Macromol. Symp. **2010**, 294-I, 91–101 DOI: 10.1002/masy.201050808

Study on Flow Induced Nano Structures in iPP with Different Molecular Weight and Resulting Strength Behavior

Achim Frick,[1] Claudia Stern,[2] Goerg Michler,[3] Sven Henning,[3] Martin Ruff[1]*

Summary: Polypropylene samples in a wide molecular weight range between approx. 100 kg/mol to 1 600 kg/mol were processed by injection molding to thin walled micro specimens with respect to study shear induced crystallization phenomena under high shear rate and subsequently possible self reinforcement effects. The specimens nano structures were investigated and related deformation behavior under tensile studied. Novel morphologies have been detect and their micromechanical mechanism interpret and summarized.

Keywords: micro injection molding; micro mechanics; nano structure; poly(propylene); self reinforcement; shear induced crystallization

Introduction

Polypropylene PP is considered to belong to the commodity plastic materials for injection molding due to its relative low mechanical performance. On the other hand the material its price is comparatively cheap of about 1 Eur/kg. This is a huge economic benefit and distinguishes PP why it becomes selected for several applications. Regarding e.g. Polyetheretherketone PEEK which is a high end polymer it performs much better than PP (Table 1), but its price is also considerable higher with 100 Eur/kg. These facts emphasize to work on possibilities to reach the theoretical strength data of PP [2–4] in molded parts under industrial like processing conditions. This would yield a capability in stiffness of about 38 times and in strength of more than 400 times (Table 1).

In the present investigation the influence of shear rate during melt processing of polypropylene PP on the development of material nanostructure was systematically approached by correlating present sample morphology and deformation behavior with resulting mechanical strength data.

Investigated Material

The investigations were performed on non nucleated isotactic polypropylene homopolymer iPP powders in a wide range of molecular weight (Table 2). The molecular weights of the samples analyzed differed about 1:16, which results significant differences in their melt viscosity and subsequently in melt shear rate when processing the different samples under same molding conditions.

In Table 2 Mw denotes the molecular weight of investigated samples and PI the polydispersity or molecular weight distribution. Mw and PI data were measured by SEC method (Waters Alliance GPCV 2000 with 3 TSK GMHXL-HT columns) except the indicted ones, where Mw data are based on rheological measurements and PI was not evaluated. NE is number of entanglements per molecular chain and is calculated by means of estimated entanglement molecular weight ME, which was found to be

---

[1] Institute of Polymer Science and Processing (iPSP), Aalen University, Beethovenstr. 1, 73430 Aalen, Germany
E-mail: achim.frick@htw-aalen.de

[2] ElringKlinger Kunststofftechnik GmbH, Bietigheim-Bissingen, Germany

[3] Martin-Luther-University, Halle-Wittenberg, Germany

Table 1.
Properties of plastics[1]

Polymer Properties	PP	PEEK	*PP* *theoretical*
Young modulus [MPa]	1 300	4 000	*50 000*
Strength [MPa]	38	104	*16 000*

6730 g/mol for the PP according equation 1.

$$ME = \frac{\rho \cdot R \cdot T}{G'(\omega)_{\tan\delta\,\min}} \tag{1}$$

In equation 1 ρ denotes the sample density, R the gas constant, T the temperature and $G'(\omega)$ the storage modulus of the material measured by means of oscillatory rheometer test when its loss tangent $\tan\delta$ becomes minimum. The reference temperature was considered to be 200 °C.

The zero viscosity η_0 of the samples varies in a wide range which is depending on MW and yields to have characteristic relaxation times t_0 for the PP macromolecules different in length a split second till almost 20 s. The characteristic relaxation time t_o was evaluated from rheological measurements using equation 2.

$$t_0 = \eta_0 \cdot J_e^0 = \eta_0 \cdot \lim_{\omega \to 0} \frac{G'}{G''^2} \tag{2}$$

Melt Processing

For melt processing the iPP samples a commercial injection molding machine type Arburg 220 S Allrounder with special plasticizing unit with a 12 mm diameter flat thread screw was used. The maximum injection pressure the machine allows is about 2 000 bar. Neat iPP samples were shaped into dumbbell specimens by micro injection molding using a 2 cavity mold to receive the specimens for morphological characterization and mechanical tests.

