before compression molding, a better homogeneity can be reached. The weights of the product before and after compression are reported in Table 4.

Table 4: Mass of the samples before and after pressing.

| Sample | Mixture mass (g) | Plate mass (g) | Variation (%) |
|--------|------------------|----------------|---------------|
| 1 | 34.00 | 32.50 | -4.41 |
| 2 | 32.05 | 30.50 | -4.84 |

The table shows that the weight variation is slightly higher, that can be explained by the more difficult preparation of the sample before compression, due to its volume distribution.

4.1.2 Production of dumbbell specimens

In Figure 7-a the dumbbell specimens produced in compression molding without compounding are displayed. As it can be seen, these specimens are characterized by low isotropy and homogeneity of the mixture. This will be a probable issue when mechanically testing and in resistance to flame propagation. Since the flame retardant is a weakener of strength (it introduces organics with poor adhesion and thus stress intensifiers), these specimens may have higher deformation at break than the more homogeneous ones produced in melt compounding, showed in Figure 7-b.

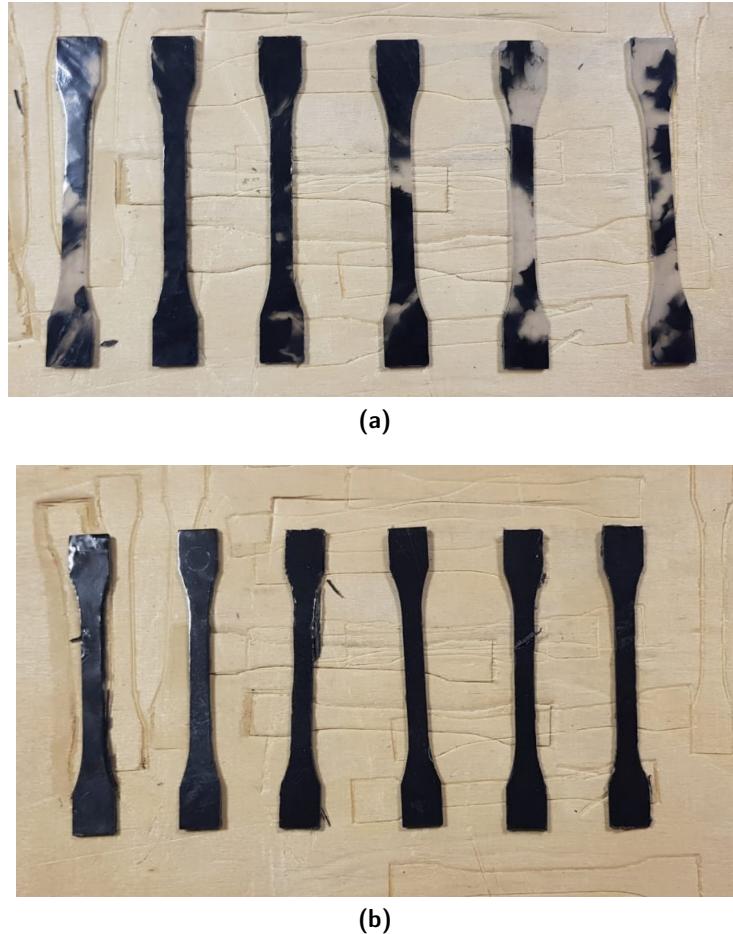


Figure 7: Produced specimens from compression molding plate after compounding.

These specimens have been then used during laboratory activity of Prof. Pegoretti for flexural tests in order to evaluate their mechanical properties according to ISO 527 standard.

4.2 Injection molding: sample evaluation

ISO type specimens are reported in Figure 8.

