Rheol Acta (2011) 50:461–468
DOI 10.1007/s00397-011-0542-5

ORIGINAL CONTRIBUTION

Recovery of shear modification of polypropylene melts

G. Breuer · A. Schausberger

Received: 1 December 2010 / Revised: 9 March 2011 / Accepted: 9 March 2011 / Published online: 12 May 2011
© Springer-Verlag 2011

Abstract Long-chain branched polypropylenes (LCB-PP) of different degrees of branching (up to 1 branch/10^4 carbon atoms) and a linear polypropylene (L-PP) are deformed at different shear conditions (rate, time and deformation) leading to reversible modifications of the entanglement structure. These modifications recover with time. Because of it the intensity of the modification and the rate of recovery are studied. At shear rates between 1 s^{-1} and 10 s^{-1} lower rates modify stronger. The intensity increases with shear time to a maximum at times of about 1 h where the final deformation does not control the intensity. Obviously, the disentanglement created by shearing competes with the Brownian motion coupling entanglements. Also, the intensity increases with the degree of LCB where the increase is stronger at low degrees. The rate of recovery not influenced noticeably by the initial modification strongly depends on the degree of LCB. The pertinent recovery functions grow exponentially to the limiting value of the unmodified state. Three different recovery processes are found. The fastest one with a recovery time shorter than 10^3 s is assigned to linear chains. The process with a time of about $5{\cdot}10^3$ s independent of the degree of LCB is assumed to describe the recovery of the backbones. The times for the very slow recovery of the side chains increase with the degree of LCB (between 10^4 and 10^5 s for the investigated samples). The recovery strength reflects the initial modification and depends on the degree of LCB. By that, the recovery behaviour provides information on the molecular structure.

Keywords Shear modification · Modification of entanglement structure · Recovery of modification · Long-chain branching · Polypropylene

Introduction

It is well known that rheological properties of polymers strongly depend on the processing history the melt has undergone before (Cooper and Pollett 1969; Dealy and Tsang 1981; Fujiki 1971; Kim et al. 1998; Prichard and Wissbrun 1969; Prooyen et al. 1994; Ram and Izrailov 1986; Ritzau et al. 1989; Rudin and Schreiber 1983; Schreiber 1960; Yamaguchi et al. 2003; Yamaguchi 2006). Mainly branched but also linear polymers are affected by shear deformation changing the entanglement structure of the macromolecules and reducing, as a result, the viscosity. Consequently, the entanglement structure influences, e.g. the crystallization process (Eder et al. 1990). The elasticity is reduced even more, e.g. effecting the residual stress frozen by solidification. These effects labelled shear modification, shear refining or melt homogenization also control the behaviour in elongation. For example, strain hardening important for the processability is reduced substantially. To complicate matters, shear modification

---

This paper is dedicated to Professor Helmut Münstedt, Friedrich-Alexander Universität Erlangen-Nürnberg on the occasion of his 70th birthday.

G. Breuer (✉)
Transfercenter für Kunststofftechnik GmbH,
Franz-Fritsch-Straße 11, 4600 Wels, Austria
e-mail: gerold.breuer@tckt.at

A. Schausberger
Institute of Polymer Science, Johannes Kepler University
Linz, Altenbergerstrasse 69, 4020 Linz, Austria

recovers with time and the history of fading depends on the molecular structure again.

This all has been studied extensively on low-density polyethylene (LDPE) for a long time. Several authors found out that continuous shearing of molten LDPE reduces the swelling ratio, but finally attains a steady value. However, the swelling is completely recovered by solvent or heat treatment (Baker et al. 1993; Rokudai 1979; Teh et al. 1985). Increase of MFR has also been reported (Hanson 1969). Münstedt (1981) has reported that extruded LDPE shows significantly lower extensional viscosity compared to the untreated sample, whereas the shear viscosity remains nearly unchanged. The origin of shear modification has been believed to be a disentanglement mechanism (Hanson 1969; Teh et al. 1985) for a long time, but this idea was confuted by Leblans and Bastiaansen (1989). They found out that reduced interpenetration of the molecules cannot be the reason for the lower elongational viscosity. Thus they support the idea of alignment of side chains along the backbone as the origin of shear modification. Yamaguchi and Gogos (2001) observed the most significant modifications on the storage modulus (G') in LDPE. They applied the shear treatment in a cone and plate rheometer quantified by the deformation and described the relation between annealing time and storage modulus of the sheared LDPE samples with a simple exponential function of first order. Similar results were obtained from the melt strength measurements.

Only scant information is available regarding the influence of shear treatment on long-chain branched polypropylenes (LCB-PP). Commercial PP with a linear chain architecture, e.g. linear polypropylene [L-PP], has weak melt strength. However, the melt strength can be improved by introducing branches on the L-PP backbone. This material, still available from manufacturers, offers new possibilities in a wide range of applications, such as film blowing, foaming and thermoforming.

