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Advances in Film Blowing, Thermoforming, and Foaming by Using Long-Chain Branched Polymers

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Summary: In many extrusion processes the uniformity of the geometry of the processed items is of great importance for their quality. It is shown how the uniformity of the wall thickness of a beaker thermoformed from polypropylene and of films blown from polyethylene can be improved by using long-chain branched materials. Furthermore, a beneficial effect with respect to an increase of the expansion ratios of foams is observed for long-chain branched polypropylenes. The common characteristics of all these three processing operations are pronounced biaxial elongational deformations. It is demonstrated that the occurrence of strain hardening is the key factor for an improvement of uniformity. As long-chain branches are decisive for the amount of strain hardening it is shown how they contribute to a better quality in extrusion.

Keywords: biaxial deformation; long-chain branching; strain hardening; uniaxial elongation; uniformity of extruded items

Introduction

Besides others film blowing, thermoforming, and foaming are extrusion processes in which elongational flow plays a dominant role. It is well known from literature that elongational properties of a polymer melt cannot generally be derived from those in shear, e.g. Auhl *et al.*[1] Therefore, special experimental methods are necessary to measure the behaviour of polymer melts in extension. As long-chain branches significantly influence rheological properties of polymer melts it is worthwhile investigating their effect on processing operations in extrusion. This topic has become of particular interest, as it has got possible during the last years to systematically change the branching structure of polymers.[1–5] A characteristic quantity which correlates elongational properties with the homogeneity of extruded items is the so-called strain hardening. It describes the increase of elongational viscosity at different times or elongations over the corresponding linear quantities.

Materials and Experimental

A commercial linear and a commercial long-chain branched polypropylene were used for the thermoforming experiments. Foaming was carried out on blends of these two products. In film blowing a commercial long-chain branched polyethylene (LDPE) and a linear low density polyethylene (LLDPE) were investigated.

Measurements of the elongational behaviour were performed using the tensile rheometer described by Kurzbeck *et al.*,[6] for thermoforming and film blowing com-

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mercially available test equipments were used[7] and for the foaming experiments a special apparatus was built up.[8,9]

In order to get an insight into the relationship between molecular structure, elongational properties, and the homogeneity of sample deformation the experimental device described in Kurzbeck *et al.*[6] was used. The elongated sample as demonstrated exemplarily in the right part of Fig. 1 can be video-recorded at any state of deformation. Using the recorded photos the diameter of the sample along various positions on the stretched sample was determined. Fig. 1 gives the results of such measurements for a low density polyethylene elongated at a *low, medium, and high* strain rate up to a total Hencky strain of 2.9 which corresponds to a stretching ratio of 18.

In order to obtain a number for a quantitative characterization of the homogeneity a so-called inhomogeneity factor is defined. To determine it from measurements like in Fig. 1 the averaged deviation a_s of the diameters d_i measured at different positions from the nominal diameter d_{nom} is calculated according to

$$a_s = \frac{1}{n}\sum_{i=1}^{n}\sqrt{(d_i - d_{nom})^2} \qquad (1)$$

d_{nom} is obtained assuming a constant sample volume during deformation. The inhomogeneity index r follows as

$$r = \frac{a_s}{d_{nom}} \qquad (2)$$

Results and Discussion

Elongational Behavior of the Melts

The elongational viscosities of the two polypropylenes measured at various elongational rates are presented in Fig. 2.

The data of the linear polypropylene (LIN-PP) are independent of the elongational rate as expected for linear polymers. The long-chain branched material (LCB-PP) does show a significant strain hardening, i.e. the elongational viscosity becomes remarkably higher than in the linear regime described by the envelope of the curves measured at different elongational rates. According to the theory of viscoelasticity this curve should coincide with three times the linear shear viscosity η_0^+ (t) in the case of uniaxial elongation and six times this value for equibiaxial deformation. As can be seen from the results in Fig. 2 this relationship is very well fulfilled for the two polypropylenes characterized in uniaxial elongation demonstrating the reliability of the measurements.

