



PLASTICS & COMPOSITES

Assessment 2 - Part 2

TEAM #3

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Theoric part

- 1) You should get together with your teammates to solve as a group, the questions you answered in the Assessment 2-Part 1 and must write down for each question the following:
- A. Rephrase the problem indicating very clearly what you have been asked to do.
 - B. List all the data provided.
 - C. Make a list of the assumptions. justifying each of them.
 - D. Write down an algorithm for the solution you are proposing (no calculations are needed at this stage)
 - E. Answer the question
 - F. if needed check in the web for technical papers to support your answer.
 - G. List the references used in the solution of the problem.

Question 1:

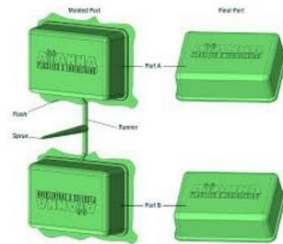
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Rephrase the problem:

In this question, we are using polypropylene for injection molding, but the product has “flash problem”, we have the list at least three causes of this problem and its solutions.

Information provided:

The information that we have is that the final product has a flash problem, we are using polypropylene and injection molding process. Also, there is this photo of the final product's defect:



Assumptions:

We assume that during the process some errors are making the defect, that error could be by the pressure during the injection or because some components of the machine are not correctly adjusted, like feeders, clamps, etc.

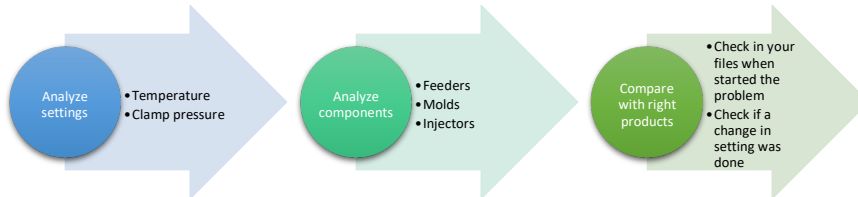


Figure 1 – Algorithm of question 1.

Answer:

Table 1 - Causes and solutions of the flash problem

Causes	Solutions
Material too hot	Adjust material flow that is too soft for parts.
The clamp pressure is too high	Adjust the pressure of the clamp.
Excessive feed	Cylinder temperature too high.
Erratic feed	Nozzle temperature too high
Poor parting line or mating surfaces	Mold temperature too high.
Overfilling cavity during the first-stage injection	Adjust the first-stage cut-off position or reduce shot size and check the machine response on switchover from filling to pack/hold the stage.
Mold shutoff surfaces not seating properly	Check the integrity of mold shutoff and increase clamp force.

References:

- Bozzelli, J. W., & Sepe, M. (2011). Injection Molding. In *Encyclopedia of Polymer Science and Technology*. Hoboken, NJ, USA: John Wiley & Sons, Inc. DOI:10.1002/0471440264.pst163.pub2
- Hagan, R. S., Thomas, D. P., & Schlich, W. R. (1966). Application of the rheology of monodisperse and polydisperse polystyrenes to the analysis of injection molding behavior. *Polymer Engineering & Science*, 6(4), 373–376. DOI:10.1002/pen.760060416
- Tan, K. H., & Yuen, M. M. F. (2000). A Fuzzy multiobjective approach for minimization of injection molding defects. *Polymer Engineering and Science*, 40(4), 956–971. DOI:10.1002/pen.11223
- Wissbrun, K. F. (1991). Injection mold flashing of liquid crystalline polymers. *Polymer Engineering and Science*, 31(15), 1130–1136. DOI:10.1002/pen.760311510

Question 2:

Commented [RF2]: Great! 1/1

Rephrase the problem:

In this question, there has been an explosion in a residential area that affected dozens of houses. That explosion happened by a gas pipe that broken and let the gas get out. We must determine the factors that affected the pipe and infer if one or all of them caused that the pipe broke and give a simple explanation of the problem because the question is asking us to explain the problem to a judge.

Information provided:

There was a high-density polyethylene (HDPE) pipe used for residential natural gas distribution. It has a 10 meters long rupture parallel to the length of the pipe as we can see in the photo.

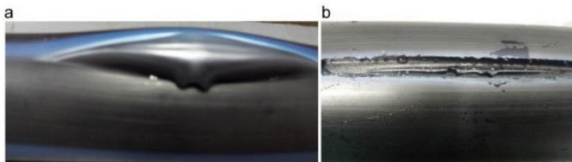


Figure from: HDPE pipes failure analysis and damage modeling. *Engineering Failure Analysis* Volume 71, January 2017, Pages 157-165

Assumptions:

We assume that the pipe has suffered wear during time by internal factors like changes in pressure, fiber alignment. And external factors like vibrations, changes of temperature, or bad maintenance. All factors frayed the pipe till it broke and the gas escaped provoking the explosion.

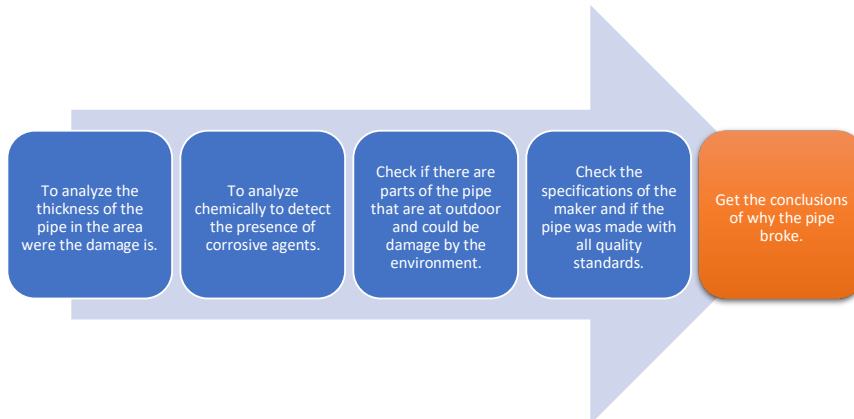


Figure 2 - Algorithm of the question 2.

Answer:

The explosion was provoked by severe damage on the pipe that compromised the structure, the internal pressure of the gas that in the end, the internal pressure overcame the resistance of the walls, which caused the gas leak.

The damage is a thickness reduction, caused by abrasion, chemical attack, or material weakening because of exposure to sun UV rays. It can also result from special intrinsic defects of the material generated during the resin preparation or the production process. If the pipe is relatively new, the main cause is for a defect in the materials during preparation, like contamination in the structure

References:

Krishnaswamy, R. K. (2005). Analysis of ductile and brittle failures from creep rupture testing of highdensity polyethylene (HDPE) pipes. *Polymer*, 46(25), 11664–11672. DOI: 10.1016/j.polymer.2005.09.084

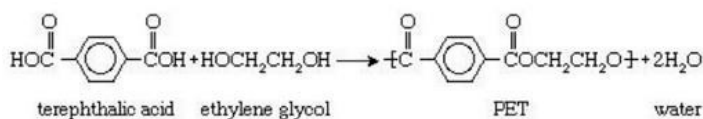
Majid, F., & Elghorba, M. (2017). HDPE pipes failure analysis and damage modeling. *Engineering Failure Analysis*, 71, 157–165. DOI: 10.1016/j.engfailanal.2016.10.002

Majid, F., & Elghorba, M. (2018). Continuum damage modeling through theoretical and experimental pressure limit formulas. *Frattura Ed Integrità Strutturale*, 12(43), 79-89. DOI: <http://0dx.doi.org.biblioteca-ils.tec.mx/10.3221/IGF-ESIS.43.05>

Commented [RF3]: You can go deeper in this section. During the production of the pipe several factors can affect the quality of the product. Most of them could be later be related to residual stresses.

Question 3:**Rephrase the problem:**

In this question, we have recycling steps of Polyethylene Terephthalate (PET) coming from drinking water bottles. The steps are (a) Cut the plastics into flakes, (b) wash the plastic in Mild Sodium Hydroxide solution to eliminate the labels and glue, (C) again washing in the water and drying (D) Pelletize the material. In the end, MFI (Melt Flow Index) has been increased. We need to know what the reason behind that is and what are the solutions.

**Information & Assumptions:**

We have the recycling process steps, so we know that what kind of external forces happened to the polymer solution such as high heating as in the end it became pelletized. We have the structure of PET; it gives us some understanding of the functional group in the structure. As mentioned in the question, the MFI has been increased, it shows that we had some changed in Rheological properties. The Melt Flow Index (MFI) is a measure of the ease of flow of the melt of a thermoplastic polymer. When we have an increase in MFI, we have a decrease in viscosity. And all of them are related to Average Molecular Weight.

Commented [RF4]: Perfect! 1/1

We can assume that during the recycling process (Washing with Acid) the polymer chains have been damaged and we have some lost in average Mw.