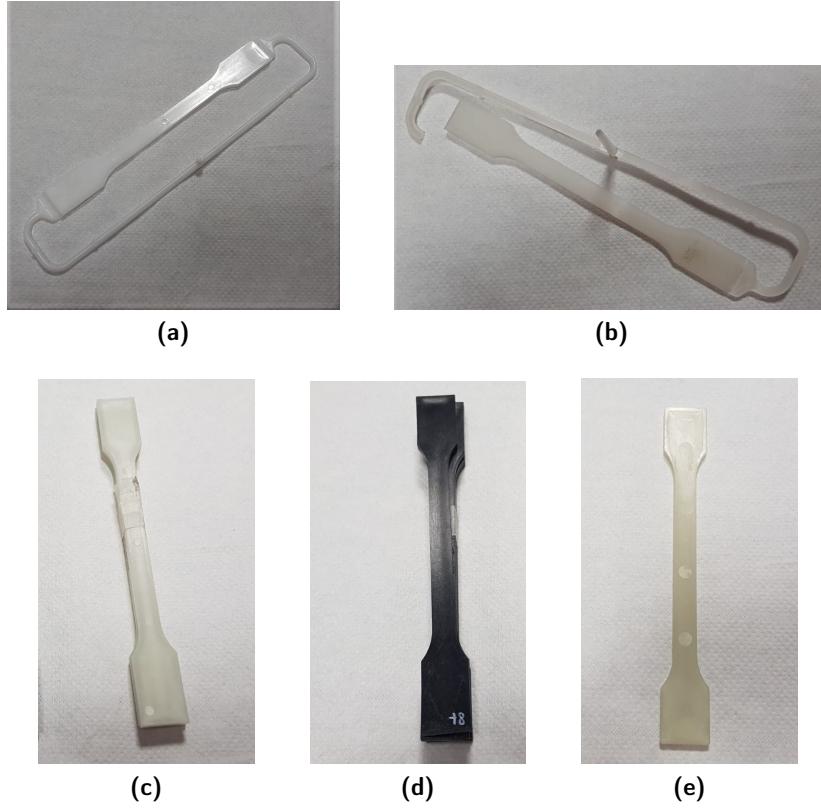


Figure 8: ISO samples: a) POM; b) PA11; c) PP-GF30; d) PP-GF35; e) PA6-GF50.

In Table 5 different types of ISO specimens are classified with their sizes.

Table 5: ISO specimens and characteristics.

| Figure | Material | Size (mm) | Weight (g) | Description |
|--------|----------|----------------------|------------|-------------------------------------|
| a | POM | 9.74 × 3.94 × 167.06 | — | white and presence of cold junction |
| b | PA11 | 9.86 × 4.05 × 168.98 | — | opaque and white |
| c | PP-GF30 | 9.88 × 4.00 × 172.11 | 10.30 | white and stiff |
| d | PP-GF35 | 9.80 × 4.00 × 171.86 | 10.72 | black and stiff |
| e | PA6-GF50 | 9.99 × 3.98 × 154.71 | 12.91 | very stiff |

It can be noticed that the higher the amount of glass fibers in the polymer, the higher is the weight of specimen.

In Table 6 the values of the shrinkage (according to Equation 1) of ISO type samples are reported.

Table 6: Shrinkage of ISO samples.

| Samples | Longitudinal shrinkage | Transversal shrinkage | Thickness |
|---------|------------------------|-----------------------|-----------|
| POM | 0.028 | 0.026 | 0.015 |
| PA11 | 0.017 | 0.014 | -0.012 |
| PP-GF30 | 0 | 0.012 | 0 |
| PP-GF35 | 0.001 | 0.020 | 0 |

4. Results and discussion

From Table 6 it can be noticed that in reinforced polymers the shrinkage is very small, almost negligible. The presence of glass fibers gives to polymers better dimensional stability during cooling. ASTM type specimens (containing dumbbell, sprue and plate) are reported in Figure 9.

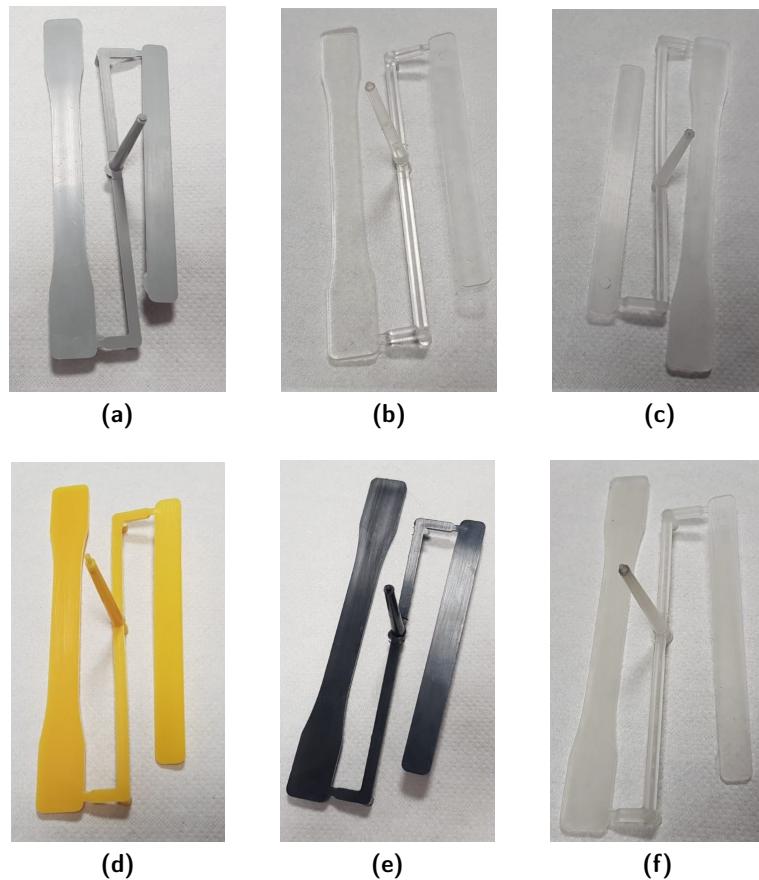


Figure 9: ASTM samples: a) ABS; b) COC; c) PP; d) HDPE; e) PE/PP blend; f) PA11.

