TU/e - Faculty of Mechanical Engineering
Polymer Technology group

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# Contact mechanics, friction and wear on semi-crystalline polymer surfaces

Preparation phase

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# 1 Introduction

With the increasing demand for high-end (corrosion resistant, light-weight, self-lubricating, etc.) products, the application of (thermoplastic) polymers in various types of machinery becomes more important every day. In widely different types of equipment polymers play a crucial role, e.g. in bearings in automotive industry, or in medical equipment like artificial hip-joints. To increase the lifetime of, and decrease the mechanical energy loss between relative moving parts, the study of contact mechanics is crucial; in the design of such parts minimum dissipation of energy and wear rate are key factors. Whereas in metals the concept of contact mechanics, friction and contact fatigue is widely known, there are no clear guidelines for the surface design in technical polymer applications.

To speed-up the design proces, accurate numerical simulations are being developed within our group, to supersede the conventional trial-and-error approach. In the recent past, combined experimental and numerical techniques have characterizied the contact mechanics and contact fatigue of neat amorphous polymer systems (e.g. polycarbonate (PC) and polymethylmetacrylate (PMMA)) [1, 2], as well as soft and hard nano-filled systems of the before mentioned matrix material [3, 4, 5, 6]. Extending the existing analysis for amorphous materials, the aim is to use similar techniques to simulate indentation and single asperity scratch experiments in neat, semi-crystalline, unoriented and oriented polymeric systems and at a later stage, in filled semi-crystalline structures. For semi-crystalline polymers this is less straightforward as compared to amorphous systems. The main issue is the post-yielding response of these polymers.

For semi-crystalline systems the intrinsic properties are strongly dependent on crystal structure, which on its turn strongly depends on processing conditions. Hence a fundamental comprehension of both the processing/structure relation and the structure/properties relation is key. This project focusses on the influence of processing conditions (e.g. cooling rate and/or draw ratio) on the tribological properties of semi-crystalline isotactic polypropylene (i-PP), in an ultimate attempt to relate intrinsic material properties to deformation and fatique of the polymeric contact surface (i.e. wear).

# 2 Research plan

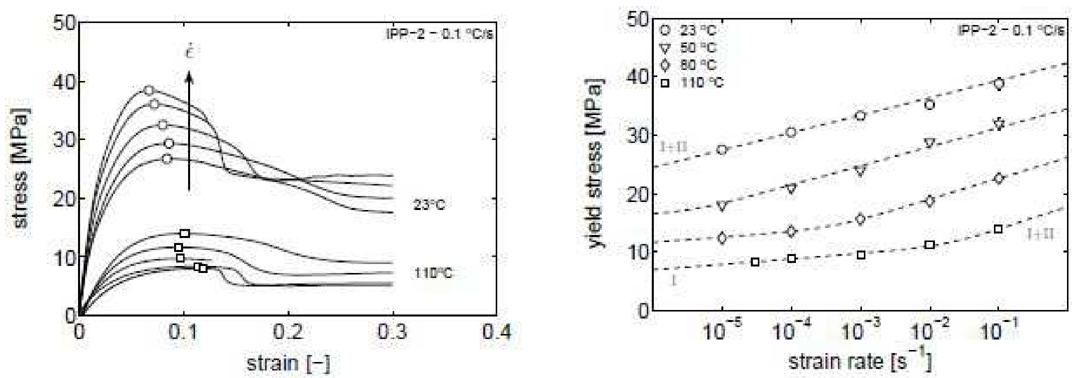
## 2.1 Research objectives

Whereas for amorphous systems the contact mechanics of touching polymer surfaces can be predicted accurately in terms of penetration depth and friction force as function of sliding velocity and normal force, for semi-crystalline polymers these phenomena strongly depend on the crystal orientation. To get a better understanding of the structure/properties relation for these materials, this project will deal with:

- Verfying if the pronounced effect of sliding velocity and normal force on surface properties for amorphous materials also applies to semi-crystalline surfaces.
- Study by controlling the crystal-structure development originating from processing (e.g. extrusion, drawing and cooling) its influence on tribological properties.
- Study the effect of orientation on the surface properties; indentation, scratch resistance and wear.

