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(54) Method for the preparation and regulation of thermobonding skin-core type polyolefin fibers and of nonwoven fabrics made therefrom

(57) The first object of the new innovation is both to improve and regulate the production conditions for skin-core type polyolefin fibers so that the product fibers have better physical characteristics than before. The second object of the innovation is to manufacture from the said fibers nonwoven-fabrics with strength and softness characteristics that are better than before.

The method is especially adapted for large-scale productional melt spinning apparatuses having a short cooling system.

One part of the method is aimed at controlled molten-state polymer oxidation and the other part at the control and modification of the molecular weight distribution of the said polymer, by adding thereto, if necessary, prior to the spinning nozzle, a very short chain polymer of the same quality.

Characteristic features of the regulation method are in addition

- a low draw ratio, temperature and nozzle diameter at spinning,
- measurement of the dynamic deformation of the molten filament as a function of time and distance, in order to ensure the supply of oxygen to the filament in the correct place, quantity and temperature,
- carrying out the oxidation of the filament using an oxidation nozzle separate from the quenching nozzle as a targeted oxidation and, if necessary, using oxygen enriched air
- increase of the dispersion value of the molecular weight distribution of the product filament when the molecular weights decrease as the oxidation degree increases,
- decrease of the thermobonding temperature for the product fibers, regulation of the product fabric strengths and their relationship as a function of the degradation degree of the polymer.

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Description

[0001] A first object of the present innovation is to both improve and regulate as well as monitor the manufacturing conditions of skin-core type polyolefin fibers so that the product fibers will have improved physical characteristics. A second object of the innovation is to prepare from the said polyolefin fibers nonwoven fabrics with improved strength and softness characteristics.

[0002] The preparation and regulation method according to the new innovation is based on substantially improving and regulating the polymer molecular chain degradation process following molten state autogenous oxidation of the surface layer of spinning fibers. The method is applied especially to high-capacity meltspinning apparatuses having a short cooling system.

[0003] The object of the invention is thus a method for regulating the oxidative degradation of the molecular chains in the surfaces areas of molten polymer filaments, which method is applicable in a polyolefin, especially a polypropylene shortspinning system for the production of filaments, according to which the stabilized polymer is extruded and melt spun and the spinning filaments formed are oxidized and quenched, the method being characterized in that

- the oxidation of the molten spinning filament is carried out as a targeted oxidation by directing an oxidizing gas onto the filament bundle from an oxidation nozzle which is arranged separately from the quenching nozzle,
- under unchanged spinning conditions, an equation of the form MFI = c_1v_{02} - c_2v_i + c_3, is used as the regulation equation in the targeted oxidation for defining the level of oxidative degradation, in which equation
  MFI is the melt index value of the polymer, which can be replaced by the value for the spinning melt viscosity corresponding to low shear rate, v_{02} is the velocity of the oxidizing gas multiplied with the oxygen partial pressure, that is the partial pressure velocity, v_i is the velocity of the quenching gas, c_1, c_2, and c_3 are experimentally determined, polymer- and process-specific constants, the oxygen partial pressure velocity being used for regulating, in addition to the molecular chain degradation of the polymer surface area of the filament, the magnitude of the dispersion of the molecular mass distribution.

[0004] In the above equation, the constant c_1 is a function of the position of the oxidation nozzle both with respect the spinning nozzle and the filament bundle, the dimensions and temperature of the oxidizing gas jet, the spinning deformation of the melt filament; the constant c_2 is a function of the position of the quenching gas nozzle, the dimensions, the composition, the temperature of the quenching gas jet; the constant c_3 is a function of the level of oxidative degradation of the filament caused by the quenching gas phase, the nozzle diameter, the spinning temperature, the molecular weight distribution of the polymer matrix, and the level and type of additive addition.

[0005] According to a preferred embodiment, a short-chain polyolefin of the same polymer type, especially polypropylene, is added to the starting polyolefin, especially polypropylene having a melt index in the range of 350 - 800 and molecular mass distributions in the range of M_w = 125 000 - 95 000, M_n = 35 000 - 20 000 and D = 3.5 - 5.0, the quantity added preferably being at the most 15 % by weight of the supplied polymer.

[0006] According to a further embodiment, in addition to the conventional regulation of the temperature and velocity of the quenching gas phase, the molecular chain degradation occuring during quenching of the molten polymer filament is regulated by regulating the oxygen partial pressure of the quenching gas phase.

[0007] According to the invention, the thermal molecular chain degradation of the molten polyolefin can be regulated in the extruder by regulating the melt temperature and extrusion delay time, especially so that the polyolefin is extruded in a temperature range of 250 - 290 °C, the delay time of the spinning melt in the extruder and the ducts being 5 - 15 minutes.

[0008] In the method, the melt index value of the polymer fed to the extruder is preferably 1.5 - 15, and the values for the molecular mass distributions are in the range of M_w = 500 000 - 240 000, M_n = 65 000 - 50 000 and D = 7.0 - 5.0.

[0009] The molten filament is preferably quenched under conditions, where the volume, velocity and temperature of the quenching gas are in the range of 400 - 1100 Nm^3/h, 20 - 60 m/s and 25 ± 5 °C, respectively, the amount of polymer supplied being 20 - 40 kg/h per nozzle plate.

[0010] According to one embodiment, a gas poor in air and free oxygen, such as a combustion gas mixture, is used as the quenching gas, the oxygen partial pressure being in the range of 0.01 - 0.21 bar.

[0011] In the method, a product filament is preferably obtained which after quenching has melt index and molecular mass values in the range of 25- 50, and M_w = 185 000 - 200 000, M_n = 40 000 - 50 000.

[0012] According to a further preferred embodiment, the quantity, velocity, temperature and oxygen partial pressure of the oxidizing gas fed to the oxidation nozzle are 0.01 - 0.8 Nm^3/h, 0.1 - 48 m/s, 25 - 60 °C and 0.21 - 0.98 bar, respectively, the constant c_1 for the oxygen partial pressure velocity in the regulation equation being maintained in the range c_1 = (-0.2) - (+2.0).

[0013] The amount and velocity of the quenching gas is preferably regulated so that the tensile strength applied to the melt filament at the solidification point is below the value of approximately 30 mN/m^2, whereby, depending on the spinning nozzle diameters (0.70 - 0.25 mm), at a nozzle plate capacity of 30 - 32 kg/h and a spinning melt temperature of 285 - 290 °C, the amounts and velocities (25 °C) of the quenching gas are 350 - 750 Nm^3/h and 20 - 45 m/s, and are relative to these values at other spinning conditions, and whereby the polymer-specific constant c_2 of the regulation equation varies in the range $c_2 = 0 - 3$. The constant c_3 typically has a value ≥ 5.

[0014] According to one embodiment, for producing layers of desired thickness at the surface of a spinning filament having a very low molecular weight (polymerization degree:a few monomers) and correspondingly melting at a very low temperature, the number average molecular mass values of the filament polymer is reduced at the most by 30 % and its dispersion values are increased at the most by 40 % from the values prior to nozzle oxidation, by using an oxygen partial pressure velocity in the oxidation gas and at the same time an oxygen partial pressure correspondingly within the range 0.1 - 25 m/s and 40 - 100 % by vol. O_2 and simultaneously preventing, by regulating the velocity of the quenching air, an increase of the maximum values for the filament tension above appr. 30 mN/m^2.

[0015] In the method according to the invention, the oxidation nozzle for the filaments is suitably adjusted into the position $\alpha = 5\text{-}20$ °, $x = 60 \pm 5$ mm, $y = 25 \pm 5$ mm, wherein α is the angle between the central plane of the oxidazing gas jet and the spinning nozzle plane, x and y are the distances of the center line of the free opening area of the oxidation nozzle from the vertical central plane of the polymer spray (x) and the spinning nozzle plane (y), and the filament quenching nozzle is adjusted in the position: $\alpha = 25 \pm 3$ mm, $x = 50\text{-}75$ mm, $y = 40\text{-}50$ mm, wherein α is the angle between the central plane of the quenching gas jet and the spinning nozzle plane, x and y are the distances of the center line of the free opening area of the quenching nozzle from the vertical central plane of the polymer spray (x) and the spinning nozzle plane (y).

[0016] Also, when oxidizing using the oxidation nozzle in the position $\alpha = 2 \pm 1°$, $x = 32 \pm 5$ mm, $y = 2 \pm 1$ mm in the immediate vicinity of the plane of the spinning nozzle surface, the spinning nozzle is preferably internally heated, for example using an effect of 0.25 kW/kg of weight unit of the nozzle plate to prevent the nozzle from cooling.

[0017] The invention also concerns an apparatus for the regulation of the oxidative degradation of the molecular chains in the molten polymer filament surface areas of polyolefins, especially polypropylene, in a filament production method, comprising a melt spinning device with spinning nozzles, and means, especially a quenching nozzle for quenching the polymer filaments, which apparatus is characterized in that it contains means for oxidizing the polymer filaments, especially an oxidation nozzle, which is separate from the quenching means.

[0018] Preferably the size of the free openings of the quenching and oxidation nozzles are correspondingly (10-20) x 480 mm and (0.5-1.5) x 460 mm, *i.e.* the relationship between their surface areas is 7 - 42.

[0019] The invention also concerns the use of the method according to the invention for regulating the temperatures and bonding strengths in a process of thermobonding fibers produced by the said method, especially the melting point and melt quantity of the partial melts formed from the filament surface during thermobonding, as well as the quality characteristics of fabrics made from the fibers.

[0020] The invention further concerns a method for regulating the thermobonding of skin-core-type fibers made by degrading the molecules in a filament surface layer based on a controlled autogenous oxidation of the molten-state spinning filaments made from polyolefins, especially polypropylene, which method is characterized in that

a. the fibers to be thermobonded are made by means of the regulation method according to the invention so as to give fibers with desired surface layer structures and molten areas as determined both by the melt index and by the degree of surface degradation indicated by the molecular mass values

b. the thermobonding is regulated using polymer-specific regulation equations simulating the strength values of the product fabrics, the equations for the tensile strength and the elongation being

$$\sigma(\in) = c_{01} \times [MFI/(MFI)_O]^{n(o1)} \times T^2 \times \exp(-E_{01}/RT)$$

the common envelope equation after reaching the maximum values for the strengths being

$$\sigma(\in) = c_{02} \times T^2 \times \exp[+E_{02}/RT]$$

c. the ratio between the tensile strength and the elongation of the product fabrics is regulated by the polymer-specific regulation equation for bonding

$$\sigma_{II}/\in_{II} = c_{03} \times [MFI/(MFI)_o]^{n(o3)} \times \exp[-E_{03}/RT].$$

[0021] As an example, in such a method a starting polymer can be used having $M_w = 255\,000$, $M_n = 49\,250$, $M_v =$

209 000, D = 5.15, from which, using molten-state filament oxidation, a fiber series is made, wherein the melt index ratio varies 2 - 4.5, which fibers are used for making thermobonded fabrics (appr. 22 g/m^2) which in the regulation equations for bonding have the following factors corresponding to the strength values and their ratio ($\sigma_{\parallel}$, $\sigma_{\parallel}/\in_{\parallel}$): $c_{01} = 5.442 \times 10^{19}$, $n_{01} = 1.811$, $E_{01} = 47180$; $c_{02} = 2.377 \times 10^{-10}$, $E_{02} = 11920$; $c_{03} = 3.235 \times 10^{6}$, $n_{03} = -0.794$, $E_{03} = 12390$, whereby the regulation equations corresponding to the transverse strength values are formed from parameters corresponding to these, and which fabrics will have the following differences in the maximum strength values, using bonding regulation, at the melt indices

$$\text{MFI} = 1.98 \text{ and } 2.90;\ \Delta\in_{\parallel} = 105\ \%,\ \Delta\in_{\perp} = 73\ \%,\ \Delta T = 4{,}5\ °\text{C}$$

$$\text{MFI} = 1.98 \text{ and } 4.07;\ \Delta\sigma_{\parallel} = 8\ \%,\ \Delta\sigma_{\perp} = 39\ \%,\ \Delta T = 11{,}1\ °\text{C}.$$

[0022] The new regulation method is thus a combination of several partial methods and is based on a large number of measurements and observations. The regulation method is divided into a main part and a side part. One part is directed to the molten state, controlled oxidation of the polymer, and the second part, if necessary, to controlling and changing, prior to spinning oxidation, the polymer molecular weight distribution, *i.a.* in the radial direction of the nozzle filament, by mixing therewith, prior to the spinning nozzle, a very short-chain homopolymer of the same polymer quality. Characteristic features of the new method are *i.a.* :

- In a shortspinning system, the cooling or quenching distance of the molten polymer filament exiting from the spinning nozzle is appr. 25 mm (in a longspinning system appr. 1500 mm). At this short distance and during a few milliseconds, the filament is drawn at spinning (cold draw ratio: 150-1600) from the nozzle diameter (0.25-0.80 mm) to almost the final fiber diameter (15-30 μm), that is, its volumetric and surface deformation and corresponding speed changes are very big. Simultaneously with the said dynamic filament deformations, the filament temperature decreases (for polypropylene appr. 150-200 °C), the polymer solidifies and its crystallization sets in.
- In order to guarantee high-quality fine fibers, the new method aims at a low spinning draw ratio, that is simultaneously at using a small spinning nozzle diameter. Consequently the number of nozzles in the spinning apparatus has to be increased in order to reach a sufficient production capacity, whereby the controlled homogenous oxidation and quenching of the filament bundle within the said very short distance becomes technologically difficult.
- In the new method, the size of the dynamic deformation surface of the filament and the changes therein are measured as a function of distance and time, in order to provide to the molten filament the oxygen needed for the oxidative surface degradation, in the right amount, temperature and site. In the deformation measurement, also the tensile strength applied to the filament and the corresponding orientational changes in the molecular chains of the molten filament polymer (after the post-nozzle chain disorientation caused by the relaxation of the shear forces) have to be taken into account as also the effects caused by the supplying of oxygen both in the deformation surfaces and in the filament tension.
- Based on studies carried out it can be concluded that the oxygen diffusion to the filament surface and matrix is rate-controlling in the degradation of the molecule chains, because the oxidation of thermal radicals is extremely rapid at the melt temperature and also the degradation of the generated oxidation products (*i.a.* hydroperoxides) takes place in a broad temperature range, wherefore none of these reactions is primarily overall rate-controlling.

Guided by the deformation measurements the oxidation of the filament always has to be aimed, at the beginning of the area of largest deformation, where the filament oxidation area is the largest, the filament tension the lowest, the decrease in filament temperature as small as possible, the deformation delay time the longest and the polymer birefringence and correspondingly the molecular chain orientation the lowest.

- Because of the said very short quenching distance and the small amount of oxygen required, a separate oxidation nozzle is used for the oxidation, the position of which can be adjusted and which is arranged in the vicinity of the spinning nozzle, immediateley above the quenching nozzle, the oxidation nozzle having a nozzle opening with a very small free surface area. The separate oxidation nozzle arrangement makes it possible to perform a targeted oxidation, which is directed to the filament bundle exiting from the spinning nozzle using the correct quantity, temperature and site, to jet the oxidation gas, if necessary, through the quenching zone without the gases being intermixed to any higher degree, to heat or cool the oxidation gas, to economically use oxygen enriched oxidation air, to increase the oxygen concentration gradient and thus of the oxygen diffusion flow in the gas phase and the filament surface portion, to control the quality of the oxidation products, to utilize the net heat between the endothermic evaporation reactions and the exothermic oxidation reactions, to regulate the deformation surface changes by means of the oxygen concentration, *etc.*

The angle of direction of the oxidation nozzle with respect to the surface of the spinning nozzle, as well as its distances from the nozzle surface and the filament bundle are essential for carrying out the oxidation method. If the oxidation nozzle is positioned one- or two-sidedly (that is oxidizing one or both sides of the filament bundle) in the immediate vicinity of the spinning nozzle surface, it is possible that the oxidation gas jet cools the nozzle surface excessively, in which case, if necessary due to polymer condensation, the nozzle is provided with a low-power electrical resistance to maintain the nozzle surface at a temperature corresponding to that of the spinning melt.

