COST EFFICIENT PRODUCTION OF CARBON FIBRES

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Abstract

Carbon fibres feature excellent mechanical properties (up to 7 GPa strength) combined with a low density (~ 1.8 g/cm³). However, due to their energy demanding production process carbon fibres are still not used for mass applications (e.g. automotive industry) because of their high price (15 – 25 €/kg) [3, 8]. Therefore the production costs of carbon fibres need to be reduced.

The main bottleneck in the conversion of polyacrylonitrile (PAN) fibres to carbon fibres is the stabilization process with temperatures up to 300 °C and process times up to two hours [3, 4]. Nearly 50 % of total conversion costs are account by stabilization [2]. The approach of this research work is the reduction of stabilization times in order to minimize the total production costs of carbon fibres.

The results show, that the residence times in the first zones can be drastically reduced. The majority of the reaction force is going on in the last two zones. The total stabilization time was reduced by more than 40 %. Furthermore, it could be shown that through the application of drawing profiles the formation of a core mantle structure can be minimized. The strength of the carbonized samples is comparable to a Toray T300 fibre.

1. Introduction

Because of their outstanding mechanical properties combined with low density carbon fibres are in the last years increasingly used for light-weight applications in the transport or the energy industry. Wind power plants, especially for offshore applications, can achieve wingspans of 150 meters and more with the use of carbon fibres [7]. Through higher wingspans the energy yield of wind power plants is increased, by which the total efficiency is enhanced. Modern airplanes, like the Airbus A350 or the Boing 787 “Dreamliner” consists of more than 50 % carbon fibre reinforced plastics (CFRP) [6].

Figure 1 illustrates the historical and projected global carbon fibre demand for the next 5 years [1, 6]. Until 2020, the projected constant annual growth rate (CAGR) will be 17 %. In total, the global demand will increase from 62,000 tons to 138,000 tons (+ 225 %). The global outlook for the carbon fibre market is promising. However, compared to other reinforcement fibres like glass fibres the global demand is still very low. The current global demand of glass fibres is with 5.2 Mio tons more than 80 times higher compared to carbon fibres [8]. One reason for this is the high price of carbon fibres (15 – 25 €/kg) [3].

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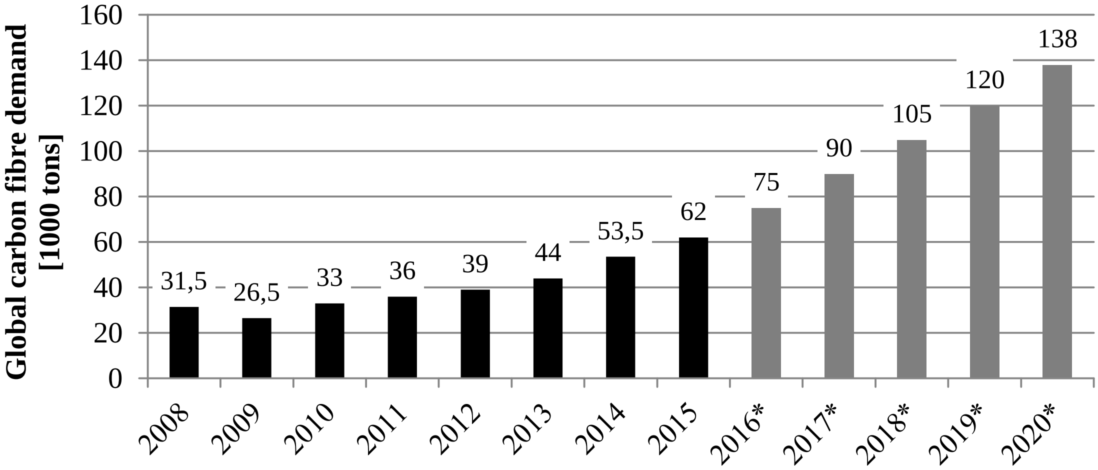

Figure 1. Historical and projected global carbon fibre demand [1, 6]

2. Deficits of the carbon fibre production process

Today's production process of carbon fibres is time-, energy- and therefore cost-intensive. One bottleneck in the thermal conversion of polyacrylonitrile (PAN) based precursors to carbon fibres is the process step of stabilization. Stabilization requires temperatures up to 300 °C and process times up to 120 minutes. Process control and process parameters depend strongly on the properties of the precursor material (precursor composition, comonmers etc.) [3, 4]. During stabilization, the fibres are prepared for carbonization to prevent a disintegration reaction [9]. The fibres become infusible and non meltable. Furthermore, the polymer chains form a pyridine ring structure, which consists of 1 nitrogen atom and 5 carbon atoms [3, 4, 9]. The stabilization reaction is exothermic. The three main reactions during stabilization are cyclization, dehydrogenation and oxidation. Cyclization and dehydrogenation are mandatory for the formation of the characteristic pyridine ring structure. Oxidation is needed for dehydrogenation, but attacks and destroys the pyridine ring structure (Figure 2) [4].