## 2.2 Current state of the art

As mentioned before, due to recent progress made by our group, the surface mechanics as well as the onset of damage, can be predicted accurately for amporphous materials such as PC and PMMA (see [1, 2]), using just the intrinisic material response as input. For (thermoplastic) semi-crystalline systems, such as polypropylene (PP) or polyethylene (PE), these intrinsic parameters depend strongly on the orientation of the crystals, i.e. the amount of anisotropy [7]. In the first part of this section the dependence of yield stress on various loading conditions is discussed for isotactic polypropylene (i-PP) and ultra-high molecular weight polyethylene (UHMWPE). In the latter part previous work on contact mechanics, deformation and failure is summarized.



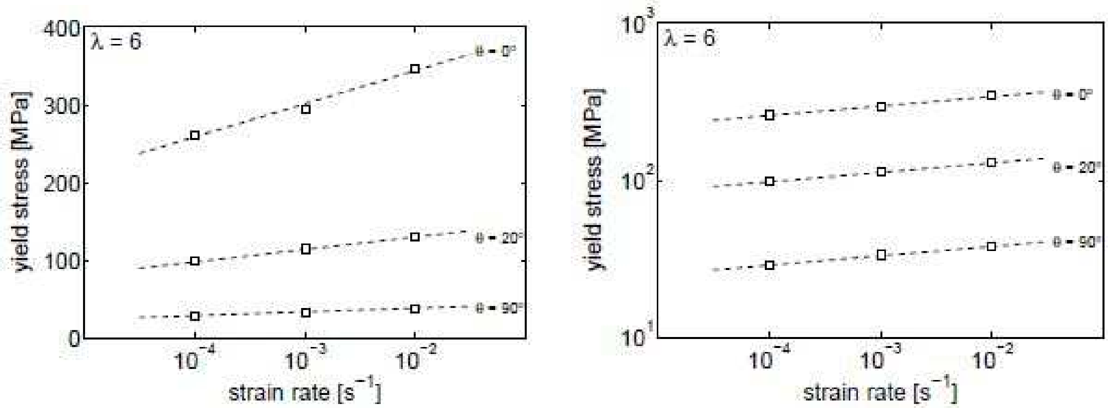

(a) (b)

Figure 1: Example of neat $\alpha$-phase i-PP (a) stress-strain response during uniaxial tensile tests at different temperatures and strain rates, (b) strain rate and temperature dependence of the yield stress. Figures are taken from Van Erp [8].

Extensive work on four model systems i-PP is done by Van Erp in his PhD thesis [7, 8, 9]. The influence of strain rate on the yield kinetics is determined at different temperatures. For the monoclinic $\alpha$-phase in i-PP, an example of the strain rate dependence is shown in Fig. 3. High deformation rates impede relaxation of polymer chains, leading to the observed increase in yield stress with increasing strain rate. On the other hand, an elevated temperature facilitates molecular movement, hence the decrease in yield stress (Fig. 1a). Analogous to the amporphous PMMA, the semi-crystalline i-PP samples exhibit thermorheological complex behavior, i.e. multiple molecular deformation processes contribute to the yielding. Fig. 1b depicts the horizontal shift on the onset of the second process with temperature. The experimental results are modelled with the modified Ree-Eyring equation [10, 11], accounting for the second molecular process. Similiar experiments were carried out on mesomorphic phase samples, yielding an almost identical dependence of strain rate on the yield kinetics. Therefore the rate dependence of yield stress can, for i-PP, be considered independent of crystalline phase.

