

# Reactive extrusion and melt spinning—A new technological route to special fibres\*

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This paper outlines the results of an online coupling of a twin screw (TS-) extruder with a melt spinning head. It deals with both theoretical and experimental investigations and the practical realization of such a (up to now rarely used) technological route in melt spinning to produce an elastomeric polyolefin fibre. This paper is a detailed continuation of former presentations (R. Beyreuther *et al.*, in 14th PPS-Meeting, Yokohoma, Japan, June 98, Ext. Abs. S717–718; M. Hoffmann *et al.*, in 15th PPS-Meeting, Hertogenbosch, NL, May/June 1999, Proc. Paper 144; M. Hoffmann *et al.*, *Chem. Fibers Int. (CFI)* **49**(5) (1999) p. 410; M. Hoffmann *et al.*, in Polymerwerkst. '98, Tagungsab., S. 582, Merseburg, Germany, September 1998; R. Lü and H.-G. Fritz, in Polymerwerkst. '98, Tagungsab., S. 572, Merseburg, Germany, September 1998; R. Beyreuther *et al.*, in 3rd ESAFORM Conf. on Mat. Forming, Proc., Stuttgart, Germany, April 2000, p. I-3; R. Beyreuther *et al.*, in Int. Pol. Proc. XI, 1996, p.154; R. Beyreuther, H. Brünig and R. Vogel, in "Polymeric Material Encyclopedia: Synthesis, Properties and Applications," Vol. 6 (CRC Press, Boca Raton, FL, 1996) p. 4061; R. Vogel, G. Schauer and R. Beyreuther, *Chem. Fibers Inter. (CFI)* **45** (1995) p. 268).

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## 1. Introduction

Melt spinning can be characterized as a special case of a polymer formation process. This is based on the enormous surface/volume ratio of the formed fibres during the extremely short period of time which is smaller than 150 ms and where the isotropic melt state changes into the more or less oriented fibre state. Up to now most industrial melt spinning processes have been carried out by means of a single screw extruder. The use of a twin screw extruder (following TS-extruder) coupled with a spinning head of melt spinning equipment is relatively unknown, and publications do not exist in this context. Economical considerations seem to be the reason for this fact: Namely, a TS-extruder requires 1.5 to 2 times higher investment costs at the same productivity compared to a single screw extruder and its automatic control design has to be more sophisticated and consequently more expensive. Nevertheless, theoretical and practical considerations led to the idea and/or the necessity to connect a TS-extruder and a spinning head in the melt spinning process. Technological goals, automatic control problems and a realized melt spinning process of polyolefine elastomeric fibres by means of an online coupled reactive extrusion process will be explained below.

## 2. Technological goals

Spinning experiments with special polymers, modified polymers and polymer mixtures showed in the past that

good homogeneity as well as a smallest possible polymer degradation during the extruder passage are unrenounceable assumptions for the spinnability of the corresponding polymer melt. But, the necessary mixing effect as well as a sufficient homogeneity can often not be reached by means of a single screw extruder. The detour over an additional offline twin screw extrusion step for the homogeneous mixing before the real melt spinning leads to chemical, oxidative and/or hydrolytical damage of the material (molecular weight degradation and shifting of the molecular weight distribution), also in special cases to the dehomogenization. Very often a regranulated polymer is not spinnable in the real melt spinning step (what means a 2nd thermic stress). By means of a TS-extruder it is possible to unite both processes into one continuous extrusion step. Good melt homogeneity is achievable and polymer damage, which could be caused by granulation with the modifier, can be avoided. The last and/or an insufficient melt homogeneity lead usually to the reduction or even to the loss of the polymer spinnability. "Spinnability" in this connection is defined as a continuous, fibre-break-free fast formability of the polymer melt into fibres. Further explanation of this can be found in [1, 2].

In conclusion there are two groups of technological goals which appear favourable or even unrenounceable for the integration of a TS-extruder into a melt spinning process:

1. Melt spinning of fibres from a polymer which has to be modified before the spinning. By using a spinning

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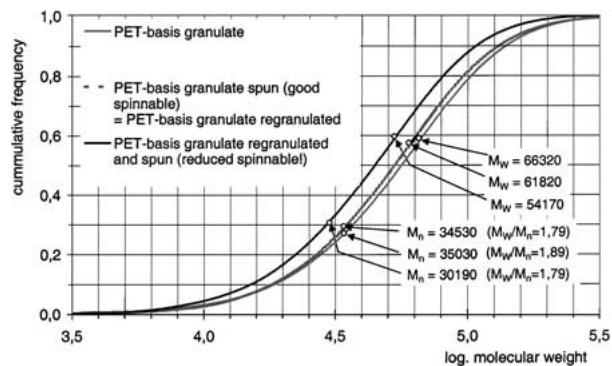


Figure 1 Molecular weight shifts caused by repeated extrusion stages.

head online coupled with a TS-extruder it is possible to combine two processes into one continuous extrusion step [3, 4].

2. The melt spinning of polymers which first have to be treated through a reactive extrusion. In this case it is also the goal to combine two single process steps into one continuous process (reactive extrusion carried out in TS-extruder and melt spinning are usually separated).