- When measuring the level of oxidative degradation by means of the melt index of the filament, the regulation equation for the filament melt oxidation is of the form MFI = $c_1v_{O2} - c_2v_i + c_3$, where
  v_{O2} = the partial pressure velocity of oxygen, that is the velocity of the oxidation gas multiplied with the oxygen partial pressure thereof, v_i is the velocity of the quenching air and c_1, c_2 and c_3 are polymer specific constants (under constant spinning conditions). An increase in the velocity of the quenching gas decreses, and an increase in the oxygen partial pressure velocity increases the level of degradation. The value of the constant c_1 is primarily affected by the position of the oxidation nozzle and the dimensions of the oxidation gas jet, and the constant c_2 by the position of the quenching nozzle and the dimensions of the quenching gas jet, the gas temperatures, *etc.* The constant c_3 is a function of the level of oxidative degradation by the quenching gas, the nozzle diameter, the spinning temperature, *etc.* The level of oxidative degradation can naturally be measured directly from the changes in the polymer molecular weights or viscosities, in which case the constants in the regulation equation change. The constants for the regulation equation are determined experimentally polymer-specifically for use in regulating the spinning process in production.
- When using large nozzle diameters in spinning, resulting delayed cooling of the filament and corresponding long delay times, increases substantially the oxidative degradation caused by the quenching air in the polymer. This level of degradation can be regulated by means of the spinning temperature and also by the choice of polymer additives, both of which also affect the regulation function. When using small nozzle diameters, the filament is thinned out and its temperature decreases so rapidly that the delay time for the quenching degradation is too short. When it is desired to maintain the spinning polymer in preferably long-chain form and the velocity and oxygen content of the actual oxidation gas reasonable, the new method contemplates to include as a part of the process, a small addition of a very short-chain polymer to the spinning polymer. The ratio of the melt indices of the short- and long-chain polymers used for this addition became high, that is appr. 100-200. It was hereby observed that at speeds corresponding to production capacity, the shear forces applied to the filament in the nozzles at low nozzle diameters are sufficient to enrich at least part of the short-chain polymer in the surface portion of the filament, whereby *i.a.* in this surface portion both the quenching and the controlled oxidation degradation are sufficiently intensified. An important consequence of this addition with respect to the oxidation and control process is the fact that already a fairly small addition of short-chain polymer makes it possible to lower the spinning temperature (even 20-50 °C), whereby the thermal degradation in the filament matrix decreases and simultaneously the molecular weight of the polymer chains within the filament remains high and, due to the intensified degradation, decreases strongly in the filament surface portions.

It can also be concluded that in the spinning conditions for the said homopolymer mixture, the oxidized product filament is readily solidified in a smectic structure, which can be taken advantage of, especially in fiber-thermobonding, through controlled matrix crystallization, as a substantial increaser of bonding strength. This part of the new regulation method is very applicable and useful especially when spinning fine fibers using small nozzle diameters, especially for high-quality nonwoven fabrics.

- In the new method, the changes in the polymer (number and weight average) molecular weights and dispersion during the extrusion process are, according to measurements, conventional and correspond to known multiextrusions, that is all the said values decrease in a regular manner (approximately logarithmically in a linear manner) when the melt index increases. In the nozzle oxidation following extrusion the molecular weights decrease further when the melt index increases, but in a manner different from the previous changes. The dispersion value increases as the melt index increases in a manner deviating from the conventional behaviour. This behaviour is specific for the molecular weight distribution, especially under the effect of a peripheral short-chain layer, as is easily deductable from statistical distribution values.
- The polymer-specific bonding equation simulating the fiber nonwoven strength values (Ø) is of the form $Ø = c \times T^2 \times \exp[-E/RT]$, where
  Ø is (here) the tensile strength or elongation value. The activation energy values in bonding corresponding to the strength values in thermobonding in a direction parallell to the carding direction of the fiber nonwoven or perpen-

dicular thereto are mutually of the same magnitude. The activation energy values corresponding to tensile strength and elongation are usually of different magnitude.

The strength values in thermobonding have a maximum value with respect to the temperature. The temperature ranges above and below these maximum values have their own equations of the same form. The theoretical maximum value for the bonding strength lies in the intersection point of these equations. The same polymer has, within the limits of accuracy of measurement, at bonding strength values corresponding to different degradation levels, the same bonding equation at the temperature ranges exceeding the bonding strength maximum values, that is, the strength values coincide on a common envelope.

As a result of oxidative degradation, the strength value functions and the maximum strength values are shifted toward low bonding temperatures, and thus the bonding strengths increase as the degradation increases in accordance with the bonding equation, polymer-specifically and restrictedly.

From the equations simulating the strength values, the polymer-specific regulation equation for the relationship between the tensile strength (σ) and the elongation ($\in$) as a function of the melt index ratio and temperature is obtained directly: $\sigma_{II}/\in_{II} = [MFI/(MFI)_o]^{-n} \times c_4 \times \exp[-\Delta E/RT]$, where the exponent value for the melt index ratio is $n < 1.0$.

A similar type of equation is obtained also for the transverse strength values.

In turn, by means of the ratios for the product fabric elongation and strength, *i.a.* the tactile characteristics (softness, flexibility, elasticity *etc.*) and energy to break of the fabrics are regulated.

[0023] In the method according to the invention, a starting polymer is used which has been stabilized in a known manner, whereby especially peroxide degradation agents, such as phosphite-phosphonite mixtures come into question, typically in an amount of not more than appr. 0.5 %.

[0024] In order to elucidate the state of the art relating to the melt spinning oxidation of a polymer filament, the natural scientific principles relating to both polymer melt spinning and its thermal oxidation are reviewed. In many innovations *i.a.* from the last years relating to spinning and oxidation of melt filaments, the effects in the spinning process of *i.a.* increasing the spinning melt temperature, delayed cooling of the melt filament, increasing the spin nozzle diameter and increasing the capacity, are taken advantage of. For this reason, the results obtained in known experimental spinning models are shortly reviewed with respect to the nature and effect of the factors.

The differential equations concerning polymer melt spinning dynamics (before crystallization) (S.Kase, T. Matsuo, 1965, 67) with respect to the heat, force and material balances are /1/

$$v(\delta T/\delta y) + (\delta T/\delta t) = (2\sqrt{\pi h}/\sqrt{A}\ \rho\ C_P)\ (T-T^x) \qquad /1/$$

$$(\delta v/\delta y) = F/\beta A \qquad /2/$$

$$v(\delta A/\delta y) + (\delta A/\delta t) = -A\ (\delta v/\delta y) \qquad /3/$$

The independent variables in the equations are time: t, s and position: y, cm, measured from the spinning head; dependent variables are the temperature: T, °C, filament speed: v, cm/s and cross-section area: A, cm^2.

The draw viscosity: β, $gf{\cdot}s/cm^2$ is presumed to be a function only of temperature and internal viscosity, $|\eta|$ and the spinning tension: F, gf a function only of time. The filament density: ρ, g/cm^3 and the isobaric specific heat: Cp, cal/g. degree are presumed to be constant.

A number of studies /*i.a.* 2/ relating to fiber filament formation have been presented in the past decades. However, the said equations and their solutions /1/ are associated with fairly abundant experimental reference documentation, which in practice covers the most important spinning phenomena and technical applications.

The stationary state solutions to the differential equations /1/-/3/ give the changes in the cross-sectional area of the fiber filament, A(y), and the temperature, T(y) as a function of the distance, y measured from the spinning head under a multitude of spinning conditions. The obtained solutions are then correlated to the properties of the filament thread. The following can be said about the essential results obtained from the solutions to the spinning model equations [IBM 1401] in the melt spinning of polypropylene:

- An increase of the spinning nozzle diameter without changing the winding speed or
- the gauge, shifts the A(y)- and the T(y)-functions in the direction of the y-axis and thus slows down the cooling and increases filament tension (measurement range: D_s = 0.4-1.6 mm).
- An increase in the thermal activation energy for the draw viscosity, β shifts the T(y)-function in the direction of increase of the y-axis and that of the A(y)-function in the opposite direction.

- By lowering the quenching air temperature or increasing its velocity, the A(y)- and T(y)-functions are made to shift in the direction of the y-axis toward decreasing values, that is, an even faster thinning out of the filament and increase of the filament tension is brought about.
- An increase in the flow rate (capacity) of the polymer, at constant winding speed, greatly increases the distance needed for filament solidification, that is slows down polymer cooling and thinning.
- By mounting an insulating cylinder below the spinning head, around the fibre bundle, makes the A(y)- and T(y)-functions shift as a function of the length of the insulating cylinder, toward high y-values, that is, the insulating cylinder retards the cooling and thinning of the polymer and lowers the F-values.
- The Barus-effect and the temperature distribution in the direction of the filament cross-section become significant with respect to the functions A(y), T(y) and F(y) only at very high polymer flow values.

[0025] The polypropylene filament threads crystallize rapidly in melt spinning, which makes the crystallinity and orientation important. When the molten filament becomes thinner, the birefringence, Δn, increases rapidly. It can be shown that the birefringence of the thread is directly proportional to the tensile strength at the solidification point, (F/A). In melt spinning, filament crystallization takes place subject to molecular orientation under non-isothermal conditions. The kinetics of the crystrallization mechanism can, however, be described by the following Avrami-type equation used in isothermal kinetics

$$\kappa(t) = 1\text{-}\exp\{-[\int K(T(t))dt]^n\}, \qquad /14/$$

wherein the time exponent corresponds to the isothermal situation and the rate constant K(T(t)) stands in a simple relationsship to the Avrami rate constant (Ziabicki /2/).

[0026] The degree of crystallization (κ) can be obtained from the equation at any desired point of time provided the rate temperature dependance and the cooling function of the system are known. The temperature function of the isothermal crystallization rate is an almost symmetrical bell function with respect to the maximum rate value. The maximum value for the crystallization rate is below the polymer solidification temperature for polyolefins. The filament crystallinity is, in addition to the crystallization rate, dependant on the length of time the polymer spends at the temperature range where it has its highest crystallization rate. This can be expressed in a quantitative manner as the length of time the polymer needs to cool one degree, that is

$$Dt/DT = (\rho A/P)(dy/dT))_{T^*}, \qquad /5/$$

wherein Dt/DT is the "cooling time" and $(dy/dT)_{T^*}$ is the temperature change along the spinning filament in the vicinity of the maximum temperature for the crystallization rate. Assuming that the temperature for the maximum crystallization rate for the polymer, T*, is a material constant, the crystallization degree (density) of the filament can be calculated. Some correlations between the properties of the polypropylene thread and the stationary state solutions for the spinning equations can be mentioned:

- When the nozzle temperature increases, the birefringence, Δn, decreases when F/A_w(maximum) decreases and the density, $\rho(\kappa)$, decreases when the cooling time Dt/DT decreases.
- An insulating cylinder placed down from the spinning head provides for the maintenance of a high air temperature and almost zero air velocity within the cylinder and reduces all values: $\rho(\kappa)$, Δn, Dt/DT and F/A_w. The provision for reduced crystallization by decelerating the cooling of the molten polymer can be explained by the fact (equation 5) that as the insulating cylinder slows down the cooling, the filament is thinned out and reaches simultaneously a high speed during the time the filament cools to a temperature of appr. 100 °C. This provides for a short cooling time and simultaneously for less crystalline filaments.
- When the velocity of the cooling air increases, all values: ρ, Δn, F/A_w and Dt/DT increase.

[0027] The information needed for the evaluation of the melt oxidation of the polymer filament and the subsequent chain degradation and relating to the changes in the filament cross-section (and skin) areas, as well as in filament temperature and the progress of filament solidification as a function of the distance measured from the nozzle and time can, according to the above assessment, be obtained from dynamical studies of spinning.

Autogenous polymer oxidation at low temperatures (< 140°C) has been extensively studied /5/. In contrast thereto, there are hardly no elaborate studies relating to the polymer melt range at temperatures below linear pyrolysis. The oxidation of polypropylene with molecular oxygen can be shown with the following partial formula:

$$ROOH \xrightarrow{K_1} RO\cdot + OH\cdot \qquad (01)$$

$$RO\cdot + RH \xrightarrow{K_2} \text{products} + R\cdot \qquad (02)$$

$$R\cdot + O_2 \xrightarrow{K_3} RO_2\cdot \qquad (03)$$

$$RO_2\cdot + RH \xrightarrow{K_4} ROOH + R\cdot \qquad (04)$$

$$2RO_2\cdot \xrightarrow{K_5} \text{products} \qquad (05)$$

[0028] Molecular oxygen oxidizes the polymers over a mechanism of free radical chains. In the case under consideration, free radicals are formed primarily under the effect of both thermal and mechanical energy.

Carbon radicals react with the oxygen molecule ($3O_2$-radical) very rapidly ($K_{03} \sim 10^8 - 10^9\ M^{-1}s^{-1}$). The oxidation reaction is, however, reversible and the reverse reaction becomes important when the oxygen pressure is low, the temperature is high or the carbon radical is stabilized.

An important rate and product governing partial reaction (formula 04) is the formation of hydroperoxides as a product of hydrogen abstraction by peroxy radicals. The hydroperoxides are most often primary main products of polymer oxidation, and they play, as initiators of autogenous oxidation, an important role in the oxidative degradation.

The rate constants for the main reactions in the oxidation reaction scheme are at the temperature range 71 - 140°C:

$$K(01),\ s^{-1} = 5.45 \times 10^{10} \times \exp(-25000/RT)$$

$$K(04),\ 1M^{-1}s^{-1} = 1.61 \times 10^{7} \times \exp(-12080/RT)$$

$$K(05),\ 1M^{-1}s^{-1} = 1.11 \times 10^{13} \times \exp(-11600/RT)$$

[0029] Polypropylene oxidation is kinetically of first degree order. The apparent rate of the oxidative pyrolysis is:

$$-d[RH]/dt = K_{04}(K_{01}[ROOH]_s/K_{05})^{1/2} \times [RH] \qquad /6/$$

The hydroperoxide concentration under stabilized condition is:

$$[ROOH]_s = K_{04}{}^{2}[RH]^{2}/(K_{01}K_{02}) \qquad /7/$$

By inserting the values for the rate constants into the equation /6/, the following apparent rate constant for the oxidative degradation is obtained:

$$K = 1.128 \times 10^{6} \times \exp[-18780/RT] \times [ROOH]_s \qquad /6/$$

The following equation for simulating the change in hydroperoxide concentration in the temperature range of 110°-289°C is obtained:

$$[ROOH]_s,\ Ml^{-1} = 2.981 \times 10^{-5} \times \exp[7381/RT] \qquad /7/$$

[0030] The reaction rate constant corresponding to first order kinetics for the oxidative pyrolysis of a polypropylene melt as measured thermogenometrically /5/ in the temperature range of 240-290°C, is of the form

$$\text{iPP: } K,\ s^{-1} = 7.75 \times 10^{3} \times \exp(-15240/RT) \qquad /61/$$

$$\text{aPP: } K,\ s^{-1} = 4.83 \times 10^{4} \times \exp(-17190/RT) \qquad /62/$$

When comparing the numerical values calculated, in the melt-range temperatures, from the rate constants for the oxidative degradation of a solid polypropylene sample (/6,7/) to the corresponding measurement results in the melt range (/61, 62)/, it can be concluded that the values from both series are of equal magnitude within the limits of accuracy of measurement. From this it can be assumed that also the reaction mechanisms are the same in both the molten and the solid phase polypropylene regions.

It has experimentally been shown /8/ for solid polypropylene that in case of a flat sample the maximum oxidation rate is directly proportional to the oxygen pressure in the oxidative gas phase. It has also been shown that the concentration of the primary oxidation product, hydroperoxide, is directly proportional to the oxygen concentration. For the flat form, in case of thick samples, one obtains

$$[O_2] = [O_2]_0 \times \exp[-(KD)^{1/2} \times X] \qquad /81/$$

$$[ROOH] = [ROOH]_0 \times \exp[-(KD)^{1/2} \times X], \qquad /82/$$

where the index 0 refers to the initial concentration, X to the distance from the sample surface and D is the oxygen diffusion constant.

The concentration distributions of oxygen and hydroperoxide are then of importance for the amount and quality of oxidation products distributed in the oxidation system. Similar phenomena evidently take place also in melt-phase oxidation.

[0031] The products from the oxidative pyrolysis of polypropylene at the temperature 289°C was determined /5/ IR-spectrofotometrically from the GC-fractions and partly using mass spectrometry. The semiquantitative product yield order was: ethanol, acetone, butanol, methylvinylketone, C_6-ketone, propylene, methanal, methanol, propanol, 2-methylpropanol, 2-pentanone, C_5-aldehyde, 3-methyl-3,5-hexadiene.

There is a mutual variation among the first components as a function of the pyrolysis time.

The appearance of the hydrocarbon products ethane, propane, propylene etc. in the oxidative degradation indicates that the oxygen diffusion limits the process. Many of the hydrocarbon components are conventional products of polypropylene pyrolysis in an inert atmosphere. When the atmosphere contains sufficiently oxygen, the primary oxidation products are further oxidized, whereby both the order of appearance and the product quality change as a function of the oxygen content of the oxidation gas:

$$5\ \%\ O_2\text{: } H_3C\text{-}CO\text{-}CH_3,\ H_3C\text{-}CHO,\ H_2O,\ H_3C\text{-}CH = CH_2,\ H_3C\text{-}CH\text{-}CHO,\ CO_2\ldots$$

$$20\ \%\ O_2\text{: } H_2O,\ CO_2,\ H_3C\text{-}CO\text{-}CH_3,\ H_3C\text{-}CHO,\ H_3C\text{-}CH = CH_2\ldots$$

$$50\ \%\ O_2\text{: } CO_2,\ H_2O,\ H_3C\text{-}CH = CH_2,\ H_3C\text{-}CHO,\ H_3C\text{-}CO\text{-}CH_3$$

$$100\ \%\ O_2\text{: } CO_2, H_3C\text{-}CH = CH_3,\ H_2O$$

When the oxygen concentration of the atmosphere increases, ethanol, acetone, butanol and water decrease to insig-

nificant quantities, and the carbon dioxide yield increases. The effect of thermal and thermal-oxidative degradation on the polypropylene molecular weights and their distribution is briefly examined.
A sustainable theoretical and practical relationship between the thermal (not oxidative) degradation kinetics of polypropylene and the changes in molecular weights corresponding to the degradation and their distribution has been observed (Chan & Balke, /6/). For the practical needs in this study, the equations simulating the resulting changes in the molecular weights in the study are

$$(M_w)_O - M_w = 1.3662 \times 10^8 \times T^{0,1316} \times \exp[-8056/RT] \qquad /9/$$

$$(M_n)_0 - M_n = 1.1646 \times 10^9 \times T^{0,1972} \times \exp[-12646/RT], \qquad /10/$$

where the initial values for the weight and number average molecular weights were : $(M_w)_0 = 234000$, $(M_n)_0 = 59300$, $(M_w/M_n)_0 = 3.94$, τ, h is time. The measurements were carried out in the time and temperature ranges: $\tau = 0\text{-}48^h$ and $T = 548 - 598K$.
From the equations it can be deduced that in the very short productional delay times of extrusion, it is the effect of the processing temperature on the degradation of polypropylene which is essential.

