

Thermal and mechanical properties of commodity polymers

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1 Abstract

The purpose of this project was to investigate commodity polymers. Two commercial polymers, high-density polyethylene (HDPE) and low-density polyethylene (LLDPE), as well as polystyrene (PS), synthesised by free radical polymerisation were investigated in terms of molecular characteristics, thermal properties and a clear difference between the polymers was noted. Additionally, the mechanical properties of HDPE and LLDPE were investigated and most interestingly, a difference in the tensile strength of HDPE and LLDPE was observed, even though they consist of the same monomer and just vary in their macromolecular architecture.

2 Introduction

Polymers (plastics) have become a major part of our daily life, whether it is in the form of clothes, packaging or electronics, and today's living standards heavily rely on their numerous properties. These properties are due to the variety of polymer types and structures available. Consisting of many repeating units, called monomers, polymers are very large molecules with generally more than 1000 atoms. The properties of a polymer are not only dependent on the structure of its repeating units, but the arrangement of the repeating units can also strongly affect the properties of the polymer. Sometimes the monomers do not build one long chain with a linear structure, but rather form branches. Such a difference in structure results, for example, in the different properties of linear high-density polyethylene (HDPE) and branched low-density polyethylene (LLDPE) which are both produced from the monomer ethylene.^{1,2}

The objective of the project was it to study the different properties of polymers as well as their origin. For example, HDPE and LLDPE were compared to investigate to what extent their structural difference causes their different properties. Furthermore, polystyrene was produced by free-radical polymerisation and compared to commercial polystyrene.

3 Materials and Methods

3.1 Materials

- Styrene (Sigma Aldrich)
- AIBN recrystallised (Sigma Aldrich)
- Ethanol (VWR)
- THF (VWR)
- HDPE and LLDPE were kindly donated by industrial partners
- Commercial polystyrene (Sigma Aldrich)

3.2 Characterisation

Size exclusion chromatography (SEC) was used to measure the molecular weight distribution of self-produced and commercial polystyrene. For this, the polystyrene was dissolved in THF. The measurements were taken at a flow rate of 1 ml/min and a refractive index detector was used. Polystyrene was used as standard.

The melting point of HDPE and LLDPE and the glass transition temperature (T_g) of the commercial and the self-produced polystyrene were determined with differential scanning calorimetry (DSC). Around 5 mg of each polymer was heated to 160 °C and then cooled to -20 °C at 10 °C/min. This was repeated and the second cycle was used to determine the T_m and T_g , to remove the thermal history of the polymer.

Thermogravimetric analysis (TGA) was the method used to measure the point of degradation of the self-produced polystyrene. This was done by heating around 5 mg of the polymer from room temperature to 500 °C at 20 °C/min.

To test the tensile strength of HDPE and LLDPE the two polymers were first moulded into dog bones with an injection moulding machine. The dog bones were then pulled apart by a tensile tester at 50 mm/min. The measurements were done with a 200 N module for LLDPE and a 10 kN module for HDPE.

3.3 Polymerisation of Polystyrene

The inhibitor was separated from the styrene with aluminium oxide (basic). The styrene was then stored at -20 °C. 36 mg Azobisisobutyronitril (AIBN) and a stirring bar were put in a round bottom flask, which was then sealed and later flushed with Nitrogen for five minutes. 4.4 ml styrene were transferred into the flask with a syringe. The round bottom flask and its contents were then heated to 60 °C and stirred for two hours and ten minutes. Thereafter the content of the flask was first dissolved in tetrahydrofuran and then the solution was precipitated into ethanol. The polystyrene was not soluble in ethanol and precipitated from the solution containing unreacted monomer. The mixture was centrifuged and the solution was poured off, leaving almost only polystyrene. The polystyrene was dried overnight in a vacuum oven at 50 °C. This whole polymerisation was done twice simultaneously.

4 Results

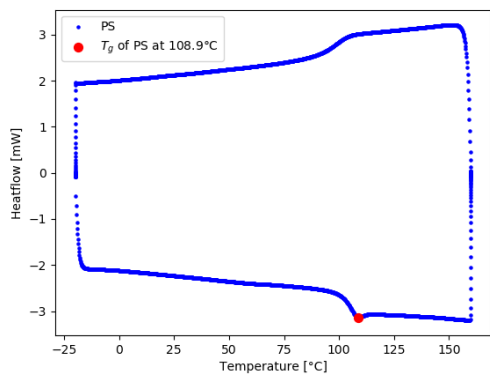


Figure 1: Differential scanning calorimetry of polystyrene (PS)

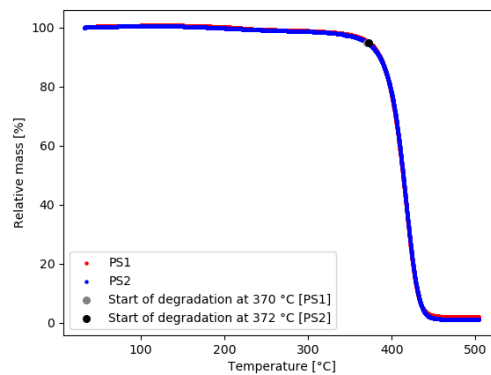


Figure 2: Thermogravimetric analysis (TGA) of polystyrene (PS)