Yamaguchi and Wagner (2006) compared LDPE, L-PP and a commercial LCB-PP after processing in an internal batch mixer. They found that the drawdown force, as a measure of melt elasticity for LCB-PP, is strongly depressed even by the short processing time in an internal batch mixer, whereas the rheological properties of L-PP are unchanged by the processing history. LCB-PP needs a longer post-processing annealing time to recover the drawdown force than LDPE. There is still a need for investigations on the influence of processing history on LCB-PP as well as on blends with L-PP and the fading of this influence. The rheological effects occurring are of importance in the attempt to extrapolate material behaviour under process conditions.

In this work, the influence of shear on the rheological properties of blends of a L-PP and a LCB-PP and especially the fading of it were studied in detail. For this, a strong shear is applied in a cone–plate rheometer and immediately after that the linear storage modulus, G', is recorded as a measure for the shear modification.

Experimental

Materials and measurement

For this study, two commercial polypropylenes from Borealis with different chain architecture were chosen. Daploy™ WB130HMS (MFR [ISO 1133] = 2.4 g/10 min; M_w = 600 kg/mol; M_w/M_n = 6.6) is a homopolymer long-chain branched polypropylene with about one long-branch/10^4 C-atom (Ratzsch et al. 2002). HD120MO (MFR [ISO 1133] = 8.0 g/10 min; M_w = 370 kg/mol; M_w/M_n = 4.9) is a homopolymer linear polypropylene. Blends of these two PPs with LCB-PP contents of 5, 25, 50 and 75 wt.% were compounded at 220°C in a Thermo Prism TSE 24HC co-rotating twin screw extruder (500 rpm rotational speed) with a length-to-diameter ratio of 28, a gravimetric dosing system, a water cooling bath and a pelletizer. Notation and characteristics of the sample used in this study are listed in Table 1. The plates for the rheological measurement were moulded for 20 min in vacuum between two flat steel plates to a thickness of 0.5–1.2 mm at a temperature of 180°C.

Rheometry was performed in an Anton Paar Physica MCR501 torsional rheometer at 180°C under nitrogen atmosphere to prevent oxidation. For the characterization, the dynamic moduli were measured in a plate–plate geometry (diameter: 25 mm; gap: 1 mm). The shear modification was investigated in a cone–plate system (angle: 2°; diameter: 25 mm) at 180°C. For this, the samples were sheared at shear rates $\dot{\gamma}$ between 1 and 10 s^{-1} for times t_s between 90 and 3,600 s. Immediately after the shear treatment, the fading of the

Table 1 Notation, LCB-PP fraction, zero shear viscosity (η_0) at 180°C, first zero-normal stress coefficient ($\Psi_{1,0}$) and the terminal relaxation time ($\tau_d = \Psi_{1,0}/2\eta_0$) of the investigated samples

Sample	LCB-PP fraction (wt.%)	η_0 (kPa s)	$\Psi_{1,0}$ (kPa s^2)	τ_d (s)
L-PP	0	6.04	109	9
P5	5	6.59	158	12
P25	25	8.31	582	35
P50	50	12.4	2,380	96
P75	75	20.9	8,955	214
LCB-PP	100	41.8	58,300	698

shear modification was recorded by the storage modulus, G', at a deformation amplitude of $\gamma = 0.3$ at the frequency $\omega = 0.1$ rad/s. This frequency appears to be suitable because pronounced shear modification can be observed on one hand and on the other hand it allows taking measuring points, all at 63 s, i.e. after one oscillation.

Results and analyses

The thermal stability of the samples was tested by time sweeps at a constant angular frequency of $\omega = 0.1$ rad/s. Figure 1 shows the storage moduli of the time sweep, $G'(t)$, normalized to the starting value, $G'(t = 0)$. Within the recording period no changes were found for L-PP, whereas the moduli of the samples containing LCB-PP slightly increased with time. This is attributed to the reformation of the entanglements between the molecules disentangled by the preparation process. As Stange et al. (2005) reported a remarkable influence of the preparation process, we studied intensely different mixing procedures (Duscher 2008). The samples investigated in this paper were prepared under conditions that create modifications smaller than 5%. Therefore the influence of the extrusion process is not separated in the analysis of the recovery.

For an overall impression, the influence of shear modification on different material functions is shown in Fig. 2.