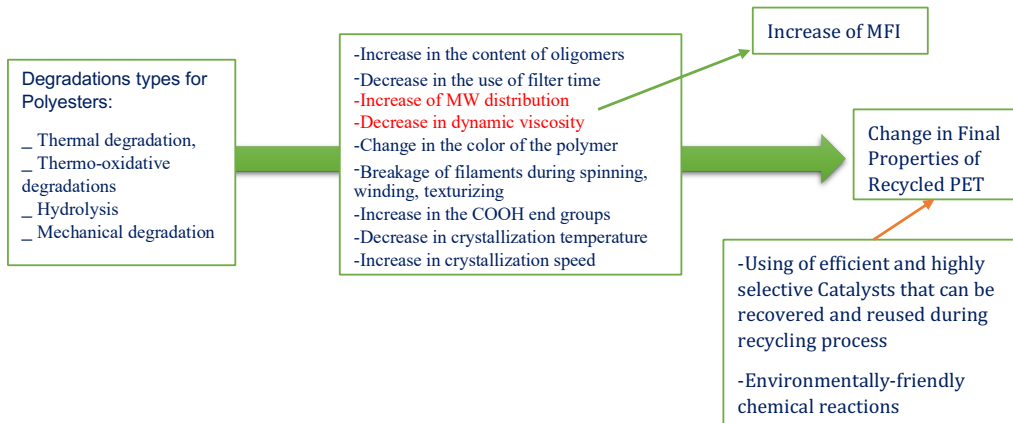


Figure 3 - Algorithm of the question 3.

Answer: PET is semi-crystalline, thermoplastic polyester of characteristic high strength, transparency, and safety. The PET bottles were patented in 1973 by Nathaniel Wyeth and began to be used popularly to produce disposable soft drink bottles in the 1980s. In 1987, more than 700 million pounds of PET were consumed in their production (Al-Sabagh, Yehia, Eshaq, Rabie, & ElMetwally, 2016). Recycling processes are the best way to economically reduce PET waste. However, **it has some problems:**

Table 2 - Problems with PET production.

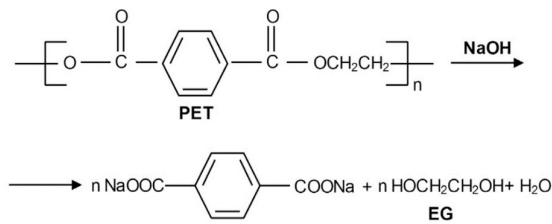
The major problem encountered in melt reprocessing of any PET **is the reduction in melt viscosity**, which is **caused by thermal and hydrolytic degradation**.

Melt reprocessing can generate **cyclic and linear oligomers**, which **can affect the final product properties such as printability or dyeability**

Contaminants such as PVC, polyvinylidene chloride (PVDC), glues, ethylene-vinyl acetate (EVA), paper, etc. **generate acidic compounds**, which **catalyze the hydrolysis of the PET's ester linkages** during thermal reprocessing.

A major obstacle in the recycling of post-consumer PET is the **yellowing of the polymer**. The color is due to intramolecular cross-linking and oxidation reactions. Yellowing is a significant problem for PET that is reused in bottle production.

According to the question, we had an Alkaline medium for washing, so the Hydrolysis process is happened like the below figure. Alkaline hydrolysis of PET is usually carried out with the use of an aqueous alkaline solution of NaOH, or KOH of a concentration of 4–20 wt%.

**Answer:**

Since the discovery of PET and the start of PET chemical recycling in 1950s that attracted great interest from the research community, PET glycolysis has gone a long way, back when zinc acetate was first used as a catalyst until when ionic liquid catalysts have been finally utilized. Studies have already dealt with most of the problems dealing with PET glycolysis, including impracticability of the reaction due to long reaction times, low yields, undesirable conditions, and pollution obstacles. Researchers have developed catalysts to increase the reaction rate, catalysts that can be recycled and reused, a method that does not require catalysts, and many others. However, PET recycling is still far from its summit. Researchers have found ways to solve each problem separately; there is still no way to solve them all simultaneously. The main issue that stands now is to **deliver an efficient environmentally friendly way to chemically recycle PET**. This may be an opportunity for researchers to try to develop **efficient and highly selective catalysts that can be recovered and reused** (Abdelaal, Sobahi, & Makki, 2008; Altun & Ulcay, 2004; Frounchi, 1999).

References:

- Abdelaal, M. Y., Sobahi, T. R., & Makki, M. S. I. (2008). Chemical Degradation of Poly(Ethylene Terephthalate). *International Journal of Polymeric Materials*, 57(1), 73–80. <https://doi.org/10.1080/00914030701329080>
- Al-Sabagh, A. M., Yehia, F. Z., Eshaq, G., Rabie, A. M., & ElMetwally, A. E. (2016). Greener routes for recycling of polyethylene terephthalate. *Egyptian Journal of Petroleum*, 25(1), 53–64. <https://doi.org/10.1016/j.ejpe.2015.03.001>
- Altun, S., & Ulcay, Y. (2004). Improvement of Waste Recycling in PET Fiber Production. *Journal of Polymers and the Environment*, 12(4), 231–237. <https://doi.org/10.1007/s10924-004-8150-4>
- Frounchi, M. (1999). Studies on degradation of PET in mechanical recycling. *Macromolecular Symposia*, 144(1), 465–469. <https://doi.org/10.1002/masy.19991440142>
- MATSUBARA, T. (2003). Recycling of Polypropylene Fiber Products. *FIBER*, 59(7), P.216-P.219. https://doi.org/10.2115/fiber.59.P_216

Question 4:

Rephrase the problem:

Commented [RF5]: Great! 1/1

In this problem, we must propose a solution to the given problem. The problem says that the final product of an injecting plastic process presents some black marks in some corners. We need to discover why these black marks are been producing during the process and propose a solution for them.

Information provided:

The final product presents some black marks in some corners of the pieces like you can see in the image, that pieces are made by in injecting process.



Assumptions:

We assume at first that the black marks could be “burn marks” because they are in corners and as we can see in the image; they are not close to the injection zone. That is because in the frontal face of the piece there isn’t a mark of the plastic injector, and by its geometry; the injection must be in other parts so that the injected polymer could be distributed uniformly for all the mold.

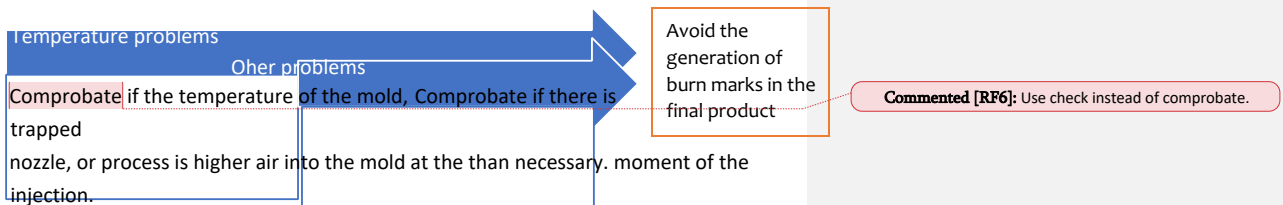


Figure 4 - Algorithm of question 4.

Answer:

Table 3 - Causes and solutions for burn marks.

Causes	Solutions
Frictional burning of cold granules against one another and/or the cylinder walls	Relocate plunger and allow sufficient tolerance to permit air to escape back around the plunger.
Plunger off-center; frictional burning of material between plunger and cylinder wall	Avoid finely ground material that can come between the plunger and the wall.
Burning in a nozzle that is too hot	Use externally lubricated plastic.
Wide cycling of nozzle temperature	Lubricate regrind. Raise rear cylinder temperature. Reduce the nozzle temperature. Avoid the "on-off" controller. Use a variable transformer.
Injection speed is too fast	Low the injection speed
Trapped air into the mold	Eliminate the air from the mold, it would be useful to add some respirators to the mold or improve the air removal process in the processing machine.

References:

Injection Molding Handbook. (2000). Injection Molding Handbook. Springer US. DOI:10.1007/978-1-46154597-2

Question 5:**Rephrase the problem:**

The question mentioned that they are producing some polypropylene pellets by Extrusion. The final product of these pellets is Fibers. What will happen if we add some Peroxide while the polymer is extruded?

Our polymer is Polypropylene. The structure is here (below) It has a repeating unit of $(C_3H_6)_n$. The processing method is extrusion. The final Product is fiber.

Data provided and Assumptions:

In the question mentioned that the final product is Fiber. So, we can assume that by mentioning that he wanted us to consider that the High mechanical properties are needed as the fiber are stiff and strong. For this matter, we need High Molecular Weight polymer. However, we have Peroxide as highly active material in the system. In Extrusion, we have Heating & Peroxide at the same time as our polymer.

