

Article

## Polyethylene-Based Carbon Fibers by the Use of Sulphonation for Stabilization

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**Abstract:** Polyethylene has great potential as an alternative material for carbon fiber production. Polyethylene can be processed in the economic melt spinning process. These precursors are prepared for the subsequent process step of carbonization by using chemical stabilization (sulphonation). The strategy is to adjust these precursor properties by the melt spinning process, thus resulting in a precursor, which can be stabilized sufficiently by sulphonation. The objective is to find the correlation between precursor properties and the results of the sulphonation. In this paper, the chemical stabilization is described and the results of the chemical stabilization are discussed. The novelty in this paper is that the results of the sulphonation are brought in correlation with the precursor properties. It can be shown that the filament diameter and the polymer structure (e.g., the crystallinity) of the precursor have an influence on the sulphonation process.

**Keywords:** polyethylene; precursor; sulphonation; carbon fiber

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## 1. Introduction

Carbon fibers have excellent properties with a low density at the same time. Due to the complex manufacturing process, the production costs of polyacrylonitrile-based carbon fibers are at a high price of 15 to 25 €/kg. This is the reason why carbon fibers for large-volume applications of carbon fibers, e.g., in the automotive or renewable energy industry, are not widespread [1]. The production of the polyacrylonitrile (PAN) precursor is the main cost factor (50%–65%) [2]. These high costs are due to the use of the complex solvent spinning process. The solvent, the solvent recovery and the raw material PAN are the main cost drivers [2]. Using new raw materials instead of PAN can be an option to reduce the costs. New raw materials are Lyocell, Lignin and polyethylene. There are a lot of studies on those materials [3,4]. The focus of this paper is on the experimental study for polyethylene-based carbon fiber production. Advantages of polyethylene (PE) are the high availability of the material, the low material price (1–1.5 €/kg) and the good suitability as precursor [5].

## 2. Experimental Section

PE has a simple chemical structure. Based on the density, PE can be classified. For the melt spinning experiments a high density PE (HDPE) was used. The company Saudi Basic Industries Corporation (Riad, Saudi Arabia) provided the material. The material has a melt flow index (190 °C, 2.16 kg) of 20 g/10 min. The use of HDPE can be explained by the fact that carbon fibers based on HDPE achieved the highest tensile strength among carbon fibers based on polyolefin precursors [6]. The idea is that the precursor properties have an impact on the sulphonation.

For this reason, precursors with different single filament diameters and different crystallinity were spun. The crystallinity and the single filament diameter were controlled by the spinning process. The data of the spun precursor are listed in Table 1. A method of analyzing the crystalline structure of the polymer is the wide angle X-ray diffraction (WAXD). The filament diameter was determined by optical light microscopy. The sample labeling is composed of P for precursor and S for sulphonation, PE for polyethylene, HDPE for high density polyethylene and 41–44 for the number of the samples which were produced.