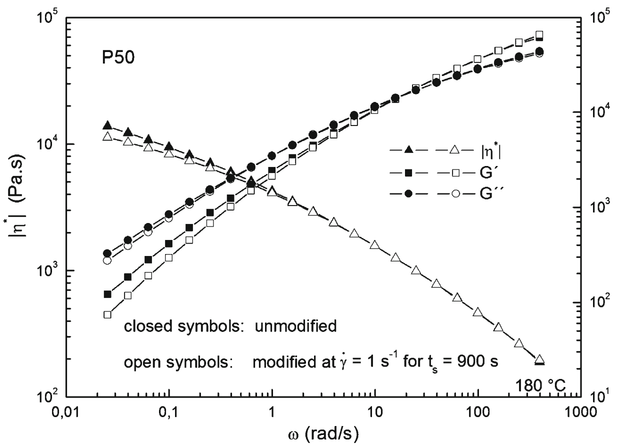

Fig. 2 Complex viscosity ($|\eta^*(\omega)|$), storage modulus (G') and loss modulus (G'') as a function of the angular frequency, ω, of the sample P50

G' is more altered than G'' and $|\eta^*(\omega)|$. Thus the storage modulus is chosen for quantifying shear modification. In Fig. 3, the G'_s values of materials sheared for $t_s = 900$ s at $\dot{\gamma} = 1\ \mathrm{s}^{-1}$ are reduced by the values of the original material, G'_o, for better illustration. The change of the storage modulus is more pronounced in the lower frequency region. This is reasonable in terms of the fact that long time relaxation mechanisms, such as entanglement couplings associated with long-chain branches, are mainly responsible for the level of G' in the low-frequency region. In the case of L-PP, no influence of shear treatment could be found within the analyzed frequency region. This is why the modified structure recovers sooner before the moduli at low frequencies are measured. The magnitude in change of storage modulus is larger for materials with higher degrees on long-chain branching. The sample P75 shows a behaviour similar to LCB-PP.

One has to consider, however, that the modified samples are not in a steady state during the frequency

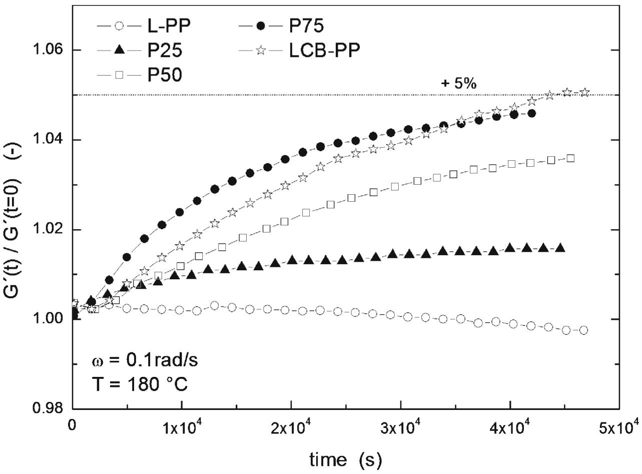

Fig. 1 Normalized storage modulus, $G'(t)/G'(t = 0)$, as a function of time

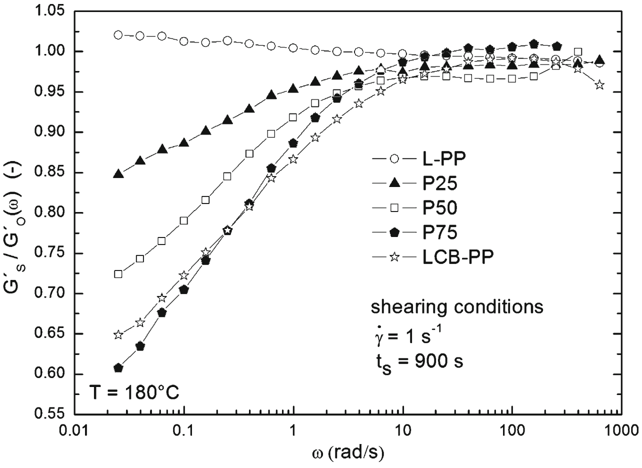

Fig. 3 Reduced storage modulus, G'_s/G'_o, of samples sheared for $t_s = 900$ s at $\dot{\gamma} = 1\ \mathrm{s}^{-1}$

sweep. Therefore the fading is recorded at a constant angular frequency of $\omega = 0.1$ rad/s. This is a compromise between the low frequency and variation of G' within the time needed for taking a measuring point. For the evaluation, a recovery function, $\Phi(t)$, growing with the time, t, to the final value $\Phi(t) = 1$ (fully recovered) is defined as

$$\Phi(t) = \frac{G'_s(t)}{G'_o} \text{ or } \Phi(t) = 1 - \phi(t) \tag{1}$$

with

$$\phi(t) = \frac{G'_o - G'_s(t)}{G'_o} \tag{2}$$

The time $t = 0$ is the stop of the shear treatment and the start of the recovery. The function $\varphi(t)$ is a measure for the intensity of the modification ($0 < \varphi(t) < 1$).