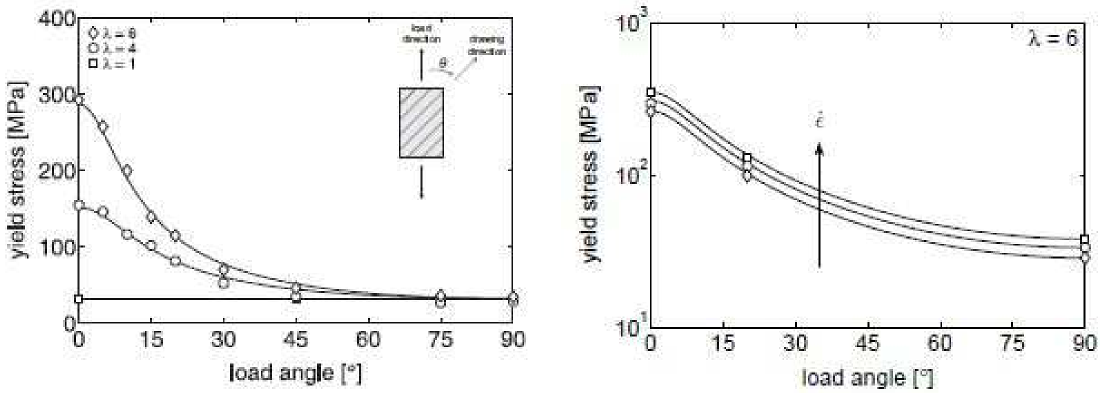
Besides the effect of temperature on the rate dependence of the yield stress, there is a much more pronounced effect on yield stress in oriented systems. All above results are obtained for i-PP samples. In the following, Van Erp's work on oriented i-PP systems is summarized. Solid state drawn i-PP tapes are investigated, to obtain the effect of draw ratio, load angle and strain rate on its yield kinetics. For each tape, the yield stress is measured for different strain rates at various loading angles (Fig. 2a). However the rate dependence is most pronounced for loading in orientation direction, it is however still considerably large for loading in the perpendicular direction. Moreover, in a double logarithmic plot the yield stress dependence on strain rate is equal for the measured loading angles (Fig. 2b), which implies that this dependence is factorizable, i.e. the effect of strain rate and load angle can be separated in a multiplicative way.

This pronounced effect of orientation, is also found to be strongly dependent on the amount of pre-stretch present in the material. For different draw ratios ($\lambda \sim$ 1-6) the yield stress is measured as function of the loading angle (Fig. 3a). Especially for a slight off-axis loading, the yield stress is a strong function of the pre-stretch, and the anisotropy in the material is huge for higher draw ratios. In perpendicular direction, all tapes are considered "isotropic" (read: yield stress is independent of draw ratio). Then again, for different loading angles the influence of strain rate is measured to verify analytical predictions made by Van Erp (Fig. 3b). On a double-logarithmic scale this results only in a vertical shift, implying that for a given draw ratio the influence of orientation and strain rate on the yield stress can be decoupled multiplicatively.




(a) (b)

Figure 2: Yield stress dependence on orientation and strain rate of neat $\alpha$-phase i-PP on (a) semi-logarithmic scale, (b) double-logarithmic scale. Figures are taken from Van Erp [7].




(a) (b)

Figure 3: Yield stress dependence of neat $\alpha$-phase i-PP on (a) draw ratio and loading angle for a fixed strain rate, (b) strain rate and load angle for a fixed draw rate. Figures are taken from Van Erp [7].

It is important to note that this difference in mechanical response caused by processing conditions, originates from the materials micro-structure. In i-PP, nuclei are known to crystallize in either a monoclinic $\alpha$-phase, a trigonal $\beta$-phase, an orthorombic $\gamma$-phase or an unstable meso-phase, depending on the cooling conditions (i.e. temperature, pressure, amount of flow). Under isothermal and quiescent conditions neat i-PP crystallizes only into $\alpha$-phase, since spontaneous nucleation of $\beta$-polymorphs are rare. Nevertheless, $\beta$-phase can easily nucleate with the use of a selective $\beta$-nucleants (calcium pimelate or calcium suberate among others). Moreover, $\beta$-phase is found to nucleate in neat i-PP in the presence of a temperature gradient [12] or by application of a shear flow to the polymer melt [13, 14]. When i-PP is quenched, i.e. cooled down from the melt at a rate of at least 100 K/s, a nodular meso-phase structure develops. Next to that, at elevated pressures, $\gamma$-phase crystallizes concomitantly with $\alpha$-phase, in a specific structure often referred to as "shish-kebab", where oriented parent lamellae (shish) develop in flow direction, on which daughter phases can nucleate and grow (kebab). These two cases, where $\beta$- and $\gamma$-polymorphs nucleate and grow together with $\alpha$ in the same polymer melt, are important phenomena in polymer processing, and therefore in this project it is important to make the processing-structure coupling, in order to eventually understand mechanical bulk and surface properties. Structural information is easily extracted from differential scanning calorimetry (DSC) heating scans, since the polymorphs of i-PP exhibit a large difference in melting point, and from single shot WAXD (wide angle X-ray diffraction) patterns.