The negative effect that regranulation causes to the shift of the molecular weight distribution and—connected with this—to the spinnability of in itself good spinnable basis granules can be demonstrated by means of the Fig. 1. The spinnability has been evaluated on the basis of the fibre breaks at spinning tests under comparable conditions with an industrial near designed lab spinning equipment during 10 minutes. The diagram shows the shift of the molecular weight distribution curve, if a regranulation (e.g. for the additive modification purpose, here realized by means of a Buss-cokneader) of the spin granules took place before the real spin extrusion. Already the relative small reduction of the average molecular weight from  $M_W = 66320$

to  $M_W = 61820$  g/mol through the regranulation step causes a clear decrease of the spinnability. It was also observed that the fibres which were spun after the regranulation (they were thermally stressed two times), suffered a significantly higher molecular weight decrease (from  $M_W = 61820$  to  $M_W = 54170$  g/mol) than the only one time stressed original granules (namely only from  $M_W = 66320$  to  $M_W = 61820$  g/mol). The technological goals named above were realized by the online coupling of a corotating TS-extruder with a spinning head on the lab spinning equipment of the Institute (Fig. 2).

Nevertheless, a particularly meshed automatic control system had to be developed for the combination of twin screw extrusion and melt spinning.

### 3. Meshed automatic control system

An investigation of international data banks CA and DERWENT under the descriptor combination “TS-Extruder and melt spinning” (time period 01/1980 until 06/1998) results in 7 patents [5–11]. These patent announcements describe and claim material and process technological aspects. However, the patents do not deal with possible problems to be solved, if a TS-extruder must be coupled online with a spinning head. The following conditions had to be fulfilled by an automatic control system for such a coupling:

1. The extrusion pressure  $p_E$  between extruder output and the spinning pump input must be constant.
2. The peculiarity of a melt spinning extrusion system is given by the gear pump (spinning pump) at the extruder head which enforces a constant throughput  $th$  through the spinning die and—backwards—simultaneously to the extruder too. This pump is indispensable for a melt spinning process because the fineness of the spun fibres depends directly on it.

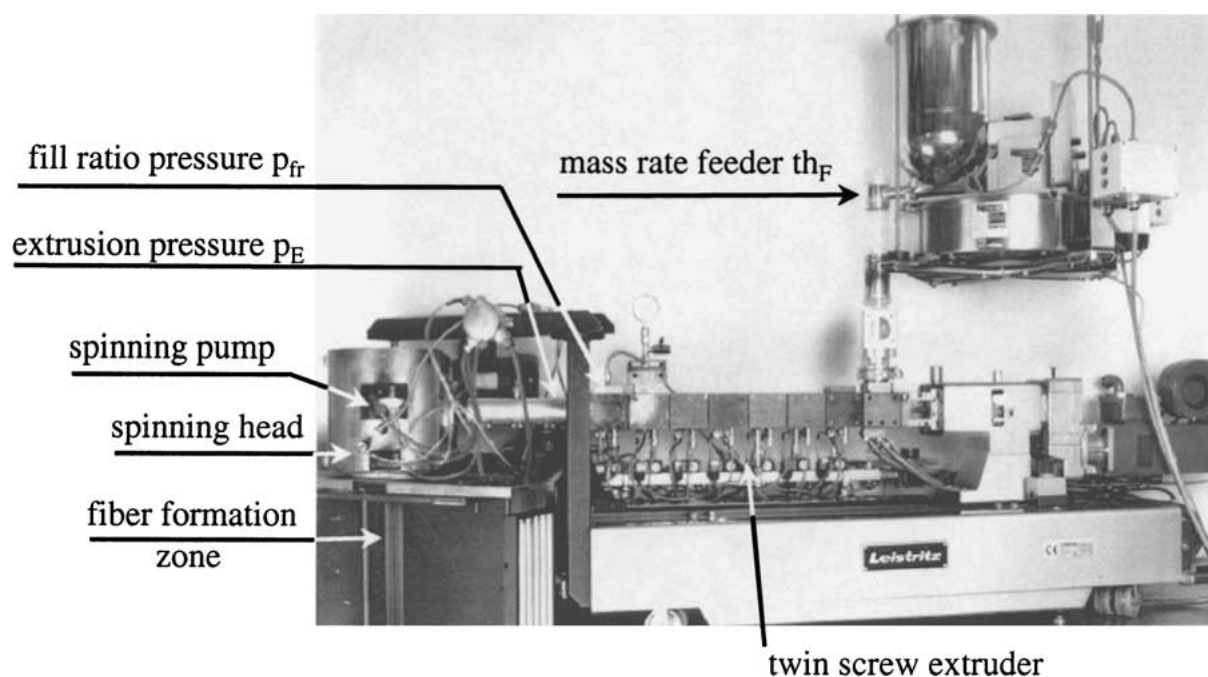


Figure 2 TS-extruder Micro 18 GL-40D (Comp. Leistriz, Nuremberg) coupled with spinning head (practical realization).

3. Because a TS-extruder can only work in a partially filled state, the fill ratio  $FR$  of the TS-extruder must be (generally)  $<100\%$  and also has to be controlled.

4. The mass rate feeder  $th_F$  has to be controlled by the fill ratio  $FR$  as well as by the adjusted throughput of the spinning pump  $th$ .

Considering this conditions two meshed automatic control systems had to be designed: An automatic regulator which controls the extrusion pressure  $p_E$  between the extruder head and the spinning pump by adjusting the screw speed  $rpm$  automatically (PID control; circuit drawn in dotted lines; white box). Additionally an automatic control circuit for the chip mass rate  $th_F$  is necessary. It consists of two regulators in series arrangement in order to control the gravimetric feeding of the polymer pellets. Because a direct measurement of the extruder fill ratio  $FR$  could not be carried out, we used an indirect measurement quantity. We found out that the pressure in the middle of the last extruder barrel, the so called fill ratio pressure  $p_{fr}$ , is a representative value for the fill ratio of the extruder and can be used as main control size for both automatic regulators  $p_{fr}$  and  $th_F$  (circuit drawn in compact lines; grey boxes; Fig. 3).