The chosen type of the specimen was 1A according DIN ISO 527 but 8 times miniaturized in all its dimensions. This micro specimen shows a width B = 1,25 mm in the parallel zone and a thickness H = 0,5 mm at an overall length L = 25 mm. mm. It was gated by a film gate.

For processing the specimens the melt temperature was settled 210 °C respectively 250 °C and the mold temperature 60 °C. The injection speed was taken 10 mm/s to be constant.

It is obvious the shear rate $\dot{\gamma}$ in the micro specimen during filling becomes huge, due to its very thin wall thickness H at the given volume rate. Considering a Newtonian flow behavior according Hagen-Poiseuille-law the shear rate is calculate (equation 3).

$$\dot{\gamma} = \frac{6 \cdot \dot{V}}{H^2 \cdot B} \tag{3}$$

According equation 3 the shear rate becomes 21 715 1/s. This number fits in its order of magnitude with the data based on Moldflow Plastics Inside (MPI) software simulation calculation, which were performed, and verify those. The simulation results predict shear rates during filling of the micro specimen up to 75 000 1/s, which

Table 2.
Properties of investigated samples [5,6]

Sample	Mw	PI = Mw/Mn	NE = Mw/ME	η_o	t_o
	[kg/mol]	[–]	[–]	[Pa s]	[s]
PP 1600	1 600*	na	238	156 100	19,3
PP 1120	1 120	6,4	166	76 700	6,6
PP 833	833	6,6	124	40 040	4,5
PP 462	462	7,2	69	6 250	1,7
PP 361	361	6,8	54	2 640	1,5
PP 320	320	6,8	48	2 260	1,2
PP 244	244	7,3	36	1 090	0,4
PP 153	153	7,3	23	290	0,3
PP 101	101*	na	15	90	0.3

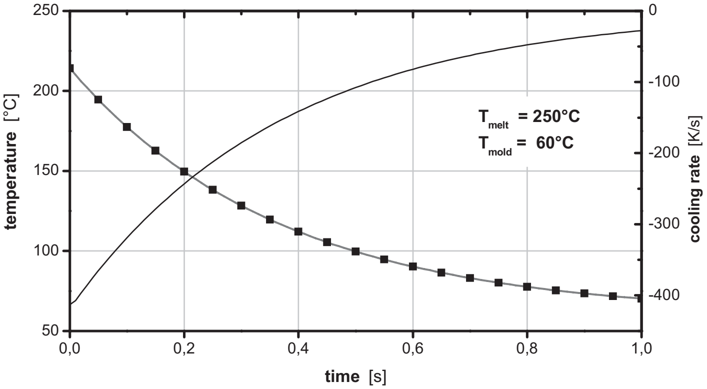


Figure 1.
Temperature profile in the core of the molded micro specimen depending on cooling time.

is about 750 times higher as compared to the shear rate when molding a standard 1A specimen with a 4 mm wall thickness.

The cooling of the processed iPP-melt during solidification proceeds very rapidly due to thin wall thickness of the micro specimen (equation 4) [7].

$$t_{cooling} = \frac{3}{2} \cdot H^2 = 0,375s \tag{4}$$

The solidification process has to be considered highly non isothermal, where the average temperature during solidification can be calculated approximately according equation 5 [8], where a means the thermal conductivity of the sample, which is about 0,06 mm^2/s for PP material. Figure 1 shows the cooling curve for the molded specimens.

$$\overline{T} = T_{mold} + \frac{8}{\pi^2} \cdot (T_{melt} - T_{mold}) \cdot e^{-a \cdot \frac{\pi^2}{H^2} \cdot t} \tag{5}$$

The theoretical temperature profile and its derivative which is shown in Figure 1 give an idea on the rapid cooling condition with a cooling rate more than 100 K/s. It cannot be considered to be exact because an additional heat input, caused by dissipation effects in the molten material processed under high shear rate, has taken into account, which will increase the melt temperature certain amount. Equation 6 calculates heating rate based on viscous shear dissipation [7].

$$\frac{\Delta T}{\Delta t} = \frac{1}{\rho \cdot c} \cdot \eta \cdot \dot{\gamma}^2 \tag{6}$$

Due to high shear rate and rapid cooling, which both can be easily performed, the micro injection process is capable to manufacture specimens under shear induced crystallization. When considering the crystallization temperature of iPP of about 100 °C the molded specimen will be already solidified after 0,5 s completely (Figure 1). This approach fits quite well to the calculated result using equation 4. With respect to the characteristic relaxation times of the investigated iPP samples varying in a wide range between 0,3 s and almost 20 s (Table 1) it is possible to manufacture solid state specimens from iPP samples with mainly isotropic till highly oriented morphology. It is expect the sample with low molecular weight and therefore short characteristic molecular relaxation time will create a spherulitical crystalline structure during solidification from melt whereas the high molecular weight sample with long relaxation time will show highly shear induced crystallinity.