Commented [R7]: Great! 1/1 But before saying that degraded PP is not suitable for fiber production it is important to analyze the level of degradation. A material that is barely degraded could achieve the viscoelastic properties to be processed as fibers.

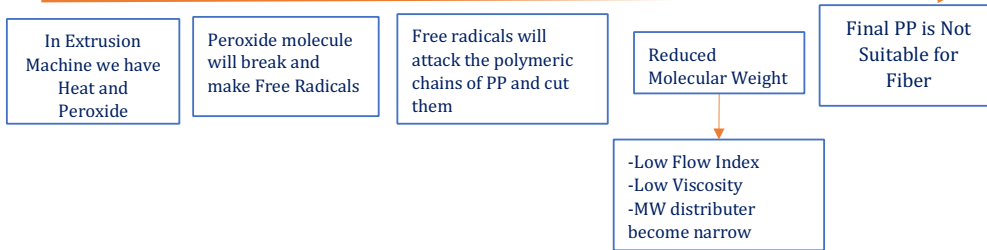


Figure 5 - Algorithm of the question 5.

Answer:

Polypropylene (PP) is a partially crystalline thermoplastic polymer with numerous applications in the fiber spinning, injection molding, and film extrusion industries. Modification of the molecular structure of PP during reactive extrusion after polymerization by the action of peroxide-generated radicals is known as controlled rheology or vis-breaking. The product of this process is so-called the **controlled-rheology polypropylene (CRPP)** (Azizi, Ghasemi, & Karrabi, 2008). Here, is the PP degradation can happen in the presence of Peroxide. Free radicals will be produced by activated Peroxide, and due to Hydrogen Abstraction; the polymeric chains will cut to the smaller parts (Dickson, Tzoganakis, & Budman, 1997).

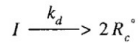
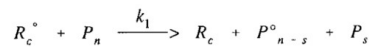
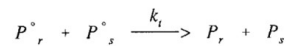
Initiation**Hydrogen Abstraction and Chain Scission****Termination**

Figure 6 - Polypropylene degradation scheme used in the kinetic model.

The process involves the blending of appropriate peroxides with PP. During melt extrusion of this mixture the peroxide thermally decomposes to produce Peroxy radicals. These radicals attack the polymeric chains. This process converts the low melt flow index (MFI) commodity resins to polymers with higher MFI (up to 100 times the original value) that have superior processing properties because of the reduced viscosity and elasticity. The advantages of CRPP are less elasticity, less shear sensitivity, less part warpage and better physical properties such as clarity and gloss. There is a large body of publications that describe peroxide degradation of PP (Azizi et al., 2008).

Several experimental results of the peroxide-degradation process of polypropylene (PP) in a co-rotating twin screw extruder to produce controlled-rheology polypropylene (CRPP) are presented. It was found that the rheological properties of PP change significantly during reactive extrusion. Melt flow index (MFI) increased with Peroxide concentration. Complex viscosity decreases with increasing Peroxide concentration. Degraded resins showed more Newtonian behavior than the origin resin. Cole-Cole plots indicated that mean relaxation times of CRPP resins are shorter than for virgin PP, and

the relaxation mechanism is more uniform for modified samples. From dynamic rheological data, molecular weight (MW) and molecular weight distribution (MWD) were calculated. Results indicated that MW decreases and MWD becomes narrower with increasing peroxide concentration (Azizi et al., 2008).

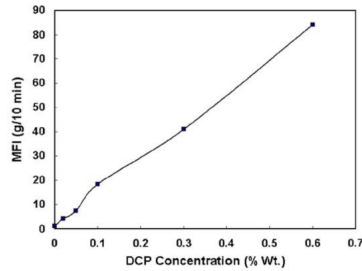


Figure 8 - With Increasing the concentration of Peroxide, MFI has been Increased.

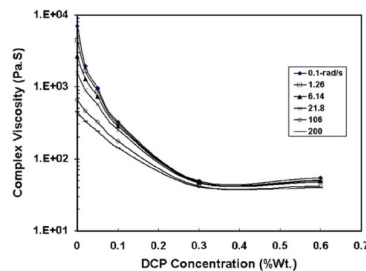


Figure 7 - With Increasing the concentration of Peroxide, Complex Viscosity has been decreased. (Different frequency at 230 °C).

References:

- Azizi, H., Ghasemi, I., & Karrabi, M. (2008). Controlled-peroxide degradation of polypropylene: Rheological properties and prediction of MWD from rheological data. *Polymer Testing*, 27(5), 548–554. <https://doi.org/10.1016/j.polymertesting.2008.02.004>
- Dickson, S. B., Tzoganakis, C., & Budman, H. (1997). Reactive Extrusion of Polypropylene with Pulsed Peroxide Addition: Process and Control Aspects. *Industrial & Engineering Chemistry Research*, 36(4), 1067–1075. <https://doi.org/10.1021/ie960288u>

Question 6:

Rephrase the problem:

In this problem, we must decide if we would buy the HDPE resin of the vendor. That decision must be made considering the fact of the product of this vendor is 15% cheaper, but we need to know if his product will have all quality facts that the current product that we are using. Also, we must **Information provided:**

You have a **blown film** business and you use HDPE resins. A vendor wants to become your supplier and ask you to consider his HDPE resin. He claims that the resin he is trying to sell to you has the same MFI and the same shear viscosity curve as the one you are using. The price of the resin is 15% cheaper than the one you are using. Would you buy the resin?

- In order to answer this question you need to justify it from the processing as well as from the rheological point of view

Commented [RF8]: Great 1/1

Solution:

In terms of processing the vendor can be using a manufacturing process cheaper than mine. For instance, he can be recycling the material. The recycled waste polymers have advantages over the virgin materials such as lower manufacturing cost, properties are compatible with virgin material, less use of the natural resources as compared to the production of virgin material (Singh, Fraternali, Farina, & Hashmi, 2018). Additionally, processing conditions can be accurately optimized by using a capillary rheometer to measure the viscosity of polymer melts as a function of temperature and rate of deformation. Considered a controlled-shear-rate test, capillary rheometers ensure that testing conditions are truly representative of processing conditions, especially for high-pressure and high-speed techniques like injection molding.

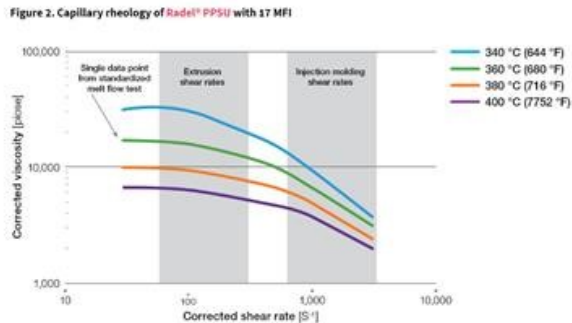


Figure 9 - Viscosity of polymer melts as a function of temperature and rate of deformation (Solvay, 2020).

Considering the rheological point of view, it has been found that required rheological properties of a given polymer can be obtained by an appropriate adjustment of M_x (average molecular weight), q (molecular weight distribution M_w/M_n) and LCB (long-chain branching), or in other words, the same flow characteristics are found for samples with various values of M , MWD, and LCB (Dobkowski, 1963). Furthermore, the material can be acquired for our company by considering that Melt flow data must be interpreted cautiously because the MFI test method has several shortcomings. First, the equipment setup is a pressure-limited configuration. The standardized weights create a constant load that forces the melt through the orifice. It is a constant-shear-stress test that provides a single point on a viscosity curve based on a single shear rate and temperature. Second, and more importantly, most plastics are shear thinning (meaning their viscosity decreases under shear strain) and they are processed at much higher shear rates than those observed during the MFI measurement (Solvay, 2020).

Finally, with these considerations in mind, we decided to buy the HDPE resin.

References:

Singh, R., Fraternali, F., Farina, I., & Hashmi, M. S. J. (2018). *Experimental Investigations for Development of Hybrid Feed Stock Filament of Fused Deposition Modeling. Reference Module in Materials Science and Materials Engineering*. Elsevier Ltd. DOI:10.1016/b978-0-12-803581-8.10392-3

Solvay, consulted on July 12th, 2020. <https://www.solvay.com/en/chemical-categories/specialty-polymers/healthcare/understanding-medical-plastic-data-sheets-melt-flow-index>.




Question 7:

Commented [RF9]: Great! 1/1

Rephrase the problem:

We must give an opinion about change polypropylene resins by using polyester resin, and advise about how to keep the quality of the product if we change the raw material.

Information provided:

-  The company currently is using Polypropylene resin.
-  The company wants to switch by Polyester resin.
-  We must keep the quality of the product.

Assumptions:

We must focus on the chemical and physical properties of every resin and compare all of them to have a big panorama about the possible changes and considerations that we'll do in the production line to keep the quality of the final product. At the same time, it's probably that we have to modify the list of stabilizers and additives and how they will affect our final product.

