



Measuring the orientation of chains in polypropylene welds by infrared microscopy: A tool to understand the impact of thermo-mechanical treatment and processing



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ABSTRACT

The superstructures developed in the welds between injection molded plates made from α -nucleated and non-nucleated isotactic polypropylene (iPP) were analyzed by infrared (IR) microscopy, polarized light microscopy (PLM) and differential scanning calorimetry (DSC). Layers of distinct structures and size formed during welding in the welds were identified by PLM. Deformation of spherulites occurred in the weld seams due to the sheared melt flow. The orientation of the polymer chains in the welds, which is the result of melting and recrystallization, was quantified by IR microscopy for the first time: In the injection molded plates the chains were oriented along machine direction (MD), whereas this pattern changed to normal direction (ND) at the weld seams. Two positions at the welds were inspected to study the orientation of the chains: In one of these the PLM image depicts two well defined weld seams, while at the other, the weld seams were absent. DSC analysis of microtomed sections revealed the presence of both iPP polymorphs in the injection molded plates, whereas in the weld seam and weld core the α - and β -phase, respectively, were found. The degree of crystallinity (X_c) of the welds of iPP calculated using DSC and IR microscopy showed a homogeneous profile across the welds.

The antioxidants (AOs) and the nucleating agent were profiled across the weld using IR-microscopy. A significant consumption of AOs during welding could be shown, and, using the principle of IR-dichroism, thermo-oxidative degradation of iPP chains was observed, even in the presence of AOs. The nucleating agent was homogeneously distributed across the weld.

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1. Introduction

IR spectroscopy is one of the most important techniques for the characterization of polymers as it delivers information about the composition, structure and conformation of macromolecules. The macroscopic properties of the polymer depend on chain orientation, particularly in the case of stretched specimen and, therefore, an explanation for the mechanical properties of a final product or semi-finished good made from polymers has to include the orientation of the polymer chains as an important morphological parameter. A variety of analytical techniques such as X-ray

diffraction (XRD), PLM [1], sonic modulus [2] and IR spectroscopy [3] have been used previously to study the extent of orientation in polymer specimen. However, these techniques fail to provide information about the orientation with spatial resolution. XRD and IR spectroscopy can be modified in terms of spatial resolution as XRD imaging and IR microscopy respectively. Determining the orientation function from the diffraction planes of crystalline domains has been well developed in XRD imaging. However, in the case of semicrystalline polymers, XRD fails to retrieve the extent of orientation in the amorphous phase. Since IR microscopy is based on energy absorption by molecular vibrations, it delivers distinct information for both crystalline and amorphous regions, which makes it unique for this purpose.

Quantitative analysis of polymer chain orientation by IR microscopy is possible using the principle of dichroism (D), where D is

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defined as the ratio of the absorbance of a vibration when the incident radiation is polarized parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the transition moment vector of the vibration (Eq. (1)).

$$D = \frac{A_{\parallel}}{A_{\perp}} \quad (1)$$

Using the concept of D [4,5] in IR spectroscopy, the orientation of polymer chains in uniaxially and biaxially stretched polymer specimens has been determined previously [6–8]. Temperature and the rate of stretching are the main parameters which affect the orientation of chains in both crystalline and amorphous regions. Kissin [9] reported the change in the orientation of iPP chains in crystalline and amorphous regions during stretching at different temperatures and rates of elongation using IR spectroscopy.

In order to determine the chain orientation using IR spectroscopy, the axes have to be predefined in such a way that the MD is the direction of orientation. Rode et Al. [10] extended Fraser's model with the aim to calculate the orientation of polymer chains along the three dimensions of a sample by IR microscopy from two perpendicularly microtomed sections. According to this model the Fraser's orientation function (f) can be calculated as in Eq. (2).

$$f_z = \frac{3 \cdot \frac{A_z}{A_x + A_y + A_z} - 1}{2} \cdot \frac{D_0 + 2}{D_0 - 1} \quad (2)$$

f_z is the orientation function along the z axis for independent absorptions A_x , A_y and A_z measured along the x , y and z axis respectively, and D_0 is the correction factor for the angle between the vector of the transition moment and the polymer chain axis (Eq. (3)),

$$D_0 = 2 \cdot \cot^2 \alpha_T \quad (3)$$

where α_T is the angle between the transition moment vector and the chain axis.