A series of jump time transfer function measurements at a lab TS-extruder (Micro 18 GL 40D from the *Leistritz Company*) coupled with the spinning head were carried out to determine the time transition behaviour between the adjustable control input variables of the regulators (extruder screw speed  $rpm_E$  and feeder screw speed  $rpm_F$ ) and the most important extruder output variable pressure  $p_E$ . Figs 4 and 5 show  $p_E$ -

effects to  $rpm_E$ - or  $rpm_F$ -jumps: The evaluation of the different time response functions showed: The cause-effect-relation between the extruder screw speed  $rpm_E$  and the extrusion pressure  $p_E$  is a proportional action with first-order factor (proportional-action factor  $K_P = \Delta p_E / \Delta rpm_E = 1.9 \text{ bar/rpm}$ ; delay time constant  $T = 1.1$  until  $1.5 \text{ min}$ ); by contrast the cause-effect-relation between the feeder screw speed  $rpm_F$  and the extrusion pressure  $p_E$  is an integral-action with dead time. The integral-action factor amounts at our lab extruder  $K_I = \Delta p_E / t \cdot \Delta rpm_F = 0.3 \text{ bar/min-rpm}$ , the dead time  $T_d = 0.3$  until  $0.7 \text{ min}$ . On this basis it was possible to qualify the signal cause-effect-diagram of the meshed automatic control system (Fig. 6).

The results received by the jump response time function measurements enabled us to optimize the setting of the three automatic regulators for  $p_E$ ,  $p_{fr}$ , and  $th_F$ .

Fig. 7 shows the results of time functions for the observed values extrusion pressure  $p_E$ , and fill ratio pressure  $p_{fr}$ , and the connected and adjusted values extruder screw speed  $rpm_E$ , and feeder mass rate  $th_F$  [18].

#### 4. Reactive spinning of elastomeric polyolefin fibres

The newly developed equipment was used for the realization of a tailor-made polymer modification and a fibre formation in a single extrusion step.

A series of tests was performed where it was decided to carry out a peroxide generated graft polymerization of organosilane on the ethylene-octene copolymer inside a corotating TS-extruder. Fig. 8 shows the material concept where the peroxide generated

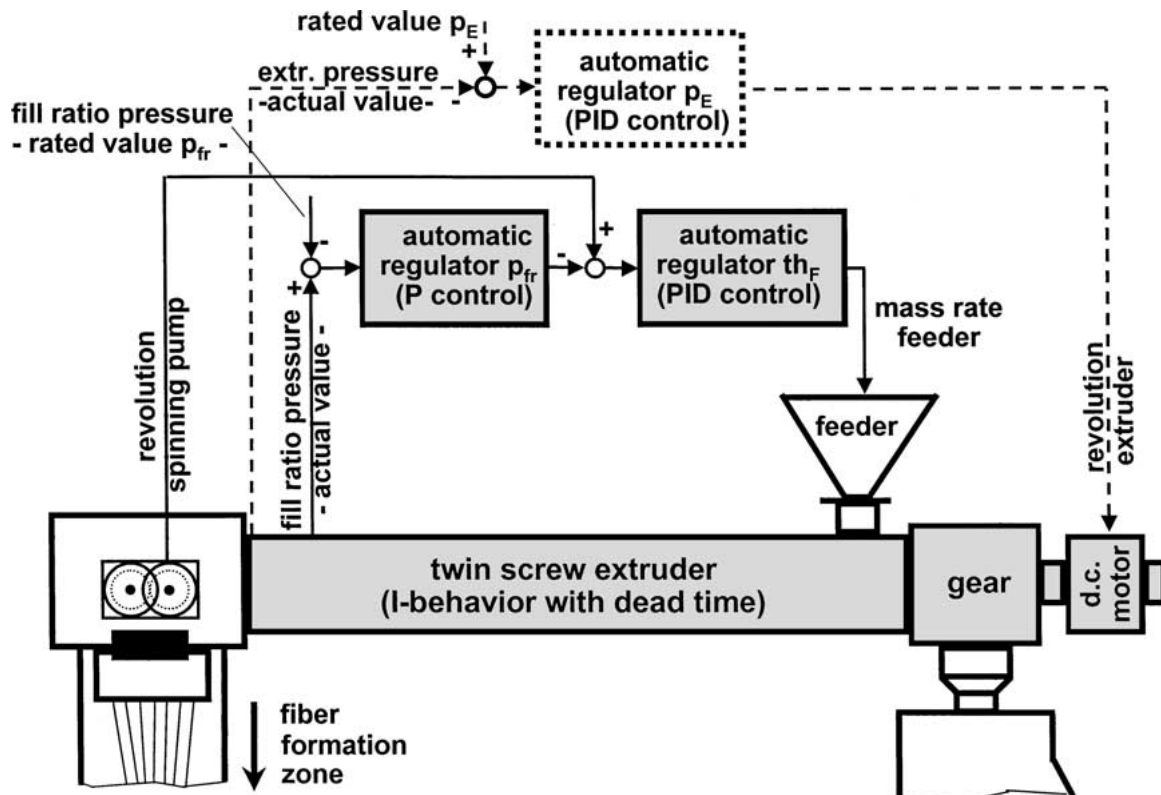


Figure 3 Scheme of the designed meshed automatic control system.