Answer:

We must consider the application that will be given, we suggest that if it is to make fibers you can make the change from polypropylene to polyester.

We need to examine that one polypropylene is a homopolymer (propylene) while polyester is a copolymer composed of Dimethyl terephthalate and Mono Ethylene Glycol. In **Figure 10** we can observe the two molecules

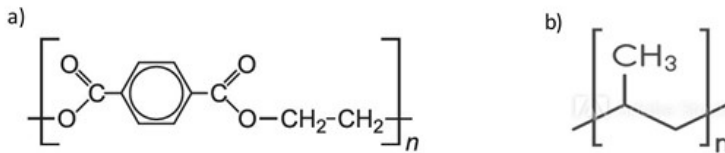


Figure 10 - a) Polyester molecule b) Polypropylene molecule.

If the rheology behavior and MFI are the same I buy it, but I also check the M_z , M_n , and M_w , because of the PDI is different the process it will be different and you need other parameters to change, but if all is the same I Buy it, the rheological part indicates how its flows under a shear rate and how the viscosity change, if we have a different behavior is because of the M_n or M_w is different or the PDI and this tell us that for your blown film process it doesn't work.

From a geometrical point of view, we have that polyester has a higher molecular weight than polypropylene (different viscosity and MFI), aside from that we have, in the case of polyester, benzene which gives it different rheological and thermal properties than polypropylene. Additionally, we need to consider that the polypropylene is a more linear polymer than the polyester.

We would also like to emphasize that polyester has two double bonds which make it a more reactive molecule, so we must consider the use of antioxidants or additives for extrusion.

Moreover, polypropylene is a semicrystalline thermoplastic material and polyester it could be thermoplastic or thermoset. Also, Polyester is available in higher tenacity grades compared to polypropylene, giving requirements and specifications more easily. Polypropylene is not commonly used for sewing threads because of its low melting point. Elongation is better in polypropylene, gives better elasticity for the material (Deeken, Abdo, Frisella, & Matthews, 2011).

The density of polypropylene is much lower than that of polyester. The diameter of polypropylene fiber is consequently proportionately higher than the polyester fiber of the same denier. It is therefore much easier to achieve color with polypropylene.

The melting point of polypropylene is lower than that of polyester. Flame retardancy by burning rate is minor with polypropylene than with polyester. Also, we need to consider the glass transition temperature (Balasubramanian, 2007).

We need to add a UV stabilizer during the manufacture of polypropylene to improve its resistance to UV light. in the case of polyester, we do not need that ('What Is the Difference Between Polyester and Polypropylene', 2008).

We must consider the MFI and the rheological behaviors, to have quality control as well as the flowability according to the ISO and ASTM standards. For that the time that the polymer is in the extrusion machine, temperature, screw, pressure, and velocity we require to change to produce Polyester fibers.

References:

Balasubramanian, N. (2007). Polyester vs Polypropylene - Fibre2Fashion. Retrieved 12 July 2020, from <https://www.fibre2fashion.com/industry-article/1972/polyester-vs-polypropylene>

Deeken, C. R., Abdo, M. S., Frisella, M. M., & Matthews, B. D. (2011). Physicomechanical evaluation of polypropylene, polyester, and polytetrafluoroethylene meshes for inguinal hernia repair. *Journal of the American College of Surgeons*, 212(1), 68–79. DOI:10.1016/j.jamcollsurg.2010.09.012

What Is the Difference Between Polyester and Polypropylene. (2008). Retrieved 12 July 2020, from <https://china-webbing.com/what-is-the-difference-between-polyester-and-polypropylene.html>

Question 8:

Rephrase the problem:

Commented [RF10]: Great! 1/1

We need to analyze how to correct a defect on our final product without compromising the pipe highpressure specifications and avoid hard problems for our customers in the future derived by the defect in the product.

Information provided:

Our company produces polymer pipes, but a customer told us that it has a defect due to the product being out of specifications on the diameter. So we need to correct this defect in the product without compromise its pressure capacity.

Assumptions:

We assume that the defect on the product could be derived by a wrong setting in the calibration of the machines of the line production. Perhaps the error will not be hard to solve.

Answer:

We must consider the cause of this difference in diameter, we reflect that it is something of the mold, therefore we propose different solutions since if the polymer change is carried out, we could risk having a structural failure and may cause a rupture in the pipeline.

The main causes are:

1. Variations in elastic stresses in the melt caused by the folding of the polymer melt in the channels of a twin-screw extruder.
2. Incorrect design of the flow channel of the extrusion die can destabilize the melt flow, creating waves in the pipe.
3. Incorrect temperatures of oven and screw can create temperature differences that influence the discharge of the melt from the screw channels. In this case, wall thickness variation is related to screw speed.
4. In multi-layer pipe extrusion viscosity differences between the layers can cause flow variation. This is referred to as a wave of instability or interfacial instability.
5. In some operations, unmelted polymer particles reach the discharge end of the extruder. These can create waviness in the pipe.
6. The frictional force of the melt against the calibration sleeve may be greater than the melt strength – this causes velocity variation. This problem is more likely to occur in a thin-walled pipe; it is sometimes referred to as slip-stick in the calibration sleeve. This problem can also occur with improper alignment between the extrusion head and the calibrator.
7. In some situations, the cleats of the puller do not have enough traction on the pipe causing slipping. This can create ring-shaped waves in the pipe.
8. In the extrusion of foam pipe, the inner wall can become irregular when the cell sizes become too large (> 0.15 mm). This is sometimes referred to as the orange peel effect.
9. The temperature levels and distribution inside the pipe wall after leaving the calibration has a significant effect on the final product geometry. Usually, it is not possible to compensate occurring melt temperature variations in the calibration, so that a non-uniform melt temperature distribution at the extrusion die leads to a non-uniform pipe temperature distribution after the calibration.

10. Most important for the final product geometry is the cooling process in the outer vacuum calibration and the subsequent thermal shrinkage caused by the temperature-dependent density of the thermoplastic material (Hiesgen, Saul, & Rauwendaal, 2016) *Possible remedies are:*

- Molding: Adjust for:
 - Clamp pressure too low.
 - Injection pressure too high.
 - Injection time too long.
 - Boost time too long.
 - Injection feed too fast.
 - Unequalized filling rate in cavities.
 - Interrupted flow into cavities.
 - Feed setting too high.
 - Inconsistent cycle, operator-caused.
- Machine: Adjust for:
 - The projected area of the molding parts too large for the clamping capacity of the machine.
 - Machine set incorrectly.
 - Mold put in incorrectly.
 - Clamp pressure not maintained.
 - Machine platens not parallel.
 - Tie-bars unequally strained.
 - Inconsistent cycle, machine-caused.
- Mold: Make correction for:
 - Cavities and cores not sealing.
 - Cavities and cores out of line.
 - Mold plates, not parallel.
 - Insufficient support for cavities and cores.
 - Mold not sealing off because of foreign material (flash) between surfaces.
 - Something other than flash keeping the mold open (e.g., foreign material in leader pin bushing so that leader pin is obstructed when entering the bushing, keeping the mold open).
- Insufficient venting.
- Vents too large.
- Land area around the cavities too large, reducing the sealing pressure.
- Inconsistent cycle, mold-caused.

(*Inject. Molding Handb.*, 2000)

To conclude, a fundamental part is cooling, due to it must be checked that the cooling system is correct and that there is no pressure difference if a vacuum system is used for cooling. And it must be verified that it is cooling enough, achieving the desired cooling (*Chapter 4 PE Pipe and Fittings Manufacturing PE Pipe and Fittings Manufacturing*, 2015).

References:

Chapter 4 PE Pipe and Fittings Manufacturing PE Pipe and Fittings Manufacturing. (2015).

Hiesgen, G., Saul, K., & Rauwendaal, C. (2016). Temperature induced dimensional variation in extrusion. *AIP Conference Proceedings*, 1779, 30006. doi:10.1063/1.4965475

Injection Molding Handbook. (2000). *Injection Molding Handbook.* Springer US. doi:10.1007/978-1-46154597-2

Question 9:

Rephrase the problem:

We have to order the resins that there are in the table of the exercise.

Information provided:

Resin, Zero shear viscosity (Pa.s), and PDI.

Investigated information:

An increase of the shear rate above a critical value, critical shear rate, leads to a deviation of the viscosity from its zero-shear value so that viscosity becomes a decreasing function of shear rate. Increasing concentration or increasing molecular weight leads to a decrease in the value of the critical shear rate. Moreover, the shear rate dependence of the viscosity begins at a lower shear rate as the molecular weight increases. (Milas, Rinaudo, & Tinland, 1985). Rheological evaluation is based on the fact that most nonNewtonian fluids like molten polymers have a defined flow profile which can be modeled by the Cross equation at low shear rates molten polymers have a constant viscosity and at high shear rates they have another constant value of viscosity. These two viscosity plateaus are connected by a range of shear rates where the behavior of the polymer is shear thinning, i.e., the viscosity reduces as a function of the shear stress/shear rate. The higher the molecular weight, the higher the viscosity plateau commonly termed the Zero- Shear Viscosity (TA instruments, n.d.). This behavior can be illustrated in Fig 1 and Fig. 2 related to question 9.

