The effect of the consolidation process on structural parameters and micro-mechanical properties of PE-UHMW

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Aim

Two consolidation techniques are mainly applied for PE-UHMW: compression moulding and ram extrusion [1]. In this study the influence of these consolidation processes on structural parameters and micro-mechanical properties of non-cross-linked, orthopaedic grade PE-UHMW is investigated.

Materials

Ram extruded rods and compression moulded sheets of powder grade GUR 1050 (Orthoplastics PUR - 1050 Medical Grade UHMWPE, Orthoplastics Ltd.) were analysed (Figure 1, coloured lines). No antioxidants or processing additives are added to the samples.

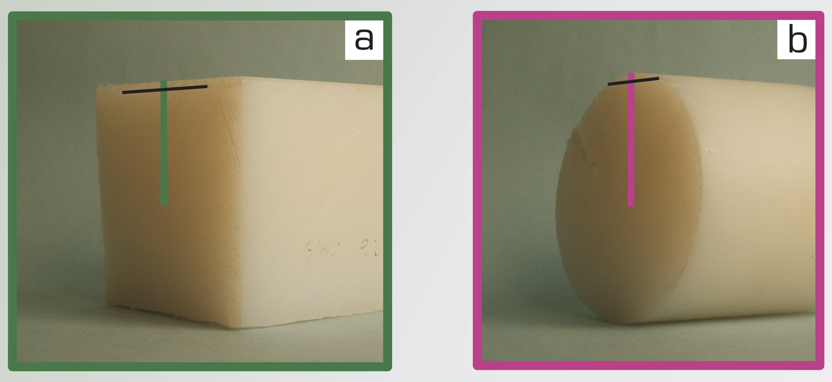

Figure 1: Investigated samples compression moulded sheet (a) - thickness: 50 mm and ram extruded rod (b) - diameter: 60 mm

Methods

Fourier Transformed Infrared Spectroscopy (FTIR):
Oxidative degradation products were analysed by means of locally resolved FTIR (Tensor 27, Bruker Optics, Germany). The spectra were taken along a line perpendicular to the surface (Figure 1, coloured lines), in transmission mode and normalized to a peak height of 0,05 a.u. at 2020 cm^{-1} [2].

Differential Scanning Calorimetry (DSC):
Microtomed slices (thickness: app. 200 µm) were taken across the surface (cut parallel to the black lines in Figure 1). Two samples per position (sample mass app. 1,5 mg) were heated, cooled and re-heated at rates of 10 K/min (DSC Q 2000, TA-Instruments, Delaware, USA). The degree of crystallinity was calculated according to (H_f = 291 J/g [1]):

$$\text{Degree of crystallinity (\%)} \quad \frac{H_{endotherm}}{H_f} * 100$$

The lamellar thickness distribution (LTD) was calculated from the melting endotherm according to [3-5]:

$$\frac{1}{M} * \frac{dM}{dL} \quad \frac{\text{Heat Flow}}{\text{Heat Rate}} * \frac{T_m^0 \quad T_m{}^2 * \quad c}{2 * \quad e * T_m^0}$$

Instrumented Nanoindentation:
The microhardness H_{IT} and indentation modulus E_{IT} were mapped (TriboIndenter®, Hysterion, Inc., Minneapolis, USA) along the cross section of the consolidated material perpendicular to the surface (Figure 1, along coloured lines). The measurements were carried out at a rate of 0,5 mN/s up to a maximum load of 10 mN, than a holding period for 30 s followed by unloading with 1 mN/s. The characteristic values were calculated according to [6] with =0,43 for PE-UHMW [7]:

$$H_{IT} \quad \frac{P}{A} \quad \frac{P}{24{,}5 \quad h_c^2} \qquad \frac{1}{E_r} \quad \frac{1 \quad {}^2}{E_{IT}} \quad \frac{1 \quad {}_i^2}{E_i} \qquad E_r \quad \frac{\sqrt{\quad} S}{2 \quad \sqrt{A}}$$

Results and Discussion

In FTIR spectra of the surface layer of ram extruded PE-UHMW a peak at 1718 cm^{-1} is observed (Figure 2b). On the contrary in the spectra of compression moulded PE-UHMW no peak is analysed at 1718 cm^{-1} (Figure 2a). The peak at 1718 cm^{-1}, assigned to the ketone group [2], allows to conclude that the ram extrusion process leads to oxidative degradation in the surface layer of app. 0,85 mm thickness. Whereas compression moulded material shows no degradation induced by the consolidation process.