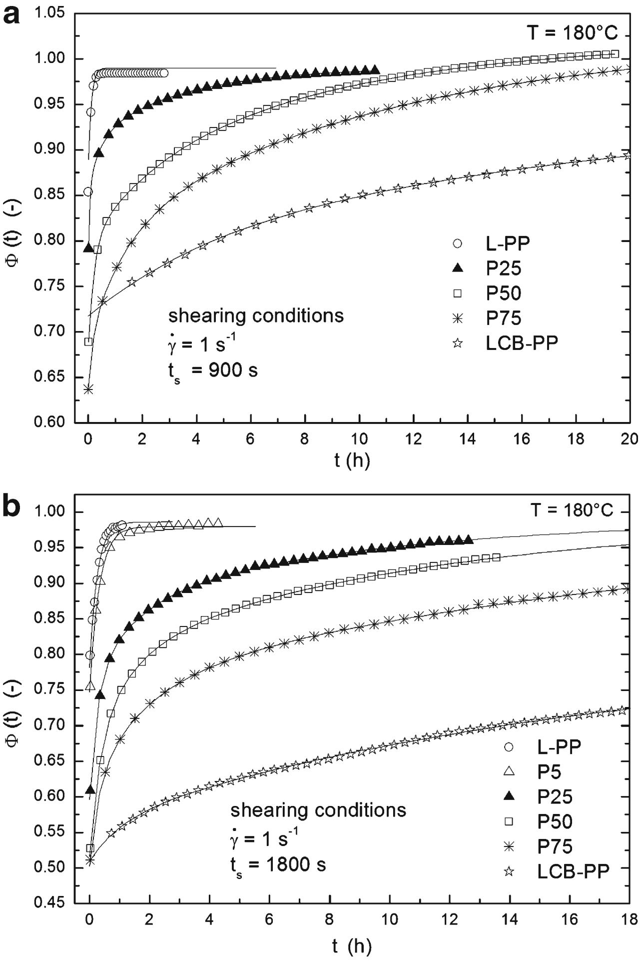

Fig. 4 Recovery function, $\Phi(t)$, of the samples modified at $\dot{\gamma} = 1\ \mathrm{s}^{-1}$ for $t_s = 900$ s (**a**) and for $t_s = 1800$ s (**b**) fits (*lines*) L-PP, according to Eq. 3; mixtures, according to Eq. 4; and LCB-PP, according to Eq. 5

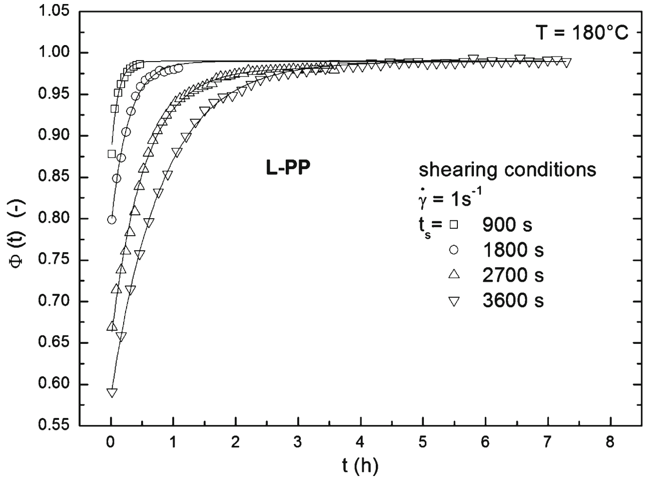

Fig. 5 Recovery function, $\Phi(t)$, of L-PP modified at $\dot{\gamma} = 1\ \mathrm{s}^{-1}$ for $t_s = 900$, 1,800, 2,700 and 3,600 s fits (*lines*) according to Eq. 3

Figure 4 show the recovery function, $\Phi(t)$, of samples sheared at $\dot{\gamma} = 1\ \mathrm{s}^{-1}$ for $t_s = 900$ s (Fig. 4a) and for $t_s = 1{,}800$ s (Fig. 4b) respectively. The earliest measuring points $G'_s(t)$ were taken at $t = 132$ s (near to zero in a scale of hours) except for pure LCB-PP. In this case, strong normal forces impair the measurement of $G'_s(t)$ early into the recording. Remarkably, the normal forces vanish faster in samples sheared longer. Obviously, samples with higher LCB-PP fraction undergo a stronger modification and their $\Phi(t)$ function needs more time to recover. As the modified L-PP recovers very fast, the behaviour of different long-modified samples is shown in a shorter time scale additionally (Fig. 5).

Notably, the recovery functions, $\Phi(t)$, can be fitted best by simple exponentials.