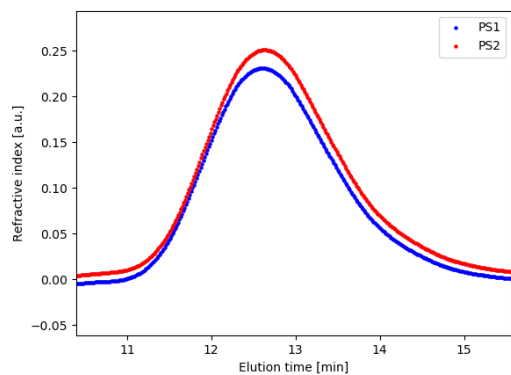


Figure 3: Size exclusion chromatography (SEC) of two polystyrene (PS) samples

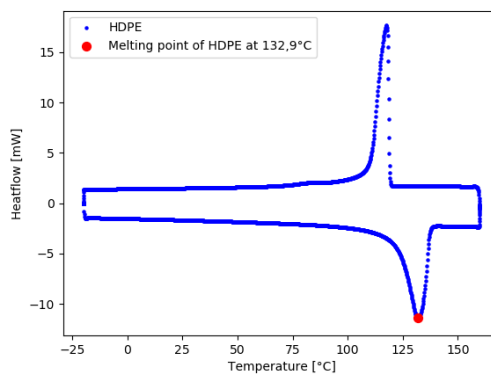


Figure 4: Differential scanning calorimetry of high-density polyethylene

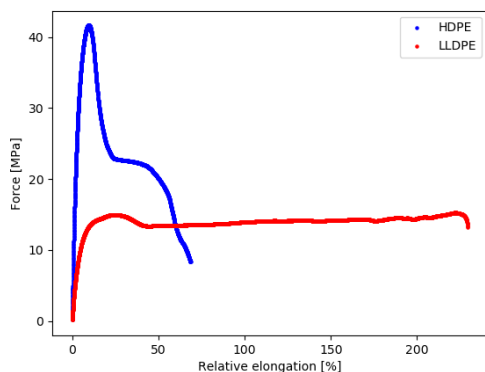


Figure 5: Tensile strength testing of HDPE and LLDPE

Table 1: Glass transition temperature and melting point of various polymers (*the value of this T_g or melting point was out of the measurable range)

Polymer	T_g	Melting point
LLDPE	*	120°C
HDPE	*	132°C
Commercial PS	108°C	*
PS1	107°C	*
PS2	109°C	*

5 Discussion

5.1 Polymerisation and properties of polystyrene

5.1.1 Polymerization of polystyrene

The polystyrene was produced by free radical polymerisation. The initiator AIBN decomposes through heat into radicals, which react with the styrene monomers and form growing radical chains. The radical chains can react with styrene monomers or with other radical chains to form longer molecules. This results in large polystyrene molecules.

5.1.2 Glass transition temperature

The glass transition temperature of the self-produced polystyrene is very similar to the one of the commercial polystyrene from the laboratory inventory. In figure 1 the glass transition temperature of commercial polystyrene is visible. During the glass transition, the polymer chains gain mobility and go from a glassy to a rubbery state which can be observed by a small decrease in the heat flow.

5.1.3 TGA

Figure 2 shows the decomposition temperature of the two self-produced polystyrene samples. When the polystyrene is heated up it decomposes into CO_2 and H_2O , so the mass of polystyrene decreases. The point when the mass starts to decrease thus shows the decomposition temperature of polystyrene, which is almost similar for both samples.

5.1.4 Molecular weight distribution

The molecular weight distributions of polymers are different since not all chains of a polymer are the same length. Since sometimes more and sometimes fewer monomers combine to form a molecule, the molecules of a polymer have different molecular weights. Figure 3 shows the molecular weight distribution of two polystyrene samples indicating the distribution of different chain lengths. Interestingly these distributions seem to be similar for two polystyrene samples made under the same conditions.

5.2 HDPE and LLDPE

Figure 4 shows the heat flow required to raise the temperature of HDPE. Once the HDPE begins to melt, more heat is needed to raise its temperature as the melting process consumes energy. The melting point of HDPE can thus be observed by the decrease of the heat flow. The higher melting temperature of HDPE compared to LLDPE is due to its linear structure. Whereas the HDPE molecules can form dense molecular arrangements, gaps are formed between the branched LLDPE molecules. Because of the smaller distances between the HDPE molecules, the attractive force is stronger and more energy is needed to make the molecules move. These stronger forces between the HDPE molecules are also responsible for the greater tensile strength of HDPE. As can be seen in Figure 5, it takes a lot more force to rupture HDPE, but it elongates less compared to LLDPE before it ruptures. While the HDPE molecules are already elongated in the polymer and therefore cannot rearrange, the LLDPE molecules are more flexible and can adapt better to the elongation by packing more closely. The HDPE and LLDPE are commercially available and an SEC could not be made since they are not solvable in THF.

5.3 Conclusion

We analyzed various polymer properties. The structure and composition of polymers have a significant influence on the thermal and mechanical properties of polymers. The influence of the structure could be observed with HDPE and LDPE which have different mechanical properties solely based on their structure. Interesting for further investigations would, for example, be polymers with narrower weight distributions and to try out methods to produce polymers with narrower molecular weight distributions.

6 References

¹ Polymer Science Learning Center, Macrogalleria, (www.pslc.ws/macrog/index.htm).

² Odian, George (2004). Principles of Polymerization, Fourth Edition. USA: John Wiley & Sons.

7 Acknowledgements

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