As can easily be derived from an experiment of thought strain hardening

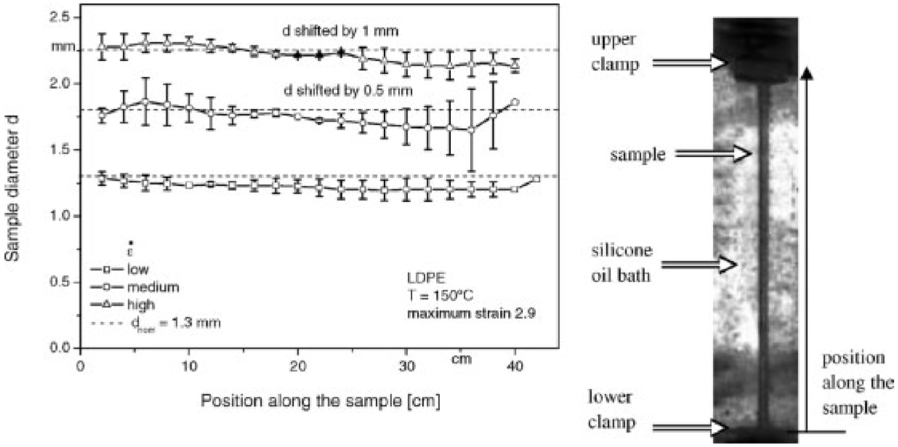

Figure 1.

Homogeneity of a low density polyethylene sample stretched at different elongational rates.

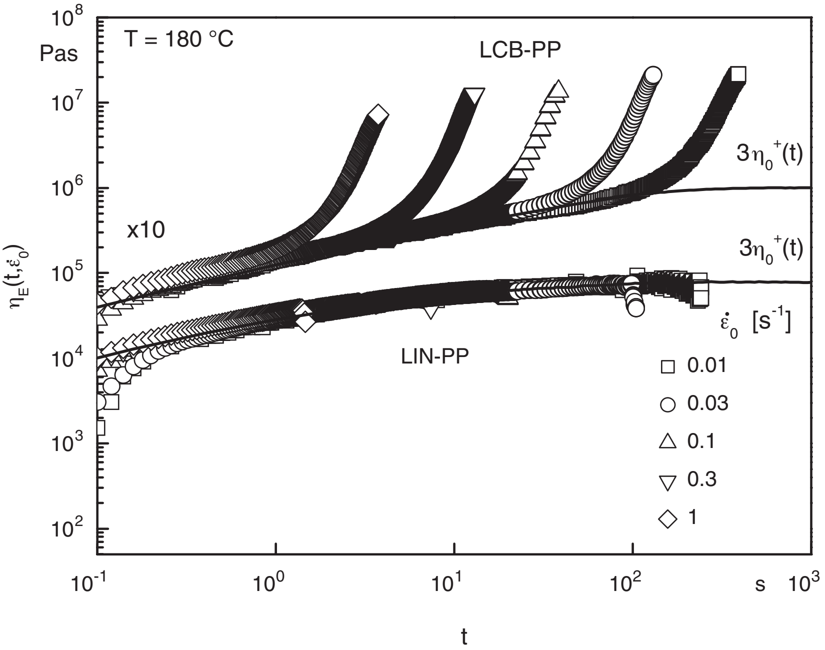

Figure 2.
Uniaxial elongational viscosities of the linear and the long-chain branched polypropylene.

gives rise to a kind of self-healing mechanism effecting a more homogeneous deformation of an elongated item in comparison to a non strain-hardening material (e.g. Münstedt *et al.*[10]). Uniaxial laboratory experiments demonstrating this effect for the two polypropylenes characterized in Fig. 2 are shown in Fig. 3 in which the inhomogeneity index determined by the laboratory method described above is plotted as a function of the constant elongational rates. The stretching ratios of the samples were 18 again.

As it is clearly seen the overall homogeneity of the LCB-PP is much better than that of the linear sample. In addition to that, the scatter of the measurements on the long-chain branched PP is much smaller indicating a more robust deformation process.

As the deformation in film blowing, thermoforming, and foaming is mainly biaxial the question arises whether the strain hardening occurring in uniaxial deformation is existent in biaxial stretching, too. Hachmann and Meissner[11] showed for a polyethylene that strain hardening in uniaxial elongation is qualitatively reflected in biaxial deformation, too. In order to investigate this relationship for the two polypropylenes of this work equibiaxial experiments were performed using the method of squeezing flow. The results taken from Münstedt *et al.*[10] are represented in Fig. 4.