The orientation of polymer chains using IR dichroism has been investigated for the case of injection molded, extruded and stretched polymeric materials [11–15]. Welding is an interesting case of polymer processing which rapidly gains importance to prepare complex structures from semi-finished goods. In welding a complex interplay between high heating and cooling rates as well as mechanical forces exists, which leads to a local extinction of the original morphology in the welding partners, and the rise to a new morphological structure in the weld. Hot plate welding is one of the widely used techniques for joining plastics in which the partners to be joined are brought into contact with a hot metallic plate until they start to melt. The molten surfaces are then compressed, and held under a constant pressure until the weld solidifies.

DSC and PLM have been widely used to monitor the crystallization kinetics and morphological structures in the weld [16–22]. In particular, DSC can be used to monitor the X_c as well as the different crystal structures formed during processing. Spatially resolved information regarding the X_c and polymorphism of a polymer sample can be obtained by mechanical preparation of samples, but it is limited to $\sim 300 \mu\text{m}$.

PLM is a known technique to differentiate the anisotropies in the superstructure developed in a weld. However, quantitative analysis of orientation using PLM fails to separate the orientations of crystalline and amorphous phase. The influence of welding parameters such as plate temperature, heating time and joining pressure on the strength of the weld seam has been reported [23] and the orientation of polymer chains highly depends on these parameters. A quantitative analysis of chain orientation may help to assess the quality of welds by relating the resultant structure in the weld seam

Table 1
Parameters used for injection molding the plates.

Parameter	PP-H1	PP-H2
Injection time (s)	1.64	1.86
Hold pressure time (s)	25	25
Cooling time (s)	25	25
Melt temperature ($^{\circ}\text{C}$)	220	200

with the weld parameters and the resulting properties. IR microscopy also holds a potential to account the distribution of additives such as antioxidants, light stabilizers, processing stabilizers, which are added to the polymer to prevent oxidation.

This article discusses about the quantitative determination of the distribution of AOs as well as the chain orientation in the welds of two grades of PP which differ in their additive composition and nucleation using IR microscopy.

2. Experimental

2.1. Materials

Plates, made from two grades (non-nucleated and α -nucleated by sodium 2,2'-methylene-bis-(4,6-di-tert-butylphenyl)phosphate) (NA11) of iPP homo polymer, PP-H1 and PP-H2, were joined by hot plate welding. The plates were made by injection molding and, thus, pre-orientation of the polymer chains along the extrusion direction was induced. The weight average molar mass of PP-H1 and PP-H2 were 8.86×10^5 and 1.73×10^6 g/mol, respectively, with reference to narrowly distributed polystyrene standards. Extrusion direction, normal direction and transverse direction are abbreviated as MD, ND and TD, respectively. The values of different parameters used or injection molding and welding are tabulated in Table 1 and Table 2.

2.2. IR-microscopy

Cuts of $50 \mu\text{m}$ thickness were prepared perpendicular (MD-TD plane) and parallel (MD-ND plane) to the weld (Fig. 1) using a Reichert Jung rotary microtome.

An IR microscope (Continuum, Thermo Nicolet (Madison, WI)) equipped with an MCT-A detector was used for analysis. It was coupled to a Nicolet-Nexus 670 FT-IR spectrometer as beam source. Hundred scans were accumulated per spectrum in transmission mode with an aperture of $50 \times 50 \mu\text{m}^2$. Consequently, the f determined at each point represents the chain orientation averaged over an area similar to that of the aperture opening. Line scans were performed with a step width of 25 and $50 \mu\text{m}$ in PP-H1 and PP-H2, respectively. A micro-vice sample holder was used to fix the microtome cuts. A ZnSe wire-grid polarizer was used for achieving linear polarized radiation.

2.3. Polarized light microscopy

A microscope (BX50 F, Olympus) equipped with UPlan objectives, a rotatable polarizer (U-POT), analyzer (U-AN360) and a

Table 2
Parameters used for welding.

Parameter	PP-H1	PP-H2
Hot plate temperature ($^{\circ}\text{C}$)	220	220
Hold pressure time (s)	190	190
Cooling time (s)	180	180

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