In Table 7 different types of ASTM specimens are classified with their sizes.

Table 7: ASTM specimens and characteristics.

| Figure | Material | Weight(g) | Size (mm) | Description |
|--------|-------------|-----------|-----------------------|--------------------------|
| a | ABS | 14.78 | 12.77 × 3.27 × 163.55 | grey and flexible |
| b | COC | 14.07 | 12.64 × 3.30 × 164.04 | transparent and glassy |
| c | PP | 12.28 | 12.60 × 3.35 × 162.29 | opaque and flexible |
| d | HDPE | 12.73 | 12.54 × 3.33 × 160.00 | yellow and very flexible |
| e | PE/PP blend | 13.30 | 12.66 × 3.31 × 161.58 | matt black and flexible |
| f | PA11 | 14.00 | 12.60 × 3.35 × 162.29 | very similar to PP |

In Table 8 the values of the shrinkage of ASTM samples (containing dumbbell, sprue and plate) are reported, following Equation 1.

Table 8: Shrinkage of ASTM samples.

| Samples | Longitudinal shrinkage | Transversal shrinkage | Thickness |
|-------------|------------------------|-----------------------|-----------|
| ABS | 0.009 | -0.006 | 0.009 |
| COC | 0.006 | 0.005 | 0 |
| PP | 0.016 | 0.003 | -0.015 |
| HDPE | 0.030 | 0.013 | -0.009 |
| PE/PP blend | 0.021 | 0.002 | -0.003 |
| PA11 | 0.016 | 0.003 | -0.015 |

From Table 8 it can be observed that semicrystalline polymers (such as PP, HDPE, PA11) have higher values of shrinkage respect to amorphous polymers (such ABS and COC). Amorphous polymers have random arrangement of molecules that produces little volume changes thus lower shrinkage. The higher values of longitudinal shrinkage in semicrystalline polymers are partially compensated by the increase of the thickness (negative values of thickness shrinkage).

In Table 9 and in Figure 10 weights and densities of ASTM samples are reported.

Table 9: Weight and density of ASTM samples.

| Samples | Weight(g) | Density(g/cm ³) |
|-------------|-----------|-----------------------------|
| ABS | 14.78 | 1.04 – 1.12 |
| COC | 14.07 | 1.02 |
| PP | 12.28 | 0.905 – 0.94 |
| HDPE | 12.73 | 0.93 – 0.97 |
| PE/PP blend | 13.30 | 0.90 – 0.95 |
| PA11 | 14.00 | 1.04 |

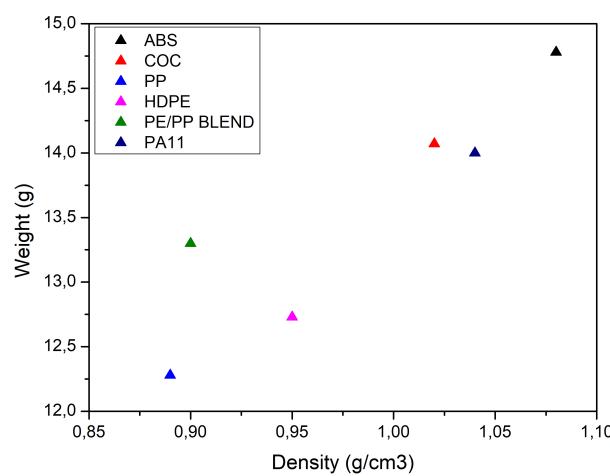


Figure 10: Weight and density of ASTM samples.

For PE/PP blend it has been considered a blend constituted by PE/PP 50%. From Table 9 it can be noticed that, for the same volume, weights of samples are in accordance with values of densities taken from literature [1].

4.3 Filament analysis

Diameter and titer measurements are reported in Table 10 according to Equation 2.

Table 10: Diameters and fineness measurements of collected fibers.

| Sample | Diameter (μm) | Fineness (dtex) | Fineness (denier) |
|--------|----------------------------|-----------------|-------------------|
| F1 | 34 | 8.2 | 7.4 |
| F2 | 87 | 53.7 | 48.3 |
| F3 | 212 | 319.5 | 287.6 |
| F4 | 248 | 437.0 | 393.3 |
| F5 | 147 | 153.5 | 138.2 |
| F6 | 41 | 11.9 | 10.7 |

Tenacities before and after drawing are reported in Table 11 following Equations 3, 4, 5, 6.