It is clearly demonstrated that the LCB-PP shows strain hardening in the equibiaxial deformation mode but the LIN-PP not which is in qualitative agreement with the findings from the uniaxial experiments in Fig. 2. The envelopes of the two curves are in good agreement with $6\eta_0^+$ (t). This result gives a hint to the reliability of the experiments. The slight upswing of the curves of the linear polypropylene (cf. Fig. 4) is due to experimental difficulties. Following from these findings it can be concluded that uniaxial experiments which

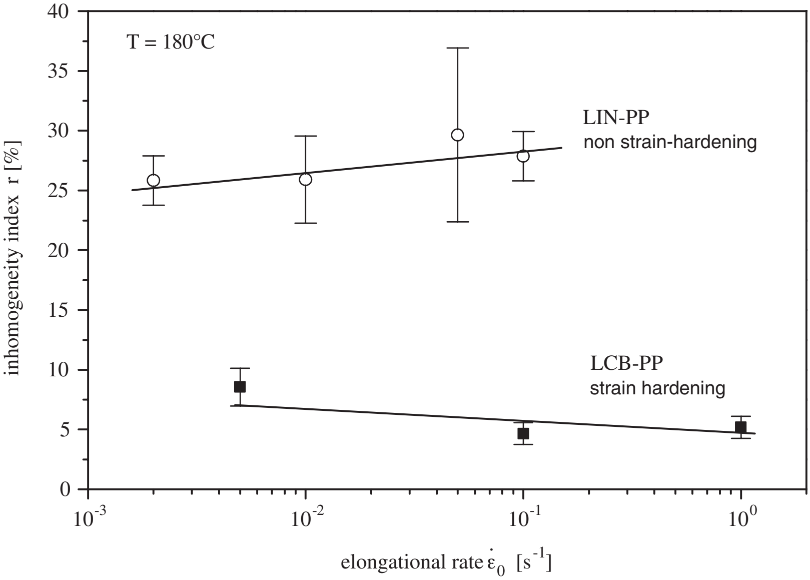

Figure 3.
Inhomogeneity index for a linear and a long-chain branched polypropylene at various constant elongational rates.

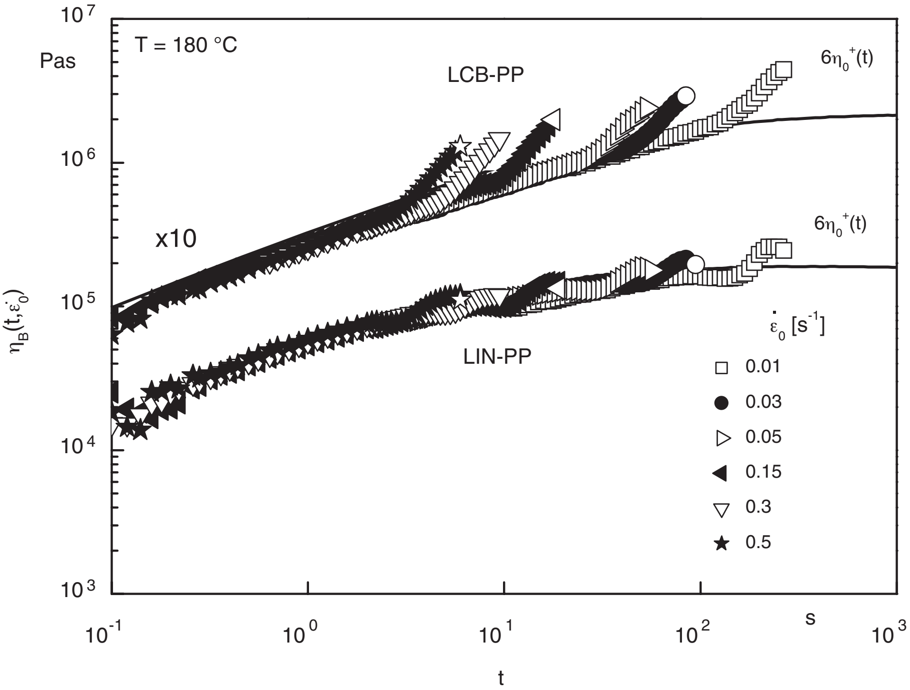

Figure 4.
Biaxial elongational viscosities of the linear and the long-chain branched polypropylene.

are much easier to perform than biaxial ones can be used for a qualitative assessment of strain hardening.