[0032] The effect of multiple extrusion of polypropylene carried out under oxidative conditions (air) on the melt index, molecular weights, dispersity and melt viscosity at low shear rates has been elucidated in a fairly new study (H. Hinsken at al. /7/). The equations relating to the relationship between the molecular weights and melt indices and approximating the results of the study are:

$$M_w = 532300 \times [MFI]^{-0.2890} \qquad /11/$$

$$M_n = 73510 \times [MFI]^{-0.1026} \qquad /12/$$

[0033] The values for the molecular weights and melt indices of the starting polymer were: $M_W = 418400$, $M_n = 78350$, $M_W/M_n = 5.34$ and MFI = 3.1. The measurement results correspond to an extrusion temperature of 260°C. Based on the results of the study it can be concluded that as a result of the multiple random degradation of polypropylene carried out under oxidative conditions, the values for the molecular weights and dispersion decrease conventionally and regularly as a function of the melt index.

[0034] The effect of the molecular mass of the polymer crystal on its melting temperature will be studied briefly, which is a factor affecting substantially *i.a.* the thermobonding of peripherally oxidized fibers. It can be shown (*i.a.* H-G. Elias, /23/) that the melting point (T_M) of a non-perfect polymer crystal with a finite molecular mass satisfies the equation

$$T_M = T_M^O - [2RT_M T_M^O/(\Delta H_M)u]\,[(\ln X)/X] + f(X), \qquad /13/$$

where T_M^O is the melting point of a perfect crystal having a finite molecular mass, $(\Delta H_M)u$ is the melting enthalpy of the polymer monomer unit and X is the degree of polymerisation. By introducing into the equation the values corresponding to polypropylene, the following approximate equation (accuracy unknown) is obtained:

$$T_M = 460 - 507.5\,[(\ln X)/X].$$

Based on the equation it can be concluded that the decrease in melting point becomes significant only at polymer values $X < 10^3$.

[0035] The development of the state of the art relating to the manufacture of fibers with skin-core structure using oxidative degradation will be examined by means of a few both old and new patent publications.

[0036] The methods according to the patents US 2.335.922, 2.715.077, 3.907.957, 4.303.606, 4.347.206 and 4.909.976 deal with many kinetic and other problems and their solutions relating to the handling of polymers in connection with the manufacture of peripherally oxidized fibers. In the process according to the patent US 2.335.922/ 060341, /11/, a synthetic textile material is produced by extruding a high polymer material. The polymer, on which air has a detrimental effect at the extrusion temperature, is extruded into a chamber containing inert gas or steam and is cooled to a temperature, where air does not have a harmful effect on the extrudate. In the method the effect of air on the polymer at the extrusion temperature is thus known, as is also the prevention thereof and both effects, in addition to a "chemical", also from a kinetic point of view.

In the method according to the patent US 2.715.077/291152,/12/, the adhesion of a polyethylene structure (film) to inks, metals, paper and polymers of different qualities is improved. In the method, the polymer is subjected to nitrous oxide containing air (5-20 % N_2O) at the extrusion temperature range (150-325°C), preferably in the presence of UV-light ($\lambda \leq 3900$ Å) and is quenched. The specification reveals a knowledge of the kinetics of nitrous oxide treatment and information is given of the treatment rate and time.

In the method according to the patent US 3.907.957/180474, /13/ the formation of oxidative layers on the nozzle surface for the exiting filaments during rapid spinning, which has a detrimental effect on the processing, is reduced or prevented. In the method, a steam blanket is fed into a chamber close to the nozzle surface and below this (prior to air quenching) a small amount of non-condensing, if necessary pre-heated inert gas. The spatial heights of the gases in the direction of the cable are optimized.

In the methods according to the patents US 4.303.606/011281 and 4.347.206/310882, /14/, one aims at preventing the detrimental draw resonance caused by (one or more) relaxation swellings (Barus effect) formed during polypropylene spinning in the melt filament immediately after the nozzle. In the method, the filaments are extruded to a short hot zone, to the extrusion or a lower temperature, before they meet the cooling air. By proceeding in this manner also the extrusion temperature can be lowered without increasing the relaxation swelling. The extrusion temperature was in the former method 204°C and in the latter 177°C.

In the method according to the patent US 4.909.976/090588,/15/, the rapid spinning process for synthetic fibers is improved by including on-line-zone heating in a conventional method. In the method, the filament exiting the spinning head is quenched to a temperature above the glass-transition temperature (e.g. a smectic structure for the product phase) and is then fed to a heating zone, where the desired fiber characteristics (crystallinity, orientation, strengths) are produced. Finally the filament is quenched again and wound up. In the specification, zone length and temperature values are given which correspond to a specific winding speed.

[0037] The development of the state of art for conventional composite polymer structures is indicated *i.a.* by the patents: US 4.680.156, 4.632.861, 4.634.739, 5.066.723, 4.840.847, 5.009.951 and EP 0.662.533A1.

In the method according to the US-patent 4.680.156/140787, /16/, the device-specific production capacity and the product quality of skin-core structural composite fibers is increased. In the method, the molten, restricted, molecularly oriented material forming the fiber core is enveloped with a molten material forming the skin layer. The combination obtained is supplied to a nozzle tool having such a temperature gradient that the outermost part of the fiber core is solidified when still in the tool. The molten surface layer forms a protective layer preventing cracks on the surface of the brittle, high-molecular weight, oriented core layer and simultaneously functions as a lubricant.

In the methods according to the patents US 4.632.861/240386 and US 4.634.739/221085, /16/, the spinning speed and capacity of a rapid spinning process for bicomponent fibers in a polyethylene-polypropylene-system are improved above the values for the end components. In the product fiber obtained, the polyethylene forms the continuous and the polypropylene the dispersive phase in the matrix. The product fiber has good thermobonding properties.

In the method according to the patent US 5.066.723/211290, /16/, polymer composites having high impact strength are made in the presence of a Ziegler catalyst. These contain polypropylene as the continuous phase and as the discontinous phase a thermoplastic polymer containing 90% polymerized ethylene and the rest other α-olefins. The mixture is heated in the presence of a free radical in order to decrease the viscosity of the system.

In the method according to the patent US 4.840.847/020588, /16/, conjugate fibers having both a superior thermal adhesion and absorption capacity are made by melt spinning. The fibers contain as one component a crystalline α-olefin and as another component an ethylene-dialkylaminoalkyl acrylamide copolymer. In the method according to the patent US 4.115.620/190177, /16/, spontaneously curly conjugate fibers with high strength characteristics are made. One component in the structure containing at least two components is comprised of polypropylene and 5-50% of a thermosetting plastic (catalyzed from a hydrocarbon containing at least four carbon atoms or a colophonium derivative) and the other of polypropylene and a varying quantity of a thermosetting plastic. In the method according to the patent application EP 0.662.533 A1/040195, /16/, multicomponent polymer filaments are made, by mounting a high speed lateral quenching unit close to the lowermost surface of one or more spinning heads having a high nozzle density, in order to prevent the aggregation of pre-fibers and/or of molten filaments. In the method, a spinning head suitable for the simultaneous spinning of several different filaments can be used (US 4.406.850, 5.162.074). Thus in the methods, a shortspinning system is applied to a complicated polymeric multicomponent rapid spinning system.

[0038] The methods according to the patents US 3.437.725 and 3.354.250 aim at decreasing the thermal degradation by shortening the processing time and reducing the temperature. In the method according to the patent US 3.437.725/290867, /17/, the spinning nozzle apparatus comprises, between the plate containing the filter space and the actual nozzle plate, an insulating space through which the polymer flows, the melt temperature being below the temperature of substantial degradation, through extended feeding tubes to the nozzles in the nozzle plate. The nozzle plate is electrically heated to produce a steep temperature gradient (≥ 60°C) in the polymer (in the feed tube and the capillary) so that the shearing stress is momentarily reduced at the capillary wall, without polymer degradation.

In the method of the patent US 3.354.250/260264, /17/, polymer powder is screw-compressed against a melting diaphragm, into which an electrical resistance plate is apertured. The screw tube is surrounded by a water cooled mantle, by means of which the temperature of the polymer powder is kept below the lowest melting point of its components. After melting, the polymer is conducted to the nozzles immediately after the filter. By means of the method, the polymer remains in a molten state for a short time.

The methods according to the patent US 5.281.378 and the patent applications FI 943072 and 942889 describe the development work carried out during the present decade in the manufacture of skin-core structured fibers using oxidative surface degradation.

The main objective of the method according to the patent US 5.281.378/200592,/18/, is to improve control of the polymer degradation, spinning and quenching stages and to produce a fiber, which is capable of providing a nonwoven product with increased strength, elasticity and uniformity values. A further object of the method is to develop the thermobonding properties of a fiber spun from a polyolefin containing melt.

According to the method, a high-strength spinning fiber is made by utilizing oxidative chain degradation of the surface of a molten spinning filament as well as a slow quenching stage for the melt filament as applied to polypropylene having a broad molecular weight distribution. According to the description, the method is applicable for use in a rapid spinning system. According to the description and the claims, the method has the following essential functions:

In a first stage of the method, the polypropylene containing melt is extruded under the following conditions:

- the molecular weight distribution of the input polymer is broad, that is the values for the dispersion are 5.5 - 7.75.
- the polymer contains a member from the group consisting of antioxidants, stabilizers or mixtures thereof, and optionally a degrading component,
- the said additives are used in an amount sufficient to inhibit or control the degradation of the polymer in the extruder.
- the polymer material (MFI: 5 - 35) is extruded at a temperature of 250-325 °C.

In the second stage of the method, quenching of the hot extrudate is carried out in an oxygen containing atmosphere, in order to effect oxidative molecular chain degradation of the surface under the following conditions:

- controlled quenching of the extrudate is carried out in an oxygen containing atmosphere by regulating the quenching rate of the hot extrudate, in order to bring about oxidative chain degradation of the filament surface.
- the controlled quenching includes delayed quenching of the hot extrudate.
- the oxygen containing quenching atmosphere comprises quenching by transverse blowing and the uppermost part of the transverse blowing is prevented up to 5.4 % (i.e. quenching and transverse blowing is not carried out in the said zone).
- the controlled quenching further comprises maintaining the extrudate at a temperature above 250 °C for a period of time which oxidatively degrades its surface.
- the product fiber contains an inner zone: M_w = 100,00-450,000, an outer zone: M_w = 5,000-10,000 and an intermediate zone, wherein the molecular weights are between the said limits.
- the inner zone has a high and the outer zone a low birefringence.

It is difficult to find a basis in the method description for the contents of the numerous patent claims.

A comparison of the fiber series A, B, C, and D of the specification shows (tables I-III) that the strength values of fibers obtained from a polymer with a broad chain distribution decrease under conditions of retarded quenching. Noteworthy is the decrease of the dispersion values for the polymers of the test series B, C and D from starting values of different magnitude, at the very beginning of oxidation (also in non-retarded quenching), to a final value of practically the same magnitude, from which it does not change any longer when oxidation increases and the melt index grows. A statistical evaluation of the molecular weight distribution does not support the assumption in the patent of short molecular chains enriching in the filament surface. It can be mentioned that the description does not indicate the diameter of the spinning nozzle, the quantity and velocity of the quenching gases, nor the length of the quenching zone. The description also lacks information relating to the fiber draw ratio, which is essential from the point of view of thermobonding strength. The following can be said with respect to the fabrics made from the fibers of the test series (table IV):

- an indication of the transverse fabric strength values without giving longitudinal or median strengths does not really prove anything about the fabric thermobonding and the real fabric strengths, as already by the plain adjustment of the carding the transverse strengths can be varied in wider limits than those given in the results of the description.
- in the result table, the fabric strengths have been indicated only at two temperatures (which are not precisely defined), which is insufficient. It is generally known that the strength values of a thermobonded fabric pass through a maximum as a function of the bonding temperature.
- the weight variation of the fabric samples in the table is too big for carrying out the necessary comparison. Based on the fabric strengths indicated it can, however, be concluded that a substantial improvement cannot be seen as a result of the retarded quenching of the fiber filament or the broadening of the molecular weight distribution of the supplied polymer.

In the method according to the patent application FI 943072/230694, peripherally oxidized fibers with a skin-core structure are produced for fabrics with high transversal strength properties in combination with even quality and flexibility. In the method, different types of spinning nozzle structures for carrying out the method are indicated. The method is applied especially in connection with shortspinning systems. In the method, the polymer composition (*i.a.* polypropylene: MFI = 0.5 - 40, $M_w/M_n \geq 4.5$) is heated in the spinning nozzle (which is e.g. induction heated) or in its immediate vicinity (e.g. by means of an electrically heated apertured plate situated immediately above the nozzle) so that the composition partly degrades. The partly degraded polymer composition is extruded to form molten filaments. The molten filaments are immediately quenched in an oxidazing atmosphere (oxygen, ozone, air) in order to effect at least a surface chain degradation thereof. It is stated in the specification and the claims that the fibers manufactured with the method can form fabric materials (23.9 g/m^2, web speed 76.2 m/min.), the transverse strength of which is at least 12.6 N/50 mm.

[0039] It can be observed that the description of the method does not support the presented broad patent claims due to the lack of many relevant data. The following can be mentioned of the ambiguities and deficiencies of the specification:

- there is no information as to the produced fiber gauges, strength values, structure, crystallinity, chain orientation, period values and other factors affecting thermobonding.
- the indication of the transverse minimum strength for the fabric does not provide any information of the fabric strength, as the corresponding longitudinal strengths and elongations are not indicated. When using conventional homogenous polypropylene fibers the said transverse strengths can be obtained only by regulating the carding.
- the microfusion process used in the method is not sufficient to prove thermobonding properties of the fibers or fiber nonwovens, nor the strength values of the obtained fabrics, as no correlation between the said method and the results from the direct strength measurements is indicated.

The lack of the said and some other relevant information prevents almost completely a comparison between the oxidation method according to the patent application with other known methods from the prior art.

By means of the method according to the patent application FI 942889/160694 /20/ heat bonding polyolefin fibers are made which are suitable especially for the manufacture of nonwoven fabrics using heated rolls. The method is based on the observation that an increase of the diameter of the nozzle duct in the extruder die to a value ≥ 0.5 mm (0.5 - 2.0 mm), results in a substantial increase in the thermobonding properties of the product fibers. According to the description, the method is suitable for use both in the manufacture of staple fibers and in spunbonding methods. When manufacturing staple fibers using a wind-up range of 30-500 m/min in spinning, the cooling distance for the melt filaments is suitably in the range of 10 - 350 mm. According to the description, the spinning temperature is in the range of 240 - 310 °C and the subsequent drawing (< 100 °C) in the draw ratio range of 1.1 - 3.5. The method is applied to polyolefins in the melt index range of MFI = 5 - 25.

The description contains a pluraility of examples for the preparation of staple fibers and spunbonding using the conditions: nozzle duct diameter: 0.4 - 0.9 mm, spinning temperature: 280 - 310 °C, cooling distance: 5 - 30 mm and wind-up speed 60 - 2400 m/min.

In the description, a new method for measuring the thermobonding properties of the fibers is disclosed, which has been used *i.a.* only in the examples. The description does not give the correlation between the results obtained by the new measuring method and those of a conventional direct measuring method for the fabric tensile strength, elongation and tenacity. It is to be observed that the result obtained from the said measuring method is ambiguous due to the hot-roll bonding of the fiber nonwoven with associated strong shear forces. As an example it can be mentioned that by using a draw ratio of 3.5 in mechanical drawing in accordance with the claims 5 and 6 of the application, on a fiber made using a single-die method, a good thermobonding value is obtained from a fiber, which is known to thermobond extremely poorly.

The results obtained for thermobonding according to the description cannot be compared to the state of the art of thermobonding of conventional nonwoven fabrics.

[0040] It can also be mentioned that the methods described in US 5.281.378 and FI 942889 are directly derivable from known melt spinning models (e.g. Kase & Matsuo, /1/) and both have the same natural-scientific basis.