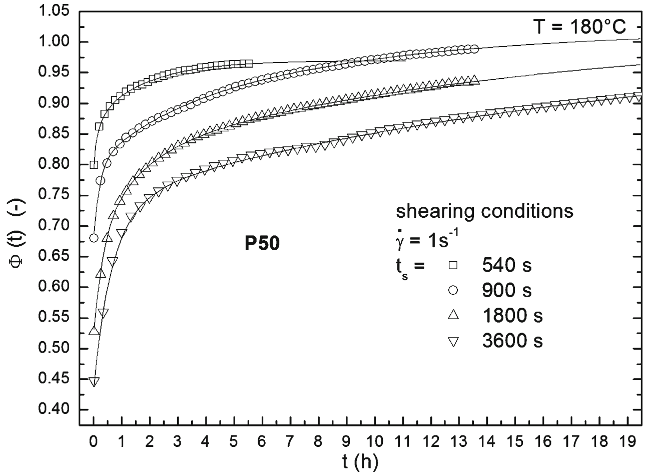

Fig. 6 Recovery function, $\Phi(t)$, of P50 modified at $\dot{\gamma} = 1\ \mathrm{s}^{-1}$ for $t_s = 540$, 900, 1,800 and 3,600 s fits (*line*) according to Eq. 4

L-PP shows a single recovery process:

$$\Phi(t)_{\mathrm{L-PP}} = 1 - \phi_1 e^{\frac{-t}{\tau_1}} \tag{3}$$

The parameter φ values the initial modification and by that the recovery strength. The parameter τ (recovery time) quantifies the rate of recovery.

Mixtures with LCB-PP show two additional slower recovery processes

$$\Phi(t)_{\mathrm{mixtures}} = 1 - \left(\phi_1 e^{\frac{-t}{\tau_1}} + \phi_2 e^{\frac{-t}{\tau_2}} + \phi_3 e^{\frac{-t}{\tau_3}}\right), \tag{4}$$

as illustrated in Fig. 4 and in Fig. 6.

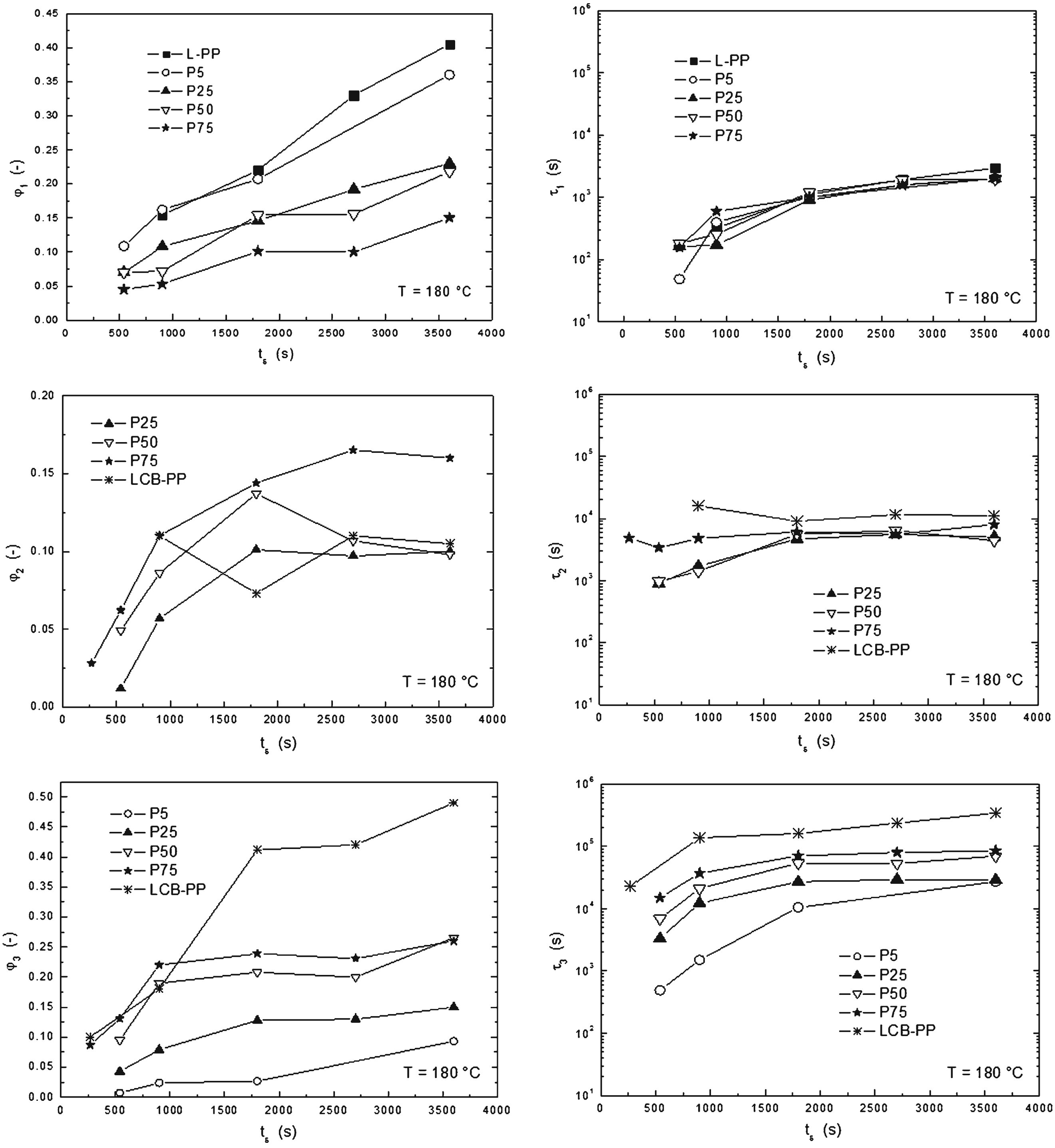

Fig. 7 Recovery parameters φ and τ as a function of modification time t_s for samples modified differently long at $\dot{\gamma} = 1\ \mathrm{s}^{-1}$