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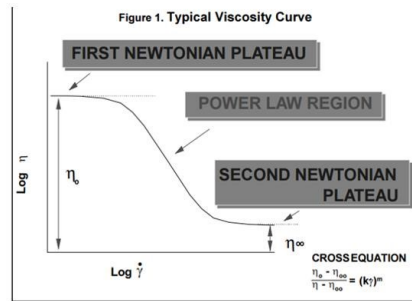


Figure 11 - Cross equation model.

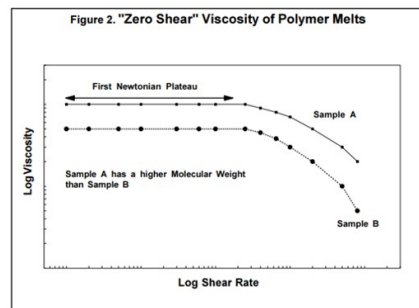


Figure 12 - The Zero-shear viscosity.

Where 5 = highest and 1=lowest.

Answer:

Table 4 - Where 5 is the highest and 1 is the lowest.

Resin	Zero Shear Viscosity (Pa.s)	Mw	PDI	shear thinning
A	1.8×10^5	4	2	1
B	2.1×10^6	5	4	2
C	3.1×10^4	3	14	5
D	8.9×10^3	1	6	3
E	2.5×10^4	2	8	4

References:

Dębkowski, Z. (1963). Rheologica acta. *Rheologica Acta*, 3(1), 1–1. doi:10.1007/bf01974447

Milas, M., Rinaudo, M., & Tinland, B. (1985). The viscosity dependence on concentration, molecular weight and shear rate of xanthan solutions. *Polymer Bulletin*, 14(2), 157–164. doi:10.1007/BF00708475

Singh, R., Fraternali, F., Farina, I., & Hashmi, M. S. J. (2018). *Experimental Investigations for Development of Hybrid Feed Stock Filament of Fused Deposition Modeling. Reference Module in Materials Science and Materials Engineering*. Elsevier Ltd. doi:10.1016/b978-0-12-803581-8.10392-3

Testing, Q. C., Polymers, O. F., Molecular, F. O. R., & Distribution, M. W. (n.d.). Rheology Solutions Qc Testing of Polymers for Molecular Weight.

Question 10:

In the question, recycling of some polymers like PP, PE, and ABS are considered. We need to define what kind of problems we will face and what can be our solutions.

Information: We have the structure of each polymer as below; we should consider the recycling process and its effect on this kind of polymers. One way of classifying polymers is to break them up into two classes. The basic property that separates a thermoplastic polymer from a thermosetting polymer and it is the polymer's response to being heated. When the thermoplastic polymer is heated, it melts, softens, and can be reformed when cooled. All these three polymers are Thermoplastic and when heated, they become soft.

Assumptions: As we have the structures of these polymers, and due to their nature, which they are thermoplastic, we will have heating in the process of recycling (Chemical/ Thermo Mechanical Recycling). Based on the structure we expect some Chemical degradation during the process which at the end may lead to chain degradation and Molecular weight loss.

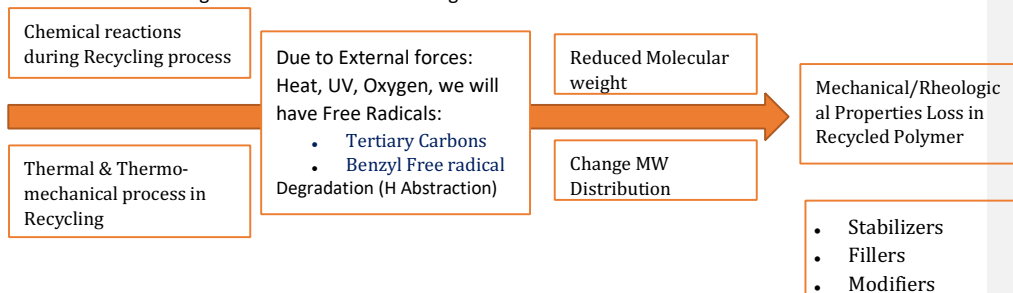


Figure 13 - Algorithm for question 10.

Possible solutions: As for all the homogeneous polymers, the main problems in the recycling of them arise from the easy degradability of this polymer both during their lifetime' (mainly by photooxidation) and during processing and recycling operations. Heat, mechanical stress, and ultraviolet radiation strongly modify the structure and the morphology and thus the characteristics of polymers. Elongation at break and impact strength are the properties most influenced by the degradation phenomena, but other effects must be considered, as well. Although the degradation behavior is common to all polymeric materials, **the effects of photooxidative and thermomechanical degradation on PP and ABS are**

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dramatic because of the **Tertiary Carbon present** in the chain of this polymer. In the following, we explain specifically on PP, but it's the same for ABS and in less degree for PE (MATSUBARA, 2003).

To determine the degree of substitution, count the number of carbons connected to the carbon of interest: **C** - carbon of interest, **C** - carbons connected to it.

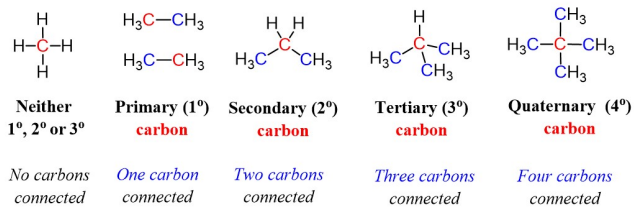


Figure 14 - Types of connections between carbons.

Degradation & Recycling:

The degradation of PP occurs through the following series of reactions describing the oxidative degradation of the polyolefins:

External Forces:

- Heat
- Mechanical Stress
- Ultraviolet radiations

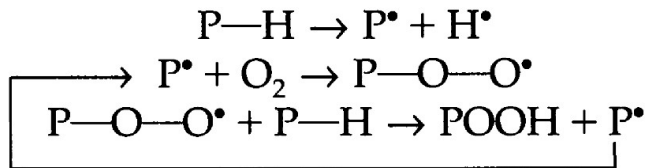


Figure 15 - Diagram of the chemical reaction.

The degradation kinetics depends on many factors, on the type and level of the external stresses and on some molecular and morphological characteristics of the polymer

(molecular weight, crystallinity, etc.). Finally, oxygenated groups, formed during oxidative degradation, act as catalysts of the reactions, accelerating the degradation rate. The main effects of the degradation phenomena on the PP structure are decrease of the molecular weight, change of the molecular weight distribution (MWD) and formation of oxygenated

functional groups. Because of these structural changes, the morphology of PP can also be modified. The properties (rheological, mechanical, electric, etc.) strongly alter as a result of changes in the structure and morphology (MATSUBARA, 2003).

Answer:

Stabilizer: As already mentioned, the dramatic reduction of the properties of the recycled PP is due to the easy degradation of this polymer not only during its lifetime but mostly during the reprocessing operations.

By adding suitable stabilizers (re- or post-stabilization) the degradation kinetics can be

slowed down, and the mechanical properties retained even after many recycling steps (MATSUBARA, 2003).

Fillers & Modifiers: By adding inorganic fillers or polymeric impact modifiers, some mechanical properties of recycled PP can be improved. Inorganic fillers, such as mica, calcium carbonate, glass and wood fibers, etc., enhance the elastic modulus, dimensional stability, and the thermal resistance while at the same time a reduction of the elongation at break is observed. Because recycled PP is generally used for injection-molding items, the decrease of the elongation at break does not play an important role (MATSUBARA, 2003).

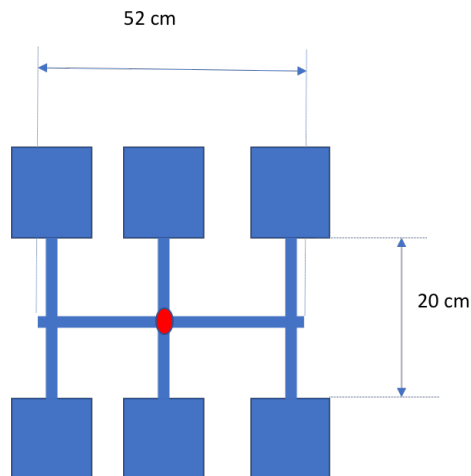
References:

MATSUBARA, T. (2003). Recycling of Polypropylene Fiber Products. *FIBER*, 59(7), P.216-P.219.
https://doi.org/10.2115/fiber.59.P_216

PROBLEMS

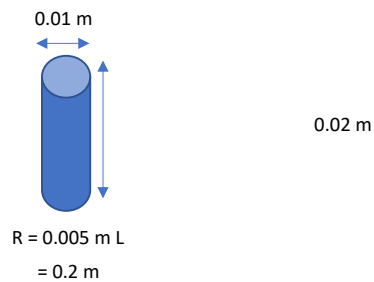
PROBLEM 1:

1. Calculate the pressure required to fill the mold.

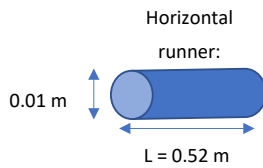


- The dimensions (in cm) of each cavity are 10x10x1
- The runners diameter is 1 cm and their length are indicated in the drawing.
- The polymer is a PP with a density of 0.9 g/cm^3
- The viscosity curve for the resins is given in the document called PPVIS 2020:
- **We Will work with PAR0**
- The injection is done at the red dot.