[0041] In the limited survey of publications relating to the oxidative surface degradation of polymer melt spinning filaments, no all-inclusive method or regulation model has been found for a shortspinning system.

In the following examples, some operational principles relating to the new melt spinning method employing oxidative degradation are discussed in detil.

Example 1.

[0042] In the example 1., the basis for the new invention and essential observations relating thereto, are disclosed by means of detailed examples.

Subexample 1.1

[0043] The subexample 1.1 discloses the manufacturing equipment and operation thereof for fibers and fabrics corresponding to the examples of the description of the invention and used for developing the method.

[0044] In the manufacture of the fiber sample series for use in the description of the new inventive method, the so-called short spinning-method and corresponding apparatuses were used.

The spinning and drawing test series were generally performed on pilot scale apparatuses which differed from production scale apparatuses only to the number of spinning units, but not to their size. The pilot apparatuses were better equipped from a measurement technical standpoint as compared to the production apparatuses.

The nozzle diameters (mm) and nozzle numbers in the spinning nozzle plates used for the test series were: 0.25 and 0.30/30500, 0.40/22862 and 0.70/12132.

The capacity (g/min) of the spinning device was $P = 45.88 \times \rho \times n_r$, where ρ (=F(T)) is the polymer density (g/cm^3) and n_r is the speed of rotation of the polymer pump (min^{-1}). For comparison (*i.a.* the spinning draw ratio) of the hot and cold speeds (nozzle and godets) the hot speed is calculated as the cold speed (cm/min) that is:

$$v_s = 45.88 \times \rho(T) \times n_r / \rho(298) \times N \times A_s \qquad /14/$$

where $\rho(T)$ is the hot density (g/cm^3), N is the nozzle number and A_s is the area of cross-section of the nozzle (cm^2). The hot density of the polymer is obtained from the equation $\rho^{-1} = 8.1383 \times 10^{-4}\, v + 1.1525$ and the cold density is $\rho(298) = 0.903$.

[0045] The parts of the shortspinning-drawing apparatus used in the pilot tests, Figure 1, were: 1. extruder, 2. melt-spinning device, 3. l-godet, 4. drawing oven, 5. 2-godet, 6. 2-finishing (avivage), 7. crimping device, 8. stabilizing and drying oven and 9. staple fiber cutter.

[0046] The deformational changes of the molten-state spinning filament after the nozzle under varying spinning conditions was photographed with a CCD camera and the information recorded on magnetic tape. The record analysis and measurements were performed using image-analysis methods. Part of the samples used for analyzing details of the invention were made under controlled conditions on a Haake-Rheocord-90-apparatus, which was provided also with a mechanical drawing apparatus with oven.

The fiber structure was analyzed using X-ray WAXS- and SAXS-technique (Philips PW 1730/10, PW 1710/00, Kratky-KCSAS), AFM-technique (TME-rasterscope 2000) and electron microscopy (Cambridge 360 and Cameca Camevax Microbeam). The conventional apparatus used in the production of the fiber nonwovens and bonding was according to the Figure 2. The parts of the apparatus are:

1. opener, 2. fine-opener, 3. storage silo, 4. feeder, 5. carding apparatus, 6. bonding rolls and 7. winding apparatus.

All the apparatuses shown in the drawing are of production scale. The production and bonding speed of the fiber web on the bonding line were adjustable in the range of 25-100 m/min. The upper roll provided with diamond or round protrusions and the smooth lower roll of the bonding apparatus were temperature and pressure adjustable. The diameter of the bonding roll was of production scale, but its width was only 2.2 m.

[0047] In the fiber bonding mechanism studies, so-called fiber loop bonding and direct bonding tests were carried out with a mechanical and dynamic-mechanical thermonanalyzer (Mettler 3000/TMA40 and Seiko 5600/DMS-200). The isothermal and dynamical oxidation-evaporation tests were performed thermogravimetrically (Mettler 3000/T650).

[0048] The relative positions of the quenching, oxidation and spinning nozzles of the melt spinning apparatus used in the pilot tests are shown in the Figure 3.

The position of the quenching nozzle was decided based on the best spinning result. The angle between the central plane of the quenching nozzle (1) and the spinning nozzle surface was appr. 24 ± 1°. The distance of the longer center line of the rectangular nozzle opening from the spinning nozzle plane was 42 ± 2 mm and its distance in the direction of the angle of the nozzle from the central plane of the cable bundle (6) was appr. 49 ± 2 mm, the diameter of the spinning nozzle being 0.70 mm. When the spinning nozzle diameter was 0.25 mm, the values for the distance were only 0-10 mm shorter than the above mentioned. The size opening of the quenching nozzle was maintained constant in the tests, *i.e.* 11.2 x 478 mm.

The positions of the oxidation nozzle (2) were a, b and c in the test runs (Figure 3). The directional angles corresponding to the nozzle positions were 7.5 ± 0.5°, 17.5 ± 0.5° and 2 ± 1°, the distances in the nozzle direction were 62 ± 5, 64 ± 5 and 32 ± 5 mm and in the height direction (as measured from the longer center line of the rectangular nozzle opening) 27.5 ± 3, 27.5 ± 3 and 1 ± 2 mm. The size of the nozzle opening of the oxidation nozzle was 0.6 x 460 mm. Targeted oxidation from the nozzle position c at small nozzle distances and high gas velocities resulted in a decrease in the surface temperature of the spinning nozzle plate and aggregate formation on the nozzle plate surface. For this reason, especially when using small nozzle diameters (0.30 mm), electrical heating of the nozzle was used to maintain its temperature at the same value as that of the spinning melt. The electrical heating comprised mounting an adjustable resistance (5) in a groove in the spinning nozzle. The resistance pack (4 units) used was 3.3 x 485 mm in size and had a capacity of 270 W.

Subexample 1.2

[0049] The subexample 1.2 studies the dynamic deformation during quenching of a molten polymer filament exiting the spinning nozzle in a production scale spinning system.

[0050] Application of the correct amount of oxygen to the surface of a molten state filament, at the correct temperature and site, is essential in a method based on thermal oxidative degradation of the filament surface layer. From the point of view of generating an oxygen concentration in the surface, its diffusional transport and the regulation thereof, it is important to know the size of the molten state filament surface suitable for oxygen transport and the changes therein. In the shortspinning method in question, the deformational changes are very rapid due to the short quenching distance. In order to evaluate the surface changes, the deformation of the molten spinning filament was measured with a video camera as a function of the distance from the nozzle surface in the direction of the filament axis.

[0051] The Table 1 contains the spinning conditions for samples used in one series for measuring the deformation of the molten filament, and the corresponding results calculated from the filament profile are given in the Figure 4. In the measurements, the changes in the filament cross-section and shell surfaces (A(y) and $A_v(y)$), the temperature ($\vartheta(y)$) and spinning delay time (T(y)) as a function of the distance (y) calculated from the nozzle in the direction of the filament axis were determined.

[0052] It can be concluded that the measurement results given in the Table 2 and Figure 4 correspond to their behaviour to the results of the spinning model of Kase & Matsuo /1/ referred to earlier. From the measurement results for the melt filaments it can be concluded that as in the model /1/, an increase in the winding speed (v_1), spinning temperature (ϑ), nozzle diameter (D_s) and nozzle capacity (P) (the other conditions remaining unchanged) shifts the functions (A(y) and $\vartheta(y)$) in the direction of increase of the y-axis and *i.a.* an increase in the velocity (v_i) of the quenching air in the direction of decrease of the y-axis (as measured from the nozzle surface, y = 0). The change in the shell area of the spinning filament, $A_v(y)$, is opposite to that of the A(y)- and $\vartheta(y)$-changes. When making the comparison it should be observed that the spinning model /1/ simulates a long-spinning system, whereas the object of comparison is a shortspinning system. As an example, the values of deformational change of the filament no. 1 of the model and the filament no. 319 of the Figure 4 in the range of the filament solidification temperatures are given:

$10^3 \cdot P$ cm^3 : 8.185(no 1) = 10.2 x 0.8040 (no 319); y mm: 200 = 31.7 x 6.3; $10^2 \cdot A_v$, cm^2 : 105.2 = 23.0 x 4.58 and τ, ms : 945 = 1.71 x 552.

[0053] In the following Table, some comparison values are given from the filament profile measurement values of Figure 4 in the filament solidification range (ϑ ~ 115 °C, A(y) standardized). The values given in parenthesis are the filament values corresponding to the distance y = 0.6.

Quantity - no	3	319	14	18
$10^5 A_v$, cm^2	615	4582	348	662
$10^6 A$, cm^2	5.04	6.16	4.53	7.07
τ, ms	75	552	41	80
$A_v/A_v(319)$	0.143	1.000	0.076	0.144
$10^4 P_s$, cm^3/s	3.12	8.04	2.06	2.06
λ	274	1305	181	181

(continued)

10^4Kl, mN/cm^2	13.4	41.7	24.9	11.5
$y_{sol.}$, mm	2.1	6.3	1.2	2.1
D_s, mm	0.30	0.70	0.30	0.30

[0054] According to the table, an increase in the nozzle opening size (no 3 - no 319) results in a strong retardation of the cooling effect and of the thinning of the filament, wherefore, during melt deformation, the difference especially in the shell surfaces increases to be substantially bigger than the difference between the nozzle capacities (in the samples the production capacities are of equal, but the nozzle capacities of different magnitude). In this case also the overall delay time of filament deformation increases substantially. An increase in the nozzle opening size thus affects very advantageously oxygen transport and a favourable implementation of the oxidative degradation in the filament.

[0055] The force balance equation (2) of the melt spinning equations was of the form $\delta v/\delta y = F/A\beta$, *i.e.* the deformation rate is directly proportional to the line tension and inversely proportional to the polymer melt draw viscosity. From the balance equations, also the dependencies $F \sim \beta v^n_y/\rho c_p$ is obtained, that is the tensile force acting on the filament is directly proportional to the draw viscosity and the quenching air velocity. From the equations also the dependency $dA/dy = v^n_y A/c_p\rho \sim \rho\ FA/\beta G$ is obtained, that is, the gradient of the A(y)-function is directly proportional to the line tension and inversely proportional to the nozzle capacity ($G = \rho\ Av$) and to the draw viscosity (also, the greater the activation energy of the draw viscosity ($p = K \exp(E/RT)$), the closer A(y) is to the position y = 0 and the faster the filament thins out below the spinning nozzle). By means of the equations it is also possible to show that the birefringence and simultaneously the polymer chain orientation are directly proportional (at the filament solidification point) to the line tension, that is $\Delta n = (F/A)(K/T)$. According to the Tables, the nozzle capacity for the samples no. 14-18 is constant, and the quantity and velocity of the quenching air vary. In the samples no. 14-16, the line tension decreases when the quenching air velocity decreases, whereby correspondingly the deformation rate ($\delta v/\delta y$) and the gradient dA/dy decrease (Figure 4). In the sample no. 18, a separate oxygen nozzle has been used, whereby the oxygen dissolved in the filament decreases the melt viscosity and consequently also the line tension force, the deformation rate, the dA/dy-gradient and also the polymer chain orentation (Table 2, Figure 4).

[0056] In the following, the diffusional oxygen transport through the molten filament surface formed in spinning and subject to deformation as a function of time, will be briefly studied. The lack of sufficiently precise oxygen solubility and diffusion data in the molten polymer, prevents a quantitative assessment of diffusion. In diffusional oxygen transport, the quantity of material transported per time unit (dm/dt) is directly proportional to the diffusion constant (D), to the surface (A) perpendicular to the diffusion stream and to the concentration gradient (dc/dx) in the direction of the diffusion stream, that is, according to Fick's law /21/

$$dm/dt = D \text{ x } A \text{ x } (dc/dx). \qquad /15/$$

Thus in melt spinning, the shell surface formed over the deformation zone extending from the nozzle temperature to the solidification temperature is suitable for diffusion.

[0057] The Table 2 and the Figure 4 show the surface-areas of the filaments as a function of time, temperature and distance from the nozzle. In this connection, the values for the filament surface and the corresponding deformation time obtained at the distance y = 0.6 and the solidification point are compared using the Table and the Figure. The filaments used for comparison correspond to the nozzle diameter values 0.70 mm (no. 319) and 0.30 mm (no. 14). The sample 0.30 mm (no. 18) is included in the comparison for establishing the effect of oxygen. For the product N x A_v x τ (cm^2·s) which is proportional to the level of oxygen transport, the following values are obtained at the said distances: N x A_v x τ/no: 3.426/319 - 0.327/14 - 0.742/18 and (115 °C) 30.69/319 - 0.436/14 - 1.615/18.

From the results it can be seen that under the conditions studied, the effect on the oxygen transport of the difference in deformation surfaces of filaments corresponding to the large and small nozzle diameter is very big. The effect of oxygen on the diffusion system as a result of the change in deformation surface, can increase to be important.

It is also to be noted that the difference between the oxygen diffusion constants corresponding to the spinning and solidification temperatures is approximately 1.5-2 decades. As a coarse approximation, the value for the amorphous polypropylene phase at low temperature was selected for the value of the diffusion constant (/5/, Jellinek: $D_o = 1.5$, $E = 8700$ cal/mol) without any correction for orientation, oxygen concentration *etc.*

Based on the changes in filament surface area, deformation time and molecular chain orientation the results of the subexample 1.2 clearly show that the oxidation nozzle has to be placed in the immediate vicinity of the spinning nozzle surface. In order to increase the values for the oxygen surface concentration (solubility) and correspondingly the concentration gradient (the force behind diffusion), the oxygen partial pressure in the oxidative gaseous phase should be as a high as possible.

Subexample 1.3

[0058] The subexample 1.3 concerns the implementation of an autogenous oxidation-degradation process of a molten-state spinning filament surface and a corresponding regulation method by means of pilot test series.

[0059] Based on measurements carried out on the spinning profile of a molten filament (subexample 1.2), it is evident that the oxidation has to be directed to the very beginning of the largest filament deformation area, where the oxidation area of the filament is largest, the spinning line tension (SLT) lowest, the temperature decrease low, the deformation delay time longest and the polymer molecular chain orientation after the nozzle at its lowest.

[0060] In a shortspinning system, the quenching distance of the filament after the nozzle is only 25 mm, that is very short compared to the 250-1500 mm of the longspinning system. Due to the very low processing space, the oxidation and quenching nozzles for the filament are separated from each other in the method according to the invention. In the method, oxidation is carried out as a targeted oxidation using a very narrow nozzle gap (0.60 x 460 mm) and sufficently high velocity, so that the oxidation gas phase, if necessary, is able to penetrate the tail part of the quenching gas stream into the filament space. The method of blowing is based on the poor mixability of the gases under the said conditions /22/. The position of the oxidation nozzle with respect to the filament bundles and the spinning nozzle surface has to be adjusted carefully (Figure 3) for the oxidation to be successful.

[0061] Although the amount of oxygen needed in the filament oxidation and thus that exiting from the nozzle is small, oxygen enriched air is used in the oxidation and in the adjustment thereof, if necessary. An increase in the oxygen level in the blowing air affects the steepness of the radial oxygen concentration gradient in the filament /21/, and simultaneously the level and site of molecular chain degradation.

By decreasing the oxygen deficiency in the filament surface and outside, it is possible to affect the quality and quantity of evaporating oxygen compounds. In difficult spinning conditions (small nozzle diameter, production of fine filaments, *etc.*) it is possible to effectively use, in the spinning, the net heat between the oxidation and endothermal evaporation reactions (which is a function of the oxygen concentration) for heating the surface areas of the polymer filament.

[0062] Several pilot spinning test series were made for developing the spinning oxidation and its regulation system. Measurement results from these test series are given in the Table 3 and the Figure 5.

[0063] By means of the test series no. 309, the performance of the regulation system according to the invention was tested with respect to the operation of the quenching and oxidation nozzles. The initial molecular weights and the melt index of the polymer in the test series were: M_w = 255000, M_n = 49250, D = 5.25 and MFI = 13.5. The temperatures of the extruder heating zones and the spinning spinneret were: 255-265-265-280-290-290 °C and 295 °C. The spinning melt temperature was 286 °C. The capacity of the spinning pump was P = 42.78 dm^3/h. The diameter of the spinning nozzle was D_s = 0.70 mm and the corresponding nozzle positions for the quenching and oxidation nozzles have been given in the subexample 1.1 and the Figure 3. The sample numbers 7-16 of the Table 2 correspond to the position b of the oxidation nozzle and the sample numbers 21-25 correspond to the position a. From the measurement results of the Table 2, the following regulation equations for the oxidation with respect to the velocities of the quenching air and oxygen are obtained:

$$\text{309-b: MFI} = 1.914 \times v_{O2} - 2.427 \times v_i + 93.248 \qquad /16/$$

$$\text{309-a: MFI} = -0.165 \times v_{O2} - 2.427 \times v_i + 93.248 \qquad /17/$$

The volume and flow rates of the Table 3 are not of STP-type, but correspond to production conditions (ϑ = 24 ± 1°C, p = 1.0 bar). It was established that the simple regulation equation obtained could be applied with sufficient accuracy when using the so called partial pressure velocity as the oxygen flow velocity, that is $v_{O2} = P_{O2} \times v$, where v is the velocity of the oxygen enriched air. For the samples no. 7-12 of the test series, the quenching gas velocities and corresponding spinning line tensions (SLT) were approximately of the same magnitude, but for the samples no. 13-16, the said values differ considerably from each other. The values calculated from the equation correspond in all samples quite well to the values obtained by direct measurement. From the Figure 3 of the subexample 1.1 it can be concluded that when the oxidation nozzle is in the position a (samples: 309-21-25), the oxidation jet intersects the major part of the quenching jet. According to the Table 2, the flow velocities of the oxidation jet do not exceed those of the quenching jet, and consequently the regulation equation changes from the former to be according to that of the equation /17/. The slightly negative factor for the oxygen flow indicates the cooling effect of the oxygen in the system.

