CHEMICAL ENGINEERING TRANSACTIONS
VOL. 43, 2015

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-34-1; **ISSN** 2283-9216

DOI: 10.3303/CET1543284

Production of Polyethylene Based Carbon Fibres

Andreas De Palmenaer*, Gisa Wortberg, Felix Drissen, Gunnar Seide, Thomas Gries

Institut für Textiltechnik, RWTH Aachen University, Otto-Blumenthal-Str. 1, 52074 Aachen, Germany
Andreas.DePalmenaer@ita.rwth-aachen.de

Polyolefins, especially polyethylene, have great potential as an alternative precursor used for carbon fibre production. Polyethylene can be processed in the economic melt spinning process. In this paper, the melt-spinning process of such polyethylene precursors and their conversion to carbon fibres in a chemical stabilization (sulfonation) and carbonization process are presented. Furthermore, the results of the chemical stabilization and the carbonization are discussed.

1. Introduction

Carbon fibres impress with their excellent mechanical properties and low density. Due to the complex production process, production costs (15 - 25 €/kg) are high and carbon fibres are not appropriate for mass application in the automotive or energy sector (renewable energy) so far (Leon y Leon and Schimpf, 2000). The main cost factor, 50 - 65 % of the carbon fibre production costs (Wilms, 2013), is the production of the polyacrylonitrile (PAN) precursor. These high costs mainly arise because of the complex solvent spinning procedure, the solvent's preparation and PAN's high commodity price of 2 - 5 €/kg (Wilms, 2013). Alternative polyolefin-based precursors are an option to reduce costs for the carbon fibre production. Especially polyethylene (PE) is, due to its high availability, the low material price (1 - 1.5 €/kg) and the good suitability as precursor, a promising material (Platts, 2013). Furthermore, the production costs could be reduced up to 30 %, because melt spinning is used to produce PE-precursors instead of solvent-spinning, which is used for the production of PAN-precursors. Because the complex and cost-effective solvent's preparation does not apply, melt-spinning is faster (up to 6,000 m/min), more energy efficient and more environmentally friendly.

2. Materials and methods

2.1 Precursor material

PE has a simple chemical structure. The peculiarity of the material is in the macromolecular structure. PE can be classified according to its density. For the melt-spinning experiments a commercial high-density PE (HDPE) was used. It was made by LyondellBasell with a melt index (190 °C, 2.16 kg) of 28 g/min in Ziegler-Natta polymerization. The decision on HDPE was made, because carbon fibres based on HDPE have shown to achieve the highest level of tensile strength among carbon fibres based on polyolefin precursors. An overview on several fibre properties taken from different papers and studies is given in Table 1.

2.2 Melt-spinning process of polyethylene

Melt-spinning is the preferred production method for polymeric fibres. The granulated material is melted in an extruder and pumped through the spinneret, creating the filaments. The solidification of the molten filaments takes place by air quenching. After leaving the air quenching area, the solidified filaments are drawn off at a well-defined speed and taken up by a winder on a bobbin. The melt-spinning experiments were carried out with a semi-industrial melt-spinning plant. The spinneret chosen for melt-spinning had 72 capillaries with a diameter of 0.25 mm and a ratio of capillary length to capillary diameter (L/D) of 2. The material was extruded

Please cite this article as: De Palmenaer A., Wortberg G., Drissen F., Seide G., Gries T., 2015, Production of polyethylene based carbon fibres, Chemical Engineering Transactions, 43, 1699-1704 DOI: 10.3303/CET1543284

at a temperature of 200 °C. The mass throughput was approximately 26.03 g/min. The take-up speed was between 2,500 and 3,000 m/min.

