



Fast cooling of (non)-nucleated virgin and recycled poly(propylenes): Effect of processing conditions on structural and mechanical properties



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ABSTRACT

In this study, the effect of processing parameters, *i.e.*, the cooling rate and pressure, on the structure–property relationships for nucleated and non-nucleated *i*-PP from virgin and recycled sources was investigated. Special attention was given to the brittle-to-ductile transition of nucleated *i*-PP from plastic packaging waste. Differential fast scanning calorimetry and dilatometry were used to mimic industrial process conditions. From the calorimetric experiments, it was observed that under ambient pressure the mesomorphic phase was formed upon fast cooling, which was confirmed by WAXD analysis. The dilatometry results showed that by applying pressure also γ -phase crystals are formed. Nucleated samples showed an increased tendency for the γ -phase formation and a decreased tendency for mesomorphic phase formation. Up to now, recycled *i*-PP showed a brittle behavior, but this study showed that by applying a sufficiently high cooling rate, the yield stress can be reduced and a stabilization of the deformation can be obtained leading to a ductile behavior for recycled *i*-PP.

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1. Introduction

Plastics are used in a wide variety of applications, including packaging products. After a short service life, the product is mostly disposed. Recycling of these plastics has gained a lot of attention in recent years. Mechanical recycling of waste plastics is considered the preferred option from the environmental point of view [1]. Commingled plastics from *e.g.* household waste are sorted with near-infrared-technology and are further cleaned. Despite improved sorting efficiencies, some polymeric contaminations are always present in post-consumer waste, which reduce the mechanical properties significantly. It was shown that a sorted polymer waste stream typically contains 5–10% contamination of another polymer [2].

One of the sorted polymer waste streams is poly(propylene) (PP). PP is a versatile polymer which is suitable for many applications because of its relatively high stiffness, tensile and impact strength. Isotactic PP (*i*-PP) is the most common form of PP. It is known that *i*-PP degrades by chain scission when reprocessing the material [3]. For sorted *i*-PP waste, contamination in

combination with degradation during lifetime leads to undesired brittle failure. Mechanical recycling of plastic waste can only be successful if the material can be used in existing processing techniques and at sufficient scale.

i-PP is a polymer which can partially crystallize upon cooling from the melt. It can crystallize in different crystal structures, depending on the processing conditions. All crystal structures have a three-fold helical conformation of the polymer chains, but differ in the packing density. The 3_1 -helix has three monomers per turn and can be either right or left handed. A further distinction can be made based on the orientation of the methyl group with respect to the chain axis, which can be either up or down. The α -crystal phase is the thermodynamically most stable phase. The α -crystal phase has a monoclinic unit cell ($a=6.65$ Å, $b=20.96$ Å, $c=6.5$ Å). A peculiar feature of the α -crystal phase is lamellar branching, also known as cross-hatching: one type of lamellae (parent lamellae) forms a nucleation site for daughter lamellae that grow under a specific angle. For *i*-PP, this angle between parent and daughter lamellae is 80° [4,5]. Despite the presence of contaminations, *i*-PP from waste materials normally crystallizes in the α -crystal phase, which was investigated by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) [6].

The β -crystal phase in *i*-PP is only formed when specific nucleating agents, such as γ -quinacridone, are added to the

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polymer or under special crystallization conditions, e.g. crystallization under temperature gradients or from an oriented melt [7,8]. It was first observed by Padden and Keith in 1959 [9]. The β -crystal phase has a trigonal unit cell ($a=b=11.01 \text{ \AA}$ and $c=6.5 \text{ \AA}$) containing three isochiral helices. The lamellae in the β -crystal phase are not cross-hatched but parallel, thereby providing greater chain mobility within the lamellae under load [10]. The β -crystal phase is a metastable phase and recrystallizes to the α -crystal phase when heated above $145 \text{ }^\circ\text{C}$, a process which is known as the β - α transformation [11–13].

The γ -crystal phase is formed when crystallization takes place under high pressures and moderate cooling rates. This crystal phase is typically formed more easily in lower molecular weight polymers [14–16] or in the presence of an α -olefin comonomer [17]. The γ -crystal phase has an orthorhombic unit cell ($a=8.54 \text{ \AA}$, $b=9.93 \text{ \AA}$, $c=42.4 \text{ \AA}$) containing layers of non-parallel organized chain segments. Lamellae of the γ -crystal phase generally nucleate on the α -lamellae by an epitaxial mechanism that is comparable with the cross-hatched structure within the α -crystal phase, but under an angle of 40° [1,5].

The mesomorphic phase is formed when *i*-PP is quenched to 0 – $40 \text{ }^\circ\text{C}$ from the melt at ambient or high pressures [18–20]. It consists of parallel chains with a high degree of order in the longitudinal direction (the helical structure is preserved), but no crystallographic register in the lateral packing [21–26]. The mesomorphic phase can be considered as an intermediate, frozen-in state of order in the crystallization process. Upon fast cooling the folding of polymer chains into lamellae is hindered. Its form is metastable and undergoes a transformation to the α -crystal phase when the polymer is heated (typically between 40 and $80 \text{ }^\circ\text{C}$).