[0064] In the test series no. 314 the same test conditions have been used as in the series no. 309, but the spinning nozzle diameter was only $D_s = 0.25$ mm. The oxidation nozzle was in the position b. The obtained oxidation function [$MFI = 29.8 + 0.376 \times v_{o2}$] has been drawn in the Figure 5, which, as does the Table 3, shows ineffective oxidation (corresponding to the spinning deformation) of the samples in the series. The initial, that is the quenching oxidation of the samples was also quite low.

[0065] In the test series no. 325 and 326 the spinning nozzle diameter $D_2 = 0.30$ mm was used. The oxidation nozzle was moved to the position c (Fig. 3) and it could be used either 1- or 2-sidedly (series no. 325 and no. 326). As the oxidation nozzle, operating in the near vicinity of the spinning nozzle surface, cools the same small electrical resistances have been mounted in the spinning nozzles to increase the surface temperature of the spinning nozzles to correspond to the spinning temperature and at the same time to eliminate polymer surface growth. As a result of nozzle and temperature corrections, the regulation system for oxidation corresponds essentially to the result of the test series no. 309, but the quenching oxidation is still very low
(Fig. 5.). The oxidation equation for the test series no. 325 is of the form

$$MFI = 1.914 \times v_{o2} - 0.7363\, v_i + 62.645 \qquad /18/$$

The use of a two-sided oxidation nozzle improves the oxidation result. Decreasing the free opening of the oxidation nozzle increases flow rates and correspondingly the oxidative degradation, which is to be taken into account especially as a factor decreasing the oxidation gas levels when using a 2-sided nozzle.

[0066] The basic factors affecting the level of quenching oxidation and degradation are the temperature, nozzle size and corresponding spinning deformation, feed capacity, oxygen content of the quenching gas, molecular weight distribution, *etc.*

[0067] The use of oxygen enriched air in quenching for increasing degradation is not economically feasible in the large amounts needed for a production scale operation. In the spinning conditions used for the test series no. 309, the overall capacity corresponding to the nozzle plate being constant, the effect of the nozzle size on the melt index is approximately: D_s, mm/MFI: 0.25/27 - 0.30/30 - 0.40/35 - 0.70/41. Due to the high spinning draw ratio, the use of a large-diameter size nozzle results in quality problems in production scale manufacture of fine-gauge fibers.
A high spinning melt temperature facilitates the quenching degradation, but its applicability is governed by the rheological properties of the polymer and the quality requirements for the spinning product. A high temperature also results in a strong thermal degradation in the extruder, which weakens the mechanical properties of the fiber and also the effect of a successfully accomplished peripheral degradation.

[0068] Economical, production scale manufacture of high-quality, fine-gauge fibers requires *i.a.* the use of as small as possible quantity of oxidative air, low oxygen enrichment, a small nozzle diameter, a low spinning temperature.
For further developing the regulation method according to the invention, test series were carried out to modify the supply polymers to suit the filament peripheral oxidation in a shortspinning system. Hereby the starting point was the mixing together of very low and very high molecular weight propylene polymers, whereby it was assumed that also at low nozzle speeds in the shortspinning system the short-chain polymer would be enriched in the surface portion of the filament, due to the big viscosity difference. At the same time, the short-chain polymer would act as a softener in the mixture, especially during extrusion. In case of successful mixing, also a degradation rate increase in the system caused by non-random molecular chain end initiation could be taken advantage of. Also the temperature of the spinning melt could be lowered, whereby the level of thermal degradation in the extrusion would decrease and a properly surface degraded fiber would be obtained without a substantial decrease in the mechanical properties of the product fiber.
In the test series no. 331, molten-state filament oxidation is performed on a mixture of two propylene polymers of highly differing chain length. In the test series, a 1-sided oxidation nozzle was used in the position c., the spinning temperature was 265 (270) °C and the spinning nozzle 0.25 - 30500. The spinning mixture contained 5 and 10 % by weight polymer with a melt index of 400 (no. 032) mixed with a polymer (no. 031) having a melt index of 4.4. In the results given in the Table 2, the former mixture is represented by the sample numbers 5-10 and the latter by the sample numbers 1-3 (see also Fig. 5 and the subexample 1.4).
For the regulation equation for spinning oxidation one obtains as a function of the oxygen flow partial pressure velocity (without recognizing the quenching rate)

$$5\ \%\ \text{no. } 32\text{: } MFI = 1.293\, v_{02} + 28.61 \qquad /19/$$

$$10\ \%\ \text{no. } 32\text{: } MFI = 4.026\, v_{02} + 47.89 \qquad /20/$$

From the results it can be seen that an addition of 5 % by weight of PP-32 does not increase the quenching degradation to any higher degree (as compared to the other values for the small nozzle diameter series) but at higher additions the value for the quenching degradation increases rapidly (the shear viscosity logarithms being essentially linear with respect to concentration). By suitably modifying the spinning polymers, very favourable and required regulation values can be obtained when operating at small nozzle diameter values and production-scale feed capacities.

Subexample 1.4

[0069] The subexample 1.4 studies the changes in the polymer molecular distribution and the melt indices occuring in the molten state peripheral oxidation of the filaments of the test series of the subexample 1.3.

[0070] The following Table gives the results from the GPC analyses (solvent TCB, 135 °C and columns TS 9S & TS 10S) and melt index values (ASTM D 1238: 21.6 N/230 °C) of some melt oxidized spinning filaments as well as supply polymers of the test series no. 309 (and 331) from the subexample 1.3.

Sample	M_w	M_n	M_v	M_w/M_n	MFI
no	g/mol	g/mol	g/mol	-	g/10 min
0	255000	49250	109000	5.25	13.5
7	192000	43400	160500	4.40	41.5
11	196000	44500	163500	4.40	47.2
15	189000	42700	157500	4.50	51.3
9	171000	33400	142500	5.00	59.8
12	186500	35000	154000	5.50	76.3
031	407500	58200	320500	7.00	4.4
032	124450	32280	105480	3.86	400
033	98412	22149	82180	4.44	800
035	277900	53210	-	5.33	12.1

[0071] The following equations were obtained for simulating the largely thermo-mechanical and simultaneous slight chemical degradation occuring in the extrusion process carried out in a normal air atmosphere in the test series no 309:

$$M_n = 6.602 \times 10^4 \times (\mathrm{MFI})^{-0.1126} \text{ and } M_w/M_n = 7.727 \times (\mathrm{MFI})^{-0.1485}.$$

[0072] The obtained result can be compared to the extrusion results obtained both under a protective gas and air atmosphere.

[0073] From the time-temperature functions simulating the distribution results in the thermal degradation study of Chan & Balke /6/ (under the delay time and melt temperature conditions corresponding to the 309 series: $\tau = 5$ min, $\vartheta = 286°C$) one obtains for the unstabilized polymer only slightly lower molecular weight decreases than in the series no. 309 (Δ M_w and Δ M_n:C&B: 69485 and 8111, *i.e.* - 29.8 and -13.7 %; no 309: 63000 and 5850 *i.e.* -24.7 and-11.9 %). Thus a conventional amount of antioxidant in the polymer of the test series no. 309 (phosphite-phosphonite mixture + antiacid: 0.2 %) is not of great importance in decreasing the thermal degradation.

The degradation results obtained in the test series 309 in an extruder correspond to conventional multiple extrusion results in the presence of air, *i.a.* from the MWD-MFI-measurements of H. Hinsken et al /7/. The slope of the functions ln M_w, ln M_n and ln (M_w/M_n) / ln MFI simulating the measurement results are approximately the same in both series.

[0074] The level of chemical degradation caused by the quenching air after the extruder is dependent on the spinning conditions (subexample 1.3). Under the spinning conditions used in the area of study this level is low as compared to the thermal and mechanical degradation. The use of an oxidation nozzle (side nozzle) in correspondence with the novel method results in substantial changes in the slopes of the ln M/ln MFI functions simulating the degradation effects, as compared to the above mentioned functions obtainable from the measurement values of Hinsken /7/. The ln Mw-values of the samples in the series no. 309 decrease less and the ln Mn-values more steeply as a function of the oxidation degree than the afore mentioned measurement values. The most essential change, however, takes place in the dispersion values, which increase rather than decrease as is the case in conventional oxidative degradation. In the side nozzle oxidation of the test series no. 309, the following equations simulating the number average molecular weight and dispersion results are obtained:

$$Mn = 2.159 \times 10^{5} \times (MFI)^{-0.420} \text{ and } Mw/Mn = 0.925 \times (MFI)^{+0.411}; \text{ (/7/: } Mn = 7.351 \times 10^{4} \times (MFI)^{-0.103} \text{ and } Mw/Mn = 6.700 \times (MFI)^{-0.1635}). \qquad /21/$$

[0075] The broadening of the polymer molecular weight distribution as a results of the oxidation is not conventional. It can, however, be shown with MWD-balance calculations that in non-random degradation, which degradation following surface oxidation also is, the dispersion of the overall distribution in the filament increases with increased oxidation (the dispersion values of the parts simultaneously decreasing in the radial direction of the filament). It can be mentioned that a similar increase in the dispersion values has been found in solid-state surface degradation (S. Girois et al. /10/, J. E. Brown et al. /9/).

[0076] In the examples contained in the description in the US patent 5.281.378 /18/ relating to peripheral oxidation, only the Mw/Mn- and MFI-values are given for the oxidized samples (the Mn- and Mw-values are lacking). In the test series B, C and D falling under the scope of the claims, the initial values for the ratio Mw/Mn were 7.75, 6.59 and 7.14. The Mw/Mn-ratios for the test series are almost of the same magnitude after oxidation (5.3 ± 0.3) and independent of the MFI-values (or decrease slightly when the melt index increases). The behaviour of the test series A is similar, but the starting and final values are: Mw/Mn = 5.35 and 4.49 ± 0.08. The distribution values given in the method behaved anomalously and do not support the occurence of layered surface degradation.

[0077] It can also be mentioned that, as is known, broadening of the molecular weight distribution according to the new oxidation-degradation method is a change facilitating the thermobonding of the product fibers.

[0078] The Figure 6 represents a differential molecular weight graph corresponding to the distributions given in the above Table. It shows that the distributions are shifted under the effect of oxidation toward low molecular weights. Based on the distribution graph, it is not, however, possible to evaluate the Mn- and Mw/Mn-changes during oxidation as especially the effect of the Mn-changes on the total distribution is low. The Figure 7 shows an AFM-image of a cross-section of an etched ($CrO_3 + H_2SO_4$) filament sample. From the image it can be seen that a radial surface layer of the fiber has dissolved, which also shows the weaken-ing of the structure as a result of the oxidation of the filament surface layer and the change in the molecular weight distribution.

The Figure 8 shows a BSE-image of cross-section of an oxidized filament sample. From the image the lighter diffusion area (impoverished zone) of the surface layer caused by the oxidation as compared to the inner structure of the filament can be seen. The surface layers of the sample were not able to resist the bombardment from the electron gun sufficiently to carry out a line analysis (apparatuses: SEM, 360 Cambridge and EPMA, Cameca-camevax microbeam).

Subexample 1.5

[0079] The subexample 1.5 studies thermobonding of staple fibers from molten-state, peripherally oxidized polypropylene filaments made according to the invention.

[0080] The basics relating to thermobonding of a nonwoven fiber web from synthetic fibers are disclosed in detail in the patent application FI 961252/18.03.96 (EP 97660030.4/14.03.97).

The constant terms for the fabric tensile strength and elongation equations which quite accurately simulate the obtained test results, are indicated in the Table 4. The logarithmic graphs of the equations corresponding to the tensile strength values of the test fabrics are presented in the Figure 9. The fibers corresponding to the numbers 1-7 and 12 in the Table and the Figure are prepared by oxidizing to various degrees of degradation and processing the same starting polymer. The fabrics corresponding to numbers 8, 9, 10 and 11 are for comparison. The fiber no. 11 is a conventional productional fiber made by shortspinning. The fibers no. 8, 9 and 10 are skin-core imported fibers. These fibers are made by longspinning and their detailed production conditions are not known. The properties of the test fibers of the Table 4 are collected in the Table 6.

From the theoretical maximum values for the fabric strengths of the Table 4 and the Figure 9 it can be concluded that when the level of peripheral oxidation increases (the MFI-values increase and the Mw- and the Mn-values decrease: subexample 1.4), the strength functions of the fabrics are shifted toward low bonding temperatures. The values (E) for the fabric bonding activation energies are within the limits of accuracy of measurement of the same magnitude for fibers made from the same starting polymer. The tensile strength and elongation ($\sigma_{||}, \in_{||}$) bonding equations at high bonding temperature of nonwovens from the fibers seem to join and form an envelope of maximum strengths (Fig. 9.: no. 00 and equations no. 1-7, 12). The joining of the equations is not precise for the strength values in the direction perpendicular to the carding direction ($\sigma_{\perp}$, $\in_{\perp}$) which could be due to the wider spread of the measurement values than in the former case.

The envelope curve clearly shows that the fabric strength values increase when the bonding temperature decreases, the degradation degree of the fiber surface layer increasing. The improvement in bonding can be derived from an increase in the surface melt quantity of the fiber, the easier relaxation of the draw orientation at decreasing chain length (whereby the orientation derived shrinkage, which is detrimental to bonding, decreases), improvement in the melt-solid-contact, *etc.* It can also be concluded that the use of a solid-state mechanical drawing process after spinning for increasing fiber strength requires a precise heat treatment also for surface degraded fibers.

[0081] From the values in the Table 4 it can be concluded that the difference in the maximum strengths for the fabrics corresponding to the fiber samples no.1 and no. 5 is 28.3 % ($\sigma_{||}$) and correspondingly 175.7 % ($\in_{||}$). The increase in tensile strength, due to oxidative degradation, between the said samples is thus modest, but the increase in elongation is substantial. The tensile strength ratio for the fabrics from the same series of is the form

$$\sigma_{||}/\in_{||} = [\mathrm{MFI}/(\mathrm{MFI})_O]^{-0.794} \times 3.235 \times 10^6 \times \exp[-12390/RT] \qquad /22/$$

Thus, in the test series, an increase of the melt index ratio and the bonding temperature has a decreasing effect on the $\sigma_{||}/\in_{||}$-ratio, whereby the effect of the change in the melt index ratio is bigger than the temperature effect.
As regards the elongation and tensile strength ratios it can be concluded from the test results that in the said test series the elongation ratio, $\in_{\perp}/\in_{||}$ decreases slightly and correspondingly the tensile strength ratio, $\sigma_{\perp}/\sigma_{||}$ remains constant or increases slightly when the MFI-values increase.
It can be mentioned that the $\sigma_{||}/\in_{||}$-ratio for the fabrics corresponding to the comparison fibers no. 10 and no. 11 are correspondingly of the form:

$$\sigma_{||}/\in_{||} = 2.443 \times 10^7 \times \exp[-13780/RT] \text{ and } \sigma_{||}/\in_{||} = 0.808 \qquad /23/$$

(i.e. e.g. T = 433°k,($\sigma_{||}/\in_{||}$)/no: 1.04/1, 2.70/10 and 0.81/11).

[0082] From the thermobonding results for the fiber nonwovens it can be generally concluded that the tensile strength and elongation results obtainable with the fabrics are strongly polymer-specific. The increase in fabric tensile strength as a result of oxidative surface degradation of the fibers is rather limited (limited both by the polymer characteristics and by the textile characteristics of the fabrics). Regulation of the fabric elongation by means of surface degradation is possible within fairly broad limits. By varying the polymer quality (Mw, MWD, softeners and other adjuvants and additives), an application system with its regulation ranges is obtained analogous to that described for the effect of fiber surface degradation, but corresponding to different strength values.

Subexample 1.6

[0083] The subexample 1.6 studies the performance of some product fibers peripherally oxidized in a method according to the invention when subjected to oxidizing evaporation and loop bonding. The aim is to recognize possible kinetic differences in fibers oxidized as molten filaments, as a result *i.a.* of changes in the molecular weight.