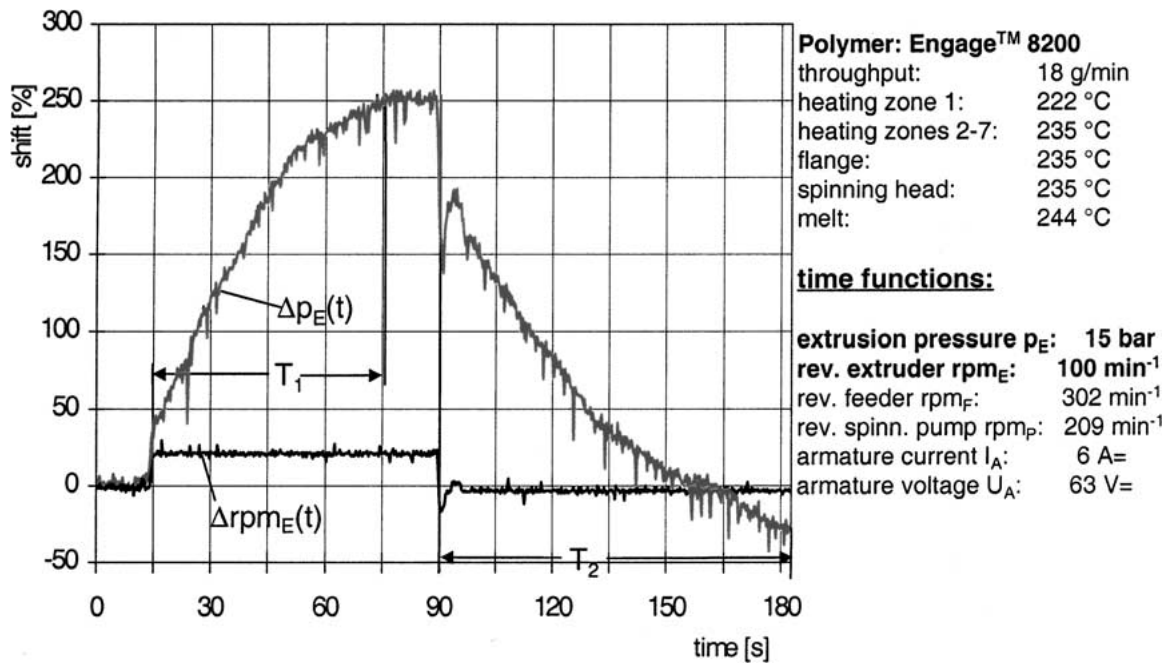


Figure 4 Jump time transfer function of the extrusion pressure  $p_E$  after negative and positive extruder number of revolutions adjustments  $\Delta rpm_E = \pm 20\%$ .

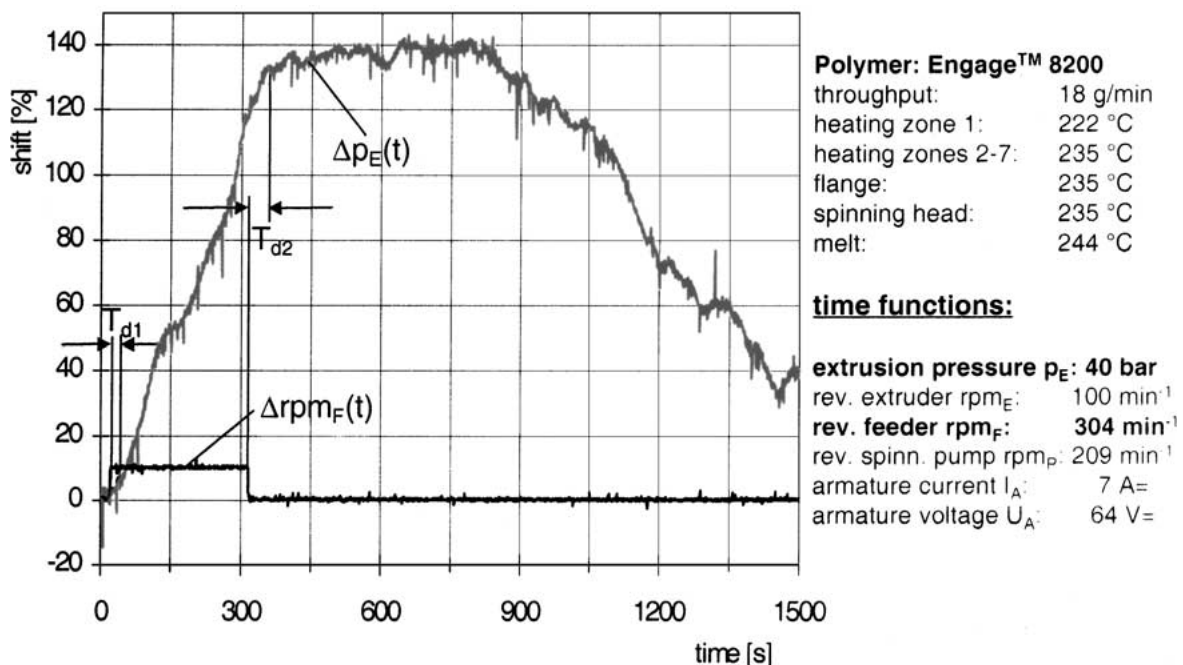
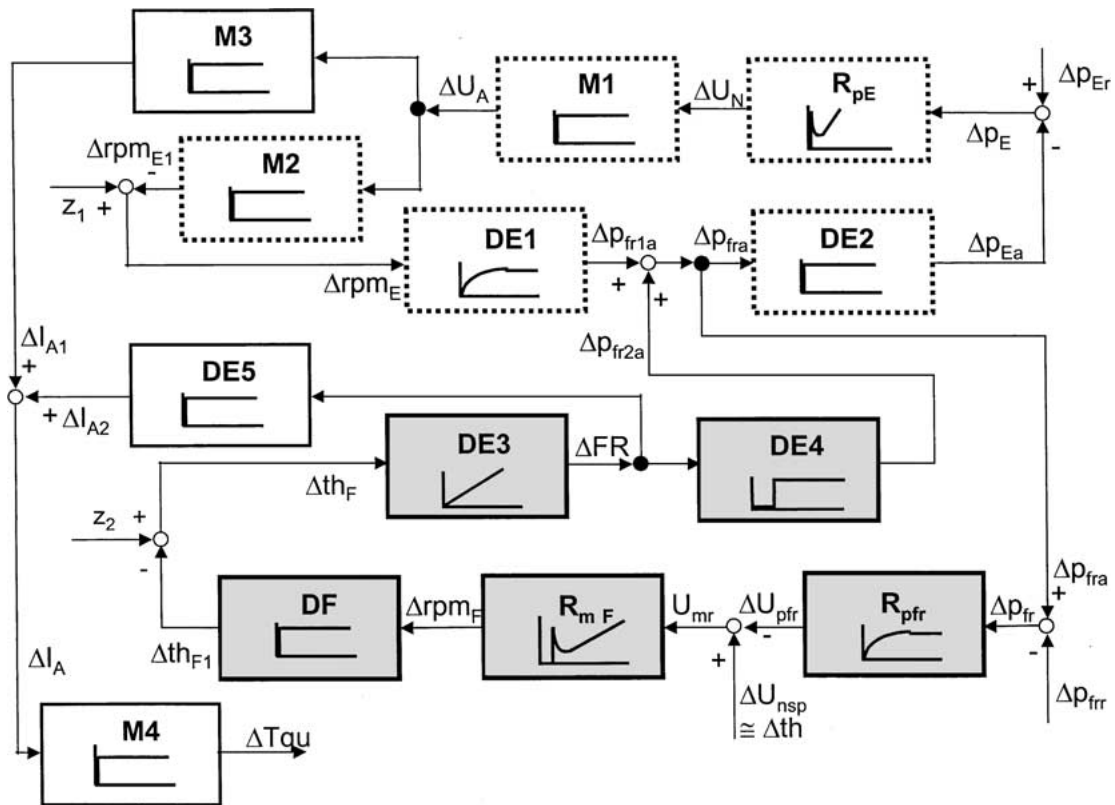