Experimental Part

Rheology

Rheometer measurements provide melt viscosity and visco elastic data of analyzed polymeric sample. The rheological investigations were performed using a Bohlin Instruments Gemini 200 type plate-plate rheometer.

The melt viscosity curves were tested in rotational mode at the temperature of 200 °C.

The shear modulus of the molten polymer samples and its frequency depending behavior was obtained by oscillatory mode test. A sinusoidal strain amplitude of 1% was applied at a melt temperature 200 °C and the angular frequency was subsequently varied from 0,01 Hz to 100 Hz.

The measuring cell was purged in all cases with nitrogen to avoid any sample degradation.

Differential Scanning Calorimetry

Calorimetric analysis (DSC) allows measuring the melting and crystallization of investigated sample and its crystalline fraction. The DSC investigations were carried out using a Mettler-Toledo DSC type 821^e calorimeter in the temperature range of 30 °C till 280 °C and the heating rate was settled to 20 K/min. The measurements were performed under nitrogen atmosphere, where the sample mass was chosen for about 5 mg and the samples placed into 40 μl crucible.

Tensile Test

For mechanical characterization tensile tests were performed in order to estimate on the stress-strain curve, the stiffness and ultimate strength of the different samples. Two different testing devices were used.

Uniaxial tensile tests were performed using a Gabo Qualimeter Eplexor 150 N type DMA in quasi static testing mode. The distance between the clamps (initial length) came to 15 mm, the strain rate was settled to 1,8%/min and the tests were realized at a temperature of 25 °C.

The micro tensile specimens were also tested by using MINIMAT materials tester at a cross head speed of 1 mm/min at room temperature. Stress-strain curves were recorded in both cases.

Scanning Electron Beam Microscope

Scanning electron beam microscopy (SEM) allows studying the surface pattern of investigated specimen under high magnification with excellent depth of field.

In order to investigate the morphology and deformation pattern of iPP specimens by SEM in a cross section along the specimen symmetry line after tensile test, to observe any structural changes introduced by plastic deformation during uniaxial testing, it needs to prepare the samples. The samples were sectioned using a LEICA microtome type RM 2165 to reach a smooth surface representing the section of interest. To reveal the details of the semi crystalline morphology and the deformation pattern, the samples were etched for 20 min at room temperature using a modified, permanganate based etching agent proposed by Olley et al. After surface etching the prior to inspection in the SEM the samples were coated with an Au/Pt layer of approximately 12 nm, what was performed by using a EDWARDS sputter coater S 150 B.

For the SEM investigation a JEOL JSM 6300 scanning electron beam microscope was used, the acceleration voltage was settled 10 kV.

Transmission Electron Microscopy

Transmission electron microscopy (TEM) allows the observation of the nano structure of investigated sample. It requires the preparation of ultra thin sections. For the present study sections with a thickness of about 80 nm were taken from the center of the parallel zone of the molded specimens to be able to transmit by electron beam. The ultra microtomy was performed using microtome type Leica Ultracut and Diatome diamond knife.

Prior to TEM inspection the microtome sections were stained with RuO_4 in order to enhance the contrast between amorphous and crystalline phase of the sample. The TEM images were taken at an acceleration voltage of 200 kV using a Jeol JEM 2010 type TEM.

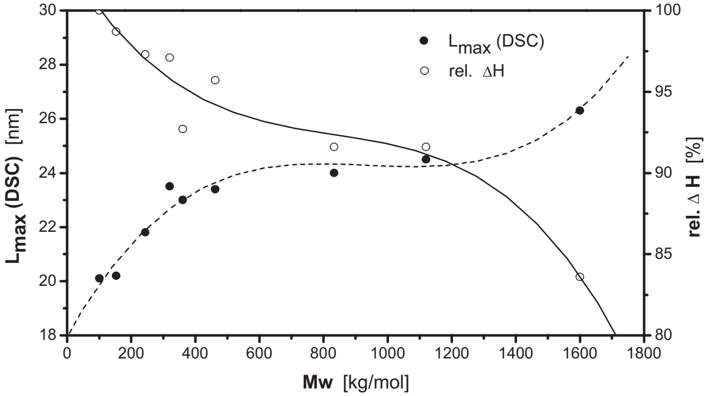


Figure 2.
Maximum lamella thickness and relative melt enthalpy of molded specimens manufactured from iPP with different molecular weight; values evaluated from DSC 1st heating curves.

