



Molecular structure and design of thermoplastic polymers for 3D printing

One of the main advantages of polymers over metals is that they possess low temperature processability and a low density, which makes them attractive materials, especially for many light-weight applications. Logically, polymers have also found their way into 3D print technology such as Fused Deposition Modeling (FDM), by which complex geometries can be generated. However, many variations in molecular structure have major impact on their performance and require in depth understanding.

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In the shaping of thermoplastic polymer products, geometries are generated in the liquid state and preserved through solidification by fast cooling from the melt. For conventional shaping technologies, the intrinsic material properties of the polymers can be correlated to the performance of the finished products, but for 3D printed parts via FDM the correlation is absent and the product properties are far below their intrinsic material properties. One of the biggest challenges is the poor layer-to-layer adhesion, which is also connected to slow diffusion of macromolecules through the inherent layered structure.

Another problem is that as the melted polymer cools, the molecules 'freeze' before an equilibrium

volume state has been reached (see below). Consequently, shrinkage may continue over time, leading to dimensional instability of the complex geometry. This effect is most pronounced in semi-crystalline polymers. The regular sequence of monomer units, for example, allows the polymer chains to pack in a regular and more dense structure upon cooling (crystallization). If the cooling after deposition from the melt takes place sufficiently slow, then the material can crystallize upon cooling below the melt temperature. However, if the cooling rate is too fast in comparison to the crystallization rate, the molecules will 'freeze' and the material will consequently lack ideal packing.

Cooling time critical for phase transitions

To illustrate the aforementioned effect of dimensional instability, the volume-temperature dependency of both amorphous (glassy) and semi-crystalline polymers is depicted in Fig. 1.

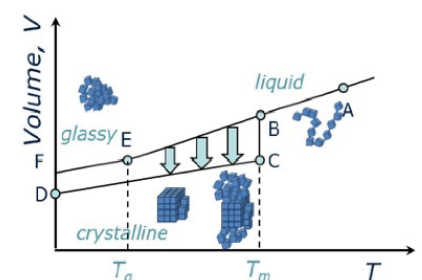


Fig. 1. Volume-temperature diagram of amorphous and crystalline phase of polymers.

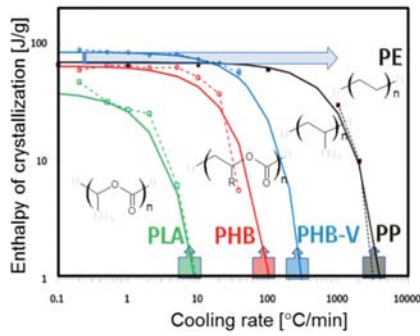


Fig. 2. Crystallisation kinetics of different semi-crystalline polymers. The enthalpy of crystallization is a measure for the crystallinity of the material.

Line A-E-F shows the volume-temperature dependency of an amorphous polymer. In the rubbery/liquid-like state, the volume decreases with decreasing temperature (AE) and follows the equilibrium line. With further decreasing temperature, the molecular motion decreases and the chains are no longer able to follow the equilibrium volume and freeze (glass transition temperature). The glass transition temperature and the specific volume are dependent on the cooling rate. If the system is cooled very quickly, too little time is allowed to approach this equilibrium state, implying that the specific volume is relatively large and shrinkage will continue overtime (though slowly) leading to dimensional instability. This effect can even be more pronounced for semi-crystalline polymers: if given sufficient time, the volume will follow the line A-B-C-D upon cooling. After passing the melt temperature, the material will crystallize, resulting in a relatively large volume decrease because of the more dense packing of the crystalline phase. When cooling is too rapid, as stated above, and crystallization does not take place (or only partially), the volume discrepancy between the actual and equilibrium state is even larger resulting in even more pronounced dimensional instability.

Problems with polymers like PLA
 Polylactid acid is an example of a semi-crystalline polymer that is often applied in 3D FDM printing. However, this

polymer is known to have a poor crystallization behavior due to large influence from its chemical structure. For example, *Auhl et al.* and *Harings et al.* have demonstrated the slow and complex crystallization behavior of PLA compared to that of other biopolymers or commodity polymers such as polyethylene (PE) and polypropylene (PP). In Fig. 2, the y-axis depicts the crystallization enthalpy (a measure for the crystallinity) and on the x-axis the cooling rate is given. As can be seen, PE crystallizes very fast upon cooling, while PP only crystallizes below a cooling rate of about 10,000 °C/min. Compared to these polymers, PLA is a very slow crystallizing polymer. This makes it surprising why it is so often applied in 3D printing, because it is doomed to lead to long production times and poor dimensional stability, since the cooling rate will easily exceed the crystallization rate.