Figure 5 Jump time transfer function of the extrusion pressure  $p_E$  after negative and positive feeder screw number of revolutions adjustments  $\Delta rpm_F = \pm 10\%$ .

graft-polymerization was executed in the Leistritz Micro 18 TS-extruder with a L/D ratio of 40 (Fig. 2) [12]. In former presentations [1, 2, 13] it was proved that the basic material (Engage™ types of Dow Du Pont Elastomers) which was investigated in this paper meets all physical and rheological requirements to be formed into a fibre through a melt spinning process. This metallocene-catalysed material possesses a well defined side chain structure, which is reached through the homogeneous incorporation of octene in the ethylene main chain. Hence with an increasing octene content the lamellae folding of the saturated chain molecules is inhibited and low crystallinity polymers with an

elastomeric behaviour are achieved [14]. The granular morphology can be imagined as a deformable network which is linked through physical network points, the crystalline domains. The thermally instable crystals melt near above room temperature (melting point  $T_M \approx 60^\circ\text{C}$ ), which is responsible for the low thermal stability of the melt spun fibres. Concerning the melt modification one had to take care that no peroxide or water induced precrosslinkage of the melt would appear, because, and this is proved in this paper, the melt-spinnability could be negatively influenced. The saturation of the macroradicals through inter- and intramolecular C–C bonds and through the grafting of



The abbreviations mean:

DE1 ... DE5	signal transfer glieder of the TS-extruder
M1 ... M4	signal transfer glieder of the extruder drive motor
DF	signal transfer glied feeder screw
$R_{pE}$	regulator for the extrusion pressure $p_E$
$R_{pfr}$	regulator for the fill ratio pressure $p_{fr}$
$R_{mrF}$	regulator for the feded mass rate $th_F$
$\Delta rpm_E, \Delta rpm_{E1}, \Delta rpm_F$	changes of the extruder number of revolutions change of the feeder screw number of revolutions
$\Delta p_E, \Delta p_{Ea}, \Delta p_{Er}$	changes of the extrusion pressure
$\Delta th_F, \Delta th_{F1}$	changes of the feded mass rate
$\Delta FR$	change of the fill ratio
$\Delta p_{fr}, \Delta p_{fra}, \Delta p_{frr}, \Delta p_{fr1a}, \Delta p_{fr2a}$	changes of the fill ratio pressure
$\Delta U_{pfr}$	change of the signal voltage depending on the fill ratio pressure
$\Delta th$	change of the spinning pump number of revolutions resp. through-put
$\Delta U_{mr}$	change of the reference input for the regulator $R_{thF}$
$\Delta U_{nsp}$	change of the signal voltage depending on the spinning pump number of revolutions
$\Delta U_N$	change of the shunt voltage of the extruder drive motor
$\Delta U_A$	change of the armature voltage of the extruder drive motor
$\Delta I_A, \Delta I_{A1}, \Delta I_{A2}$	changes of the armature current of the extruder drive motor
$\Delta T_{qu}$	change of the torque of the extruder drive motor
$z_1$	disturbance for the extruder number of revolutions
$z_2$	disturbance for the feded mass rate

Figure 6 Signal cause-effect-diagram of the meshed automatic control system; grey dotted control circuit: control of the extrusion pressure  $\Delta p_E$ ; grey colored control circuit: control of the fill ratio pressure  $p_{FG}$ .

