

# Advanced Fibre Spinning process of UHMWPE

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This article relates to an improved process for preparing ultra-high molecular weight polyethylene (UHMWPE) multi-filament yarns having excellent strength. UHMWPE yarns are typically produced through the gel-spinning method. The method encompasses dissolving UHMWPE in a solvent, for example decalin, spinning the obtained solution by extruding it through a spinneret and subjecting the obtained filaments to solvent removal by evaporation or extraction combined with and/or followed by and extensive elongational drawing of the filaments. The resulting yarns exhibit a low level of entanglements of the UHMWPE polymer chains and an extremely high molecular orientation, leading to unique properties such as high yarn strength and modulus.

However, to obtain yarns with excellent mechanical properties, the process conditions need to be precisely controlled and optimized.

The preparation of the UHMWPE solution is generally done in a mixing and heating device such as an extruder. Very often process conditions are limited by the extruder capabilities (e.g. maximum screw rotation speed or temperature) or process requirements (e.g. residence time in the extruder). It has now been found that under a set of equipment constraints the process window of an extruder can be enlarged by the use of peroxides. The use of peroxides allowed for example to reduce the screw speed which led to lower energy consumption by the extruder. Likewise, it was found that the solution can be spun at a lower temperature, which had a positive effect on the spinning stability by for example resulting in less filament diameter variation along their length. In addition, yarn drawability was improved, which resulted in less breaks per operation hour. Next to this, a lower drawing force in drawing oven(s) was observed, leading to a reduction of the required torque on the roller stands and, hence, less risk of yarn slip and filament breaks.

Moreover, it was found that the drawn yarns had better mechanical properties. This was seen in particular for UHMWPE powder with the initial elongational stress (ES) values ranging from 0.2 MPa to 1.5 MPa. It was most pronounced for UHMWPE powders having higher molar masses, characterized by ES values ranging from 0.5 MPa to 1.1 MPa.

The intrinsic viscosity ( $IV_0$ ) of the UHMWPE powder used was typically in the range of 10-50 dg/L, preferably in the range of 15-40 dg/L.

One or more peroxides could be added either to the solvent before preparation of a slurry that is fed to the mixing and heating device, during preparation of the slurry, or to the device itself. It was found that a wide variety of solvents could be applied, such as decalin, paraffin oil, xylene, etc. with decalin as optimum choice. Best results were achieved when the peroxide was soluble in the spinning solvent used to dissolve UHMWPE.

The weight ratio of UHMWPE to the solvent may be in the range of 2:98 to 15:85, alternatively in the range of 4:96 to 15:85. An excellent balance of yarn quality and economic feasibility was demonstrated to be in the range of 5:95 to 10:90.

The average residence time of the mixture resp. solution in the mixing and heating device, such as in the twin screw extruder, may be in the range of 1-10 minutes. For the twin screw extruder a residence time of 1.5-5 minutes, and even 1.5-3 minutes, was sufficient to yield desired results.

After having passed the mixing and heating device, the solution often passes through other equipment, such as solution pipes, filters, spinning heads, etc., before it reaches the spinneret(s) to form a solution yarn. The average residence time of the mixture resp. solution in the equipment between the inlet of the mixing and heating device and the outlet of the spinneret(s) may be in the range of 1-60 minutes. Shorter residence times for example 3-15 minutes or 5-10 minutes revealed to be even more beneficial. The average residence time can be defined as the free volume of the mixing and heating device (in case of extruder, barrel volume minus screw(s) volume) divided by the volumetric throughput rate. For example, an average residence time in minutes can be calculated by dividing the free volume in  $\text{cm}^3$  by the throughput rate in  $\text{cm}^3/\text{min}$ .

From environmental and process safety point of view, it is desirable that the decomposition products of the peroxide are not harmful to the environment or hardware, e. g. in general, peroxides which form acidic decomposition products are not desirable as they can lead to corrosion of hardware.

The amount of peroxide can be varied in the range from 0.01 wt% to 1 wt% peroxide relative to UHMWPE. Experiments with a concentration in the range of 0.1 wt% to 0.5 wt% or 0.15 wt% to 0.25 wt% relative to UHMWPE in solution led to good results.

The amount of peroxide may be in the range from 0.0005 mol% to 0.05 mol% peroxide relative to  $\text{CH}_2$  units of UHMWPE. A favorable range for peroxide concentration is between 0.005 mol% to 0.025 mol% relative to  $\text{CH}_2$  units of UHMWPE in solution.

Best results were achieved by peroxides which have a half-life time  $t_{1/2}$  longer than 10 hours at 23 °C, preferably in the range of 10-8000 hours, more preferably in the range of 10-4000 hours, most preferably in the range of 10-500 hours. It is further important that  $t_{1/2}$  at a

temperature range from  $T=110-130\text{ }^{\circ}\text{C}$  is in the range of 10-100 minutes, preferably in the range of 10-60 minutes, more preferably in the range of 10-20 minutes and  $t_{1/2}$  at  $150^{\circ}\text{C}$  in the range of 1 second - 5 minutes, preferably in the range of 1 second - 3 minutes, more preferably in the range of 1 second - 1 minute.