Vertical runners



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R = radius of each section (0.005m)

Q = volumetric flow rate (m³/s)

L = length of each section (0.52 m and 0.2 m)

Π = viscosity dP = injection pressure

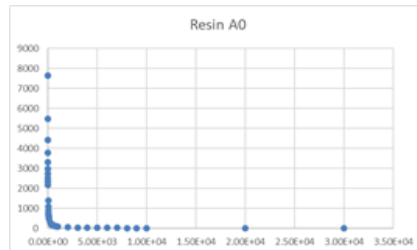


Figure 16 - Fluid behavior: shear rate (1/s) vs viscosity (Pa.s).

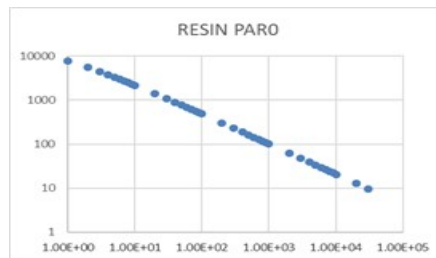


Figure 17 - Logarithm scale: shear rate vs viscosity.

Solution:

Assuming that we are using a parallel plate rheometer, the calculation for injection pressure was performed by using Hagen-Poiseuille equation in order to obtain the pressure for each section in the system (vertical and horizontal) and the total injection pressure.

$$\Delta P = \pi \frac{8\eta L}{R^4} Q$$

Most of the data is provided in the problem, but the Q values are unknown. In this case because we have the shear rates values, Q can be calculated by using the shear rate formula

$$4Q$$

$$\text{Shear rate} = \pi \frac{Q}{R^3}$$

After to compute the flow for each section we can proceed to calculate the injection pressure with the aid of the viscosity, length and radius values.

Once we have all the pressure values for each section, we proceed to compute the total injection pressure by obtaining the average pressure of the total number of sections in the system.

Table 5 - Results got from calculations of the data.

Type of resin ->	PARO									
	Viscosity (Pa.s)	R (m)	Q (m³/s)	Vertical section 3 runners L (m)	dP1 (Pa)	dP2 (Pa)	Horizontal section 1 runner L(m)	Q (m³/s)	dP (Pa)	Total injection pressure (Pa)
shear rate (1/s)										
1.00E+00	7634	0.005	9.82E-08	0.2	6.11E+05	1.83E+06	0.52	9.82E-08	1.59E+06	1.52E+07
2.00E+00	5488	0.005	1.96E-07	0.2	8.78E+05	2.63E+06	0.52	1.96E-07	2.28E+06	
3.00E+00	4430	0.005	2.95E-07	0.2	1.06E+06	3.19E+06	0.52	2.95E-07	2.76E+06	
4.00E+00	3775	0.005	3.93E-07	0.2	1.21E+06	3.62E+06	0.52	3.93E-07	3.14E+06	
5.00E+00	3320	0.005	4.91E-07	0.2	1.33E+06	3.98E+06	0.52	4.91E-07	3.45E+06	
6.00E+00	2983	0.005	5.89E-07	0.2	1.43E+06	4.30E+06	0.52	5.89E-07	3.72E+06	
7.00E+00	2721	0.005	6.87E-07	0.2	1.52E+06	4.57E+06	0.52	6.87E-07	3.96E+06	
8.00E+00	2510	0.005	7.85E-07	0.2	1.61E+06	4.82E+06	0.52	7.85E-07	4.18E+06	
9.00E+00	2335	0.005	8.84E-07	0.2	1.68E+06	5.04E+06	0.52	8.84E-07	4.37E+06	
1.00E+01	2188	0.005	9.82E-07	0.2	1.75E+06	5.25E+06	0.52	9.82E-07	4.55E+06	
2.00E+01	1412	0.005	1.96E-06	0.2	2.28E+06	6.78E+06	0.52	1.96E-06	5.87E+06	
3.00E+01	1084	0.005	2.95E-06	0.2	2.60E+06	7.81E+06	0.52	2.95E-06	6.77E+06	
4.00E+01	897	0.005	3.93E-06	0.2	2.87E+06	8.61E+06	0.52	3.93E-06	7.47E+06	
5.00E+01	774	0.005	4.91E-06	0.2	3.10E+06	9.29E+06	0.52	4.91E-06	8.05E+06	
6.00E+01	685	0.005	5.89E-06	0.2	3.29E+06	9.87E+06	0.52	5.89E-06	8.55E+06	
7.00E+01	618	0.005	6.87E-06	0.2	3.46E+06	1.04E+07	0.52	6.87E-06	9.00E+06	
8.00E+01	565	0.005	7.85E-06	0.2	3.62E+06	1.08E+07	0.52	7.85E-06	9.40E+06	
9.00E+01	522	0.005	8.84E-06	0.2	3.76E+06	1.13E+07	0.52	8.84E-06	9.77E+06	
1.00E+02	486	0.005	9.82E-06	0.2	3.89E+06	1.17E+07	0.52	9.82E-06	1.01E+07	
2.00E+02	304	0.005	1.96E-05	0.2	4.86E+06	1.46E+07	0.52	1.96E-05	1.26E+07	
3.00E+02	230	0.005	2.95E-05	0.2	5.53E+06	1.66E+07	0.52	2.95E-05	1.44E+07	
4.00E+02	189	0.005	3.93E-05	0.2	6.06E+06	1.82E+07	0.52	3.93E-05	1.57E+07	
5.00E+02	162	0.005	4.91E-05	0.2	6.50E+06	1.95E+07	0.52	4.91E-05	1.68E+07	
6.00E+02	143	0.005	5.89E-05	0.2	6.88E+06	2.06E+07	0.52	5.89E-05	1.79E+07	
7.00E+02	129	0.005	6.87E-05	0.2	7.22E+06	2.17E+07	0.52	6.87E-05	1.88E+07	
8.00E+02	118	0.005	7.85E-05	0.2	7.53E+06	2.26E+07	0.52	7.85E-05	1.96E+07	
9.00E+02	108	0.005	8.84E-05	0.2	7.81E+06	2.34E+07	0.52	8.84E-05	2.03E+07	
1.00E+03	101	0.005	9.82E-05	0.2	8.07E+06	2.42E+07	0.52	9.82E-05	2.10E+07	
2.00E+03	63	0.005	1.96E-04	0.2	1.00E+07	3.01E+07	0.52	1.96E-04	2.60E+07	
3.00E+03	47	0.005	2.95E-04	0.2	1.14E+07	3.41E+07	0.52	2.95E-04	2.95E+07	
4.00E+03	39	0.005	3.93E-04	0.2	1.24E+07	3.73E+07	0.52	3.93E-04	3.23E+07	
5.00E+03	33	0.005	4.91E-04	0.2	1.33E+07	3.99E+07	0.52	4.91E-04	3.46E+07	
6.00E+03	29	0.005	5.89E-04	0.2	1.41E+07	4.23E+07	0.52	5.89E-04	3.66E+07	
7.00E+03	26	0.005	6.87E-04	0.2	1.48E+07	4.43E+07	0.52	6.87E-04	3.84E+07	
8.00E+03	24	0.005	7.85E-04	0.2	1.54E+07	4.62E+07	0.52	7.85E-04	4.00E+07	
9.00E+03	22	0.005	8.84E-04	0.2	1.60E+07	4.79E+07	0.52	8.84E-04	4.15E+07	
1.00E+04	21	0.005	9.82E-04	0.2	1.65E+07	4.95E+07	0.52	9.82E-04	4.29E+07	
2.00E+04	13	0.005	1.96E-03	0.2	2.05E+07	6.14E+07	0.52	1.96E-03	5.32E+07	
3.00E+04	10	0.005	2.95E-03	0.2	2.32E+07	6.96E+07	0.52	2.95E-03	6.03E+07	

The data obtained for the pressure values is consist with the literature in terms of parameters behavior (Castany et al., 2014) where increasing the Q values injection pressures increase and increasing the length values the injection pressures increase.