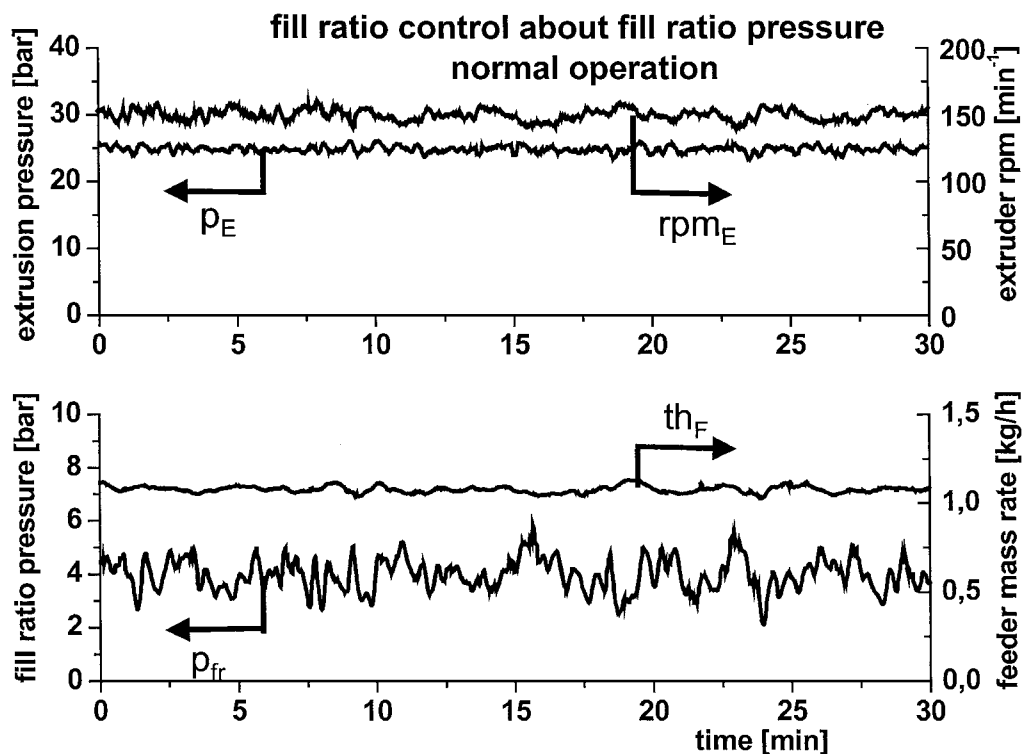


Figure 7 Time functions of the extrusion pressure  $p_E$ , extruder number of revolutions  $rpm_E$ , fill ratio pressure  $p_{fr}$  and feeder mass rate  $th_F$  for best adjustments of the three regulators.

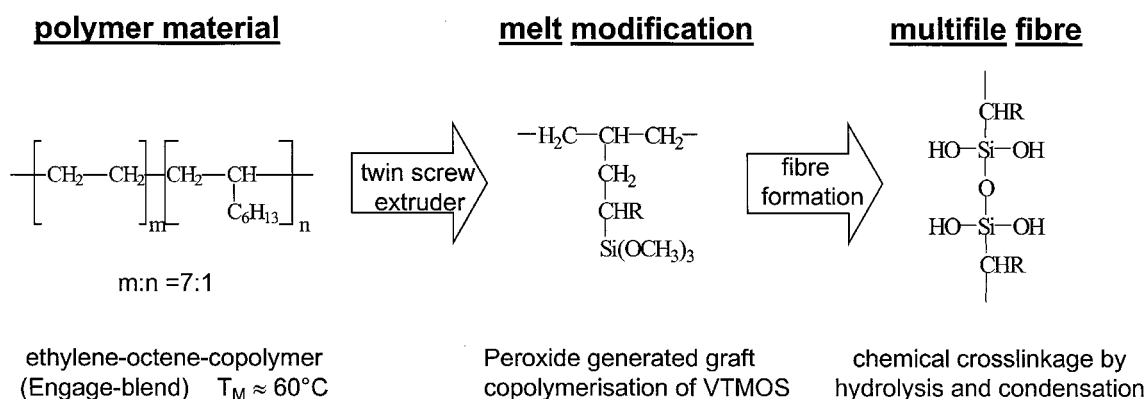


Figure 8 Basis concept of reactive extrusion and melt spinning of ethylene-octene-copolymers.

VTMOs are competitive reactions. In order to avoid the harmful gel formation, numerous rheological experiments had to be carried out and styrene was introduced as a grafting control agent. The generation of homologue blends which were obtained from Engage<sup>TM</sup> types with different flow behaviour made it possible to control the rheological properties of the basic blend as well as the rheological behaviour of the functionalised material [15]. It was surprisingly found that a higher polydispersity through the blending step did not worsen the spinnability. The silane-crosslinking of polymers is a sequential reaction, executed in two steps. The functionalization of the e/o-copolymers happens in the TS-extruder. Then the melt is extruded through the spinneret and under the variation of the spinning parameters (in this paper mainly the spinning velocity) wound up into fibres. The chemical crosslinking is executed in the solid filaments through siloxane link-

ages (Si-O-Si). The bobbins were therefore placed in a water based crosslinking solution which was mixed with 1.5 percent by weight of a tin catalyst to accelerate the hydrolysis and condensation reaction at room temperature.

#### 4.1. Experimental findings

Distributive shear sections of the TS-extruder were important factors influencing the achievable product quality and the long-lasting spinning-process. Through a high number of flow divisions one could assure that there was a constant concentration of the reactive modifying agents and the necessary residence time, primarily for the degradation of the peroxide was established. The alternating arrangement of distributive shear elements and conventional conveying elements reduced the danger of a high energy dissipation which could

have led to an undesired heating-up of the melt and in consequence of this effect to an accelerated peroxide degradation ( $\Rightarrow$  inhomogeneities). Furthermore an optimised crosslinking formulation had to ensure that no peroxide initiated precrosslinkage of the melt could occur. A devotalisation unit had to extract low molecular weight agents, which were for example received from nonreacted VTMOs or from peroxide degradation. A schematic illustration of the used TS-screw configuration can be found in Fig. 9.