Another semi-crystalline polymer that shows a strong dependence of orientation on both bulk properties and wear, is UHMWPE. Many studies have been carried out to enhance the surface properties of this material, since it is widely used in artificial joints. Various attempts to make joints more wear resistant have been made; crosslinking conventional UHMWPE decreases the wear rate with at least one order of magniture [15, 16, 17, 18], while adding vitamin E to the material prevents the crosslinked material from oxydizing [19, 20]. Next to that, different fillers ranging from metal oxides to carbon nanotubes or nano particles are used to improve the lifetime of artifical joints.

Since literature lacks fundamental studies on the wear mechanisms in semi-crystalline thermoplasts, for the scope of this project we will concern first only unfilled, thermoplastic systems, textured by orientation of the crystal lamellae. After a solid state deformation process, the oriented chains cause significant diffences in bulk mechanical properties [21, 22, 23], as well as in wear rate [24], where it was found that the cross section of the groove left on the surface is lowest for scratches made in perpendicular direction (with respect to the drawing direction). At a later stage filled systems can be considered.

In the following, previous work on contact mechanics is summarized. The Polymer Technology group Eindhoven and the Physical-Mechanics and Tribology of Polymers group of the Charles Sadron Institue Strassbourg have done extensive work on developing combined experimental and numerical (the Eindhoven Glassy Polymer model) approaches to describe and predict surface penetration, friction and contact fatique of amorphous polymer surfaces. An overview of different contact failure mechanisms is shown in Fig. 6, where the transition region from ductile ploughing to ductile machining and cracking is of highest interest, since in many applications cracking is considered the ultimate point of failure.

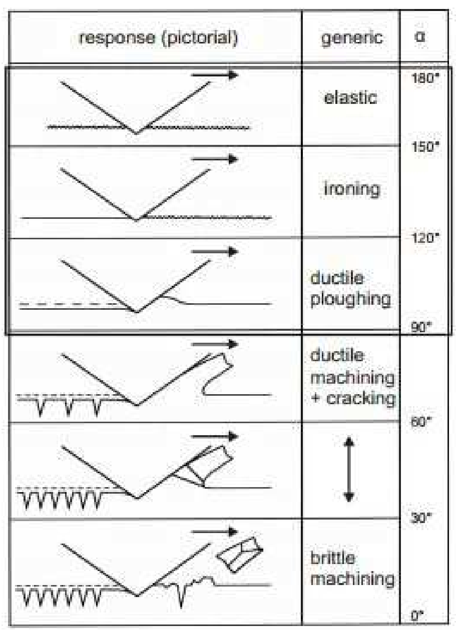
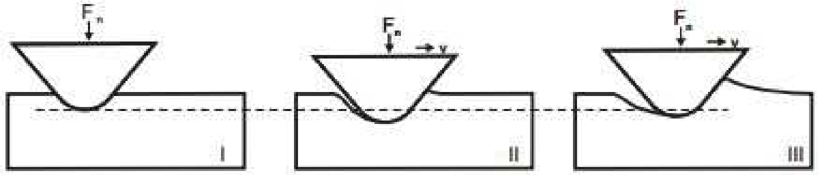
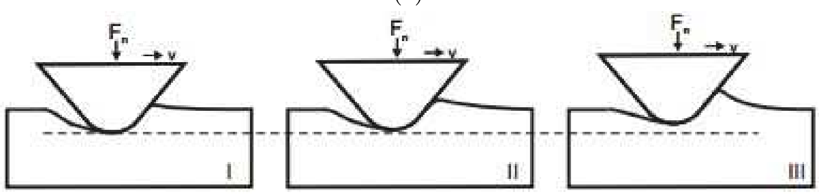



Figure 4: Schematic representation of various deformation and failure mechanisms in contact mechanics. Adopted from [25].