The activation energy for peroxide decomposition may be in the range from 140-250 kJ/mol. Satisfying results were as well obtained for peroxides having an activation energy in the range from 150-240 kJ/mol.

Aliphatic peroxides have shown to work best. The term aliphatic peroxide refers to peroxides without aryl groups, thus without aromatic moieties, such as to peroxides without phenyl groups.

The peroxides may be dialkyl peroxides, peroxyesters, peroxyketals and/or alkylperoxy carbonates. Most preferred are dialkyl peroxides. The peroxides can be used in combination. Peroxides with at least one tertiary-alkyl group are favored. Most preferred are dialkyl peroxides with tert-butyl groups

The peroxides were used in pure form, meaning without solvent and/or other chemicals. This has the advantage that solvents and /or other chemicals do not need to be removed from the process which makes the process simpler.

Suitable peroxides include tert-Amylperoxy 2-ethylhexyl carbonate, tert-Butyl peroxy-3,5,5-trimethylhexanoate, tert-Amyl peroxyacetate, 2,2-Di(tert-butylperoxy)butane, 1,1-Di(tert-butylperoxy)cyclohexane, tert-Butyl peroxyacetate, tert-Butyl peroxybenzoate, 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane.

## **Examples**

### **General Spinning procedure for producing ultra-high molecular weight polyethylene (UHMWPE) yarn**

A slurry of an UHMWPE powder in decalin was prepared and fed to an intermeshing, co-rotating, twin-screw extruder. Thereby a solution of the UHMWPE in decalin was formed. The solution was passed through a spinneret to form solution filaments. By cooling of the solution filaments gel filaments were formed. Subsequently, the solvent was removed and the filaments were drawn, thereby solid, drawn filaments were obtained.

### **Comparative Example 1**

Yarns were prepared according to the general procedure described above. UHMWPE powder with  $ES = 0.43\text{ MPa}$  was extruded in a decalin solution at a concentration of 10 wt%. After extrusion and drying the filaments were drawn in a 2-step process, first to a draw ratio of 5 (at oven temperature of  $130^{\circ}\text{C}$ ) and then, in steps, till break (at oven temperature of  $150^{\circ}\text{C}$ ). Break occurred at draw ratio of 4 in the second oven.

### **Example 1**

Exactly the same polymer and processing conditions as in Comparative Example 1 were used, but 0.3 wt% (based on UHMWPE content) 2,5-Dimethyl-2,5-di(tert-butylperoxy) hexane peroxide was added to the initial suspension of UHMWPE in decalin before extrusion. Yarn break occurred at draw ratio 6 in the second oven. Hence, the drawability has improved considerably.

### **Comparative Example 2**

Yarns were prepared according to the general procedure described above. UHMWPE powder with ES = 0.9 MPa was extruded in a decalin solution at a concentration of 4 wt%. After extrusion and drying the filaments were drawn in a 2-step process, first to a draw ratio of 8 (at oven temperature of 130°C) and then, in steps, till break (at oven temperature of 150°C). Yarn break occurred at draw ratio of 5.5 in the second oven.

### **Example 2**

The same polymer, solvent, and process conditions were used as in Comparative Example 2, but 0.2 wt% of 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane was added to the initial suspension of UHMWPE in decalin before extrusion. Yarn break occurred at draw ratio 7.5 in the second oven. Hence, the drawability has improved considerably.

### **Comparative Example 2A**

The same polymer, solvent, process conditions, and peroxide were used as in Example 2, but 0.05 wt% of 2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane was added to the initial suspension of UHMWPE in decalin before extrusion. Yarn break occurred at draw ratio 6.0 in the second oven. Hence, the drawability hardly improved compared to Comparative Example 2, where no peroxide was added.

### **Comparative Example 3**

The same polymer, solvent, and process conditions were used as in Example 2, but 0.2 wt% of tert-Butyl hydroperoxide was added to the initial suspension of UHMWPE in decalin before extrusion. Fibre break occurred at draw ratio of 5.5 in the second oven, showing no improvement. The activity of tert-Butyl hydroperoxide was too low.

## Definitions and Methods

### Peroxide

A peroxide is any chemical that contains an oxygen-oxygen (-O-O-) bond (peroxyfunctional group). An organic peroxide is any organic chemical that contains an oxygen-oxygen (-O-O-) bond (peroxyfunctional group).