Table 1: Fibre properties of polyolefin-based carbon fibres

Property	LLDPE	HDPE	UHMWPE	PP
Tensile strength [MPa]	≤ 2.160	≤ 2.673	≤ 2.100	≤ 200
Modulus [GPa]	≤ 148	≤ 139	≤ 210	≤ 26
Strain [%]	0.7 - 3	n.a.	< 1	n.a.
Diameter [µm]	9 - 17	8	n.a.	n.a.
Density [g/cm³	2 – 2.1	0.97	0.97	0.91
Carbon yield [%]	72 - 75	70 - 76	75 - 80	62 - 68
Source	Penning et al. (1991), Leon y Leon et al. (2001), Postema et al. (1990)	Horikiri et al. (1978)	Zhang (1993), Dunbar et al. (1991), Zhang and Bhat (1994)	Leon y Leon et al. (2001), Karacan and Benli (2012)

2.3 Chemical stabilization – sulfonation of polyethylene precursors

Even though general procedure of carbon fibre production based on polyolefins is similar to the conventional PAN-based carbon fibre production, one major difference applies for polyolefin-based carbon fibre production. In contrast to PAN and MPP precursors, polyolefin precursors posses a relatively low melting point (about 130 - 135 °C). For PE heat supply does not cause any chemical reaction, that leads to a stabilization of the material. PE stays inert and melts due to missing interconnections between its molecular chains, whereas for PAN cyclization ensues. Because of this temperature induced plastic deformation of PE occurs significantly sooner . An artificial interconnection of the molecules within the fibre is therefore required to withstand the high temperatures during carbonization (Zhang, 1993). For this purpose a treatment first discovered in the 1950s is applied, , the so called sulfonation (Noeske and Roelen, 1956).

The principle of sulfonation is the most common method nowadays for surface modification and stabilization of polymers (Kaneko and Sato, 2005). However the label sulfonation must be differentiated, because according to the latest state of the art, three different methods are established for the sulfonation of polyolefins. All three methods are therefore also used in the research of polyolefin-based carbon fibres. According to (Horikiri et. al., 1978) polyolefin precursors are stabilized by thermal treatment with:

- Sulfuric acid (H_2SO_4),
- Chlorosulfuric acid (HSO_3Cl) or
- Fuming sulfuric acid (solvent of sulfuric trioxide (SO_3) in sulfuric acid).

The choice of method and the respective parameters depend highly on the choice of the polyolefin. During sulfonation of the precursors, the long molecules are interconnected by the addition of sulfo groups ($-SO_2OH$-groups) and an ensuing SO_3-bridge formation. The size of the sulfo group causes a torsion of the polymer chain around its carbon capture axis. In case of complete sulfonation of the polyolefin, during the sulfonation reaction every fifth to seventh carbon atom is substituted with a sulfo group of the sulfuric acid (Younker et al., 2013). In Figure1 the dash valence formula of a substituted polymer chain is depicted.

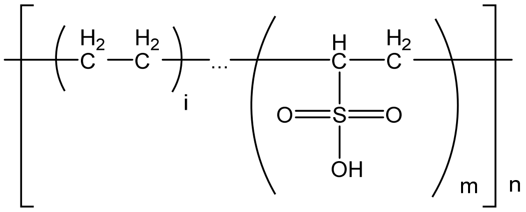

Figure1: Dash valence formula of sulfonated polyethylene (Younker et. al., 2013)

The sulfonation experiments are conducted with high concentration sulfuric acid (95 %) as the sulfonation medium. For procedures of the other two possible sulfonation methods refer to other studies, such as Hunt et al. (2012) for fuming sulfuric acid or Postema et al. (1988) for chlorosulfuric acid. For this sulfonation experiment a reaction vessel by Gebr. Rettberg GmbH (Göttingen, Germany) with a capacity of 1 litre and the temperature control unit Huber CC-K5 with Pilot ONE by Huber Kältemaschinenbau GmbH (Offenburg, Germany) are used. The double walled reaction vessel consists of borosilicate glass with an inlet and outlet for thermofluids. The lid of the reaction vessel has three connecting lines. On the middle line an overpressure valve is placed to control pressure equalization inside of the vessel. The other two lines are used as sample in- and outlet. As thermofluid the silicon oil SilOil M20.195/235.20 by Huber Kältemaschinenbau GmbH (Offenburg) is applied, and by that temperatures of up to 220 °C in the reaction vessel are possible. The silicon oil in the interior wall of the reaction vessel is used to control the temperature of the sulfuric acid inside. Additionally a magnetic mixer with a PTFE-coated flea guarantees a consistent temperature distribution of the sulfuric acid.