Thermoforming

From the two PP, beakers were thermoformed and the wall thicknesses measured. Their geometry is given in Fig. 5. The results of the wall thickness measured along the mold height clearly demonstrate that the beaker made from LCB-PP possesses a more uniform wall thickness than that from the LIN-PP. As the thinnest part of the wall is decisive for the mechanical behaviour of an item the advantages of the LCB-PP become obvious.

Foaming

For foaming the two PP were blended with each other. The uniaxial elongational viscosities of the blends are represented in Fig. 6.

As expected the elongational viscosities increase with the amount of LCB-PP resulting in a growth of strain hardening. Whereas for 2 wt.% of LCB-PP a viscosity increase is hardly visible it becomes more pronounced at higher ratios of the branched material.

The blends were foamed in a laboratory foaming equipment based on a capillary rheometer which is described elsewhere.[8,12] Azodicarbamide was used as a chemical blowing agent. The feeding temperature decisive for the decomposition of the blowing agent was 200 °C, the foaming temperature 160 °C. Electron micrographs of foamed strands are shown in Fig. 7. It can clearly be seen that the samples foamed from the pure LCB-PP and the LCB-PP with 50 wt.% of the LIN-PP possess a much more homogeneous cell structure and thinner cell walls than those of the LIN-PP and the material with only 5wt.% LCB-PP added. Particularly, in the case of the linear PP areas are discernible where foaming has not taken place.

As a characteristic property of foams their expansion ratios are plotted in Fig. 8. The expansion ratio is defined as the density of the bulk polymer related to that of the foam. The feeding temperature was 200 °C again but the foaming temperatures were chosen as given in Fig. 8. The results allow some interesting conclusions. The first one is that the expansion ratio increases with the percentage of LCB-PP, i.e. with the degree of strain hardening up to a certain level which is around three times higher than that of the linear material. That means strain hardening has a very beneficial effect on the quality of foams.

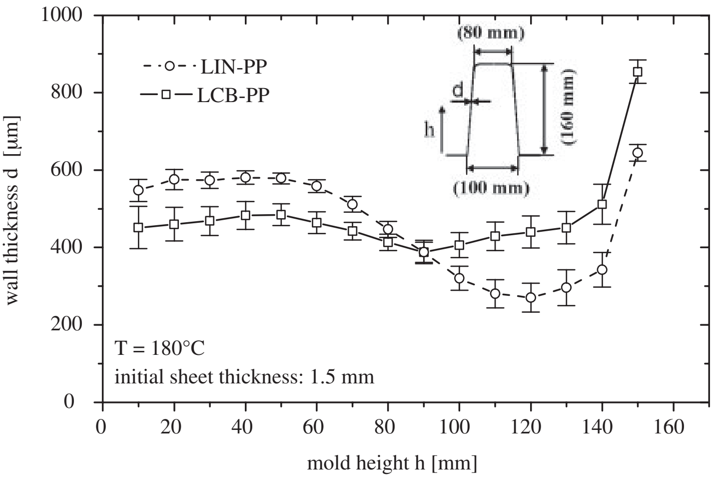

Figure 5.
Uniformity of wall thickness of thermoformed beakers from LIN-PP and LCB-PP.