Results and Discussion

Figure 2 shows on the molded micro specimens made from different molecular weight (Mw) iPP measured DSC results.

The melt enthalpy and therefore the crystallinity of the molded specimens were found to come down when Mw increases. At low molecular weight the specimens have a relative high crystalline content. The crystalline fraction passes a plateau before breaking down for about 20% for specimens from high molecular weight iPP. The lamella thickness of material crystallinity, which can be evaluated from DSC measurement as well and proposed by Thomson and Gibbs, behaves opposite.

Although the crystalline content of the molded specimens is decreasing with higher Mw the specimens produced from higher Mw iPP behave stronger in tensile experiment (Figure 3) which is supposed due to shear induced crystallization phenomena progressively, what can be proofed by TEM investigation (Figure 4). The micro specimens become stiffer with increasing Mw,

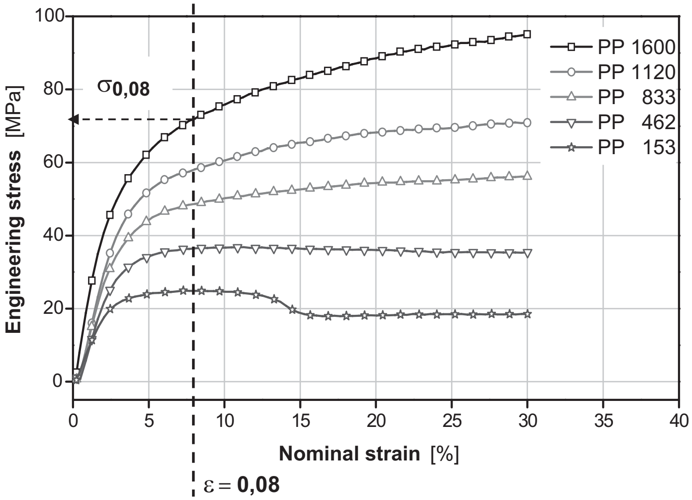
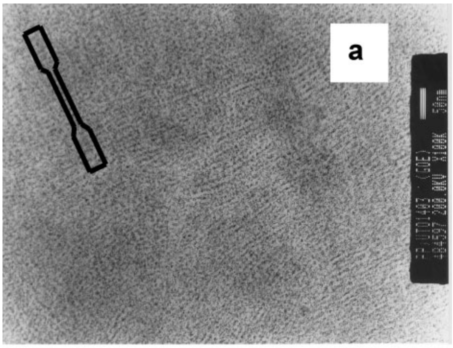
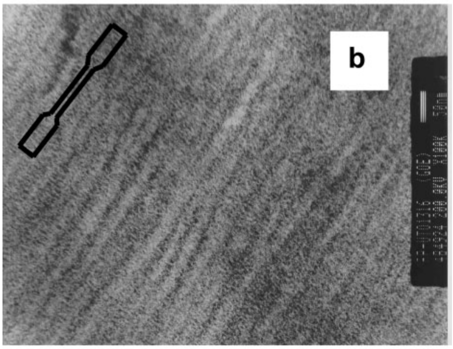


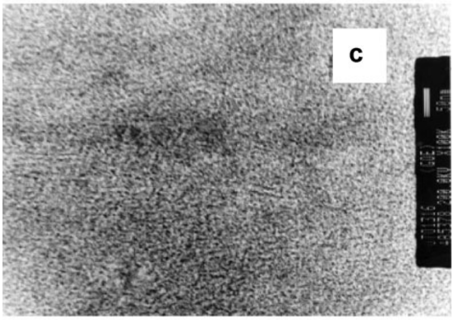
Figure 3.
Stress strain curves for the different iPP samples; measured in DMA in quasi static mode.



Mw 101 kg/mol, molded



Mw 1600 kg/mol, molded



recrystallized

Figure 4.
TEM micrographs from molded (a and b) and recrystallized (c) specimens of iPP of different Mw.

show expressed strain hardening effect at higher elongation progressively and no distinct yield point any more. For evaluation purpose therefore the stresses at 8% strain are getting compared (Table 3).