**Table 1.** Properties of polyethylene precursor.

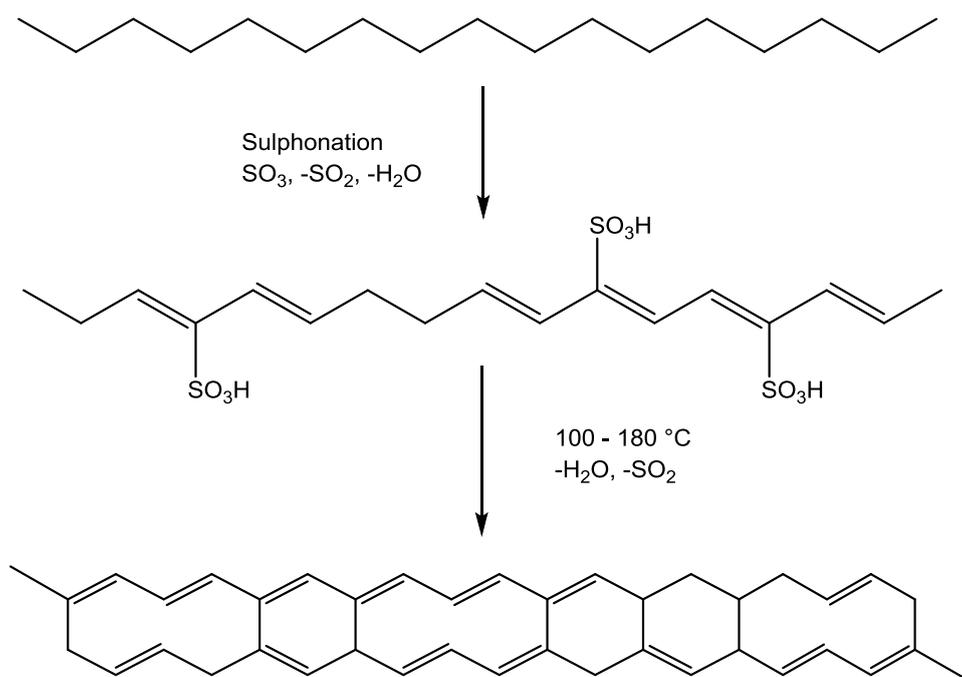
Sample	Material	Density (g/cm <sup>3</sup> )	Count of Filaments	Crystallinity (%)	Single Filament Diameter (μm)
P-PE-HDPE-41	HDPE	0.94	34	66	16.4
P-PE-HDPE-42	HDPE	0.94	34	59	19.1
P-PE-HDPE-43	HDPE	0.94	34	57	22.2
P-PE-HDPE-44	HDPE	0.94	34	34	32.8
P-PE-HDPE-45	HDPE	0.94	34	41	40.7

There is a major difference between the conversion of PAN-based precursors and PE-based precursors to carbon fibers. The stabilization of PAN-based precursors is a thermal stabilization. PE has to be stabilized in another way because of its relatively low melting point (130–135 °C). PE would stay inert and melt by using thermal stabilization, whereas for PAN cyclisation takes place. For this reason,

an artificial interconnection of the molecules within the fibers is required [6]. A chemical stabilization (sulphonation) is needed [7] which is the most common method for the stabilization of polymers [8]. The sulphonation process can be carried out by three different sulphonation materials [9]:

- Sulphuric acid ( $\text{H}_2\text{SO}_4$ );
- Chlorosulphuric acid ( $\text{HSO}_3\text{Cl}$ ) or
- Fuming sulphuric acid (solvent of sulphuric trioxide ( $\text{SO}_3$ ) in sulphuric acid).

The long molecules are linked by the addition of sulfonic acid groups ( $-\text{SO}_2\text{OH}$ ) and an  $\text{SO}_3$ -bridging effect during sulphonation process. The size of the sulfonic acid group is the reason for the torsion of the polymer chain around its carbon capture axis. Every fifth to seventh carbon atom is substituted with a sulfonic acid group, in the case of a completed sulphonation [10]. In Figure 1 is shown the sulphonation scheme and crosslinking of the PE polymer chain.



**Figure 1.** Reaction scheme of sulphonation and crosslinking, reprinted with permission from [11]. Copyright 2014 Barton *et al.*

A high concentration sulphuric acid (96%) as sulphonation material was used for the sulphonation experiments. The experiments were carried out in a double walled reaction vessel (capacity: 1 L) heated up with a temperature control unit (Huber CC-K5 with Pilot ONE) by the company Huber Kältemaschinenbau GmbH, Offenburg, Germany. One part of the double walled reaction vessel are borosilicate glass with an inlet and outlet for thermo fluids. The reaction vessel is filled with sulphuric acid where the precursor samples are put in. The acid is heated up to  $120\text{ }^\circ\text{C}$  and held at this temperature for 6 h (sampling point after each hour). Then the sulphonated samples are washed acid free and dried. To investigate the melting enthalpy of the stabilized samples the method of differential scanning calorimetry (DSC) is used. Herein, the samples are treated with a linear heating ramp with a heating rate of  $5\text{ K/min}$  from  $25\text{ }^\circ\text{C}$  to  $500\text{ }^\circ\text{C}$ .