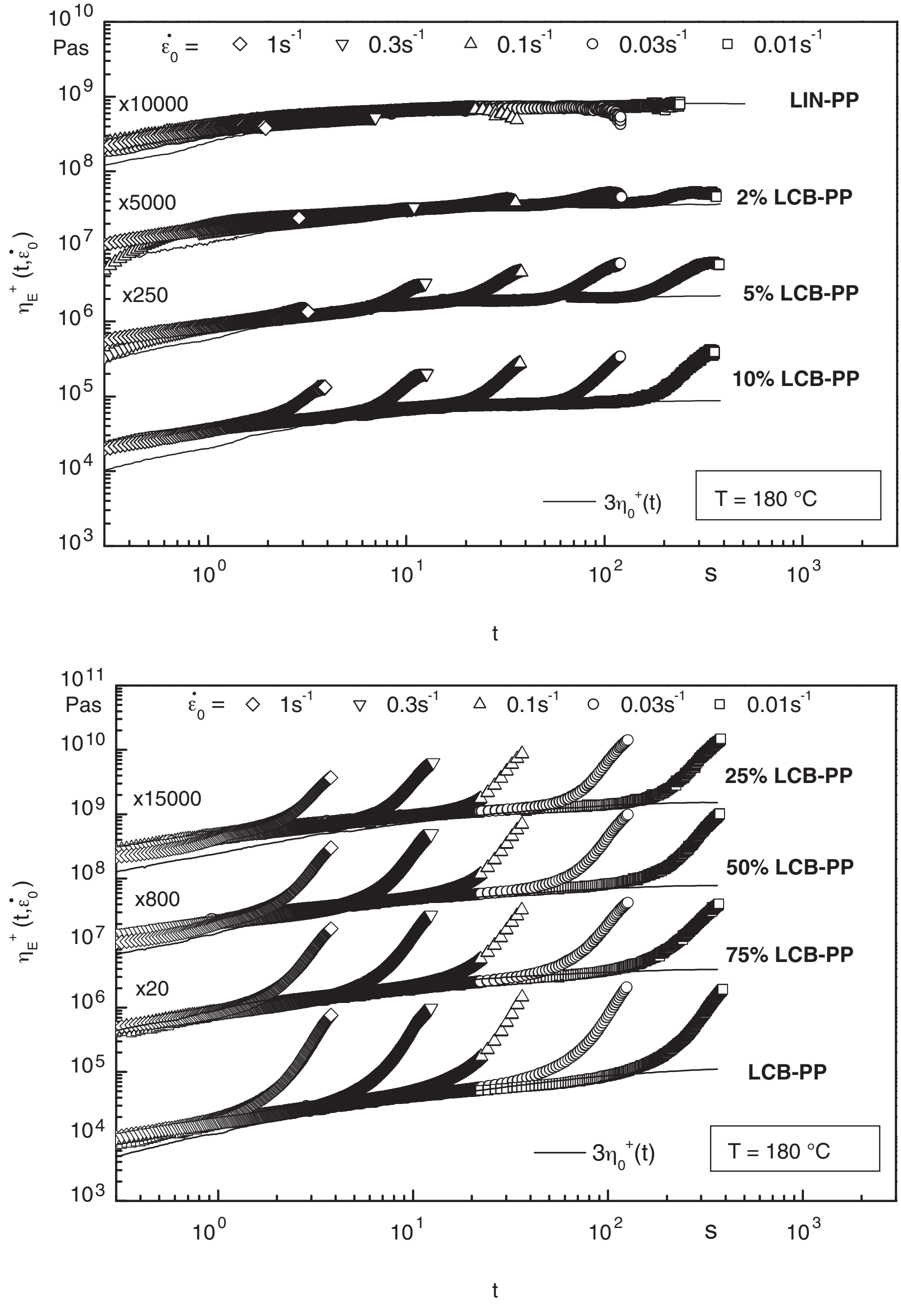

Figure 6.
Elongational viscosities of the blends from the linear and the long-chain branched polypropylene.