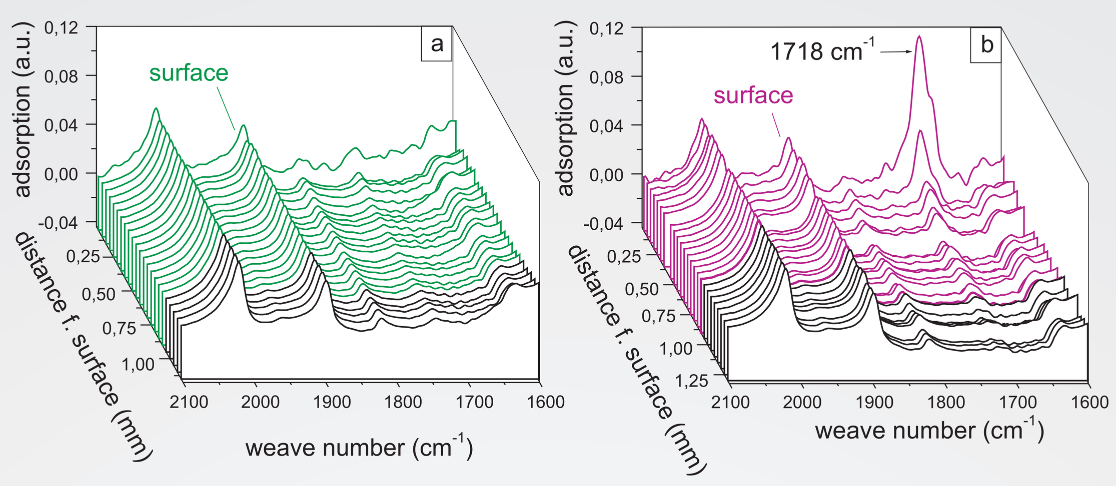

Figure 2: Locally resolved FTIR - compression moulded sheet (a) and ram extruded rod (b)

DSC experiments show that in these oxidised surface layers of the ram extruded material, the degree of crystallinity is enhanced compared with the central layers and the compression moulded material. No difference in the degree of crystallinity is measureable for non-oxidised ram extruded material and compression moulded material. This behaviour is evident in both heating runs (Table 1).

Table 1: Degree of crystallinity; surface layer: app. 0 mm - 0,8 mm below the surface, central layer: app. 10 mm - 30 mm below the surface; values are taken as the mean of the DSC results of these areas

material	sample area	degree of crystallinity (%)	
		1st heating run	2nd heating run
ram extruded rod	surface layer	59,7 ± 1,9	60,1 ± 1,8
	centre layer	53,3 ± 0,9	51,6 ± 1,0
compression moulded sheet	surface layer	53,8 ± 0,7	51,2 ± 0,6
	centre layer	52,9 ± 0,9	51,5 ± 1,2

The LTD calculated from second heating runs (Figure 3b and 4b) show a more narrow distribution than for the first heating run. This can be attributed to the controlled non-isothermal crystallisation during the cooling run of the DSC experiment.
No differences in the LTD calculated from the surface and from the centre layers were found in the compression moulded sample (Figure 4a and b).