Table 3 records the evaluated tensile strength data of the molded specimens.

It is obvious that the tensile properties are hardly but non proportional influenced by Mw. Consequently 3 different classification ranges for the material behavior can be found.[9] Starting at low Mw of 101 kg/mol the specimen behaves less ductile and ruptures at about 10% of strain. In this called ''transition range'' the material performs comparatively weak and the strength increase when Mw increases. Reaching a Mw of about 200 kg/mol the strength is becoming almost independent of Mw and less affected by a change in Mw. This 2nd range can be called ''engineering material plateau''. When exceeding about 400 kg/mol the iPP shows increasing strength performance due to shear induced morphology in the molded micro specimens and can be called ''self reinforcement range''.

Figure 4 represents clearly the change in nano structure depending on Mw which leads to the different strength behavior observed.

In case of the iPP specimen molded of 101 kg/mol low Mw polymer (Figure 4a) there is no lamellar super-structure visible. At higher magnification (100 000x) typical α-iPP lamellae, transverse to the flow direction were detected for this sample. The lamellar thickness was measured to be $l = 6\,\text{nm}$.

The 1600 kg/mol high Mw iPP specimen processed by micro injection molding (Figure 4b) shows relative thick lamellae-like structures comparatively, which are lying parallel to the flow direction. The thickness of this novel structure could be determined between 20 and 30 nm and these lamellae-like elements are not similar to common crystalline lamellae. It can be assumed that also in this sample morphology common known and short lamellae are directed transverse to the flow direction.

The detected lamellae-like structures parallel to the flow direction in high Mw sample (Figure 4b) must be responsible for its enormous strength and must be caused by shear induced crystallization due to melt processing under high shear rate. After remelting the molded high Mw specimens and slow re-crystallization of the polymer the molecular super structure has vanished (Figure 4c).

Table 3.
Tensile properties of molded specimens

sample	Mw	$\sigma_{0,08}$	$\sigma_{0,08}$	σ_B	Classification
	[kg/mol]	[MPa] "DMA"	[MPa] "Minimat"	[MPa] "Minimat"	range
PP 1600	1600	75	81	119	III
PP 1120	1120	61	62	87	
PP 833	833	51	52	68	
PP 462	462	39	41	48	
PP 361	361	36			II
PP 320	320	35	41	46	
PP 244	244	36			
PP 153	153	27			I
PP 101	101	30	–	33	

Figure 5 represents the strength data of molded micro specimens of different Mw and indicates the distinct Mw classification ranges I to III mentioned before.

For low Mw (classification range I) the stress at break σ_B and stress at 8% strain almost coincide due to brittle deformation behavior. When exceeding 150 kg/mol in Mw the sample behaves ductile in its deformation behavior and shows already distinct yield point. As higher the Mw becomes as wider the difference between yield point (stress at 8% strain) and the ultimate strength it is. The stress at break of 1600 kg/mol iPP specimens is more than 120 MPa, which was the maximum tensile stress reached before the specimen has slipped in the clamping. But even this value is quite huge when compared with standard iPP strength of about 35 MPa.

Figure 6 represents the development of nano structure in injection molded micro specimens depending on different Mw and investigated by means of TEM micrographs. Based on the specific morphology of each of the specimens different mechanical deformation behavior can be observed. The accompanying measured tress strain curves are related to each of the morphology micrographs.

The brittle performing 110 kg/mol iPP sample exhibits common α-iPP lamellae transverse to the flow direction, which are relatively thin at a lamellar thickness of 6nm. All other samples show bigger lamellae and deform ductile. The specimen molded from 320 kg/mol polymer still contains lamellae transverse to the flow direction and their thickness is 7,4 nm. Next 3 investigated samples, which have Mw more than

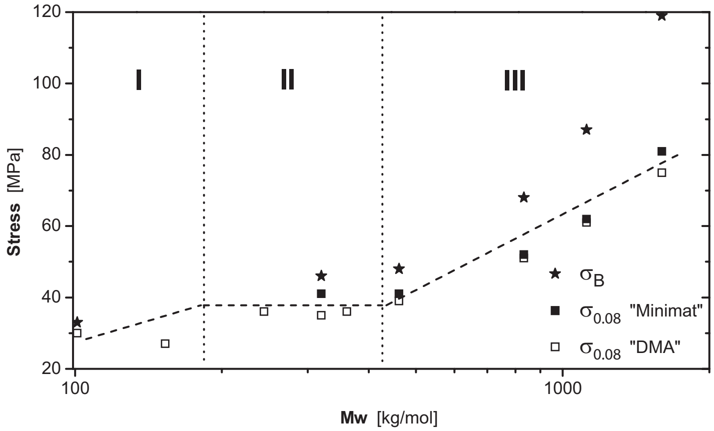


Figure 5.
Strength data of molded micro specimens of different Mw (the dotted trend line is without physical meaning).