Secondly, it is interesting that for LCB-contents higher than 50 wt.% only small additional changes of the expansion ratios are observable. This fact indicates that the addition of 50 wt.% of the LCB-PP may be sufficient to reach the lowest density of the foam. If this result can be transferred to practice it would point out a way for an optimization of costs and performance as the LCB-PP is much more expensive than

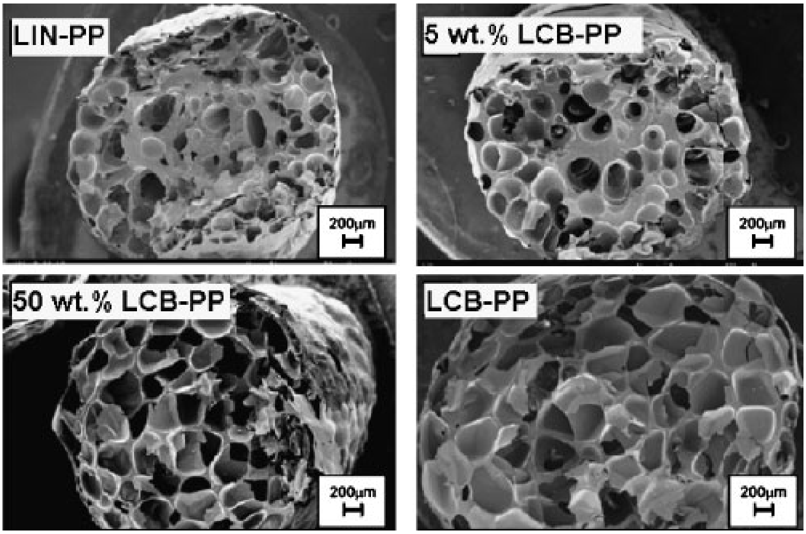

Figure 7.
Foamed strands of various blends of linear and long-chain branched polypropylenes.

the linear PP. The third observation is that the expansion ratio becomes higher with decreasing foaming temperature at least between 160 and 180 °C. This result indicates that the viscosity level may have an influence on the expansion ratio, too, as discussed in more detail by Stange and Münstedt.[9]

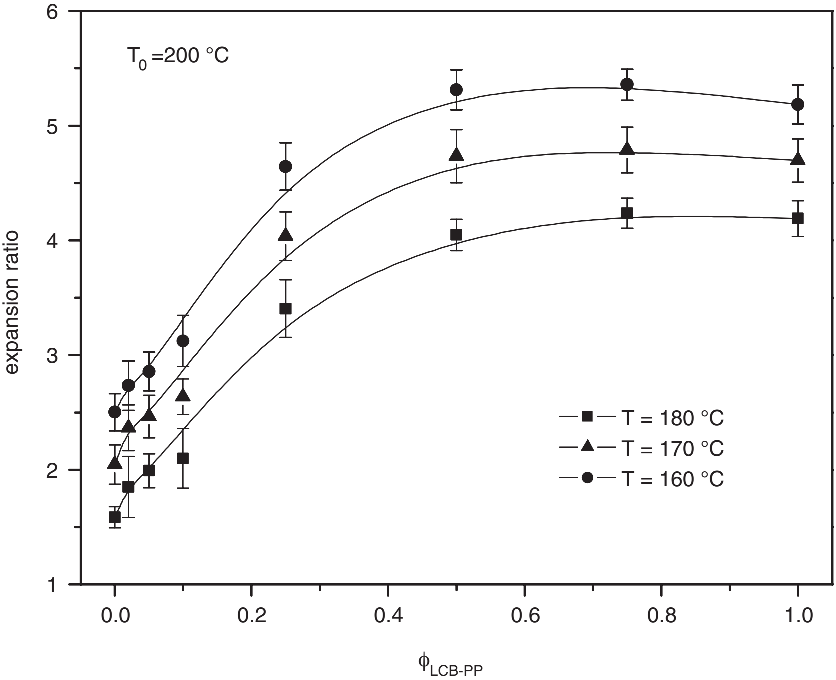

Figure 8.
Expansion ratios of foams from blends of a linear and a long-chain branched polypropylene.

As the shear viscosity of the blends decreases, however, with an increasing amount of long-chain branched polypropylene[9] it becomes evident from Fig. 8 that strain hardening has a decisive influence on the expansion ratio. This finding can very convincingly be understood by the occurrence of strain hardening. Due to the self-healing effect within strain hardening polymers the cell walls can be stretched to a higher extent than in the case of non-strain hardening before they break.

Film Blowing

For the film blowing experiments a LDPE and a LLDPE were used the elongational viscosities of which are represented in Fig. 9.