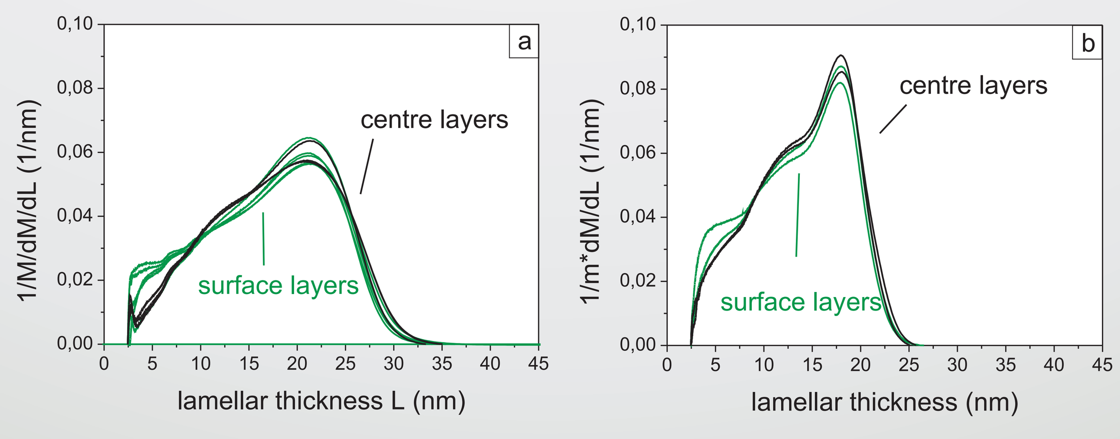

Figure 3: LTD - compression moulded sheet: 1st heating run (a) and 2nd heating run (b)

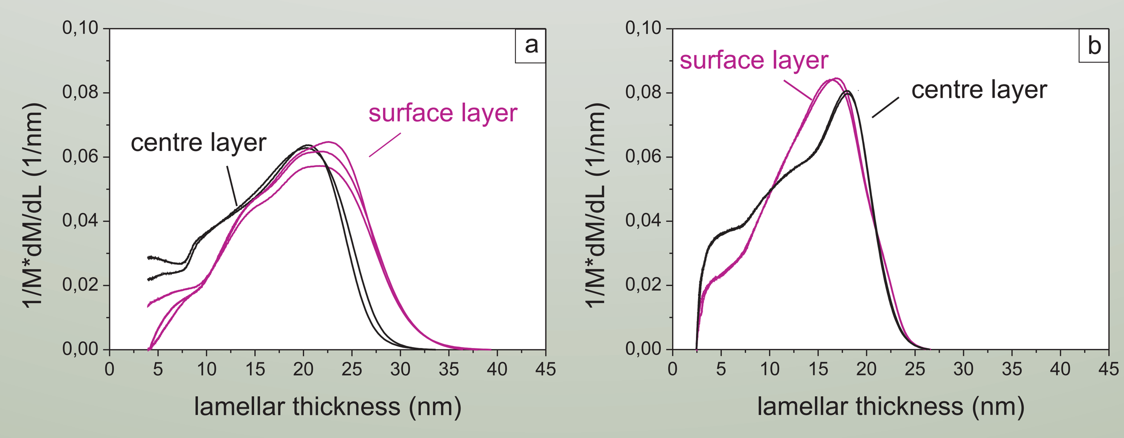

Figure 4: LTD - ram extruded rod: 1st heating run (a) and 2nd heating run (b)

In case of the ram extruded rod, the LTD of the surface layer is shifted to higher lamellar thickness in the first heating run whereas the corresponding curve is shifted to lower lamellar thickness in the second heating run when compared to the centre layers (Figure 4 a and b).
The crystallisation of samples from the oxidised surface layer of the ram extruded material starts at relatively lower temperatures compared with non-oxidised PE-UHMW (Figure 5). Crystallisation at lower temperatures corresponds to a higher degree of supercooling, which results in the formation of smaller lamellae. Hence, the LTD of the surface layer of the ram extruded rod is shifted to lower values in the second DSC heating run.