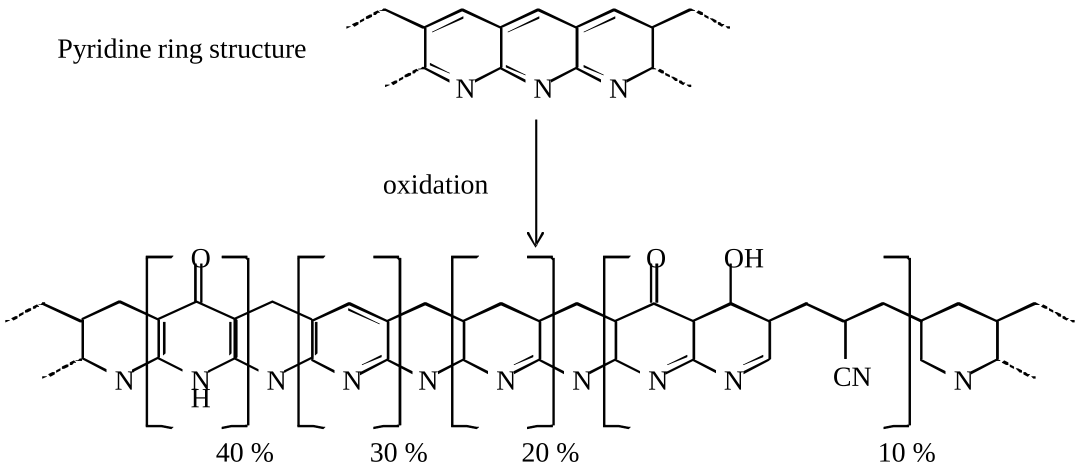

Figure 2. Oxidation of PAN precursors [4]

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It is assumed, that cyclization and dehydrogenation take place at the same time and are not fully completed prior to a starting oxidation reaction. For an optimized carbon fibre strength an oxidation reaction should be avoided.

During stabilization two different shrinkage mechanisms occur: Chemical and physical shrinkage. Shrinkage in general leads to a relaxation of polymer chains, which reduces molecular orientation and therefore the mechanical properties of produced carbon fibres [10]. Chemical shrinkage is caused by the ongoing exothermic reactions. Physical shrinkage is caused by relaxation effects [3, 9, 10]. Chemical shrinkage is caused by cyclization and dehydration, mainly because of a reduction of bond lengths [9, 10]. Chemical shrinkage starts at temperature above 200 °C [9]. The total chemical shrinkage can be up to 50 % of the initial fibre length [9]. Physical shrinkage is caused by entropic effects. After wet-spinning the polymer chains are orientated, which means they are in a condition of high entropy. After the second principle of thermodynamics the polymer chains aim at a condition with minimum entropy, which causes a physical shrinkage [9, 11]. High temperatures encourage this effect. In general physical shrinkage should be avoided while chemical shrinkage should be allowed [3, 9].

3. Materials and Methods

The methodology of this research work is illustrated in Figure 3.

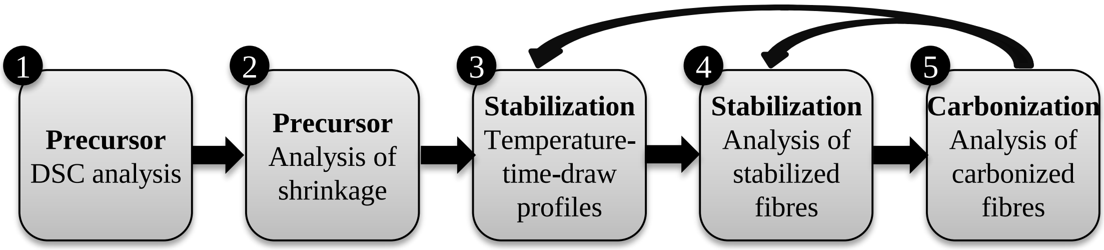

Figure 3. Approach of this research work

The basic procedure of this work is the analysis of reaction force during stabilization by DSC measurements (1), analysis of the chemical and physical shrinkage force in heavy duty draw force tester with integrated oven (Dynafil HD+) from Textechno Herbert Stein GmbH & Co. KG, (Mönchengladbach, Germany) (2), development of new temperature-residence-draw profiles (3), analysis of stabilized fibre properties (mechanical and chemical) (4) and carbonization of the stabilized samples (5). Stabilization and carbonization is carried out in technical scale continuous stabilization and carbonization ovens from Eisenmann AG (Bovenden, Germany). A standardized 4 zone stabilization profile with temperatures from 200 – 260 °C and a residence time of 100 minutes is used. Carbonization is carried out in an LT and HT oven, with max. temperatures of 750 °C and 1250 °C.

A 12k precursor from Bluestar Fibers company limited, Grimsby (UK) is used for the analytics in chapter three.