Friction is shown to be related not only the real contact area of indenter tip and polymer, but also to the (non-additive) adhesive interaction between tip and polymer surface [?, 5]. This is schematically depicted in Fig. 5, where the addition of Coulombs friction (Fig. 5b) as a model for the adhesive interaction results in a lower steady state penetration depth compared to the non-adhesive model predictions (Fig. 5a). For polycarbonate the influence of the amount of adhesion as well as the velocity dependency of the friction force is shown in Fig. 6 for a normal load of 300 mN. It is concluded that the larger part of the velocity dependence of the lateral force is due to the intricate interplay between indenter-tip and polymer adhesion and the intrinsic deformation response of the polymer.




(a)




(b)

Figure 5: Schematic representation of single asperity scratch experiment, depicting the indentation (I), the initial sliding (II) and the steady state sliding (III) for (a) deformation only, (b) combined deformation and adhesion component. Figures are adopted from [?].

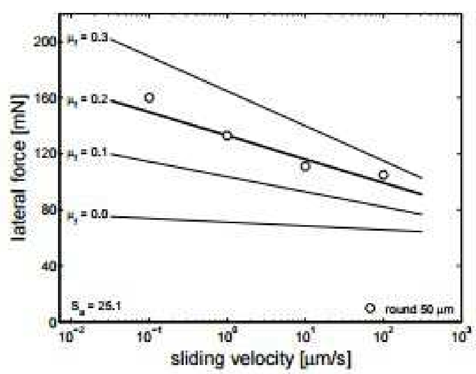



Figure 6: Sliding velocity dependence of friction force, experiments are indicated by the symbols. Drawn lines are model predicitons for different amounts of Coulombs friction. Adopted from [?].

The work on neat amorphous systems [1, 2] is extended recently [3, 4, 5, 6] to industrial coatings, i.e. particle filled systems and epoxides. A hybrid combination of experimental and numerical work resulted in quantitative predictions of scratch and wear resistance for neat, hard and soft particle filled systems. Scratch resistance, the material's resistance to permanent deformation, was found to be dominated by the yield stress. Adding hard particles, increasing the crosslink density of thermoset systems or stimulating progressive ageing in thermoplastic materials all increase the yield stress and with that decrease the amount of plastic deformation. Furthermore it turned out that adhesion was not affected by either an increase of decrease in yield stress. Vertical stratification on the other hand reduces the friction with a factor 2 or 3 by applying respectively a thin soft or hard layer on top of the coating material. The onset of wear in homogeneous coatings is highly dependent on hydrostatic pressure, which when surpassed, induces cavity formation. In heterogeneous coatings, the initiation of wear is characterized by surpassing a critical local energy per unit area.

In this study we aim to extend the knowledge of tribological properties from amorphous polymers (both neat and particle filled) to semi-crystalline thermoplastics, with special attention to the influence of crystal structure and orientation.