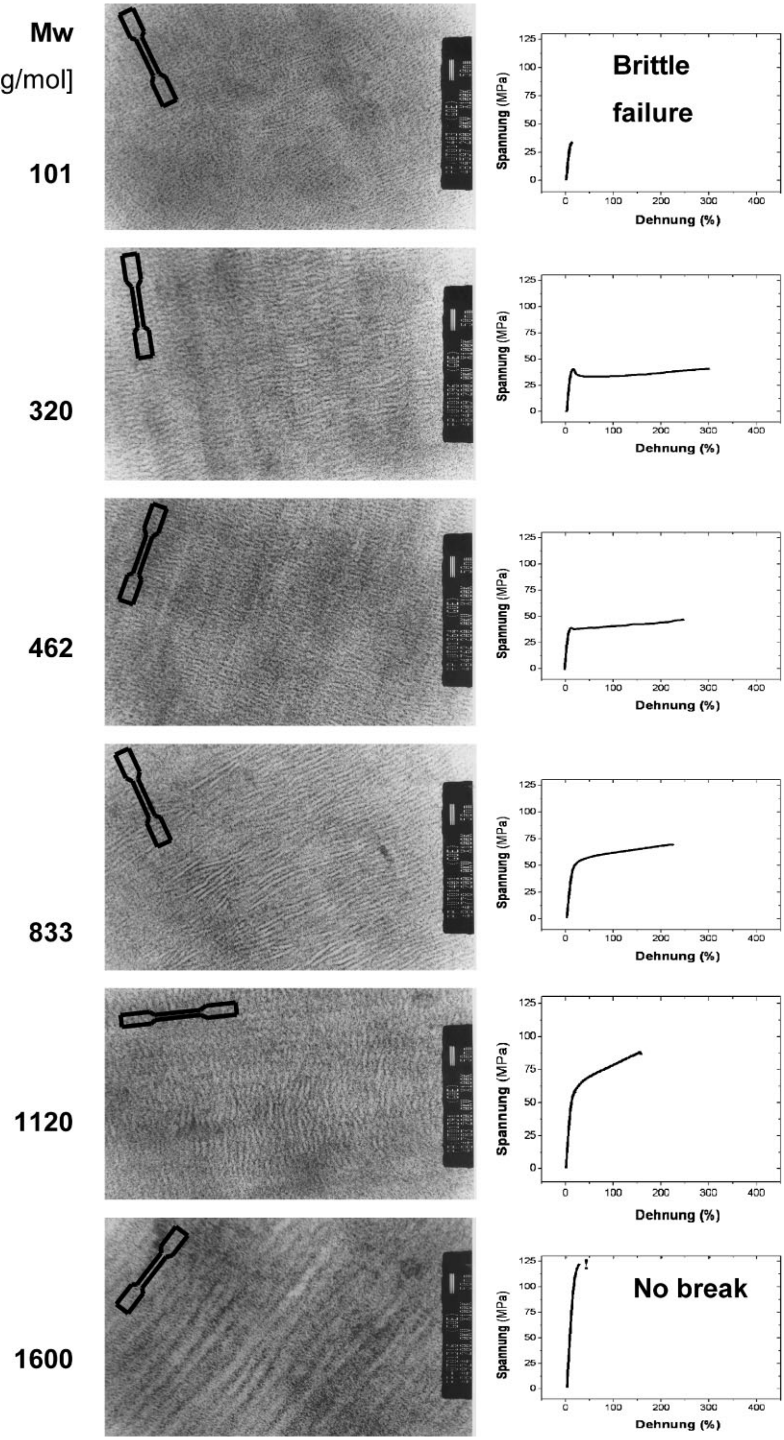


Figure 6.
Morphology of molded specimens of different Mw by means of TEM micrographs and related stress strain curves.