### 3. Results and Discussion

During the sulphonation of HDPE, an increase of the sulphonation time causes a color change of the fibers from white to brown and black (see Figure 2). The color change however, is—analogue to the thermal stabilization of PAN—no indication for a complete sulphonation. This is proven by the thermal analysis. Furthermore with increasing sulphonation time and temperature depending on the degree of crystallinity an increase of the filament diameter can be observed.



**Figure 2.** Color change of sample P-PE-HDPE-41 (crystallinity: 66%, single filament diameter 16.4  $\mu\text{m}$ ).

In Figure 3 the specific change of state enthalpies of all samples from Table 1 are plotted against the sampling points during the 6 h sulphonation. In the diagram, a significant decrease of the specific change of state enthalpy against the sulphonation time can be observed. The biggest difference of potential is shown by sample P-PE-HDPE-41. Whereby sample P-PE-HDPE-44 shows the lowest change of melting enthalpy. Figure 3 shows that the sulphonation reaction is highly depending on the filament diameter and the degree of crystallinity of the precursor. Due to the fact that the sulphonation is a diffusion controlled process, smaller fiber diameters lead to a faster sulphonation. This phenomenon can be observed in Figure 3 from sample P-PE-HDPE-41 to 44. Furthermore, bigger fiber diameters create a skin-core structure while sulphonation. Whereby the sulphonated skin of the fiber prevents the penetration of acid into the fiber core. Sample P-PE-HDPE-45 shows a domination of the influence by the degree of crystallinity on the sulphonation ability. Where P-PE-HDPE-45 is a more amorphous material, what provides a better penetration of the sulphuric acid into the fiber core and leads to a faster sulphonation.

The comparison between the melting enthalpies and density measurements (see Figure 4) of sulphonated samples in Figure 3 indicates that small filament diameters leads to faster and more efficient sulphonation reaction. This is especially recognizable by sample P-PE-HDPE-41. If the samples P-PE-HDPE-43 to 45 are considered, it can be seen that the influence of the diameter decreases to the effectiveness of the sulphonation and the influence of crystal structure increases from sample P-PE-HDPE-43-44. The reason why sample P-PE-HDPE-44 sulphonated better, what can be seen in faster increase of density, than sample P-PE-HDPE-43 and 45 is that in sample P-PE-HDPE-43 a skin-core structure is formed and only a portion of the fiber is sulphonated. Sample P-PE-HDPE-45 shows, compared to P-PE-HDPE-44, a higher diameter at approximately the same amorphous structure, which leads to a lower increase of density due to a longer diffusion route in the fiber.