### 2.3 Scientific approach

The morphology that develops upon tape drawing is strongly influenced by cooling rate, draw ratio, and hydrostatic pressure, resulting in an anisotropic material. Therefore, at a first stage, compression moulded, isotropic samples are tested in tensile and compression to obtain the strain rate dependence of the yield stress for individual $\alpha$-, $\beta$- and meso-phase i-PP. The phase content of the samples is evaluated with the use of DSC and single shot WAXD.
As a next step, extruded tape samples of about 1 mm thick are prepared with the use of our in-house tape-drawing line. In the first stages, as a model system i-PP, a widely used polyolefin, is used; not only because of its industrial relevance but also because of our group's extended knowledge on this material and its properties during processing. At a later stage the systematic approach to characterize surface properties of semi-crystalline polymers may be applied also to filled i-PP systems. The i-PP tapes will be cooled at sufficiently slow rates (to be emperically determined), to allow for crystal formation and drawing. Samples with a draw ratio of $\lambda = 1, 2, 4$, and 6 are made, and if possible also $\lambda = 8$ and 10. Challenging is that these tapes should have a surface roughness of typically below 100 nm, in order to not influence the indentation and scratch experiments.

As mentioned before, to understand and predict tribological properties of polymeric systems, a proper understanding of the intrinsic material response is key. Therefore, first uniaxial tensile tests are performed on the above mentioned tapes. Similar to the work of Van Erp [7, 8, 9, 26, 27, 28], the effect of strain rate, draw ratio and loading angle on yield stress is studied. Applied strain rates are in the range from $10^{-5}$ s$^{-1}$ up to $10^{-1}$ s$^{-1}$ and loading angles range from $\theta = 0°$ (draw direction) up to 90° (perpendicular to drawing direction). The aim is to test the tensile response of the i-PP grade used, to obtain the multiplicative decoupleable strain rate and load angle dependence. The results of this set of experiments is compaired to numerical simulations. In principle all experiments are carried out at ambient lab temperature and atmospheric pressure, since tribological analysis can only be performed under these conditions with the available experimental set-up.

After this preliminary combination of tensile tests and phase content determination, samples with various draw ratios are subjected to flat-tip indentation and successively to single asperity scratch tests, to characterize the contact mechanics, friction and fatique of semi-crystalline i-PP. In principle four different sliding velocities are applied, increasing from 0.1 $\mu$m/s to 100 $\mu$m/s. For amorphous polymers typical normal applied loads are in the range of 300 mN to 500 mN, however preliminary experiments have to verify if these machine settings are suitable for semi-crystalline materials. Subsequent topolocial analysis of the residual indents and scratches provide important insights on the elastic response of the material and therewith the overall deformation process.

# 3 Project planning

January: Setting up tape drawing line and the first attempts in using the line. Preparing and tensile testing of isotropic samples (pure $\alpha$-, pure $\beta$- and pure meso-phase i-PP) to set a reference state for the three important phases. Combined optical microscopy, DSC heating runs and X-ray analysis to check the structure and phase content of the samples. If time allows: preliminary indentation and/or scratch tests to estimate suitable parameters such as applied normal force and sliding velocity.

February: Tape preparation ($\lambda$ = 1,2,4,6 (8 and 10). Subsequent check of the phase content and orientation spectrum of the drawn tapes. Tensile tests for $\lambda$ = 1,2,4 and 6 under various loading angles between $\theta = 0°$ and $\theta = 90°$.

March: Continuation of tensile tests for $\lambda$ = 1,2,4 and 6 under various loading angles between $\theta = 0°$ and $\theta = 90°$. Start indentation and scratch tests for angles $\theta = 0°$, $\theta = 45°$ and $\theta = 90°$, on the tapes with draw ratio $\lambda$ = 1,4,6, including post-processing with the Sensofar.

April: Tensile, indentation and scratch tests for other load angles and draw ratios mentioned before. This month will also be used as a buffer for the experiments performed in the previous months.

May: Influence of cooling conditions (structural development) on mechanical and tribological properties (tensile and scratch tests for a few draw ratios and load angles). Next to that, similar tensile as scratch experiments as before are performed, but now for a $\beta$-nucleated grade of i-PP (again for only a few draw ratios and loading angles).

June: Switching to filled i-PP systems, starting with titaniumdioxyde filler, similar tensile, indentation and scratch tests are performed for isotropic material.

July: Similar tensile/compression and scratch tests on filled systems of drawn tapes and start writing thesis.

August: Continuation of the filled systems on drawn tapes and writing thesis.

September: Finishing thesis and defence before 20th of September.

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