The sensitivity of the melt properties concerning the addition of the peroxide are demonstrated in Fig. 10. The complex viscosity  $\eta^*$  was determined by dynamic-mechanical measurements. The corresponding connections between the complex shear modulus ( $G^*$ ) and the storage ( $G'$ ) and respectively the loss modulus ( $G''$ ) on one hand and the viscosity function ( $\eta^*$ ) on the other hand are described in Equations 1 and 2:

$$G^*(\omega) = G'(\omega) + iG''(\omega) \quad (1)$$

$$G^*(\omega) = i\omega\eta^* \quad (2)$$

where  $\omega$  = measuring frequency in rad/s.

The homologue (basic) blend consisted in each case of 50 percent by weight of Engage™ 8200 and Engage™ 8400. This basic blend had the lowest viscosity at zero shear rate (Fig. 9) and the highest viscous part in the viscoelastic deformation behaviour (highest  $\tan \delta$  in Fig. 10). Concerning the selected recipe formulation (3 phr VTMOs, 0.12 phr styrene) an increasing viscosity at zero shear rate and an enhancement in elastic deformation with increasing DHBP-content could be detected simultaneously. This effect finally (DHBP-content > 0.12 phr) led to inhomogeneities in the filaments, to a significant swelling effect and the onset of melt rupture at the spinneret. This finding could be explained with an increasing VTMOs grafting-rate (proved by NMR investigations) as well as a growing unintentional peroxide curing of the melt [16]. This observation also coincided with an unwanted pressure increase in front of the filter of the spinning

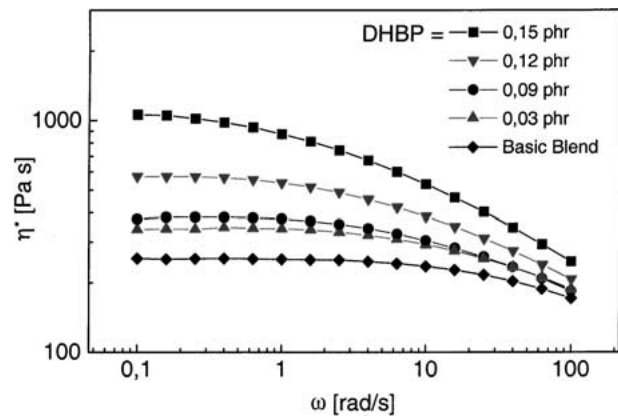


Figure 10 Melt viscosity  $\eta^*$  as a function of shear frequency  $\omega$  at variable DHBP-contents of functionalized e-o-copolymer melts (Engage™ 8200-Engage™ 8400: 50/50, 3 phr VTMOs, 0.12 phr styrene).

die (e.g.: at 0.15 phr DHBP > 100 bar/h), which was obviously caused by gel particles. These particles also led to a decreased viscous deformability of the melt (Fig. 10: increased elasticity) and meant a reduced maximum spinning velocity. Only the functionalized e-o-copolymers in the range of 0.03 phr and 0.09 phr DHBP were capable of producing fibres in broad technological diversity where in a one-stage process no significant pressure increase occurred. Through a peroxide concentration lower than approximately 0.08 phr, the desired thermal stability was not reached. It was found that a gel content of 55% (determination through hot extraction in xylene) was necessary to obtain the demanded temperature performance. Fig. 12 shows the impact of grafting on the molecular weight. An increase in weight average could as well be detected as a broadening in molecular weight distribution through the enhancement of DHBP-content. Moreover an increase in high-molecular weight content was found. This effect appeared because of the higher grafting-rate and the growing peroxide curing and was responsible for the higher melt elasticity (Fig. 11).

On one hand the mechanical properties of the functionalized elastomeric fibers were determined mainly

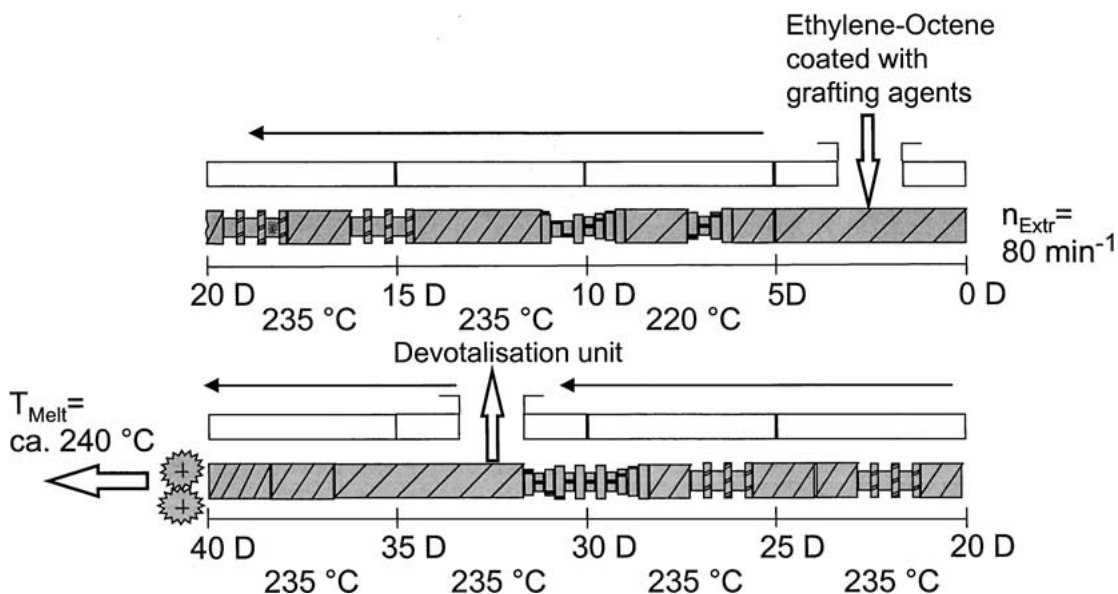


Figure 9 Screw Configuration and barrel temperatures of TS-extruder Micro 18 GL-40D (Leistritz, Nuremberg).