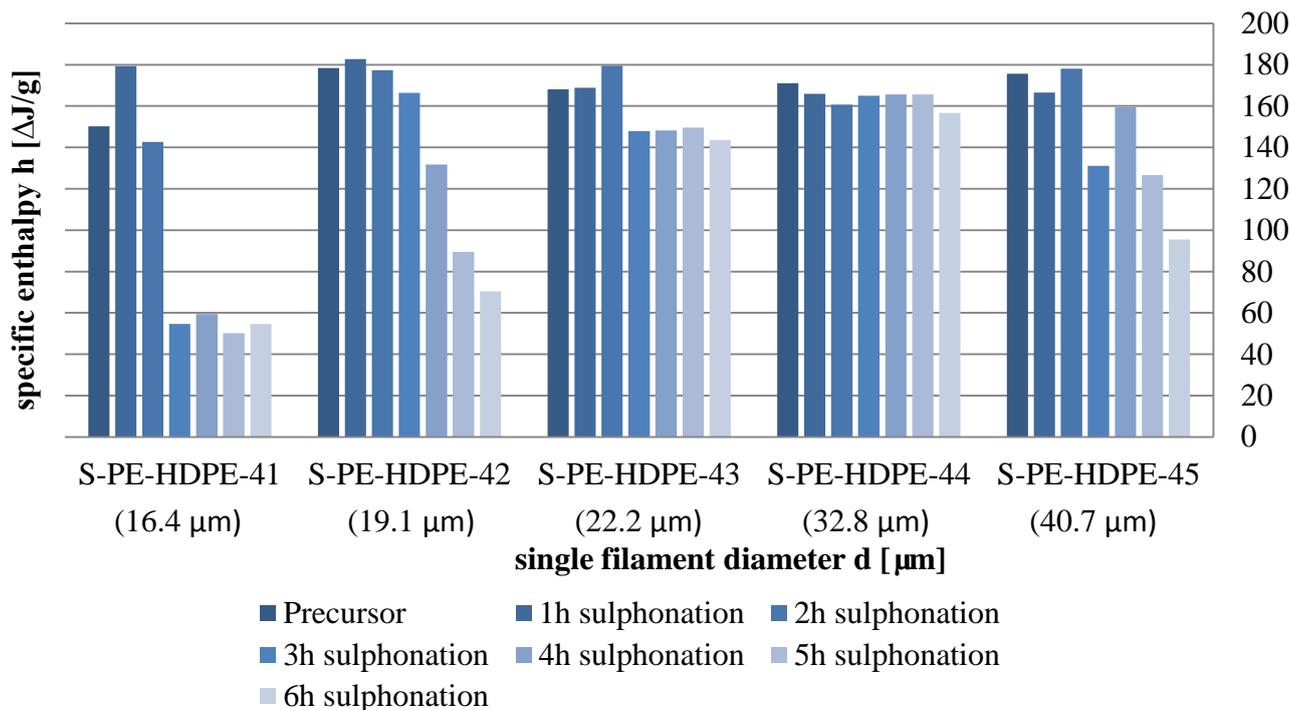


Figure 3. Change of melting enthalpy over sulphonation time over filament diameter.

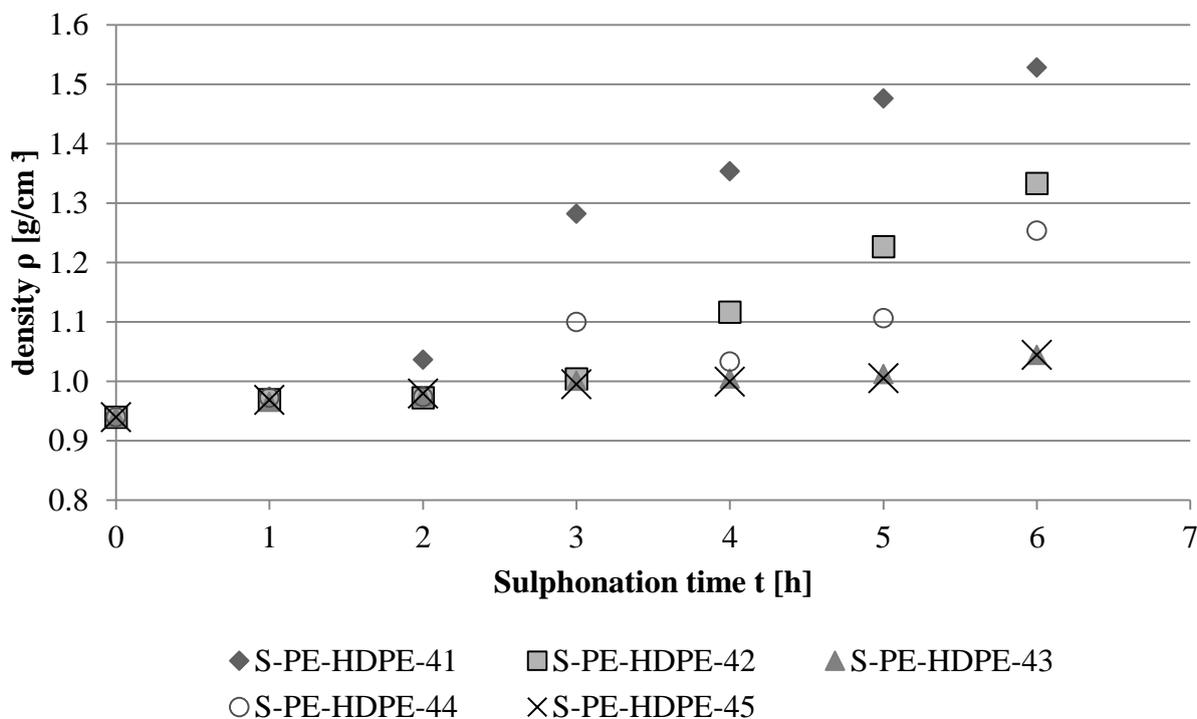


Figure 4. Results of density measurements of sulphonated high density PE (HDPE) samples.