The mechanical properties of semi-crystalline polymers are strongly dependent of their crystallinity, lamellar thickness, and type of crystal structure, which depend on the processing conditions [27]. A higher cooling rate during crystallization leads to a lower yield stress [28] and a higher strain-at-break. Lowering the yield stress of recycled *i*-PP could result in ductile instead of brittle behavior. Earlier results showed that, for the same crystallinity, the nodular mesomorphic phase was ductile with elongations-at-break up to 450% , while brittle fracture was observed for a spherulitic α -crystal phase in the same *i*-PP [29]. Another study showed that for *i*-PP's with similar crystallinities the α -crystal phase was ductile with an elongation-at-break of 300% , an elongation-at-break of over 600% for the mesomorphic phase and an elongation-at-break of over 1000% for the γ -crystal phase, which was explained in terms of a phase transition from the γ -crystal phase to the mesomorphic phase during deformation [30]. A study on the effect of stereoregularity of *i*-PP on the crystal phase formation showed that the mechanical properties of *i*-PP can be tuned using metallocene catalysts [31]. The mesomorphic phase formation was favored for stereodeficient *i*-PP. The cooling conditions were found to predetermine the morphology and shape of crystals, lamellae or nodules, while annealing offers additional options to modify the mechanical properties through the lamellar thickness, perfection, and crystallinity for slowly cooled samples. Annealing of quenched samples permits a precise adjustment of crystallinity and size of the nodular crystals without affecting the external habit of the crystals. Here, the modulus and tensile strength can be tailored while maintaining the ductility of the mesomorphic phase [32,33].

These mechanical properties are often measured in tensile testing. The yield stress σ_y , i.e., the first maximum in the stress-strain curve, indicates the transition between elastic deformation at small deformations, described by Hooke's law, and plastic deformation. Plastic deformation usually starts by the formation of

a neck, initiated by lamellar slip due to local stress concentration. After the formation of a stable neck, the neck propagates throughout the sample. The draw ratio of the material in the stable neck is better known as the 'natural draw ratio' or λ_n . After this draw ratio, a material can show strain hardening. This process is mainly governed by the increase in stress due to deformation applied on the entanglements in the amorphous phase. The slope of this regime is called the strain hardening modulus G_R . A higher entanglement density results in an increase in strain hardening modulus. The relationship between yield stress σ_y , estimated draw ratio in the neck λ_n , and strain hardening modulus G_R is well known for samples measured in compression [34,35]. In tensile deformation, the quantitative determination of strain hardening modulus is difficult, since geometrical factors have a large influence on the observed behavior after yielding of the material. However, qualitatively the following relation is valid.

$$\lambda_n \in \left(\frac{\sigma_y}{G_R} \right)$$

This relation indicates that, for similar yield stresses, an increase in natural draw ratio must be accompanied by a decrease in strain hardening modulus. Critical in the stress-strain behavior of polymers in tensile testing is the formation of a stable neck. When $\sigma_y/G_R < 3$, uniform (homogeneous) deformation will be observed. If $\sigma_y/G_R > 3$, necking is observed, and deformation can either be stable or unstable. When λ_n increases, the stress concentrates on a relatively small cross-sectional area and the smallest defect can cause failure. At high λ_n the material becomes brittle [36,37]. Furthermore, the neck stability is influenced by the presence of contaminants (failure by initiation).

High pressures and cooling rates favor the formation of either crystals with a small lamellar thickness, the γ -crystal phase or the mesomorphic phase for *i*-PP. All contribute to a lower yield stress. On laboratory scale, the formation of these phases can be investigated by dilatometry and differential fast scanning calorimetry [20,28,38,39]. This type of DSC instrument allows the use of extremely high heating and cooling rates and is ideal for the investigation of metastable structures. Samples are placed directly on a micro-electro-mechanical systems (MEMS)-based sensor using a microscope and not in crucibles as in conventional DSC. Heating and cooling rates of $1000 \text{ }^\circ\text{C s}^{-1}$ can easily be obtained. It was demonstrated that a non-isothermal crystallization model can be used to accurately describe the multi-phase crystalline evolution for the α -, β -, γ - and mesomorphic phase [20]. The relative amounts of each crystal phase were calculated from X-ray analysis [40]. With increasing cooling rate, the *i*-PP crystal phase changed from the α - to the mesomorphic phase. Differential fast scanning calorimetry studies showed that this transition occurs at cooling rates between 200 – $500 \text{ }^\circ\text{C s}^{-1}$ [41]. The transition depends on the material characteristics such as molecular weight and molecular weight distribution, but an exact correlation has not yet been found [42].

When a polymer melt gets into contact with the cold wall of the mold in compression molding or injection molding, the material in close contact to the wall cools very rapidly, which can be investigated by using non-isothermal crystallization experiments in differential fast scanning calorimetry [43]. The material cools down more slowly towards the center of the polymer product. Here, a gradient in cooling rate is observed, which can be well investigated with isothermal crystallization experiments in differential fast scanning calorimetry. To obtain a full picture of the cooling conditions in compression molding or injection molding, both types of experiments have to be considered. From non-isothermal crystallization results, continuous cooling curve

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