### Half-life $t_{1/2}$

The half-life  $t_{1/2}$  is the time required to reduce the original content of the starting material at a given temperature by 50%. The half-life temperature is the temperature at which 50% of the peroxide has decomposed at a specified time. Organic peroxide half-life temperature is usually reported for 0,1 hour (6 minutes), 1 hour and 10 hour periods.

$$-\frac{dc}{dt} = k_d c$$

Where,  $c$  = concentration

$t$  = time

$k_d$  = rate constant for the initiator dissociation in  $s^{-1}$

$$\frac{dc}{c} = -k_d dt$$

$$\int_{c_0}^{c_t} \frac{dc}{c} = -k_d \int_0^t dt$$

$$\ln\left(\frac{c_t}{c_0}\right) = -k_d t$$

$$t = \ln\left(\frac{c_0}{c}\right) / k_d$$

$$t_{1/2} = \ln 2 / k_d$$

Equation 4 is used for calculating  $k_d$  and the half-life. The concentration of peroxide at a given time ( $c_t$ ) is measured at various intervals ( $t_1, t_2, t_3$ , etc.) at a given temperature. The relative concentration ( $c_t/c_0$ ) is plotted on a common logarithmic scale against the reaction time ( $t$ ) on a linear scale. In such a diagram, the individual points should give a straight line with the gradient ( $-k_d/2.3$ ). This can be used to read off the half-life at the point ( $c_t/c_0 = 0.5$ ).

$k_d$  is temperature dependent. This is expressed by the Arrhenius equation below

$$k_d = k_{max} e^{-E_a/RT}$$

where

$k_d$  = rate constant for the initiator dissociation in  $s^{-1}$

$k_{max}$  = maximum velocity constant at the maximum rate of reaction in  $s^{-1}$

$E_a$  = Activation energy for the initiator dissociation in J/mole

$R = 8.3142 \text{ J/mole}\cdot\text{K}$  = general gas constant

$T$  = absolute temperature in K

$t_{1/2}$  = half-life in s

$[c_0]$  = original initiator concentration

$[c]$  = initiator concentration at time  $t$

$t$  = time measured from the start of decomposition in s

$$t_{1/2} = \left( \frac{\ln 2}{k_{max}} \right) e^{-\frac{E_a}{RT}}$$

$$\ln t_{1/2} = \ln \left( \frac{\ln 2}{k_{max}} \right) + \frac{E_a}{RT}$$

$$\ln t_{1/2} = \text{const.} + \frac{E_a}{RT}$$

A common logarithmic plot of the half-life at various temperatures against the reciprocal of the absolute temperature ( $1/T$ ) will give a straight line with the gradient ( $E_a/2.3 R$ ).

Kinetic data of the decomposition of hydroperoxides in monochlorobenzene are determined titrimetrically by iodometric method at a concentration of 0.1 mol/L. The peroxide solution is introduced into a number of test tubes or ampoules which are sealed and stored in a thermostatted bath at the measuring temperature until at least 75% of the original peroxide has decomposed. At specific time intervals (such as 1 hour, 2 hours, 4 hours, 6 hours, 8 hours), one sample is removed from the bath, cooled as rapidly as possible, and examined for its residual peroxide content.

The relative concentration is plotted on a logarithmic scale against the reaction time ( $t$ ) on a linear scale. By connecting the points in the graph to give a line, the half-lives can be read off from the ordinate ( $ct/co=0.5$ ).

If the correlation between the temperature and the half-life is to be determined, the same determination is carried out repeatedly at 2–3 different temperatures in stages of approximately 5–15 °C. The test temperatures are chosen so that the resulting half-lives are

in the region of approximately 1-20 hours. If the half-lives are shorter, the error of measurement increases, and with longer half-lives, the task of sampling becomes excessive. Consequently, only a limited temperature difference, namely maximum 20-30°C, can be determined with this limited time interval.

Most appropriately, the measured results can be represented on a graph by plotting the half-lives in hours or minutes as a function of the temperature in °C. A common logarithmic scale must be used for the half-life (ordinate) and the scale of inverse temperature for the other axis. In this way a straight line will be obtained from which the activation energy and the half-life for other temperatures not measured can be determined.

### **Intrinsic viscosity**

The Intrinsic Viscosity is determined according to method ASTM D1601(2004) at 135°C in decalin, the dissolution time being 16 hours, with BHT (Butylated Hydroxy Toluene) as antioxidant in an amount of 2 g/L solution, by extrapolating the viscosity as measured at different concentrations to zero concentration.

### **Elongational Stress**

The Elongational Stress, E. S., is measured according to ISO 21304-1:2019 and is defined as the stress required to have an elongation of a test piece of the material of exactly 600% in 10 minutes after starting the measurement, at a temperature of 150°C in a suitable heat transfer medium. In detail, a sample of UHMWPE powder (minimum sample size 50 g) is stabilized and pressed to make a test plate. Test pieces (dog bones) are then punched from the plate and the thickness measured. 6 test pieces are placed into the oil bath at  $150.0 \pm 0.3^\circ\text{C}$  and subjected to 6 different stresses (weights). The stresses (weights) employed are based on an estimate of the E.S. The time to reach 600% elongation for each test piece is determined (accuracy = 0.1 s) and the E.S. is then calculated using linear regression by plotting Log of nominal Stress ( $\text{N}/\text{mm}^2$ ) versus log of the time to reach 600% (minutes).