#### 4. Conclusions

Sulphonation was conducted in a high concentrated sulphuric acid (96%) at 120 °C up to 6 h. After thorough analysis by using different methods, like differential scanning calorimetry and pycnometry,

the influence of fiber diameter and crystal structure on sulphonation reaction efficiency can be shown. This leads to the conclusion that fibers with small diameters sulphonate as well as amorphous fibers with larger fiber diameters. Whether one of the parameters (diameter and crystallinity) has a lower or higher influence than the other, or if they are equal, has not yet been determined. It is also possible that the crystal size has an influence on the sulphonation of PE. The orientation of the polymer chains may also be important for the sulphonation process and on the final carbon fibers. These unsolved issues will be investigated in the next steps.

### Author Contributions

Gisa Wortberg developed the experiments and carried out the melt spinning trials for precursor production. Andreas De Palmenaer carried out the sulphonation trials. The analytical results were discussed by both.

### Conflicts of Interest

The authors declare no conflict of interest.

### References

1. Leon, Y.; Leon, C.A.; Schimpf, S. Low cost carbon fibre (LCCF) for automotive and aerospace applications Part I: Review of existing and emerging technologies. In Proceedings of the Midwest Advanced Materials and Processes Conference, Dearborn, MI, USA, 12–14 September 2000; pp. 12–23.
2. Wilms, C. Kosteneffizientes Produktionsverfahren zur Herstellung von Carbonfaser-Precursoren. Ph.D. Thesis, Institut für Textiltechnik der Rheinisch-Westfälischen Technischen Hochschule, Aachen, Germany, 2013. (In German)
3. Shunjin, P.; Huili, S.; Xuechao, H. Lyocell Fibers as the Precursor of Carbon Fibers. *J. Appl. Polym. Sci.* **2003**, *90*, 1941–1947.
4. Frank, E.; Steudle, L.M.; Ingildeev, D.; Spögl, J.M.; Buchmeiser, M.R. Carbon Fibers: Precursor Systems, Processing, Structure, and Properties. *Angew. Chem. Int. Ed.* **2014**, *53*, 5262–5298.
5. Platts. *McGraw Hill Financial: Polymerscan*; Platts McGraw Hill Financial: New York, NY, USA, 2013; Volume 36.
6. Zhang, D. Carbon Fibres from Oriented Polyethylene Precursors. *J. Thermoplast. Compos. Mater.* **1993**, *6*, 38–48.
7. Noeske, H.; Roelen, O. Process for the Chloro-Sulphonation of Polyethylene. US Patent 2,889,259, 3 March 1959. Available online: <http://www.freepatentsonline.com/2889259.pdf> (accessed on 24 June 2015).
8. Kaneko, M.; Sato, H. Sulphonation of Poly (propylene) Films with Fuming Sulfuric Acid. *Macromol. Chem. Phys.* **2005**, *206*, 456–463.

9. Horikiri, S.; Iseki, J.; Minobe, M. Process for Production of Carbon Fibre. US Patent 4,070,446, 24 January 1978. Available online: <http://www.google.com/patents/US4070446> (accessed on 24 February 2015).
10. Younker, J.M.; Saito, T.; Hunt, M.A.; Naskar, A.K.; Beste, A. Pyrolysis Pathways of Sulfonated Polyethylene, an Alternative Carbon Fibre Precursor. *J. Am. Chem. Soc.* **2013**, *135*, 6130–6141.
11. Barton, B.E.; Patton, J.T.; Hukkanen, E.J.; Bernius, M.T. Two-Step Sulphonation Process for the Conversion of Polymer Fibers to Carbon Fibers. WO002014011460A1, 16 January 2014.

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