Some $\Phi(t)$ curves in Figs. 4a and 6 reach values slightly larger than 1 (up to 1.01). Aside from experimental inaccuracies, this might be a hint of a previous modification that occurred in preparing the sample.

As mentioned above, in the case of pure LCB-PP the recovery function, $\Phi(t)$, cannot be recorded properly at short times. Maybe fast processes are not quoted correctly. Despite them, the recorded functions show two recovery processes similar to the second and third recovery process of the mixtures.

$$\Phi(t)_{\mathrm{LCB-PP}} = 1 - \left(\phi_2 e^{\frac{-ta}{\tau_2}} + \phi_3 e^{\frac{-ta}{\tau_3}}\right) \tag{5}$$

In Fig. 7, the recovery parameters φ and τ of samples sheared at a shear rate of $\dot{\gamma} = 1\ \mathrm{s}^{-1}$ are plotted as function of the shear time, t_s. For all materials, an increase of the recovery strength, $\varphi(t)$, with the shear time is observed. Furthermore, φ_1 decreases with rising LCB-PP fraction, whereas τ_1, being between 10^2 and 10^3 s, appears to be unaffected by the degree of branching. The parameters φ_2 may be estimated less exactly for LCB-PP on one side and not found for L-PP and PP5 on the other side and tend to increase with rising LCB-PP fraction. The values for τ_2 are between 10^3 and 10^4 s and also rather unaffected by the degree of LCB. Considering the third process, a remarkable increase of both φ_3 and τ_3 with the branching fraction is found. The values of τ_3 go up to 10^5 s at longer shear times and higher LCB-PP fraction.

According to Eqs. 2–4, the initial shear modification is given by

$$\varphi(t = 0) = \varphi_1 + \varphi_2 + \varphi_3 \tag{6}$$

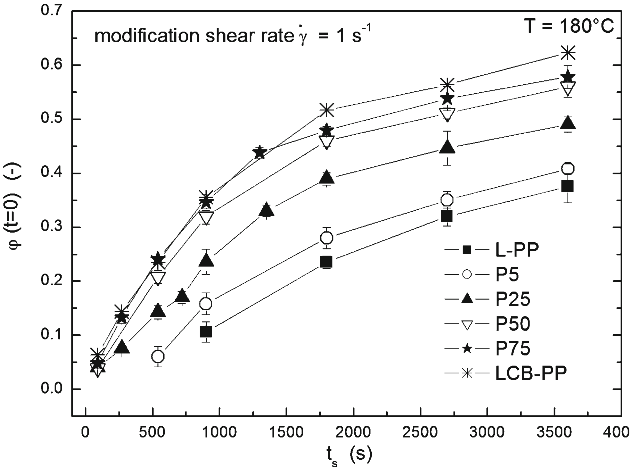

Fig. 8 Initial shear modification, $\varphi(t = 0)$, as a function of the modification time, t_s

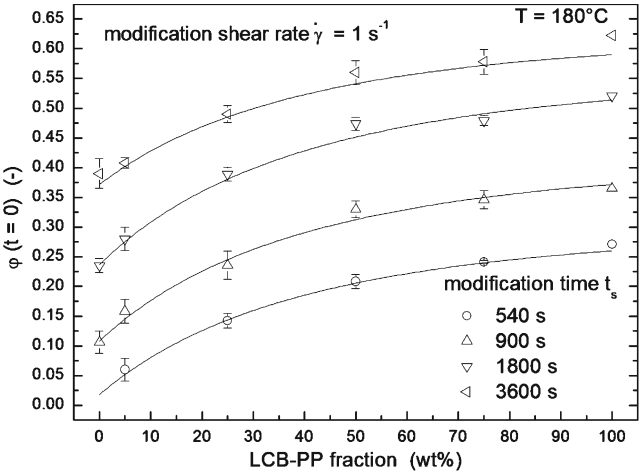

Fig. 9 Initial shear modification, $\varphi(t = 0)$, as a function of the LCB-PP fraction

These modifications, created at shear rate $\dot{\gamma} = 1\ \mathrm{s}^{-1}$, are summarised in Fig. 8 as a function of modification time, t_s. The higher the LCB-PP fraction is, the stronger the polymers are modified and the more this effect increases with shearing time. The modification, however, seems to reach a plateau at times higher than $t_\mathrm{s} = 3,600$ s. In Fig. 9, the initial shear modification, $\phi(t = 0)$, is plotted as a function of the LCB-PP fraction for different shearing times. Interestingly, it does not increase linearly with the degree of LCB, but it starts strongly and trends to reach a plateau. Samples with LCB-PP fractions higher than 50% are affected nearly equally by the same shear treatment.