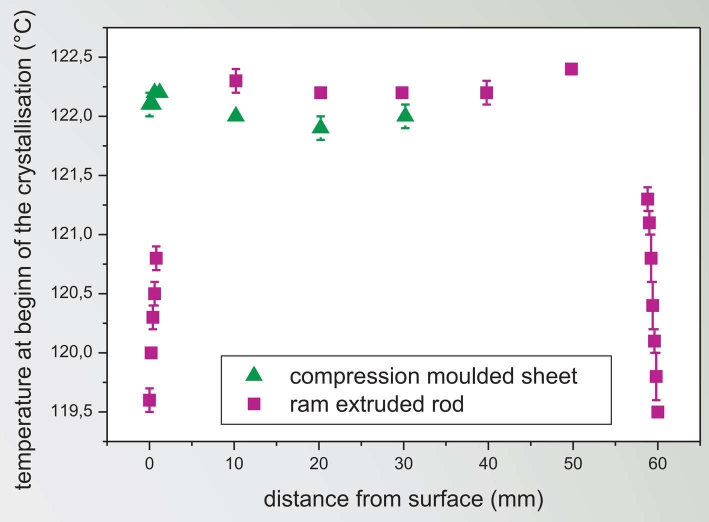

Figure 5: Onset temperatures of the crystallisation - DSC results of all conditions

Nanoindentation experiments show higher micro-hardness H_{IT} and indentation modulus E_{IT} in the surface layer (app. 0,9 mm) of the ram extruded material (Figure 6a and b). No such variations in the depth profile of H_{IT} and E_{IT} were observed in the compression moulded material. The structural reasons for the variation of H_{IT} and E_{IT} of non-oxidised ram extruded and compression moulded material have yet to be explored.

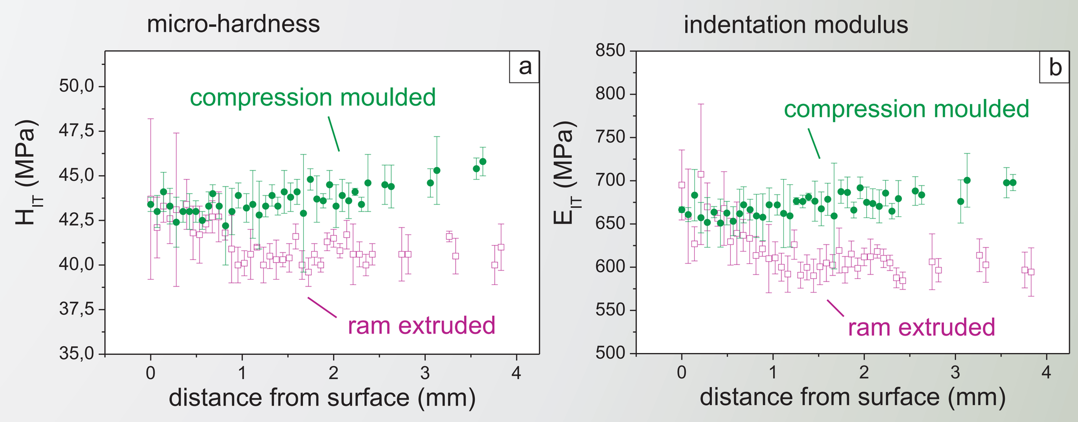

Figure 6: Locally resolved instrumented nanoindentation - microhardness (a) and indentation modulus (b)

Conclusions

- Lamellar thickness distribution (LTD) gives better insight to the manufacturing and consolidation process of PE-UHMW than characterisitic values (e.g. degree of crystallinity, melting point, ...) alone do. Hence it is a valuable tool especially for the investigation of a complex material like PE-UHMW.
- The consolidation process leads to different oxidative degradation states within the same material: In case of ram extruded material the surface layer tends to degrade. This degradation during the manufacturing process facilitates anisotropy regarding the degree of crystallinity.
- A different degree of supercooling for oxidised and non-oxidised PE-UHMW is observed in non-isothermal crystallisation. This crystallisation behaviour is reflected in the LTD calculated from the melting endotherms of the second heating run.
- It is shown, that the degree of crystallinity is enhanced in oxidative degraded areas. This can be correlated to higher values of micro-hardness and indentation modulus.

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