For the sample preparation precursors are winded on glass stirring rods and fixated with a PTFE tape, which prevents shrinkage of the fibres during sulfonation. This causes the formation of internal tension in the fibres, which influences the mechanical properties of the resulting fibre (Dunbar et al., 1992). Sulfonation is conducted with the temperature profile depicted in Figure 2. The extraction points of the samples during sulfonation are also shown in Figure 2, marked with the respective sample labels.

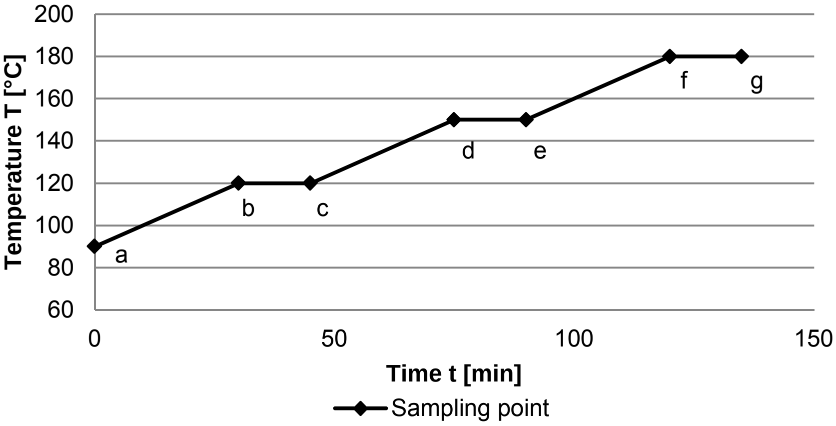

Figure 2: Temperature profile and outlet points during sulfonation

After extraction the samples are washed acid free and dried. Afterwards the thermal analysis by differential scanning calorimetry (DSC) under nitrogen atmosphere is conducted. During DSC measurement the samples are initially heated to 100 °C with a heating rate of 5 K/min. This serves the evaporation of the remaining residual moisture in the material. In an ensuing step the samples are cooled down to room temperature with 5 K/min and then again heated to 400 °C. The latter heating process is analyzed for the following evaluation of the specific change of state enthalpy.

2.4 Carbonization

Following the stabilization of the fibre, similar to the conventional PAN-based carbon fibre production, a carbonization is conducted. However, compared to PAN-based carbon fibres, carbonization temperature for polyolefin-based carbon fibres is usually between 900 and 1,200 °C From Zhang and Sun (1996), as well as Horiki et al. (1978) temperatures of 1,100 °C are reported. In Zhang (1993) carbonization occurs at temperatures of 1,150 °C. Leon y Leon et al. (2001) work with temperatures up to 1,300 °C to determine possible changes in results of the carbonization caused by different temperatures. Similar to the conventional PAN-based carbon fibre production, carbonization is conducted within several minutes and the resulting fibre possesses a high carbon concentration and good mechanical properties.

Initially the bonds between carbon an sulfur, oxygen and hydrogen are broken up by the increased oscillation between the atoms. The freed components spontaneously merge and leave the reaction. This causes a mass loss of around 20 % for the sulfonated fibre. Furthermore a linear shrinkage of about 30 % is caused by the chemical conversion (Pennings et al., 1991). Mainly water (H_2O) and sulfuric dioxide (SO_2) are freed up during the pyrolysis of sulfonated polyolefin fibres. Additional mechanisms during the pyrolysis of sulfonated polyethylene were investigated by Younker et. al. (2013) using n-heptan-4 sulfuric acid (C_7H_{16} H_4S). According to the results, during the initiation of the carbonization two reactions can be observed (Figure 3).