If increase	The injection pressures
-------------	-------------------------

Q	Increase
L	Increase

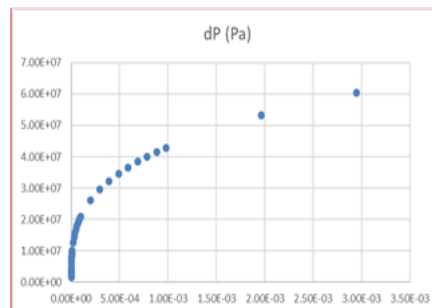


Figure 18 -Pressure behavior (dP) respect to volumetric flow rate (Q).

Furthermore, according to Propylene processing guidelines, the reported pressure for injection molding of PP are within the average of 800 to 1500 psi $\sim 1.0342 \times 10^7$ Pa. Some other companies such as Proplastics and PP solutions report their own processing guidelines with the same average injection pressures.

References:

- Fan, B., Kazmer, D., & Mukhari, R. (2004). *Real-Time Flow Rate Estimation in Injection Molding*.
Wang, K. K., & Hieber, C. A. (1988). *Injection Molding Simulation*.
Castany, F., Martinez, A., Sanchez, F., Arenaz, J., Barraqueta, D., & Gallego, J. (2014). *Diseño y desarrollo de componentes de plástico inyectado (II): La pieza*.
PP solutions, we will. *Injection*. Consulted on July 12th, 2020. <http://www.ppsolutions.com.tw/pp-processing-methods>
Proto plastic. *10 Tips for Injection Molding Polypropylene Resins*. Consulted on July 12th, 2020. <https://protoplastics.com/injection-molding-polypropylene-resins/>

PROBLEM 2:

2. You have the following information from a capillary rheometer for a HDPE resin (this is real data, so several runs were made at the same velocity due to possible variabilities in the instrument).

Velocidad (in/s)	Average load (lbf) for the L/D=40 die	Average load (lbf) for the L/D=20 die	Average load (lbf) for the L/D=10 die
0.061	170.3	92.6	55.9
0.061	171.7	92.6	54.1
0.307	420.5	216.9	121.3

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0.307	417.5	214.4	119.4
0.614	579.1	296.5	164.6
0.614	575.8	294.1	162.9
3.07	848.4	390.7	261.6
6.14	626.8	360.6	233.8
6.14	623.6	377.8	264.3
13.8	939.4	552.4	368.5
18.4	1098.4	640.3	418.0

Some of the dimensions are:

- Barrel diameter 0.68 cm
- Capillary diameter: 0.05 inches
- Die Lengths: 2 in; 1 in; 0.5 in
- The piston moves at constant velocity (inches/second)
- The load is given pound force (lb_f) and the force sensor is at the top of the piston. You are asked

to:

- Get the real shear viscosity.
- The entrance pressure.
- The elongational viscosity. Classic Newtonian flow problem:

Pressure-driven flow of fluid in a tube

- Assumptions:
- Steady State
- Well-developed
- Long tube (no Z-dependence).
- No slip at the wall.

For All fluid:

Stress at the wall: $\tau_R = \frac{\Delta P R}{2L}$

For Newtonian Fluid:

Shear Rate at the wall: $\dot{\gamma} = \frac{4Q}{\pi R^3}$

Definition of viscosity:

$$\eta = \frac{\tau_R}{\dot{\gamma}}$$

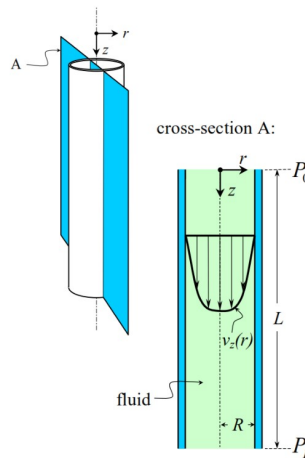
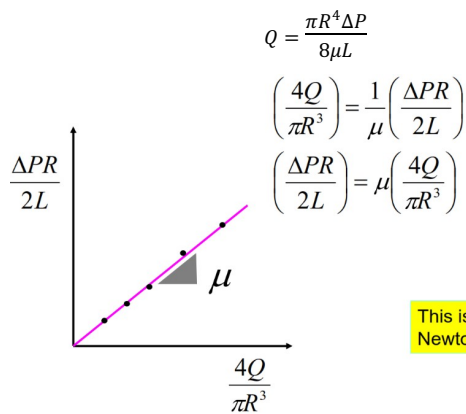


Figure 19 - Diagram of cross section.

Newtonian Fluid:

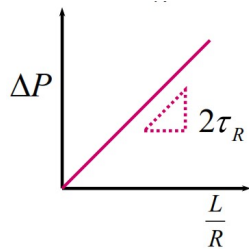
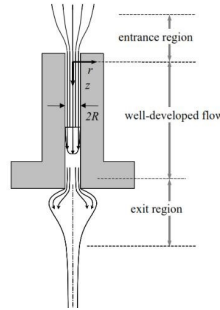
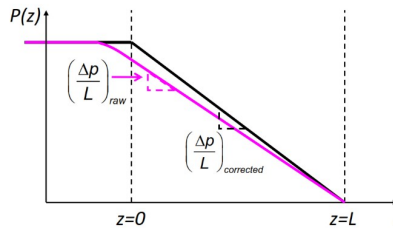
Hagen-Poiseuille Law:



This is only true for Newtonian fluids.

Corrections to Capillary Flow:

- entrance and exit effects - Bagley correction (correct the pressure drop)
- Slip at the wall - Mooney analysis (correct the flow rate) (We did not consider this correction)
- Non-parabolic velocity profile – Weissenberg Rabinowitsch correction (correct the shear rate at the wall; non-Newtonian effects)



This is the result when the end effects are negligible.

$$\tau_R = \frac{\Delta P R}{2L} \Rightarrow \Delta P = (2\tau_R) \frac{L}{R} + 0$$

Constant at fixed $\dot{\gamma}_a$

no intercept

Run for different length capillaries

Procedure:

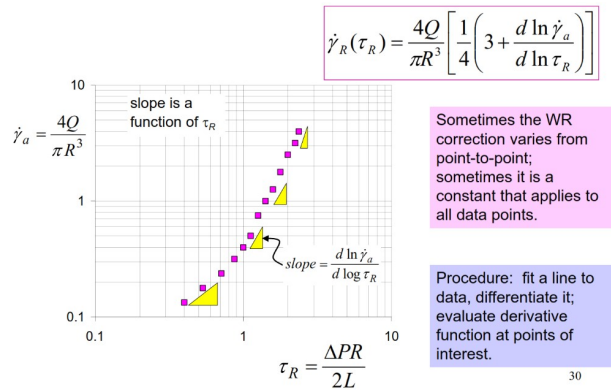
Entrance and exit effects - Bagley correction:

The pressure gradient is not accurately represented by the raw $\frac{\Delta P}{L}$

- For a standard set of apparent shear rates $\dot{\gamma}_a$, measure ΔP in capillaries of different L/R (usually different lengths).

- Plot results and infer corrected shear stress from slope.

Weissenberg-Rabinowitsch correction:



Elongational or extensional viscosity is the coefficient to define that the applied stress is extensional stress.

The formula used to calculate it were considering in terms of apparent shear rate at the orifice

$$\dot{\epsilon} = \frac{\dot{\gamma}_a}{8}$$

$$\dot{\gamma}_a = \pi \frac{4Q}{R^3}$$

Since the shear contributions are assumed negligible, the extensional normal stress difference may be expressed as:

$$\tau_{11} - \tau_{22} = \Delta P_{en}$$

Finally, the elongational viscosity can be obtained with the following formula:

$$\eta_u = \frac{\tau_{11} - \tau_{12}}{\dot{\epsilon}}$$

According to the parameters provided in the problem, we performed the calculations in order to obtain the entrance pressure, elongational viscosity and real shear viscosity. * Excel file provided as supplementary data.

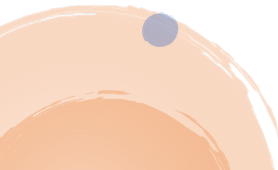
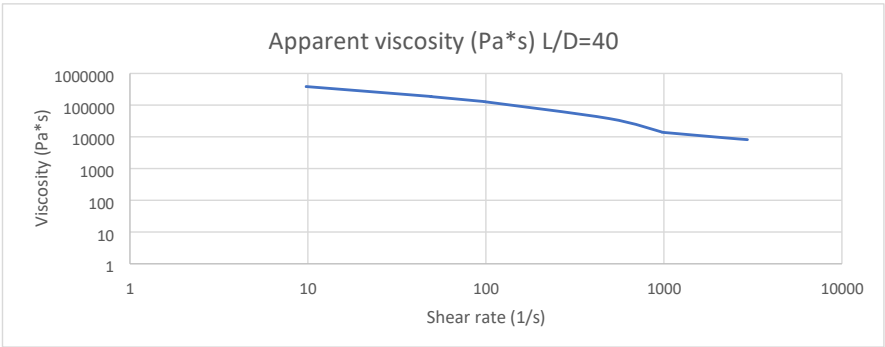
The values for the real shear rate and real shear viscosity are indicated in the tables as well as the apparent shear rate, entrance pressure and elongational viscosity.