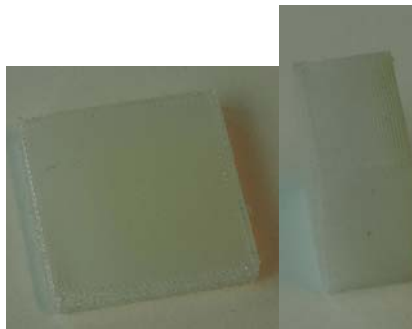


Fig. 3. (a) Top view of first layers of printed cube PLA; (b) side view of printed cube PLA .

Fig. 3 shows a printed rectangle (2*2*1 cm) from a commercial PLA grade, which was printed at 200 °C, while the chamber was heated at 70 °C.

In the left picture, when half of the part is printed, it can be seen that directly after printing, the material is transparent, indicating that the polymer is in the amorphous state. Upon further printing, the bottom part of the cube becomes opaque, while the “freshly” printed layers are transparent. The whitening of the bottom part indicates that crystallization took place several minutes after these layers had been printed.

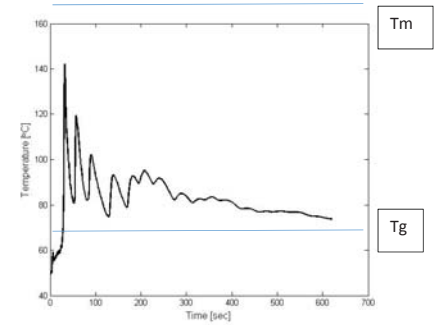


Fig. 4. Temperature profile in the bottom layer of a printed PLA cube (see Fig. 3).

To understand this phenomenon in further detail the temperature of a spot in the bottom layer of the object was measured during the entire printing process. Fig. 4 shows the resulting temperature profile. The measurements show an increase in the temperature of the bottom layer, each time the warm nozzle passes the spot in the x-y plane. With increasing printing height in vertical z-direction the temperature maximum decreases and the effects on the bottom layer diminish. As a result of the influence of the heated nozzle, the PLA is repeatedly heated far above its glass-transition temperature of 55–65 °C. At this temperature range the mobility of the polymer chains increases strongly, allowing their crystallization, which initially was suppressed by the fast cooling from the melt. Because of this crystallization the sample turned opaque and shrank, resulting in dimensional instability.

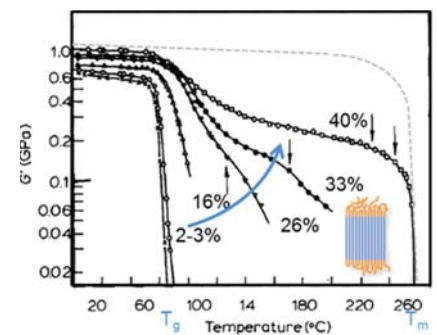


Fig. 5. Influence of temperature and percentage crystallinity of the stiffness G' of poly(ethylene terephthalate, Boyd).