Table 11: Diameters and fineness measurements of collected fibers.

| Sample | $T_{as} (\frac{\text{cN}}{\text{dtex}})$ | DR | $T_{DR} (\frac{\text{cN}}{\text{dtex}})$ | $\sigma_b (\text{MPa})$ |
|--------|------------------------------------------|------|------------------------------------------|-------------------------|
| F1 | 0.304 | 53.2 | 16.2 | 1464 |
| F2 | 0.304 | 8.1 | 2.5 | 223 |
| F3 | 0.304 | 1.4 | 0.4 | 38 |
| F4 | 0.304 | 1.0 | 0.3 | 28 |
| F5 | 0.304 | 2.8 | 0.9 | 78 |
| F6 | 0.304 | 36.6 | 11.1 | 1007 |

Accordingly to literature [1] high strength PP fibers can reach values of 2.6 GPa and 3.5% deformation at break. Since tensile strength and deformation at break follow a hyperbolic envelope, by fitting these data with the generic equation of the hyperbole (only parameter is a constant), the following can be found, expressed in Figure 11.

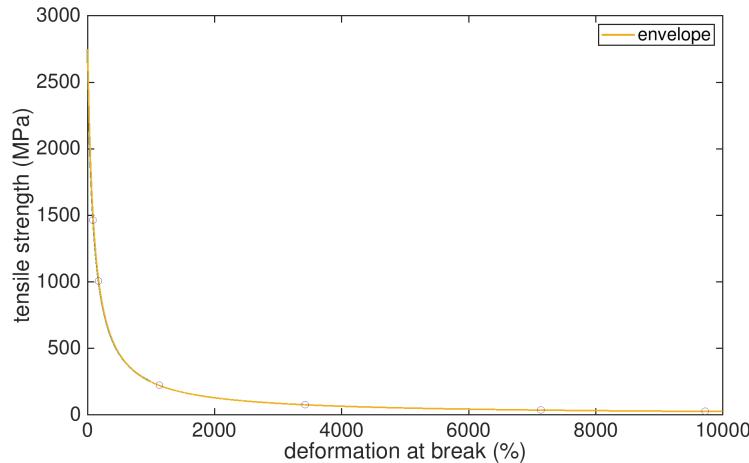


Figure 11: Stress-strain relation for PP fibers.

5 Conclusions

There are different polymer processing techniques. In this laboratory session compression molding and compounding techniques were used and samples produced by injection molding were analyzed. Several observations were made by examining the samples produced, in order to correlate the process parameters with the properties of the materials. It has been seen that a sample will be more homogeneous if subjected to compounding before compression molding; from the evaluation of samples produced by injection molding, the presence or not of shrinkage will be an index of the dimensional stability of the polymer or if it is a crystalline rather than an amorphous one; finally, by measuring the diameter of a fiber it is possible to predict some mechanical properties of the fiber itself.

References

- [1] Polymer handbook, J. Brandrup, E.H. Immergut, third edition, New York, Wiley & Sons 2003.

Appendices

A Data sheet of PP HiRONlen V15 BLACK

Table 12: Technical datasheet of PP (HiRONlen V15 Black).

| Sample | Test method | Value |
|-------------------------------------|------------------------|---------------|
| MFI (g/10min) | ASTM D1238 | 25 ± 3 |
| Density (g/cm ³) | ASTM D792 (23°C) | 0.950 ± 0.005 |
| Water absorption (%) | ASTM D570 (23°C × 24h) | 0.10 ± 0.05 |
| Shrinkage (%) | ASTM D955 | 1.0 ± 0.5 |
| Izod with notch (J/m) | ASTM D256 (23°C) | 40 ± 10 |
| Elastic modulus (MPa) | ASTM D790 | 1400 ± 150 |
| Behaviour to fire (1.6mm thickness) | ASTM UL94 | V1 |

B Weights of mixture components.

Table 13: Raw data of initial mass for the two mixing process.

| Mixing process | Mixture mass (g) | Isotactic PP mass (g) | Flame retardant PP mass (g) |
|-----------------------|------------------|-----------------------|-----------------------------|
| Manually mixing | 34 | 27.22 | 6.68 |
| Injection compounding | 40 | 34.01 | 5.99 |

C Fiber diameter

Table 14: Measured diameter of collected fiber.

| Fiber samples | Diameter (μm) |
|---------------|---------------|
| F1 | 34 |
| F2 | 87 |
| F3 | 212 |
| F4 | 248 |
| F5 | 147 |
| F6 | 41 |