[0084] The oxidizing evaporation follows first-order reaction kinetics, *i.e.* the equation simulating the evaporation effect is

$$1 - \alpha = \exp(-k \times t), \qquad /24/$$

wherein α is the evaporated weight fraction and the reaction rate constant,(K, min^{-1}), is of the form

$$K = k_O \times \exp[-E_O/RT] \qquad /25/$$

The Table 5 contains constants for the reaction rate equations for the oxidizing evaporation of some peripherally oxidized fibers (and starting polymer) under isothermal evaporation. According to the Table, the activation energy for the overall process is constant (within limits of accuracy of measurement) both in polymer and fiber evaporation. From the results it can be seen that the decrease in the evaporation rate is substantial between the starting polymer and the peripherally oxidized samples. The differences between the filament oxidized samples are, however, rather small, although also with these, the rate decreases with increasing melt index.
The change in the oxidative evaporation rate as a function of the change in melt index is of the form

$$K = 2.1945 \times 10^{7} \times [MFI/(MFI)_{O}]^{-0.172} \times \exp[-22392/RT] \quad /26/$$

[0085] For comparison, the equation constants for the oxidative evaporation of a polymer with a melt index of MFI = 30 are indicated in the Table 5, using both air and oxygen oxidation (no:s 0-1 and 0-2). The molecular weights of the polymers being compared (0-0 and 0-1) differed from each other considerably and were (before oxidation): Mw-Mn-D: 254000-49700-5.1 and 193399-34930-5.53. According to the Table, the polymers 0-0 and 0-1 have activation energy values of equal magnitude for the oxidative evaporation (within the limits of accuracy of measurement). When oxidizing with oxygen, the evaporation process is only four times faster than when oxidizing with air (with different polymers even up to 12-fold differences have been obtained in the evaporation rate values between air and oxygen oxidation). After the incubation time, the oxidation-evaporation process mechanism is similar for all the samples. The oxidation of the surface area of the melt filament is so modest that its effect on oxidative evaporation in the system studied is quite small. It can be mentioned that the kinetic equation for the oxidative evaporation of the comparison polymer, especially at high α-values, matched the Avrami-type kinetic equation ($1-\alpha = [\exp -(kt)^{n}]$) valid for a low time exponent (n = 1.20), better than the pure 1-order form.

The equation for the incubation time in the oxidative evaporation for both the starting polymer and the surface oxidized fiber series was

$$t_{O}, \text{min} = 1.584 \times 10^{-3} \times \exp[8163/RT] \quad /27/$$

A surface effect of the peripheral oxidation can thus be seen also in the incubation time, which is a function largely of the antioxidant and stabilizing agents in the polymer (*i.e.* a major part of the stabilizing agent content in the polymer is still present due to the extremely short delay time in the peripheral oxidation).

The incubation times for the oxidative evaporation of the comparison polymer in air and oxygen oxidation were correspondingly:

$$to, \text{min} = 7.112 \times 10^{-5} \times \exp[12149/RT \quad /28/$$

$$to, \text{min} = 1.755 \times 10^{-2} \times \exp[5450/RT] \quad /29/$$

Thus oxygen oxidation decreases the temperature dependency of the incubation time and shortens the incubation times.

In addition, it may be concluded from the results of the oxidative evaporation that the kinetics of the peripheral oxidation of the melt filament is polymer-specific and is affected not only by the molecular weight distribution but also by the polymer additive content.

[0086] The effect of gas phases containing nitrogen and carbon dioxide on 'oxygen-free' evaporation of polypropylene will be studied by means of dynamic thermogravimetric measurement series. The test series also shows the effect of the bound oxygen contained in the combustion gases from fossile fuels in the oxygen-free evaporation in the filament quenching stage. The molecular weights of the conventional spinning polymer used in the tests were: $M_w = 206000$, $M_n = 33450$ and D = 6.15.

The results from the dynamic measurements are not accurate but a comparison of the results indicates in a qualitative manner the direction of the reactions. In the comparison, the results have been extrapolated with respect to the temperature. This is due to the increase in the evaporation rate as a result of the increase in the oxidation degree of the carrier gas phase, whereby the optimum temperatures for evaporation in the different test series fall in different temperature areas in the range 250-500 °C.

The equation simulating the change of the evaporated fraction (α) as a function of temperature (dT/dt = 20°C/min.) is of the form $\alpha = a \times T^2 \times \exp(-E/RT)$.

The equation constants a and E (cal/mol) corresponding to different compositions of the carrier gas phase are: N_2: 3.058×10^4/35499, CO_2: 5.317/22072, $21O_2 + 79N_2$: 1.904×10^{-1}/15434 and $49O_2 + 51N_2$: 8.352×10^{-1}/16148. Compared to the evaporation values for nitrogen, the following comparison series are obtained corresponding to the temperatures 300 °C and 390°C: $49O_2 - 21O_2 - CO_2 - N_2$: 658 - 281 - 23 - 1 and 66 - 26 - 5 - 1.

The result thus shows that, compared to the oxidative evaporation values, quenching of the melt filament with combustion gases ($CO_2 + N_2$) corresponds almost to the values for non-oxidizing evaporation.

[0087] The Table 5 includes results from loop bonding tests (*i.a.* FI-application no. 961252/180396: p. 29, line 20 -

p. 30, line 9; EPO no. 079922) at high (index 2) and low (index 1) temperature for some peripherally oxidized fibers. The loop bonding equation is with respect to the tensile strength of the form

$$\sigma\text{, mN} = c_{1.2} \text{ x } T^2 \text{ x } \exp[-E_{1.2}/RT] \qquad /30/$$

From the results in the Table it can be concluded that the bonding strengths of peripherally oxidized fibers as a function of the temperature do not differ much from each other irrespective of different melt indices. This could be due to the use of a low temperature increase rate (10 °C/min) in the tests, whereby the short-chain partial melt formed at low temperature solidifies again prior to bonding. This assumption is supported also by the position of the strength function corresponding to the rather high bonding temperature. The strength function of a rapid spinning fiber (8-735), used as a comparison fiber, is positioned at the lower bonding temperature of the oxidized fibers irrespective of its higher molecular weight (12-309: 186000 - 5.2 and 8-735: 220000 - 5.5). Compared to conventional fibers, also a high temperature bonding area is evident in the thermobonding of peripherally oxidized fibers, where the change in tensile strength as a function of temperature is small, but on the other hand the increase in elongation (%) and energy to break (mN x mm) is considerable. This is due to the better wettability and spreadability of the bonding melt along the solid surfaces of the fiber body.

[0088] In the present description, the applicability of the new regulation method has been shown both for a fiber and a fabric. It is to be taken into account that the very complicated regulation method for the manufacturing process for the fibers and the nonwoven fabrics to be made from these, can be varied in very many ways within the operational area encompassed by the given examples and the claims.

TABLE 1. Measurement of the dynamic deformation of a spinning filament: Test run conditions

No	Spinning nozzle		Capacity		Quenching		Oxidation		Spinning			
	D_s mm	N_s kpl	n_r 1/min	P kg/h	V m^3/h	v_i m/s	V_s dm^3/min	v_{o2} m/s	λ_k	v_1	d_1	$10^{-4}KJ$
1	0.30	30500	15.15	31.0	887	46.02			119	31.4	5.35	13.38
3	0.30	30500	15.15	31.0	887	46.02			274	72.5	2.33	13.38
14	0.30	30500	10.0	20.4	1076	55.83			181	31.6	3.53	24.89
13	0.30	30500	10.0	20.4	888	46.08			181	31.6	3.53	20.52
16	0.30	30500	10.0	20.4	621	32.21			181	31.6	3.53	14.18
18	0.30	30500	10.0	20.4	623	32.33	150	9.06	181	31.6	3.53	11.54
319	0.70	12132	15.55	31.8					1305	163.6	2.67	41.65
310	0.70	12132	15.55	31.8	436	22.62			647	81.1	5.38	19.04

TABLE 2. Measurement of the dynamic deformation of a spinning filament: Measurement results

Sample number Quantity	3	319	14	13	16	18
10^5A_v , cm^2	615 (376)	4582 (1200)	348 (278)	437 (320)	518 (333)	662 (380)
10^6A , cm^2	5.04	6.16	4.53	5.31	6.16	7.07
τ , ms	75 (63)	552 (235)	41 (39)	79 (73)	58 (50)	80 (64)
A_v/A_v (319)	0.143 (0.314)	1.000 (1.000)	0.076 (0.232)	0.095 (0.266)	0.113 (0.278)	0.144 (0.317)
10^4P_s , cm^3/s	3.12	8.04	2.06	2.06	2.06	2.06
λ -	274	1305	181	181	181	181
10^4KJ , mN/cm^2	13.4 (0.80)	41.7 (0.05)	24.9 (3.94)	20.5 (1.86)	14.2 (0.80)	11.5 (0.78)
y , mm	2.1	6.3	1.2	1.5	1.8	2.1

TABLE 3. Oxidation of a molten-state spinning filament

Sample series Quantity	7-309	11	8	9	12	15	13	16	14-309
Quenching air V_i m^3/h	411	410	411	410	466	466	534	605	858
v_i m/s	21.3	21.3	21.3	21.3	21.3	24.2	27.7	31.4	44.5
Oxidation air V_i dm^3/min	0	300	200	300	300	300	300	375	400
$[O_2]$ vol.-%	0	21	61	61	100	47	100	74	100
v_{O2} m/s	0	3.81	7.31	11.0	18.1	8.58	18.1	16.7	24.2
SLT mN/m^2	31.5	27.1	28.1	29.3	31.3	30.1	29.6	32.3	47.0
d_1 dtex	2.80		2.95	2.68	2.93			2.84	3.12
D_s mm	0.70								0.70
MFI g/10 min	41.5	47.2	61.7	59.8	76.3	51.3	65.3	49.0	30.9
ϑ_k °C	286								286

TABLE 3. (cont.)

Sample series Quantity	21- 309	22	23	24	25- 309	1- 310	2	3	5- 310
Quenching air v_1 m^3/h	410	412	412	412	412	408	435	530	531
v_1 m/s	21.3	21.4	21.4	21.4	21.4	21.2	22.6	27.5	27.6
Oxidation air v_i dm^3/min	0	200	300	400	500	200	200	200	200
$[O_2]$ vol.-%	0	61	61	61	61				
v_{O2} m/s	0	7.31	11.0	14.6	18.3	7.31	7.31	7.31	12.1
SLT mN/m^2	30.9	36.5	41.1	39.3	41.1	35.1	22.9	20.4	26.4
d_1 dtex	2.97								
D_s mm	0.70								0.70
MFI g/10 min	41.5	39.3	36.8	37.9	36.4	-	-	-	-
ϑ_x °C	286								286

TABLE 3. (cont.)

Sample series Quantity	7-326	8	9	11	13	14-326	5-314	7	10-314
Quenching air V_i m³/h	863					863	724		724
v_i m/s	44.8					44.8	37.6		37.6
Oxidation air V_i dm³/min	0	200	250	150	200	300	0	160	220
$[O_2]$ vol.-%	0	21	21	100	61	61	0	51	64
v_{O2} m/s	0	1.27	1.59	4.53	3.65	5.48	0	4.89	8.51
SLT mN/m²	29.6	27.2	26.3	27.8	27.1	25.3	43.9	41.5	39.5
d_1 dtex									
D_s mm	0.30					0.30	0.25		0.25
MFI g/10 min	29.4	31.2	43.0	38.7	42.1	39.1	29.8	31.6	33.0
ϑ_k °C	286								286

TABLE 3. (cont.)

Sample series Quantity	1- 331	2	3	5	6	7	8	9	10- 331
Quenching air v_l m^3/h	857	857	857	712	712	712	806	788	787
v_l m/s	44.5	44.5	44.5	36.9	36.9	36.9	41.8	40.9	40.8
Oxidation air V_l dm^3/min	0	100	100	0	100	100	150	200	150
$[O_2]$ vol.-%	0	21	100	0	21	100	100	100	100
v_{O2} m/s	0	1.27	6.04	0	1.27	6.04	9.06	12.08	9.06
SLT mN/m^2	20.9	19.7	18.9	19.8	20.9	21.7	22.5	21.6	22.0
d_1 dtex	2.53								
D_s mm	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
MFI g/10 min	47.9	42.6	72.2	31.2	30.3	36.6	36.6	44,3	37,8
ϑ_k °C	265	265	265	270	270	270	270	265	265

TABLE 4. The constant terms for the bonding equations

$T < Tm: \sigma(\epsilon) = c_1 \times T^2 \times \exp[-E_1/RT]; \ T > Tm: \sigma(\epsilon) = c_2 \times T^2 \times \exp[+E_2/RT]$

Fiber no	Strength value	E_1 cal/mol	$\ln c_1$ -	σm/T N/K	E_2 cal/mol	$-\ln c_2$ -
1	σ_{II}	47179	46.3555	44.93/434.2	11917	2.1600
	$\sigma_{\perp}$	47179	44.4296	8.13/435.9	119.17	23.8241
	ϵ_{II}	34787	31.9085	40.91/434.1	42908	58.1968
	$\epsilon_{\perp}$	34787	32.6588	91.73/434.7	42908	57.3251
2	σ_{II}	47179	47.1278	51.36/429.4	11917	22.1600
	$\sigma_{\perp}$	47179	45.2068	9.30/431.0	11917	23.8241
3	σ_{II}	47179	47.3700	53.55/427.9	11917	22.1600
	$\sigma_{\perp}$	47179	45.4755	9.74/429.3	11917	23.8241
	ϵ_{II}	34787	33.0634	83.84/429.6	42908	57.9728
	$\epsilon_{\perp}$	34787	33.6212	158.6/430.4	42908	57.2448
4	σ_{II}	47179	47.7943	57.62/425.3	11917	22.1600
	$\sigma_{\perp}$	47179	46.1540	10.96/425.1	11917	23.8241
5	σ_{II}	47179	47.9294	48.67/423.1	11917	(22.1600)
	$\sigma_{\perp}$	47179	46.3161	11.27/424.1	11917	23.8241)
6	σ_{II}	47179	48.1339	61.12/423.2	11917	(22.1600)
	$\sigma_{\perp}$	47179	46.4457	11.55/423.4	11917	23.8241)
7	σ_{II}	47179	46.9030	49.40/430.8	11917	22.1600
	$\sigma_{\perp}$	47179	44.9398			

TABLE 4. (cont.)

Fiber no	Strength value	E_1 cal/mol	$\ln c_1$ -	$\sigma m/T$ N/K	E_2 cal/mol	$-\ln c_2$ -
8	σ_{II}	35026	32.9604	57.75/429.7	16062	26.8859
	ϵ_{II}	35026	32.6815	45.60/430.2	40418	55.6087
9	σ_{II}	27552	24.2510	56.64/428.9	21254	33.0306
	$\sigma_{\perp}$	27552	22.3882	9.49/429.9	21254	34.8149
	ϵ_{II}	27552	24.3986	58.84/427.6	38042	52.8314
	$\epsilon_{\perp}$	27552	24.9100	102.1/428.1	38042	52.2306
10	σ_{II}	35746	33.9019	81.5/432.2	20521	31.6406
	$\sigma_{\perp}$	35746	31.3678	7.0/433.0	20521	34.0487
	ϵ_{II}	21964	16.8906	32.2/432.7	33774	47.9609
	$\epsilon_{\perp}$	21964	17.5786	62.6/432.3	33774	47.3295
11	σ_{II}	42500	41.0216	47.91/434.0	11919	22.1023
	$\sigma_{\perp}$	42500	39.3306	11.40/436.2	11919	23.4789
	ϵ_{II}	42500	41.2353	51.25/432.7	11919	22.0687
	$\epsilon_{\perp}$	42500	42.0734	100.3/431.4	11919	21.4351
12	σ_{II}	48740	48.4556	39.48/431.1	16592	27.8304

TABLE 5. Oxidating evaporation. Loop tests.

Sample no	$\ln k_0$ -	E_0 cal/mol	$\ln c_1$ -	E_1 cal/mol	$-\ln c_2$ -	E_2 cal/mol	MFI g/10 min
3-285			53.9292	51955	19.5072	12260	-
12-309			53.9899	51955	37.7305	27770	76.3
2-247	16.9874	22790	54.0296	51955			59.9
8-735			52.8168	50507			-
5-254	16.7039	22392					45.8
1-254	17.1454	22790					26.7
0-0	17.6147	22790					13.5
0-1	16.0720	22190					30.0
0-2	18.0314	22850					30.0

TABLE 6. Properties of test fiber qualities

- symbols: fiber gauge: d, dtex; tensile strength; σ, mN/dtex; elongation: ϵ, %; energy to break: J, mN x mm; fiber length: l, mm; WAXS-cristallinity: χ, %; mechanical draw ratio: λ; weight- and number average molecular weight: M_w and M_n; dispersion: D

Fiber quality no	Fiber strength d - σ - ϵ - J dtex - mN/dtex - % - mN mm	Chain distribution MWD M_w - M_n - D	Other properties		
			l mm	χ %	λ -
1	2.11 - 22.2- 297 - 2156		40	54.6	1.44
2	2.19 - 20.9 - 388 - 1370		40	51.8	1,44
3	2.05 - 19.3 - 377 - 2275		40	-	1.30
4	2.06 - 17.4 - 450 - 1235		40	51.6	1.15
5	2.09 - 18.7 - 397 - 1165		40	-	1.43
6	2.13 - 17.5 - 430 - 1165		40	-	1.30
7	2.20 - 17.4 - 414 - 1165		40	-	1.15
8	2.24 - 16.8 - 259 - 1485		40	45.1	-
9	2.41 - 25.3 - 271 - 2608	213700 - 37300 - 5.73	40	41.5	-
10	2.19 - 35.3 - 131 - 1850	219940 - 39910 - 5.51	40	19.6	-
11	2.05 - 14.3 - 293 - 1457		40	-	-
12	1.90 - 17.6 - 343 - 1707	256000 - 48800 - 5.20	40	-	1.15
7-309	2.02 - 20.2 - 334 - 2147	190000 - 42900 - 4.4	40	-	-
8	2.12 - 19.2 - 347 - 2105		40	-	-
9	1.93 - 19.3 - 306 - 1928	175000 - 33200 - 5.3	40	-	-

TABLE 6. (cont.)