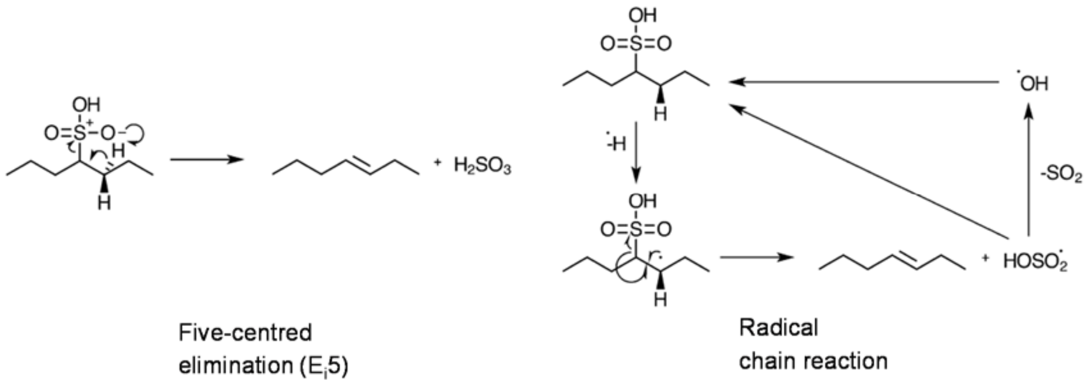

Figure 3: Schematic depiction of chemical reactions during carbonization of sulfonated PE fibres [YSH+13]

In Figure movement of the electrons is indicated with arrows. The shift of the bonds and electrons happens simultaneously. During the five centred elimination the sulfur atom tries to attract the electrons, due to its positive charge. Caused by that the bond between the hydrogen atom and the carbon chain is shifted. Simultaneously the negatively charged oxygen atom of the sulfon group (HSO_3-) takes over the hydrogen atom. The electron pair, which previously tied down the carbon chain folds onto the chain and by that forms the double bond. This creates sulfurous acid (H_2SO_3) and the carbon chain with double bonds.

During the radical chain reaction single electrons are transferred. One of the radicals on the right side (OH or $HOSO_2$) causes the hydrogen atom to be tied down to an electron. This results in one electron to remain on the carbon chain. This electron then transforms the bond to the sulfur into a double bond and an $HOSO_2$ radical is split off. This radical can either directly extract a hydrogen atom from the next chain or prior to that split off a sulfur dioxide molecule (SO_2). This causes the formation of an OH radical, which can also extract another hydrogen atom from the chain. Afterwards the whole reaction takes place again with the next carbon chain. Reactions and results in the further stages of the carbonization are not yet researched (Younker et al., 2013).

Most relevant influencing factors on the mechanical properties of carbon fibres during carbonization are temperature and sojourn time to keep the degree of orientation of the precursor fibres and achieve the optimal strength. Unfavourable influences are caused by inclusions and gaps in the fibre structure. Inner defects and surface defects cause stress cracks and lead to failure (Postema et al., 1990).

For the carbonization experiments at the Institut für Textiltechnik der RWTH Aachen University a tubular high temperature oven FRH-40-250-1500 G800 by Linn High Therm GmbH (Eschenfelden, Germany) is used. During carbonization the fibre samples are heated up to 900 °C with a heating rate of 2 K/min under a highly purified nitrogen atmosphere. For the evaluation of the carbonization a elemental analysis in relation to the carbon concentration is conducted.

3. Results

3.1 Melt-spinning process

Spinning of PE with high winding speeds is difficult because of rapid crystallization. The maximum winding speed which could be achieved by using a mass throughput of 26.03 g/min was 3,000 m/min. The single filament diameter was detected by optical microscopy. The obtained single filament diameter is between 15 and 17 µm.

3.2 Chemical stabilization

During the sulfonation of HDPE, an increase of the sulfonation length causes a colour change of the fibres from white to brown and black (see Figure). The colour change however, is - analogue to the thermal stabilization of PAN - no indication for a complete sulfonation. This is proven by the thermal analysis. Furthermore with increasing sulfonation length and temperature an increase of the filament diameter can be observed (see Figure 4). During sulfonation the fibres adjust to the glass stirring rod and harden. Due to the twisted form of the fibres an ensuing measurement of the mechanical strength is impossible.

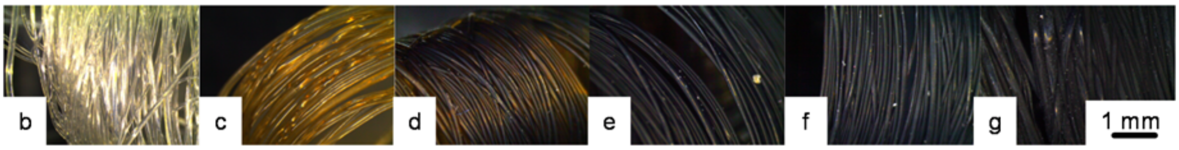

Figure 4: Colour change of the sulfonated HDPE fibres

In Figure 5 the specific change of state enthalpies of samples a to g are plotted against the temperature profile. In the diagram a significant decrease of the specific change of state enthalpy against the sulfonation length can be observed. The biggest difference of potential exists between sample d and e. After the isotherm at 180 °C and a total sulfonation length of 135 min, the specific change of state enthalpy can be completely reduced.