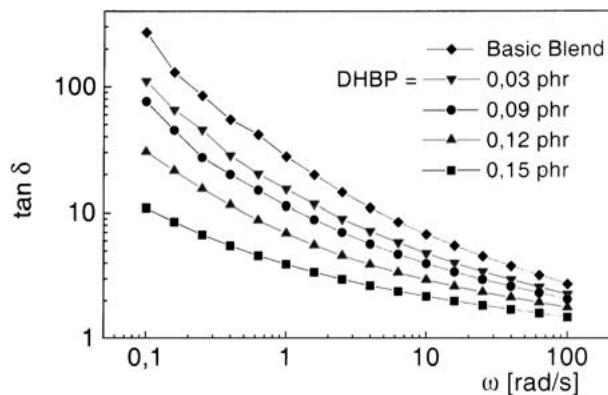


Figure 11 Influence of DHPB-content on viscoelastic behaviour ( $\tan \delta$ ) of functionalized e-o-copolymer melts (Engage™ 8200-Engage™ 8400: 50/50, 3 phr VTMOs, 0.12 phr styrene).

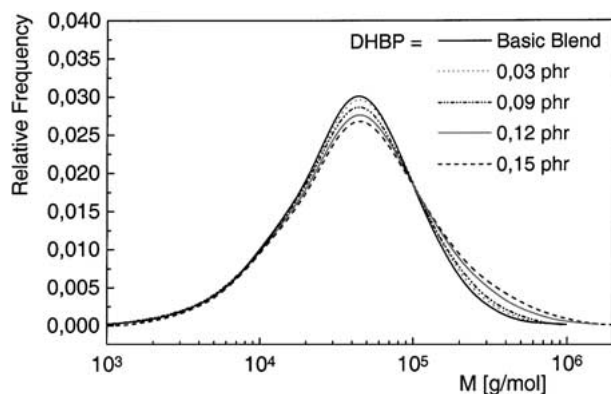


Figure 12 Influence of DHPB-content on molecular weight of functionalized e-o-copolymer melts (Engage™ 8200-Engage™ 8400: 50/50, 3 phr VTMOs, 0.12 phr styrene).

by the orientations of the amorphous phase, which were implemented in the melt-spinning process and could be detected by photoacoustic spectroscopy [16]. On the other hand the degree of functionalization and because of this the resulting gel content were other factors influencing the mechanical properties. An increasing gel content reduced the elongation at break, but led up to gel contents of about 70% to a growing tensile strength. The physical breaking stress of these fibres was independent from spinning velocity and in addition to that almost independent from gel content. Gel contents over 70% in combination with the orientation of the amorphous phase did significantly reduce the elongation at break and the tensile strength. The material behaviour of these highly crosslinked fibres resembled those of a thermoset material and could not be accepted as an elastomeric fibre anymore [2, 12, 16]. Further, these fibres did not offer a better thermal stability in comparison with those of 60% gel content [17].

Concerning the mechanical properties, an optimum gel content should influence the tensile-elongation behaviour through the additional chemical junction points in a positive way. This could be realized through a higher elongation at break or alternatively through a better tensile strength what finally should lead to an increased physical breaking stress. As well as the desired improvement of the mechanical properties it was intended to raise the thermal stability. Fig. 13 pro-

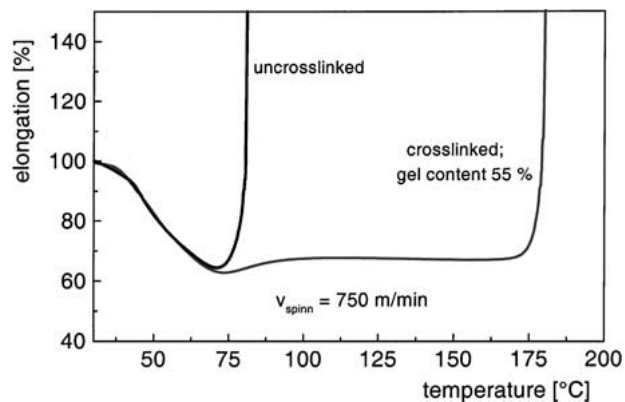


Figure 13 Improved thermal properties by means of chemical crosslinking: Functionalized and crosslinked e-o-copolymer fibres (Engage™ 8200-Engage™ 8400: 50/50, 3 phr VTMOs, 0.12 phr styrene, 0.086 phr DHPB).

vides information about a thermal-mechanical analysis. The expansion of a prestressed sample (0.025 cN/tex) was measured in a chamber that is heated simultaneously with a constant heating rate (10 °C/min). The comparison of the uncrosslinked and the crosslinked fibre clarified the significant shift of the softening temperature from 70 °C to 180 °C through the chemical network. Mainly due to the partial orientation of the amorphous phase the fibres are exposed to a thermal shrinkage which occurred parallel to the melting of the crystalline domains. The siloxane network was not able to inhibit the shrinkage. The e-o-copolymer fibres functionalised with the following crosslinking formulation (3 phr VTMOs, 0.12 phr styrene, 0.086 phr DHPB) led to a gel content of 55% and offered improved tensile behaviour through the silane crosslinking ( $\sigma_{\text{phys, funct.}} = 170 \text{ MPa} \Rightarrow \sigma_{\text{phys, crossl.}} = 220 \text{ MPa}$ ) and the desired thermal performance.

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