In order to investigate the influence of different shear rates, the material P25 was sheared at 1, 7 and $10\ \mathrm{s}^{-1}$ for various times t_s. Figure 10 shows the recovery

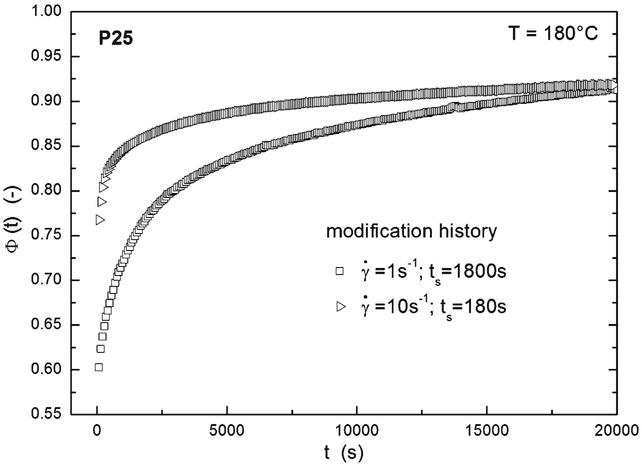

Fig. 10 Recovery function, $\Phi(t)$, of P25 sheared to a final strain of $\gamma = 1,800$ at different shear rates

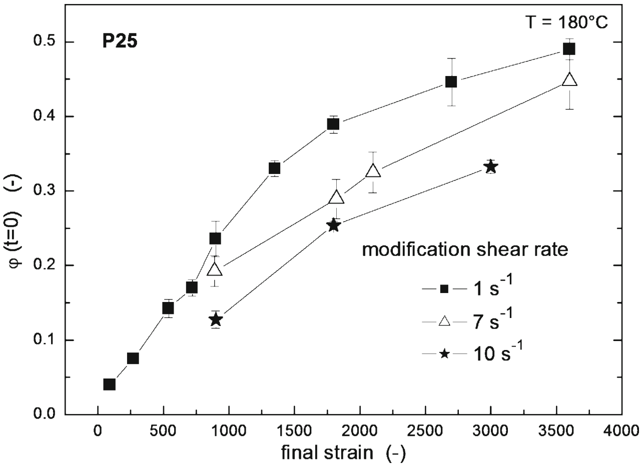

Fig. 11 Initial shear modification $\varphi(t = 0)$ of P25 as a function of the final strain applied at different shear rates

functions of P25 sheared to a total strain of 1,800 at two different shear rates. Remarkably, lower shear rates modify stronger (smaller $\Phi(t = 0)$ values) even though the final strain is equal. Obviously, the final strain does not control the rheological properties of modified samples.

In Fig. 11, the initial shear modification $\varphi(t = 0)$ at different shear rates is shown as a function of the final strain applied at different shear rates. Interestingly, at higher shear rates larger deformations have to be applied in order to create a certain level of shear modification.

Conclusion

Shear treatment of polymer melts was found to change significantly the entanglement structure of L-PP and LCB-PP (and of mixtures of them), reducing viscosity and elasticity. The intensity of the generated modification and the recovery of it depend as well as on the modification procedure and the molecular structure. Lower shear rates modify more efficiently when modifications to the same total strain (see Fig. 10) are compared. This finding initially appears to be in contrast to the results known for the steady state. In this case, higher shear rates generate stronger modifications resulting in lower viscosities. One has to consider, however, that, already at the beginning of a modification process, arranging created by shear competes with disarranging by Brownian motion. As weaker modified melts recover more slowly (due to a higher viscosity), it may happen at lower shear rates that arranging dominates at the beginning. The finding that the total (final) deformation does not control the intensity of modification confirms this kinetic phenomenon.

The rate of recovery is not influenced by the initial modification, but it depends strongly on the molecular structure. The recovery of L-PP is found to follow a single exponential. The recovery strength is equal to the initial modification, and the recovery time is about 10^3 s.