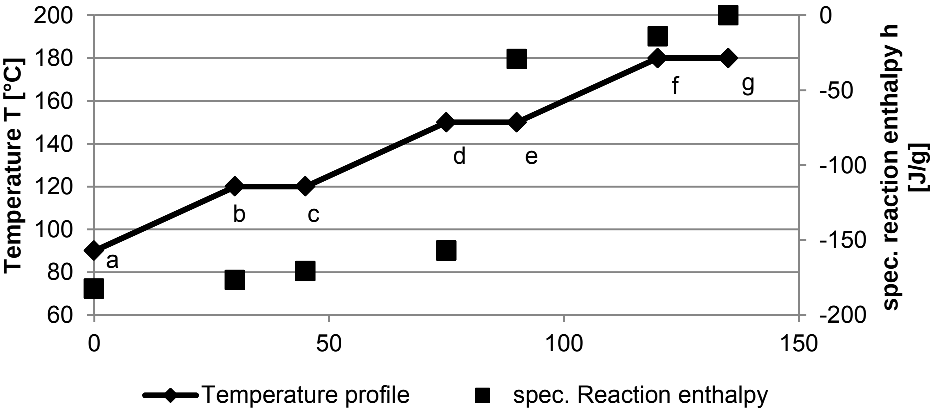

Figure 5: Specific change of state enthalpies of samples a to g against the temperature profile of the sulfonation

To give a proper overview on the elemental analysis in all sampling points as depicted in Figure 2 and *Figure* , the elemental composition in all sampling points is shown in **Errore. L'origine riferimento non è stata trovata.**. As can be seen the weight percentage of C- and H-atoms steadily reduces from sample b to sample g. Accordingly the weight percentage of S-atoms increases. The weight percentage of N -atoms within the fibre remains constant at a level below 0.05 % and should be considered as non-existent

Table 2: Results of elemental analysis of sulfonated HDPE fibres

Sample	C [wt.-%]	H [wt.-%]	N [wt.-%]	S [wt.-%]	O [wt.-%]
(b)	80.26	14.28	<0.05	1.04	4.42
(c)	80.18	14.19	<0.05	1.19	4.44
(d)	78.75	13.80	<0.05	1.38	6.07
(e)	76.21	13.07	<0.05	2.01	8.71
(f)	72.82	12.06	<0.05	2.32	12.80
(g)	62.63	7.18	<0.05	3.40	26.79

3.3 Carbonization

For the conclusive evaluation of the sulfonation samples d to g are carbonized with above described equipment. The selection of fibres complies with the measurement results of the specific change of state enthalpy from the preceding chapter 3.2. During the DSC measurement no complete decomposition was observed for samples d to g until up to 450 °C. With the exception of sample d all other samples withstood the carbonization at a temperature of 900 °C. The fibres were neither melted by the high temperature nor destroyed. Sample d was not sufficiently stabilized or sulfonated and was therefore decomposed during the carbonization process. For samples e and f heavy shrinkage (up to 50 %) and a huge weight as well as volume loss was observed. Sample g only shrank by about 30 %. The mass loss of sample g was around 45 %. By conducting elemental analysis the carbon concentration of sample g after carbonization was identified as 89 %. The remaining 11 % of the carbon fibre was only hydrogen. In addition the remaining amount of sulfur was too low to be measured.

4. Conclusion

Sulfonation was conducted in a high concentration sulfuric acid (95 %) with varying temperature and sojourn time. After thorough analysis by using different methods, a selection of sulfonated fibres were carbonized in a carbonization process. The fibres neither melted nor were they destroyed. This generally confirms the effectiveness of the sulfonation. Furthermore it was confirmed, that the specific change of state enthalpy of a fibre not necessarily needs to be completely reduced to enable carbonization. This means, the specific change of state enthalpy is no clear indication for a completed stabilization of the fibre. Additionally the necessary amount of time to create carbon fibres on an HDPE base was reduced in comparison to older research suggestions as can be seen in the temperature profile provided.