The LDPE does exhibit a pronounced strain hardening at higher elongational rates which nearly disappears at lower rates. The strain hardening of the LLDPE is just the other way round. It is hardly detectable at strain rates down to 0.1 s^{-1} but attains remarkable values at lower rates. These differences are reflected by the inhomogeneity factor as a function of the elongational rates determined in laboratory stretching experiments as described in Fig. 10.

The first result is that the inhomogeneity index of the elongated LLDPE samples is distinctly higher than that of the LDPE at larger elongational rates which means the LLDPE deforms less homogeneously than the LDPE. This behaviour can be related to the more pronounced strain hardening of the LDPE and is in agreement with the findings on the two polypropylenes (cf. Fig. 3). The much higher scatter in the case of the LLDPE indicates that the deformation process is not as robust as for LDPE. This observation supports the model consideration of a self-healing effect induced by strain hardening. The correlation between the homogeneity of elongation and strain hardening is striking insofar as the results of Fig. 10 mirror the differences in the elongational behaviour of the two polyethylene samples found in Fig. 9 very accurately. Similar to the effect of strain hardening the inhomogeneity indices approach each other at medium elongational rates. At very low rates at which strain hardening is hardly detectable any more for the LDPE its inhomogeneity index even comes to lie above the lowest value measured for the LLDPE.

The film blowing experiments were performed with an equipment described

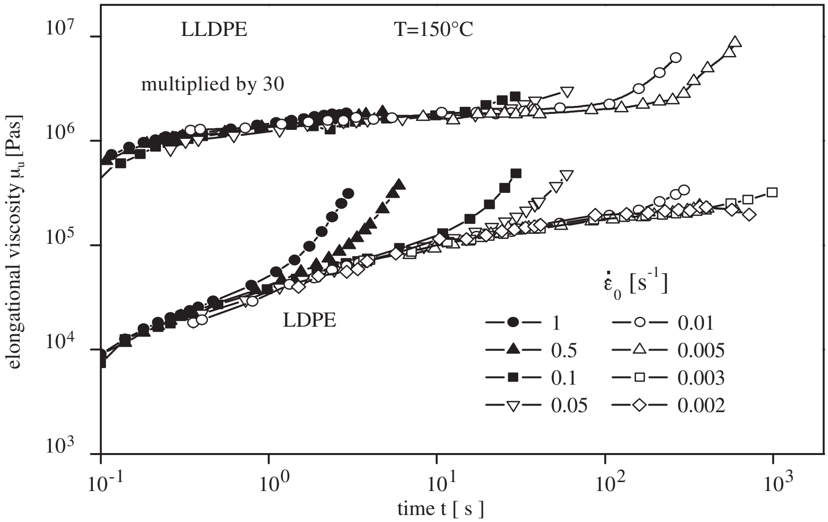

Figure 9.
Elongational viscosities of the linear (LLDPE) and the long-chain branched polyethylene (LDPE). The maximum elongation was $\varepsilon_H \approx 3$.

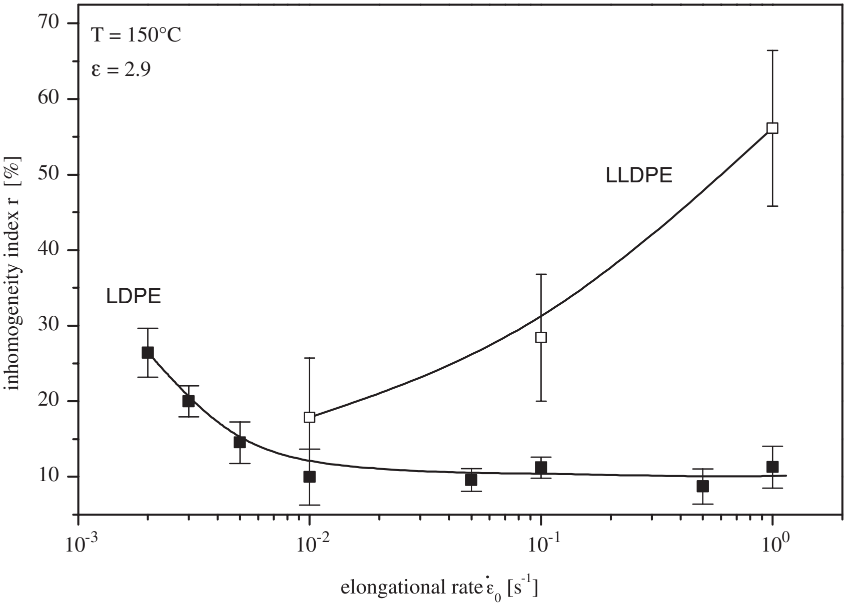

Figure 10.
Uniformity of deformation for the two polyethylene samples stretched in the laboratory apparatus.