400 kg/mol, present highly oriented structure in the flow direction with transversally aligned lamellae. The morphologies look principally same but the thickness of the lamellae increases with increasing molecular weight from 6,4 nm to 7,1 nm and 7 nm. The high Mw sample molded from 1600 kg/mol iPP finally exists from shear induced molecular super structure in melt flow direction with thickness up to 30 nm and perpendicular lamellae with a thickness of 8,8 nm. Those micro specimens could be not ruptured till a stress level of about 120 MPa.

Figure 7 and Figure 8 summarize the micro mechanics of all investigated micro specimens molded from different Mw iPP. Firstly important and descriptive material data are given, necessary to characterize basically the polymer samples and to interpret subsequently their deformation behavior.

In a scheme of the sample morphology it is shown, where the SEM images from the drawn specimens are taken. A brief description of the deformation process explains the mechanism of the deformation of the different samples. The micromechanical interpretation of the deformation principle is further given.

Mechanical deformation behavior of molded micro specimens of iPP varies upon the Mw (Figure 6). With increasing Mw a transition from brittle fracture to semi ductile behavior with neck formation,

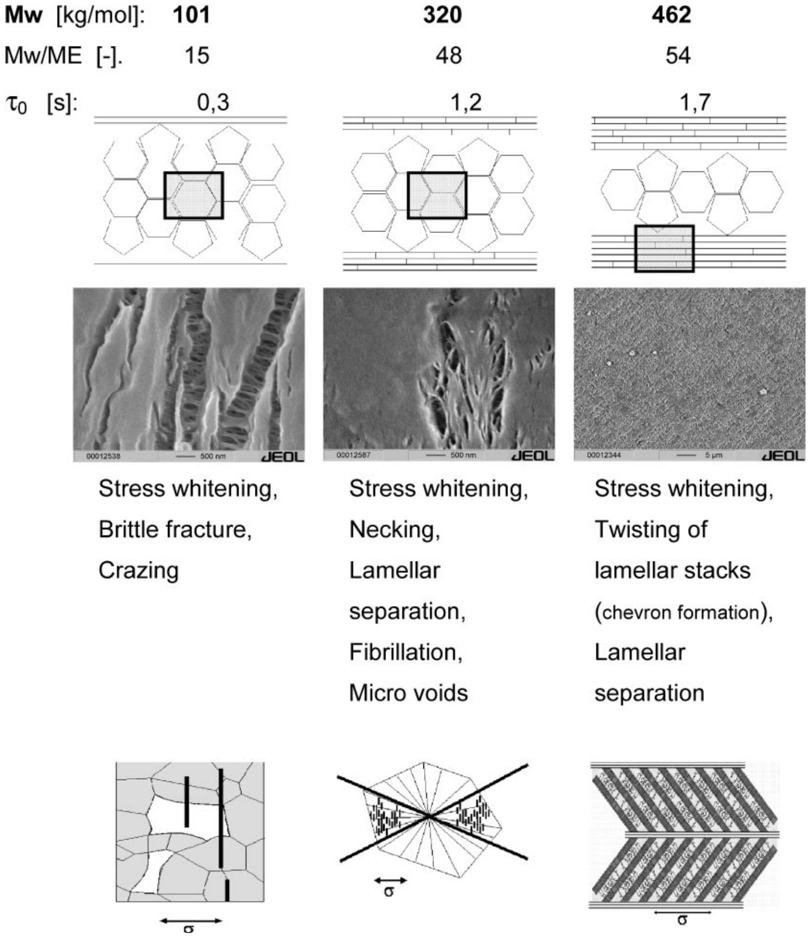


Figure 7.
Micromechanics of molded micro specimens of different Mw.