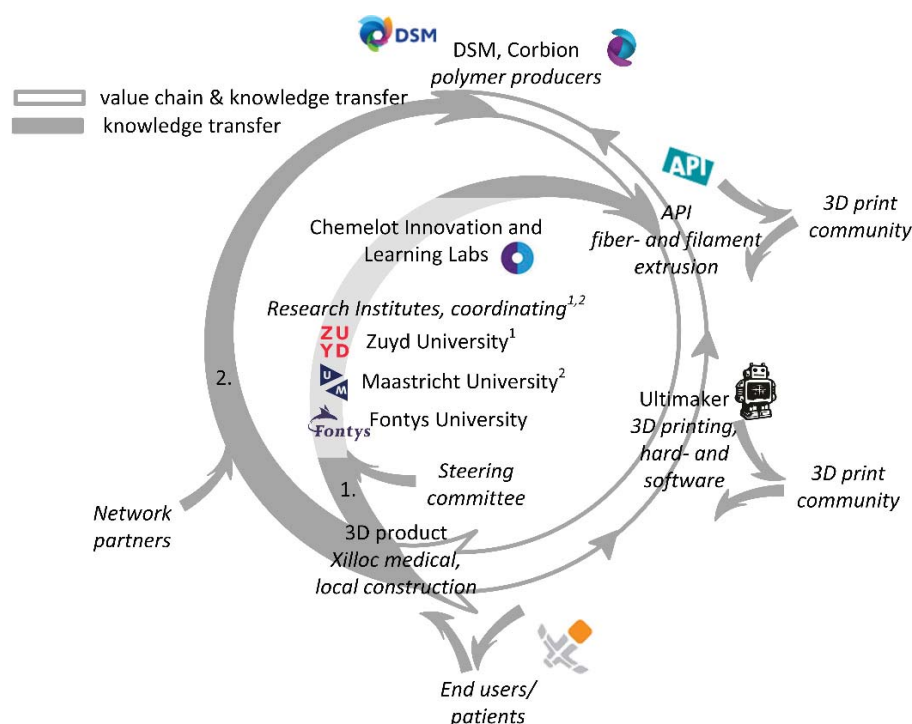


Fig. 6. Partners involved in the project

Semi-crystalline polymers

These results could give the impression that the best choice of material for 3D printing would be amorphous polymers since no interference from crystallization can take place. However, when we consider the printing of functional parts, the use of semi-crystalline polymers has a significant advantage over their amorphous counterparts because of their better intrinsic thermo-mechanical properties. For example, *Boyd et al.* have shown that the shear modulus G' , which indicates the stiffness of a material, is highly dependent on crystallinity (Fig. 5). Above the glass transition temperature T_g , the modulus of an amorphous material drops rapidly, and as a result mechanical stability and integrity is lost. This implies that the usage-range is limited by the glass transition temperature. The presence of crystals largely preserves the stiffness of the material until the melting temperature T_m - thus over a much larger temperature range. The higher the crystallinity, the better the mechanical properties such as toughness. Therefore, crystallization can be very attractive for printing functional parts since it combines better mechanical properties with a larger thermo-mechanical stability.

Polymer chain entanglements

In addition to crystallization, good mechanical properties typically require the entanglement of polymer chains. These entanglements arise when the length of polymer chains (molar mass) is sufficiently high and above a critical entanglement value of about 1–10 kg/mol. A high molar mass implies another challenge, since due to the entanglement, the melt viscosity increases strongly with the molar mass by a power of about 3.4. This means that by doubling the molar mass, the viscosity will increase by around a factor 10, which may impede the melt processability. It also limits fusion of chains between two neighboring layers, which is a necessary process to reach final product properties that reflect the intrinsic mechanical properties of a specific polymer material.

Consortium

The examples of possible issues discussed in the aforementioned paragraphs indicate that the printing of semi-crystalline polymers can be attractive in terms of intrinsic thermo-mechanical properties but it is definitely a very delicate process, where the time scales of diffusion, crystallization, and cooling must be balanced. These

time scales can be tuned by the design of the polymers, where parameters such as molecular weight and chemical composition play an important role. Chemical composition is also a parameter that can be tuned to improve the layer-to-layer adhesion, for example by making use of secondary interactions like hydrogen bonds.

To design such types of polymers that will successfully print functional parts, it is essential that all entities of the value chain of 3D FDM printing collaborate and that knowledge exchange occurs. Last year a four-year research project was started with a grant from the Stichting Innovatie Alliantie (SIA) to build up essential knowledge. In Fig. 6, the companies and institutes that are participating in the research project are outlined. This figure clearly illustrates that companies throughout the whole of the FDM value chain - from polymer producers to end-users - are taking part in the project. Maastricht University contributes fundamental knowledge and the two Universities of Applied Science (Zuyd University and Fontys) take care of the knowledge flow together with CHILL, whose mission is to strengthen the economic and social position of modern chemistry by connecting innovation and research with education. By combining broad knowledge and experience of all participants, we aim to match the specific needs in FDM product and process expectations.

References

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