References

Dunbar J. J., Weedon G. C., Tam T. Y.-T., 1992. Carbon Fibre and Process for its Production, US Patent WO 1992 003 601 A3, , http://www.google.com/patents/WO1992003601A3?cl=en, 03.02.2015

Horikiri S., Iseki J., Minobe M., 1978. Process for Production of Carbon Fibre, US Patent 4 070 446, http://www.google.com/patents/US4070446, 03.02.2015

Hunt M. A, Saito T., Brown R. H., Kumbhar A. S., Naskar A. K., 2012. Patterned Functional Carbon Fibres from Polyethylene. Advanced Mareials, 24, 2386-2389

Karacan I., Benli H., 2012. The effect of sulfonation treatment on the structure and properties of isotactic polypropylene fibres prior to the carbonization stage. Journal of Applied Polymer Science, 123, 3375-3389

Kaneko M., Sato H., 2005. Sulfonation of Poly(propylene) Films with Fuming Sulfuric Acid, Macromolecular Chemistry and Physics, 206, 456-463.

Leon y Leon C. A. Schimpf, S.: Low cost carbon fibre (LCCF) for automotive and nonaerospace applications. Part I: Review of existing and emerging technologies Midwest Advanced Materials and Processes Conference, Dearborn, USA, 12–14 September 2000., 12-23

Leon y Leon C. A., O'Brien R. A., McHugh J. J., Dasarathy H., Schimpf W. C., Polyethylene and Polyproylene as low cost carbon fibre (LCCF) precursors, 33rd International SAMPE Technical Conference, 5-8 November 2001, Seattle, USA, 1289-1296

Leon y Leon C. A., Schimpf W., Hansen B.C., Herren C.W., Frame A., Heatherly P.W., Low Cost Carbon Fibre from Non-Acrylic based Precursors: Polyethylene, 34th International SAMPE Technical Conference 4-7 November 2002, Baltimore, USA, 506-519

Noeske H., Roelen O., 1959. Process for the chloro-sulfonation of polyethylene, US Patent 2889259 A., http://www.freepatentsonline.com/2889259.pdf, 03.02.2015

Penning J. P., Lagcher R., Pennings A. J., 1991. The effect of diameter on the mechanical properties of amorphous carbon fibres from linear low density polyethylene, Polymer bulletin, 25, 405-412.

Platts, 2013, McGraw Hill Financial: Polymerscan, , Platts McGraw Hill Financial, New York, USA, Vol. 36, Issue 25, 19.06.2013

Postema A. R. Pennings A.J., 1988. Chlorosulfonation of Ultra-High strength polyethylene fibres. High modulus polymers: approaches to design and development, Dekker, New York, USA, 431-457

Postema A. R., De Groot H., Pennings A.J., 1990. Amorphous carbon fibres from linear low density polyethylene, Journal of Materials Science, 25, 4216-4222.

Wilms, C., 2013, Cost efficient production method for the manufacture of carbon fibre precursos (Kosteneffizientes Produktionsverfahren zur Herstellung von Carbonfaser-Precursoren), dissertation, Institut für Textiltechnik der Rheinisch-Westfälischen Technischen Hochschule Aachen, Shaker-Verlag, Aachen, Germany

Younker J. M., Saito T., Hunt M.A., Naskar A.K., Beste A., 2013. Pyrolysis Pathways of Sulfonated Polyethylene, an Alternative Carbon Fibre Precursor. Journal of the American Chemcial Society, 6130-6141.

Zhang, D., 1993. Carbon Fibres from Oriented Polyethylene Precursors, Journal of Thermoplastic Composite Materials, 6, 38-48

Zhang D., Bhat G. S., 1994. Carbon Fibres from Polyethylene-Based Precursors. Materials and Manufacturing Processes, 9, 221-235

Zhang D., Sun Q., 1996. Structure and Properties Development During the Conversion of Polyethylene Precursors to Carbon Fibres. Journal of Applied Polymer Science, 62, 367-373.