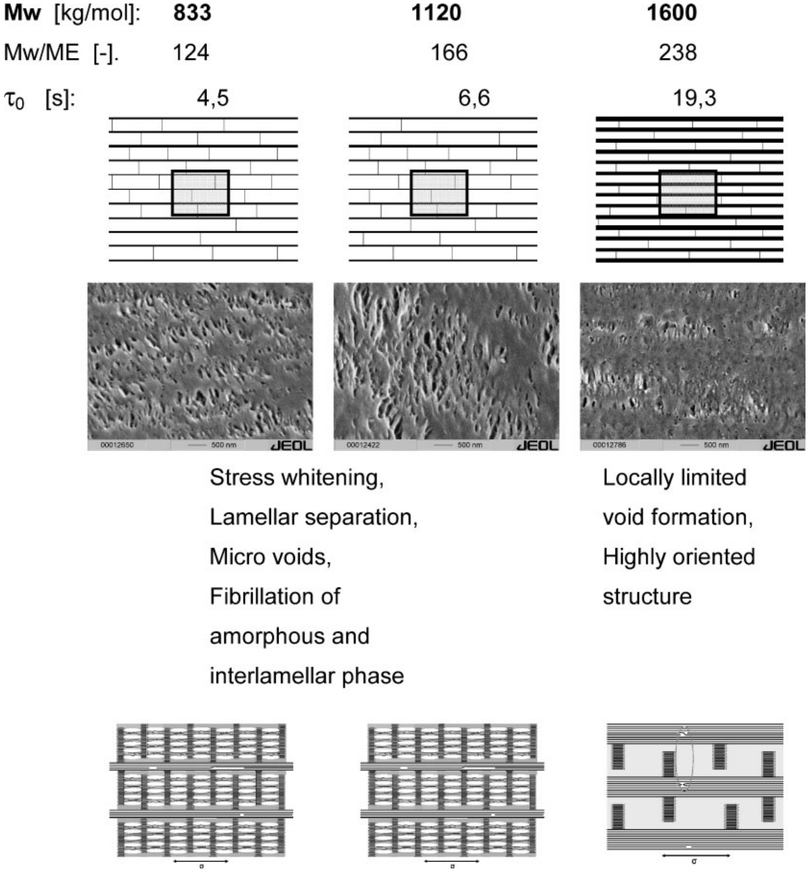


Figure 8.
Micromechanics of molded micro specimens of different Mw.

ductile deformation with neck formation und strain hardening and high strength behavior was observed.

At low Mw so called skin core morphology exists (Figure 7), which consists of a dominant spherulitic texture with narrow wide but highly oriented skin region. With increasing Mw a pronounced oriented region next to the outer layer with spherulitic core structure is recognized.

Reaching high und ultra high Mw a highly oriented bulk material without spherulitic texture is detected (Figure 8).

The observable micromechanical mechanisms during deformation are crazing, multiple crazing, lamellar separation and fibrillation, formation of micro voids, collective twisting of lamellar stacks, fibrillation of amorphous and interlamellar phase (kebab) and sporadic void formation between highly ordered macro fibrils (shishs) (Figure 7 and Figure 8.).

The present investigation leads a further understanding of micromechanics of melt processed thin walled specimens under high shear rates. It seems to be possible to manufacture molded parts with superior strength by choosing HMW-PP or UHMW-PP and suitable injection parameters.

Self reinforcement potential is specially given with respect to polymeric micro components production.

By consequent realization of this idea subsequently cost expensive engineering plastics can be substituted by HMW commodity plastics

[1] Goerg. Michler, *Kunststoff-Mikromechanik Hanser Verlag*, München, Wien 1992, p. 224.

[2] G. H. Michler, Micromechanics of polymers, *J. Macromol. Sci.-Phys.*, **1999**, *B38*(5&6), 787–802.

[3] H. Janeschitz-Kriegl, E. Fleischmann, W. Geymayer, Processing-induced structure formation in: J. Karger-Kocsis, Ed., *Polypropylene: Structure, blends and composites*, Volume, *1* Structure and Morphology, Chapman & Hall, London 1995, p. 295–344.

[4] J. Song, M. Prox, A. Weber, G. W. Ehrenstein, Self-reinforcement of polypropylene in: J. Karger-Kocsis, Ed., *Polypropylene: Structure, blends and composites*, Volume, *1* Structure and Morphology, Chapman & Hall, London 1995, 273–294.

[5] C. Stern, *On the performance of PP, PhD Thesis*, University Twente, Enschede 2005.

[6] C. Stern, A. Frick, G. Weickert, G. H. Michler, S. Henning, Processing, morphology, and mechanical properties of liquid pool polypropylene with different molecular weights, *Macromol. Mat. Eng.* **2005**, *290*(6), 621–635.

[7] Michaeli Johannaber, *Handbuch Spritzgießen*, Hanser Verlag, München, Wien 2002, p 320, 377.

[8] Keller. Sitz, *Spritzgießtechnik*, Hanser Verlag, München, Wien 2001, p. 77.

[9] = [1], p 212 ff.