Mixtures of L-PP and LCB-PP show three different fast processes, each of which also quantified by an exponential approach. Not surprisingly, a second slower relaxation process is found for the linear viscoelastic behaviour of LCB PE as well (Resch et al. 2009). The recovery time of the fastest process equals the recovery time of L-PP, and the recovery strength of the fastest process decreases with increasing LCB fraction. Therefore this process is referred to the linear molecules. Except concerning pure LCB-PP, the recovery time of the second process ($\approx 5 \cdot 10^3$ s) is not affected by the degree of LCB. The scattered values of the associated strengths may not be interpreted. Nevertheless, this recovery should be assigned to the backbone of LCB-PP. Regarding the slowest process, both the recovery strength and the recovery time increase with the degree of LCB. This increase is more pronounced at low LCB concentrations. The slowest process is assumed to describe the integral recovery behaviour of the branches, as it is possible that branches line up against the backbone during shear treatment. In the case of pure LCB-PP, the fastest process is not detected and the recovery time of the second process ($\approx 10 \cdot 10^3$ s) is found to be longer than that of L-PP/LCB-PP mixtures ($\approx 5 \cdot 10^3$ s). These two findings should not be interpreted in detail due to problems early in the recording of the recovery function. Finally, all recovery times are significantly longer than the terminal relaxation times representing the linear viscoelastic behaviour. This clearly indicates that modification is mainly associated with the molecular structure but not with the length of the molecules. Concluding the analyses of the recovery process provides useful information on the molecular structure on the one hand. On the other hand, the entanglement structure modified by shearing will strongly influence the behaviour in elongation (e.g. strain hardening) following or accompanying the shear process.

References

Baker WE, Rudin A, Schreiber HP, El-Kindi M (1993) The effect of processing on rheological and molecular characteristics of a low density polyethylene. Polym Eng Sci 33:377–382

Cooper WM, Pollett WFO (1969) The shear modulus of flowing polyethylene melts. J Appl Polym Sci 13:2313–2324

Dealy JM, Tsang WK (1981) Structural time dependency in the rheological behaviour of molten polymers. J Appl Polym Sci 26:1149–1158

Duscher B (2008) The influence of different mixing conditions on the rheological behaviour of blends from a linear and long-chain branched polypropylene. Diploma thesis, Johannes Kepler University Linz

Eder G, Janeschitz-Kriegl H, Liedauer S (1990) Crystallization processes in quiescent and moving polymer melts under heat transfer conditions. Progr Polym Sci 15:629–714

Fujiki T (1971) Concept of secondary heterogeneous structure of long-chain branched polyethylene. J Appl Polym Sci 15:47–66

Hanson DE (1969) Shear modification of polythene. Polym Eng Sci 9:405–414

Kim YC, Yang KS, Choi CH (1998) Study of the relationship between shear modification and melt fracture in extrusion of LDPE. J Appl Polym Sci 70:2187–2195

Leblans PJR, Bastiaansen C (1989) Shear modification of low density polyethylene: its origin and its effect on the basic rheological functions of the melt. Macromolecules 22:3312

Münstedt H (1981) The influence of various deformation histories on elongational properties of low density polyethylene. Colloid Polym Sci 259:966–972

Prichard JH, Wissbrun KF (1969) Reversible melt flow rate increase of branched acetal polymers. J Appl Polym Sci 13:233–239

Prooyen M, Bremner T, Rudin A (1994) Mechanism of shear modification of low density polyethylene. Polym Eng Sci 34:570–579

Ram A, Izrailov L (1986) Shear modification of polyethylene. J Appl Polym Sci 31:85–100

Ratzsch M, Arnold M, Borsig E, Bucka H, Reichelt N (2002) Radical reactions on polypropylene in the solid state. Prog Polym Sci 27:1195–1282

Resch JA, Stadler FJ, Kaschta J, Münstedt H (2009) Temperature dependence of the linear stead-state shear compliance of linear and long-chain branched polyethylenes. Macromolecules 42(15):5676–5683

Ritzau G, Ram A, Izrailov L (1989) Effect of shear modification on the rheological behavior of two low-density polyethylene (LDPE) grades. Polym Eng Sci 29:214–226

Rokudai M (1979) Influence of shearing history on the rheological properties and processability of branched polymers. J Appl Polym Sci 23:463–471

Rudin A, Schreiber HP (1983) Shear modification of polymers. Polym Eng Sci 23:422–430

Schreiber HP (1960) A study of time dependence of polyethylene flow in capillary viscometry. J Appl Polym Sci 4:38–44

Stange J, Uhl C, Münstedt H (2005) Rheological behaviour of blends of a linear and a long-chain branched polypropylene. J Rheol 49:1059–1079

Teh JW, Rudin A, Schreiber P (1985) Shear modification of low density polyethylene. J Appl Polym Sci 30:1345–1357

Yamaguchi M, Gogos CG (2001) Quantitative relation between shear history and rheological properties of LDPE. Adv Polym Technol 20:261–269

Yamaguchi M, Todd DB, Gogos CG (2003) Rheological properties of LDPE processed by conventional processing machines. Adv Polym Technol 22:179–187

Yamaguchi M (2006) Relationship between processing history and rheological properties during postprocessing annealing for anomalous polyethylene blends. J Appl Polym Sci 102:1078–1083

Yamaguchi M, Wagner MH (2006) Impact of processing history on rheological properties for branched polypropylene. Polymer 47:3629–3635