in detail elsewhere.[7] The die of the blowing head had a diameter of 36 mm, the slit width was 0.8 mm. Data on the elongational rates and total elongations which occurred during processing can be taken from Kurzbeck.[7] They are in the range of the experimental parameters for the laboratory tests underlying the results of Figs. 9 and 10. The film thicknesses were measured at several positions along the circumference of the film and along the axis. Using the equations (1) and (2) the inhomogeneity index was calculated from the geometrical dimensions.

In Fig. 11 these data are plotted as a function of the take-up ratio for the two

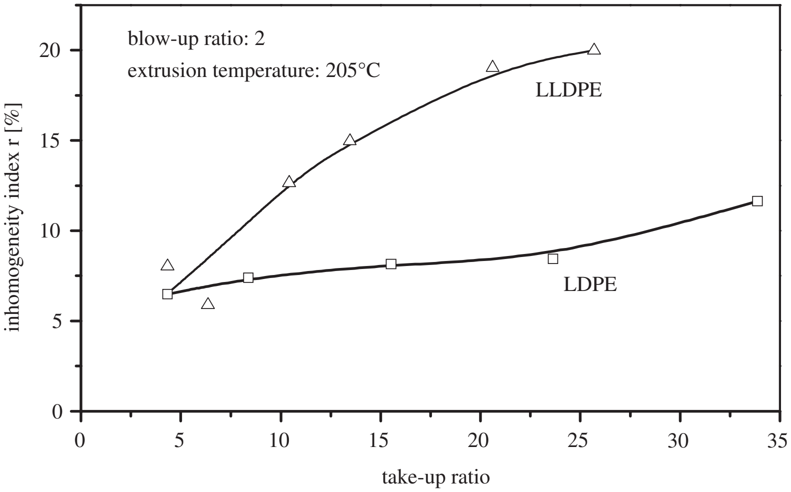

Figure 11.
Uniformity of the thicknesses of films blown from the LDPE and the LLDPE.

polyethylenes at a fixed blow-up ratio of 2. The take-up ratio is defined as the quotient of the film velocity at the frost line to the velocity at the die exit. The LDPE shows a much better homogeneity of the blown films than the LLDPE which correlates qualitatively with the results obtained from the experiments in uniaxial elongation. At the lowest take-up ratio which corresponds to the smallest elongational rate the values for the inhomogeneity are close together. This finding is in a qualitative agreement with the strain hardening behaviour of the two polyethylenes.

Conclusions

Some conclusions can be drawn from the results presented with respect to the advances of long-chain branched polymers in processing operations for which pronounced elongational flows occur. The first one is that long-chain branching leads to a better uniformity of the geometry of processed items. That was shown for film blowing of polyethylene and thermoforming of polypropylene. The better uniformity can be related to strain hardening which occurs for long-chain branched polymers. Strain hardening itself is the base of a kind of self-healing mechanism as the elongational viscosity in strain hardening melts becomes higher if the strain or the strain rate, respectively, increases resulting in a growing resistance to a further deformation of the thinner parts of a processed item.

Strain hardening can rather easily be determined in uniaxial elongational flow using highly developed laboratory equipment. As it could be shown on long-chain branched polypropylene strain hardening found in uniaxial elongation occurs in biaxial elongation, too, at least in a qualitative way. This fundamental result is the base that a discussion of some aspects of processing operations with pronounced biaxial deformation components is scientifically reasonable taking into account the results from uniaxial elongation. As relationships between the uniaxial elongational behaviour and the molecular structure of polymers are established they can be used for the development of materials with beneficial properties for thermoforming, foaming, and film blowing.

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