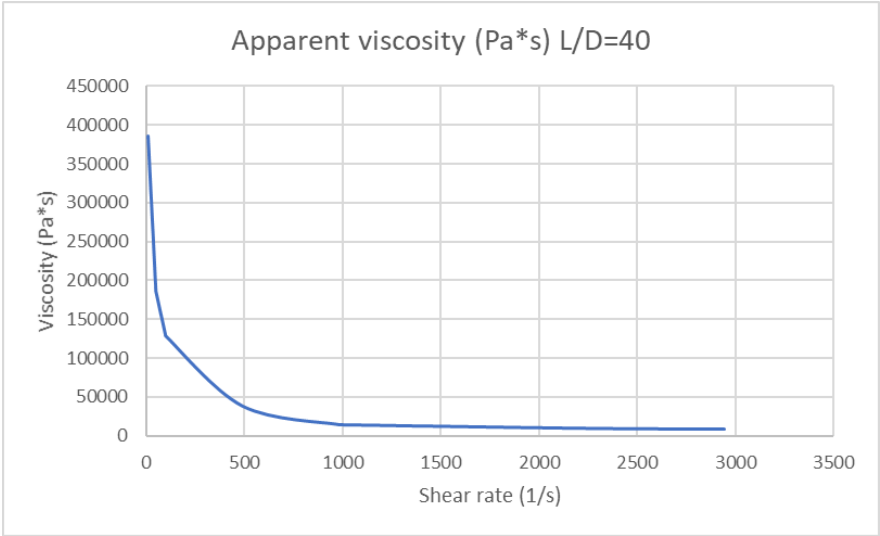
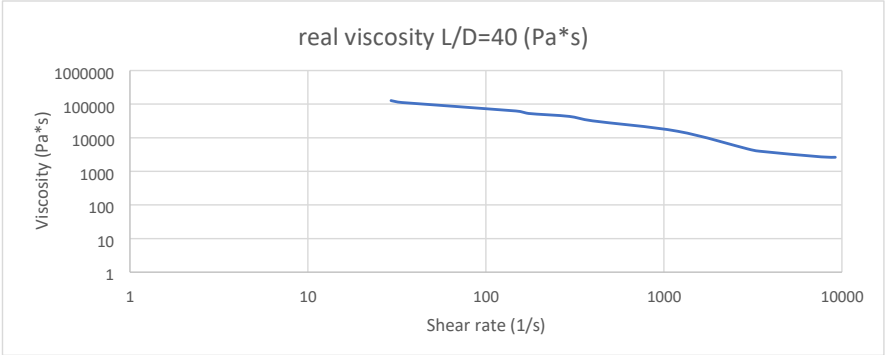
real shear rate L/D=40 (1/s)	real shear rate L/D=20 (1/s)	real shear rate L/D=10 (1/s)	real viscosity L/D=40 (Pa*s)	real viscosity L/D=20 (Pa*s)	real viscosity L/D=10 (Pa*s)
29.29485	29.29485	29.29485	127582.9	138745.4142	167513.4
33.69922	33.92974	34.18068	111820	119792.4241	138945.8
147.4347	147.4347	147.4347	62594.35	64574.14472	72225.39
173.4629	173.7027	173.9616	52822.49	54177.28156	60253.16
294.8695	294.8695	294.8695	43101.53	44136.08555	49003.71
396.9043	434.1126	378.3601	31838.67	29736.62014	37795.9
1193.03	412.0933	716.3482	15606.95	41614.70242	32058.45
2948.695	2948.695	2948.695	4665.177	5367.781601	6960.551
3434.374	3472.503	3547.446	3984.992	4775.493975	6540.49
7643.428	7703.32	7887.913	2697.313	3147.564693	4101.137
9182.531	9179.434	9174.183	2625.228	3061.727421	3999.796

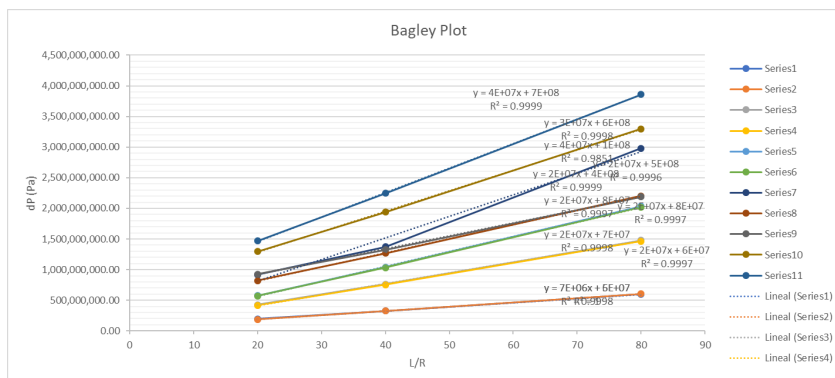
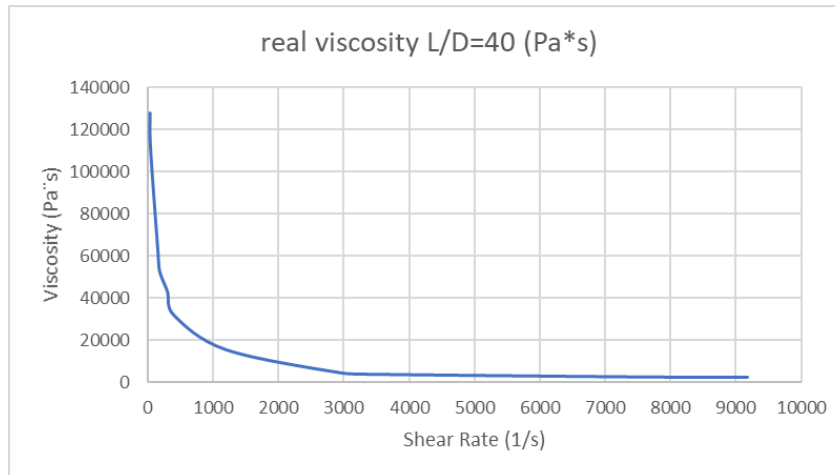
Apparent shear Rate	dPen (Pa)	Elongation Viscosity (Pa*s)
9.764950414	59870560	49049350.97
9.764950414	51091885	41857363.6
49.14491438	68473661	11146408.43
49.14491438	62679736	10203250.82
98.28982875	81817246	6659264.507
98.28982875	77427909	6302007.846
491.4491438	1.15E+08	1872014.656
982.8982875	3.54E+08	2881274.732
982.8982875	4.97E+08	4045179.497
2209.11993	6.15E+08	2227131.236
2945.49324	6.63E+08	1800717.085

The plots for apparent and real viscosity are obtained as well as the Bagley plot

The results obtained are consistent with the literature reports as shown in the graphs for apparent and real shear viscosity in view that the behavior is given in terms of a shear thinning fluid.







References:

Padmanabhan, M., & Macosko, C. W. (1997). *Extensional viscosity from entrance pressure drop measurements*, 151, 144–151.

Used formulas to solve the problem:

Concept	Formula
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Pressure dP	$dP = \frac{F}{\pi R^2}$
Flow rate (Q)	$Q = V\pi R^2$
Apparent Shear rate $\dot{\gamma}$	$\dot{\gamma}_{app} = \frac{4Q}{\pi R^3}$
Stress at the wall τ_w	$\tau_w = \frac{dPR}{2L}$
Apparent Viscosity η_{app}	$\eta_{app} = \frac{\tau_w}{\dot{\gamma}_{app}}$
Slope of ln shear rate vs stress curve	$b = \frac{\Delta \ln(\dot{\gamma})}{\Delta \ln(\tau_w)}$
Real shear rate $\dot{\gamma}_w$	$\dot{\gamma}_w = \left(\frac{3+b}{4} \right) \dot{\gamma}_{app}$
Real viscosity η	$\eta = \frac{\tau_w}{\dot{\gamma}_w}$
Entrance Pressure dP_{en} you can calculate with the interception in Y axis of the equation given by the Bagley plot that is dP vs L/R	
Also, we can consider	$\dot{\epsilon} = \frac{\dot{\gamma}_{app}}{8}$
For elongation viscosity η_u	$\eta_u = \frac{\Delta P_{en}}{\dot{\epsilon}}$

Team members contribution:

All the team members listed in this document participated equally in the elaboration of this exam and attended all the meetings to discuss, to propose solutions and to solve the problems.