Fiber quality no	Fiber strength d - σ - ϵ - J dtex - mN/dtex - % - mN mm	Chain distribution MWD M_w - M_n - D	Other properties l mm	χ %	λ -
10 (1-gal.)	2.58 - 15.5 - 389 -2257		40	-	-
12	2.09 - 18.2 - 301 - 1673	187000 - 34300 - 5.5	40	-	-
14	2.23 - 20.0 - 247 - 1718		40	-	-
16-309	2.03 - 20.5 - 293 - 1844		40	-	-
1-331	1.89 - 18.6 - 305 - 1413	171500 - 42900 - 4.0	40	17.6	1.15
2	1.92 - 19.2 - 305 - 1707		40	-	1.15
3	1.85 - 18.5 - 313 - 1435	159500 - 40600 - 3.9	40	13.5	1.15
4	2.16 - 17.5 - 271 -1459		40	-	1.15
5	2.09 - 20.6 - 305 - 1770	194500 - 48600 - 4.0	40	16.1	1.15
6	2.04 - 21.0 - 315 - 1826		40	-	1.15
7	1.98 - 20.1 - 277 - 1503		40	-	1.15
8	1.83 - 19.7 - 290 - 1431		40	-	1.15
9	2.02 - 20.2 - 271 - 1540		40	23.4	1.15
10	1.95 - 20.6 - 287 - 1608	204000 - 50000 - 4.1	40	23.3	1.15

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Claims

1. Method for regulating the oxidative degradation of the molecular chains in the surfaces areas of molten polymer filaments, which method is applicable in a polyolefin, especially a polypropylene shortspinning system for the production of filaments, according to which the stabilized polymer is extruded and meltspun and the spinning filaments formed are oxidized and quenched, **characterized in that**

   - the oxidation of the molten spinning filament is carried out as a targeted oxidation by directing an oxidizing gas onto the filament bundle from an oxidation nozzle which is arranged separately from the quenching nozzle,
   - under unchanged spinning conditions, an equation of the form MFI = $c_1v_{02} - c_2v_i + c_3$, is used as the regulation equation in the targeted oxidation for defining the level of oxidative degradation, in which equation MFI is the melt index value of the polymer, which can be replaced by the value for the spinning melt viscosity corresponding to low shear rate, v_{02} is the velocity of the oxidizing gas multiplied with the oxygen partial pressure, that is the partial pressure velocity, v_i is the velocity of the quenching gas, c_1, c_2, and c_3 are experimentally determined, polymer- and process-specific constants, the oxygen partial pressure velocity being used for regulating, in addition to the molecular chain degradation of the polymer surface area of the filament, also the magnitude of the dispersion of the molecular mass distribution.

2. The method according to claim 1, **characterized** in that to the polyolefin, a short-chain polyolefin of the same polymer type, especially polypropylene is added.

3. The method according to claim 1 or 2, **characterized** in that, in addition to the conventional regulation of the temperature and velocity of the quenching gas phase, the molecular chain degradation occuring during quenching

of the molten polymer filament is regulated by regulating the oxygen partial pressure of the quenching gas phase.

4. The method according to any of the claims 1 - 3, **characterized** in that the thermal molecular chain degradation of the molten polyolefin is regulated in the extruder by regulating the melt temperature and extrusion delay time, especially so that the polyolefin is extruded in a temperature range of 250 - 290 °C, the delay time of the spinning melt in the extruder and the ducts being 5 - 15 minutes.

5. The method according to any of the claims 1 - 4, **characterized** in that the melt index value of the polymer fed to the extruder is 1.5 - 15, and the values for the molecular mass distributions are in the range of M_w = 500 000 - 240 000, M_n = 65 000 - 50 000 and D = 7.0 - 5.0.

6. The method according to any one of the claims 2 - 5 **characterized** in that that to the polypropylene supplied to the extruder, polypropylene is added having a melt index in the range of 350 - 800 and molecular mass distributions in the range of M_w = 125 000 - 95 000, M_n = 35 000 - 20 000 and D = 3.5 - 5.0, the quantity added being at the most 15 % by weight of the supplied polymer.

7. The method according to any one of the claims 1 - 6, **characterized** in that the molten filament is quenched under conditions, where the volume, velocity and temperature of the quenching gas are in the range of 400 - 1100 Nm^3/h, 20 - 60 m/s and 25 ± 5 °C, respectively, the amount of polymer supplied being 20 - 40 kg/h per nozzle plate.

8. The method according to any one of the claims 1 - 7, **characterized** in that a gas poor in air and free oxygen, such as a combustion gas mixture, is used as the quenching gas, the oxygen partial pressure being in the range of 0.01 - 0.21 bar.

9. The method according to any one of the claims 1 - 8, **characterized** in that melt index and molecular mass values of the product filament after quenching is in the range of 25- 50, and M_w = 185 000 - 200 000, M_n = 40 000 - 50 000.

10. The method according to any one of the claims 1 - 9, **characterized** in that the quantity, velocity, temperature and oxygen partial pressure of the oxidizing gas fed to the oxidation nozzle are 0.01 - 0.8 Nm^3/h, 0.1 - 48 m/s, 25 - 60 °C and 0.21 - 0.98 bar, respectively.

11. The method according to any one of the claims 1 - 10, **characterized** in that the constant c_1 for the oxygen partial pressure velocity in the regulation equation is maintained in the range c_1 = (-0.2) - (+2.0).

12. The method according to any one of the claims 1 - 11, **characterized** in that the amount and velocity of the quenching gas is regulated so that the tensile strength applied to the melt filament at the solidification point is below the value of approximately 30 mN/m^2, whereby, depending on the spinning nozzle diameters (0.70 - 0.25 mm), at a nozzle plate capacity of 30 - 32 kg/h and a spinning melt temperature of 285 - 290 °C, the amounts and velocities (25 °C) of the quenching gas are 350 - 750 Nm^3/h and 20 - 45 m/s, and are relative to these values at other spinning conditions, and whereby the constant c_2 of the regulation equation varies in the range c_2 = 0 - 3.

13. The method according to any one of the claims 1 - 12, **characterized** in that for the production of layers of desired thickness at the surface of a spinning filament having a very low molecular weight and correspondingly melting at a very low temperature, the number average molecular mass values of the filament polymer is reduced at the most by 30 % and its dispersion values are increased at the most by 40 % from the values prior to nozzle oxidation, by using an oxygen partial pressure velocity in the oxidation gas and at the same time an oxygen partial pressure correspondingly within the range 0.1 - 25 m/s and 40 - 100 % by vol. O_2 and simultaneously preventing, by regulating the velocity of the quenching air, an increase of the maximum values for the filament tension above appr. 30 mN/m^2.

14. The method according to any one of the claims 1 - 13, **characterized** in that the oxidation nozzle for the filaments is adjusted into the position α = 5-20 °, x = 60 ± 5 mm, y = 25 ± 5 mm,
wherein α is the angle between the central plane of the oxidazing gas jet and the spinning nozzle plane, x and y are the distances of the center line of the free opening area of the oxidation nozzle from the vertical central plane of the polymer spray (x) and the spinning nozzle plane (y).

15. The method according to any one of the claims 1 - 14, **characterized** in that the filament quenching nozzle is adjusted in the position: α = 25 ± 3 mm, x = 50-75 mm, y = 40-50 mm, wherein α is the angle between the central plane of the quenching gas jet and the spinning nozzle plane, x and y are the distances of the center line of the free opening area of the quenching nozzle from the vertical central plane of the polymer spray (x) and the spinning nozzle plane (y).

16. The method according to any one of the claims 1 - 13 or 15, **characterized** in that when oxidizing using the oxidation nozzle in the position $\alpha = 2 \pm 1°$, $x = 32 \pm 5$ mm, $y = 2 \pm 1$ mm in the immediate vicinity of the plane of the spinning nozzle surface, the spinning nozzle is internally heated.

17. Apparatus for the regulation of the oxidative degradation of the molecular chains in the surface areas of - molten polymer filament surface of polyolefins, especially polypropylene, in a filament production method, comprising a melt spinning device with spinning nozzles, and means, especially a quenching nozzle, for quenching the polymer filaments, **characterized** in that the apparatus contains means for oxidizing the polymer filaments, especially an oxidation nozzle, which is arranged separately from the quenching means.

18. The apparatus according to claim 17, **characterized** in that the oxidation nozzle for the filaments is adjusted into the position $\alpha = 5\text{-}20°$, $x = 60 \pm 5$ mm, $y = 25 \pm 5$ mm,
wherein a is the angle between the central plane of the oxidazing gas jet and the spinning nozzle plane, x and y are the distances of the center line of the free opening area of the oxidation nozzle from the vertical central plane of the polymer spray (x) and the spinning nozzle plane (y).

19. The apparatus according to claim 17, **characterized** in that the filament quenching nozzle is adjusted in the position: $\alpha = 25 \pm 3$ mm, $x = 50\text{-}75$ mm, $y = 40\text{-}50$ mm, wherein α is the angle between the central plane of the quenching gas jet and the spinning nozzle plane, x and y are the distances of the center line of the free opening area of the quenching nozzle from the vertical central plane of the polymer spray (x) and the spinning nozzle plane (y).

20. The apparatus according to the claim 17, **characterized** in that when oxidizing using the oxidation nozzle in the position $\alpha = 2 \pm 1°$, $x = 32 \pm 5$ mm, $y = 2 \pm 1$ mm in the immediate vicinity of the plane of the spinning nozzle surface, the spinning nozzle is provided with internal electrical heating.

21. The apparatus according to any one of the claims 17 - 20, **characterized** in that the size of the free openings of the quenching and oxidation nozzles are correspondingly (10-20) x 480 mm and (0.5-1.5) x 460 mm, *i.e.* the relationship between their surface areas is 7 - 42.

22. Use of a method according to any one of the claims 1 - 16 for regulating the temperatures and bonding strengths in a process of thermobonding fibers produced by the said method, especially the melting point and melt quantity of the partial melts formed from the filament surface during thermobonding, as well as the quality characteristics of fabrics made from the fibers.

23. Method for regulating the thermobonding of skin-core-type fibers made by degrading the molecules in a filament surface layer based on a controlled autogenous oxidation of molten-state spinning filaments made from polyolefins, especially polypropylene, **characterized** in that

a. the fibers to be thermobonded are made by means of the regulation method according to the claims 1 - 16 so as to give fibers with the desired surface layer structures and molten areas as determined both by the melt index and by the degree of surface degradation indicated by the molecular mass values,
b. the thermobonding is regulated using polymer-specific regulation equations simulating the strength values of the product fabrics, the equations for the tensile strength and the elongation being

$$\sigma(\in) = c_{01} \text{ x } [\mathrm{MFI}/(\mathrm{MFI})_{O}]^{n(\sigma 1)} \text{ x } T^{2} \text{ x } \exp(-E_{01}/RT)$$

the common envelope equation after reaching the maximum values for the strengths being

$$\sigma(\in) = c_{02} \text{ x } T^{2} \text{ x } \exp[+E_{02}/RT]$$

c. the ratio between the tensile strength and the elongation of the product fabrics is regulated by the polymer-specific regulation equation for bonding

$$\sigma_{\parallel}/\in_{\parallel} = c_{03} \text{ x } [MFI/(MFI)_o]^{n(o3)} \text{ x } \exp[-E_{03}/RT].$$

24. The method according to the claim 23, **characterized** in that

a. from a starting polymer: $M_w = 255\,000$, $M_n = 49\,250$, $M_v = 209\,000$, $D = 5.15$, a fiber series is made, wherein the melt index ratio varies 2 - 4.5,
b. from the said fibers thermobonded product fabrics are made (appr. 22 g/m^2) having the following factors in the regulation equations for bonding corresponding to the strength values and their ratio ($\sigma_{\parallel}$, $\sigma_{\parallel}/\in_{\parallel}$): $c_{01} = 5.442 \text{ x } 10^{19}$, $n_{01} = 1.811$, $E_{01} = 47180$; $c_{02} = 2.377 \text{ x } 10^{-10}$, $E_{02} = 11920$; $c_{03} = 3.235 \text{ x } 10^6$, $n_{03} = -0.794$, $E_{03} = 12390$, whereby the regulation equations corresponding to the transverse strength values are formed from parameters corresponding to these,
c. and which fabrics will have a difference in the maximum strength values when using the melt indices

MFI = 1.98 and 2.90; $\Delta\in_{\parallel} = 105$ %, $\Delta\in_{\perp} = 73$ %, $\Delta T = 4{,}5$ °C
MFI = 1.98 and 4.07; $\Delta\sigma_{\parallel} = 8$ %, $\Delta\sigma_{\perp} = 39$ %, $\Delta T = 11{,}1$ °C.

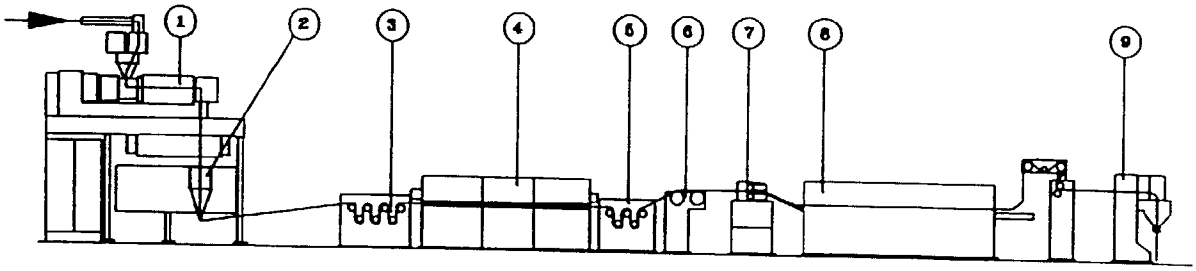


Figure 1. PP staple fiber processing line - pilot scale -

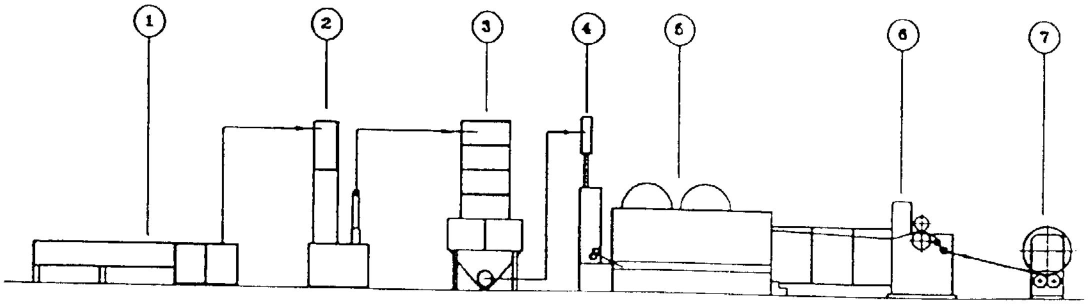
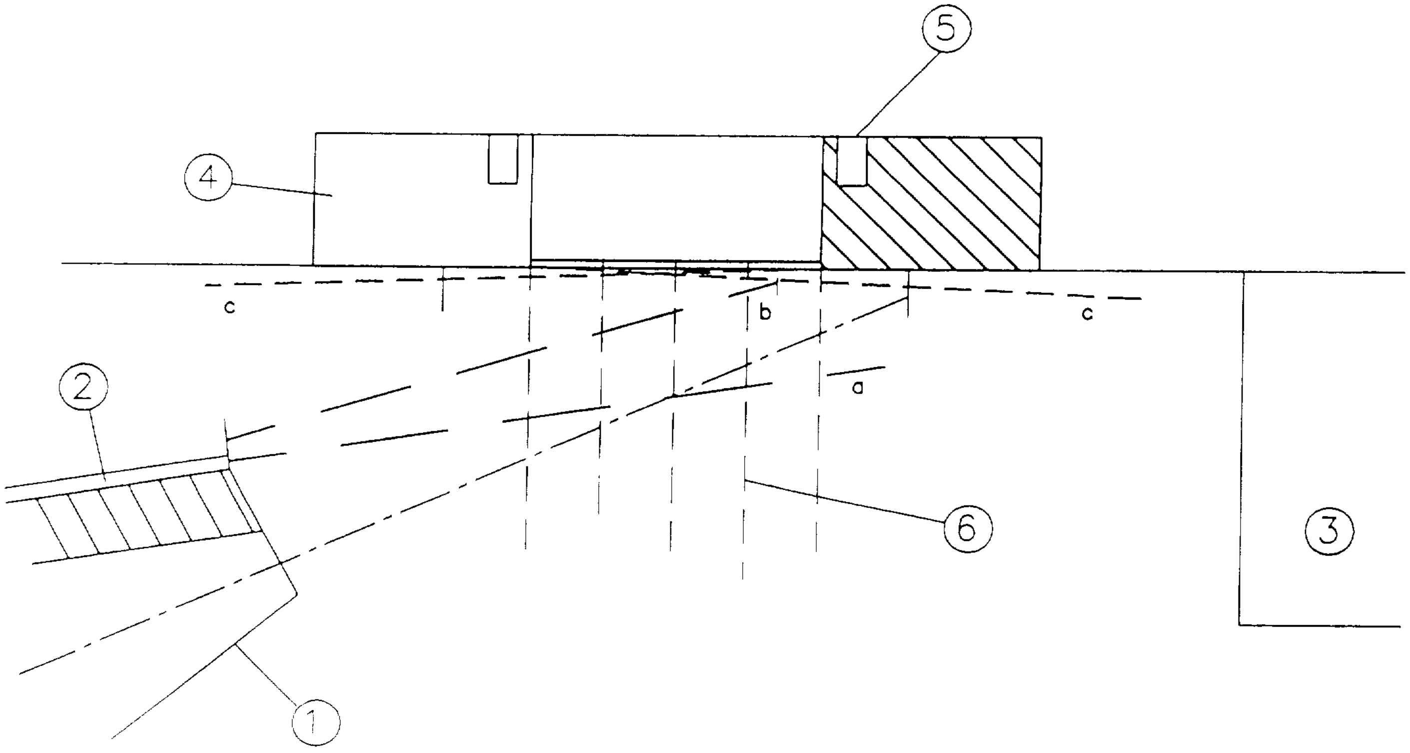


Figure 2. Conventional nonwoven processing line - pilot scale -

Figure 3. Quenching and oxidation nozzles, spinning nozzle



ratio 1:1

Figure 4. Spinning filament profile after the nozzle

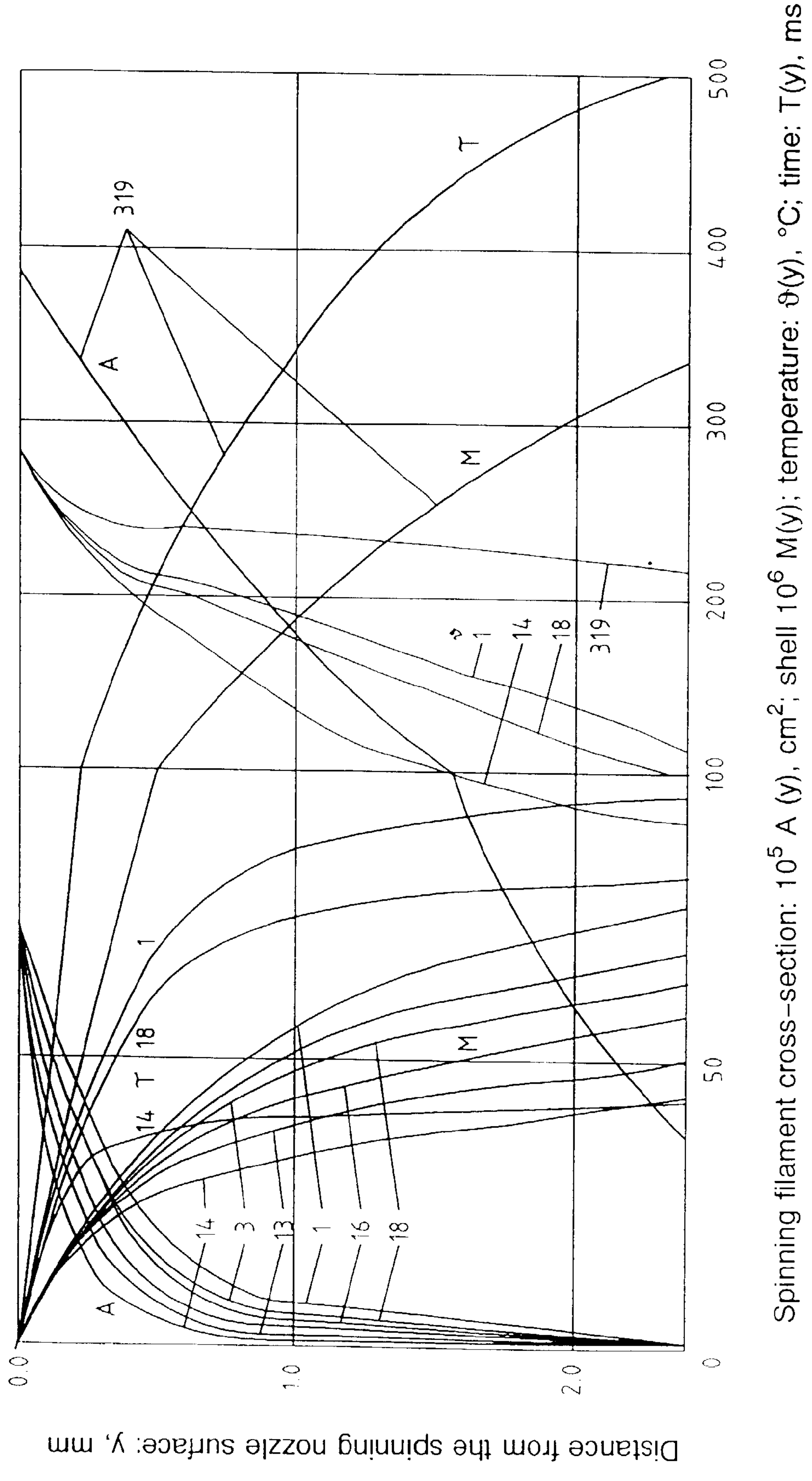


Figure 5. Filament melt index as a function of the oxygen partial pressure velocity

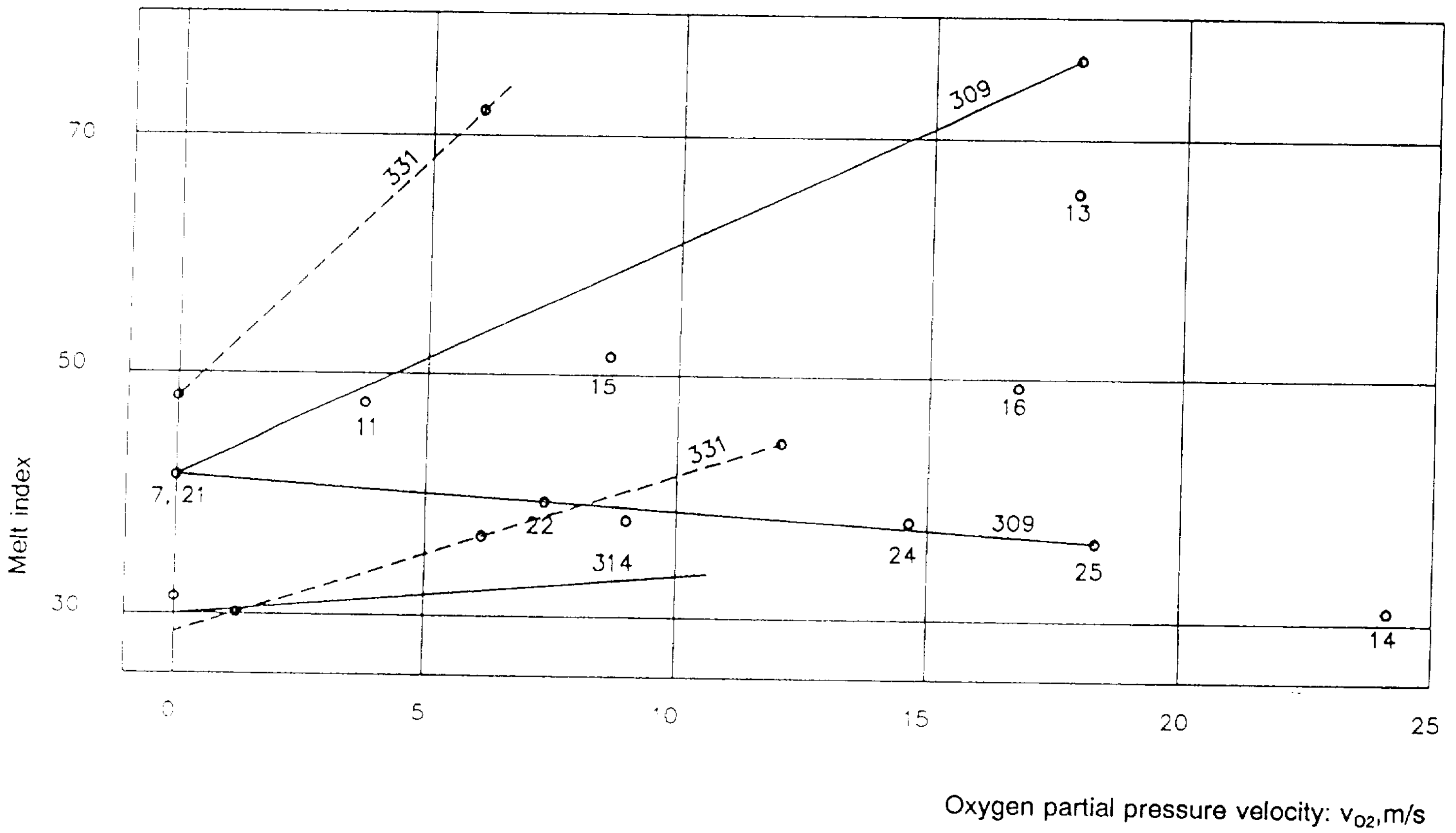
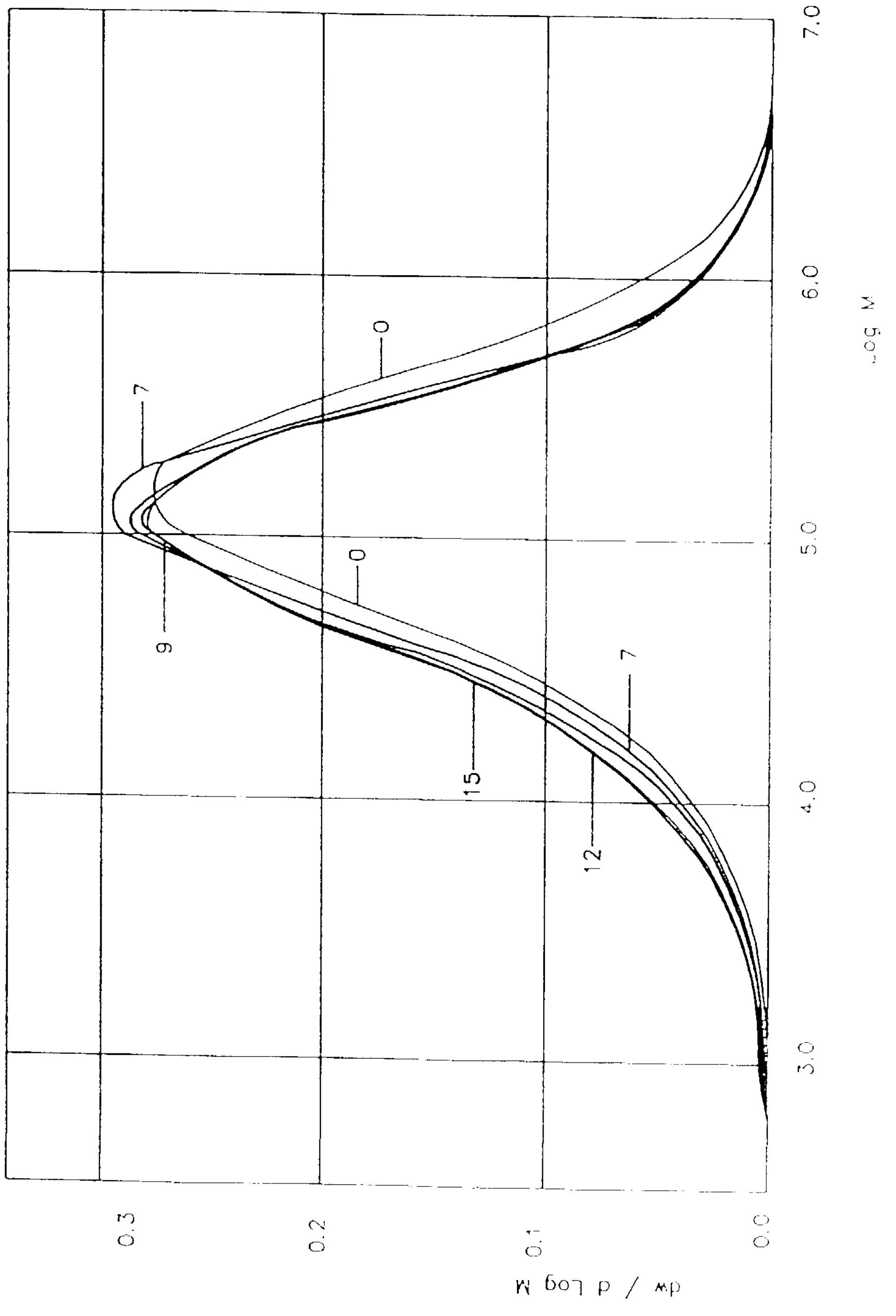


Figure 6. Differential molecular weight graphs



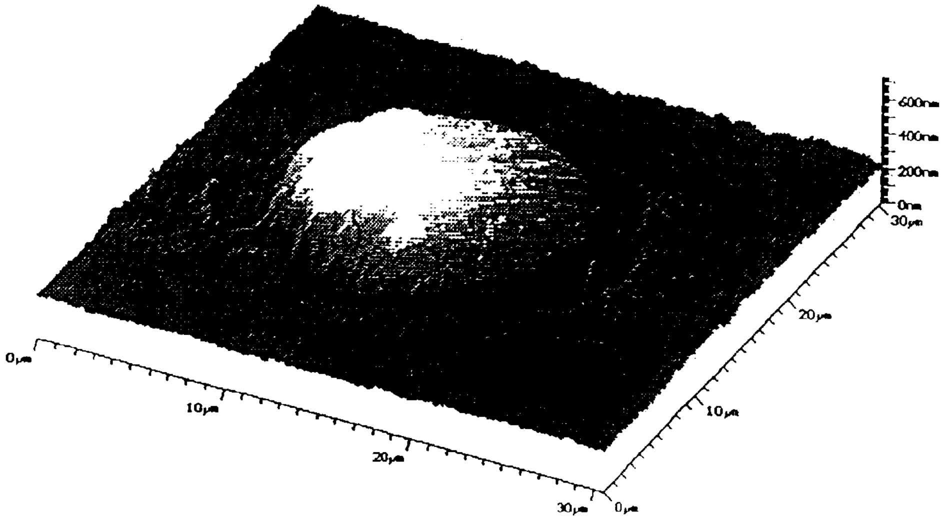


Figure 7. AFM-image of a filament cross-section

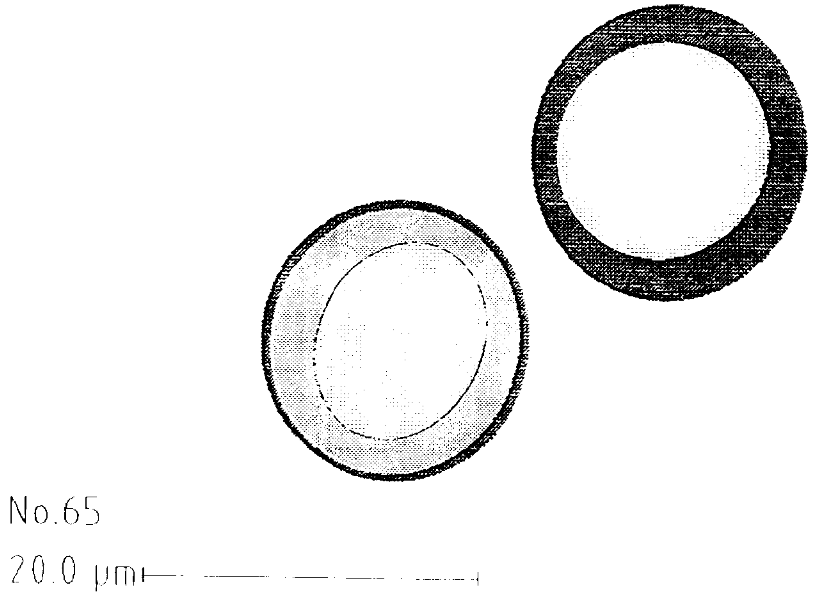


Figure 8. BSE-image of a filament cross-section

Figure 9. Bonding equation: $\sigma_{11} = C \times T^2 \times \exp[-E/RT]$