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3. Results and discussion

Figure 4 illustrates the results of the DSC analysis of the precursor material. A 4 zone stabilization profile with temperatures from 200 °C – 260 °C and 30 minutes residence time in each zone is analysed.

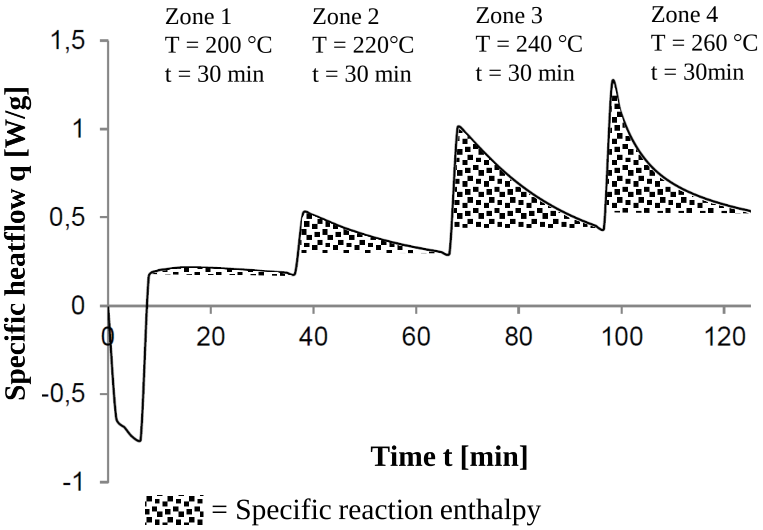

Figure 4. Specific heat flows of a 4 zone stabilization profile

It can be seen, that a majority of the reaction force is going on in the last two zones. The reactions enthalpies of each zone are listed in Table 1.

Table 1. Reaction enthalpies of 4 zone stabilization profile

	Unit	Zone 1	Zone 2	Zone 3	Zone 4	Total
Specific reaction enthalpy	J/g	54,28	115,89	423,70	374,20	968,07
Percentage	%	5,6	12,0	43,7	38,7	100

The share of zone 1 and 2 on total reaction enthalpy is only 17.6 %. This indicates that a majority of stabilization reaction is going on in the last two zones. The authors therefore assume, that residence times in zone 1 and zone 2 can be reduced.

In further investigations the influence of draw ratios and shrinkage on the stabilization reaction is analysed. Figure 5 illustrates the shrinkage force during a 5 zone stabilization profile (200 – 240 °C) with residence time of 15 minutes in each zone. As expected, shrinkage force increases with higher temperatures and higher draw ratios. At a draw ratio of 1.00, the shrinkage force increases linearly. In contrast to that the shrinkage force increases sharply from zone 1 to 2 at a draw ratio of 1.05. The increasing shrinkage force of the precursor is according to theoretical assumptions. Based on the introduced theory higher shrinkage forces are expected for higher temperatures. This statement is based on the assumption, that at temperature upon 200 °C the influence of chemical shrinkage increases [9 - 11]. Since chemical reaction force increase with higher temperatures, higher shrinkage forces are expected.

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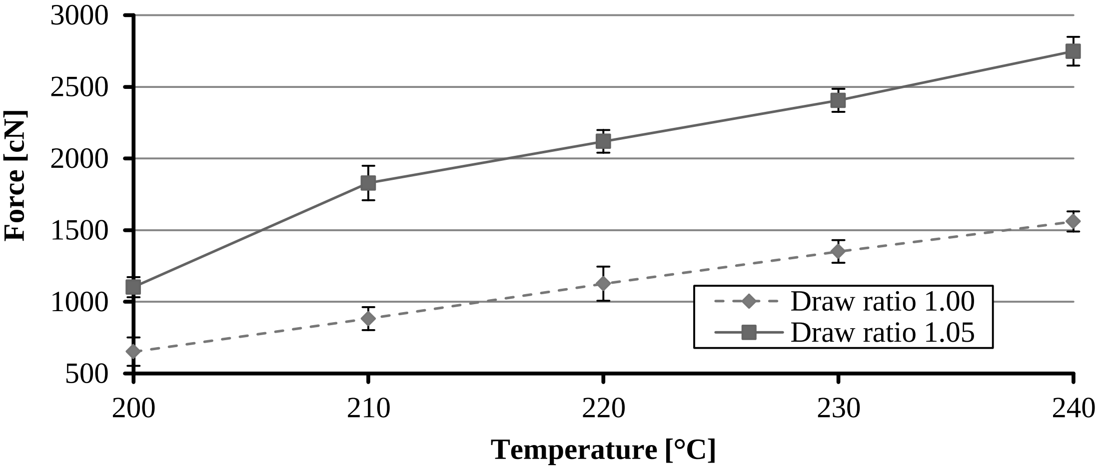

Figure 5. Shrinkage force of a 5 zone stabilization profile

In further investigations stabilized fibres (Draw ratio 1.10 and 1.00) are tested on formation of a core skin structure by optical microscopy (Figure 6).

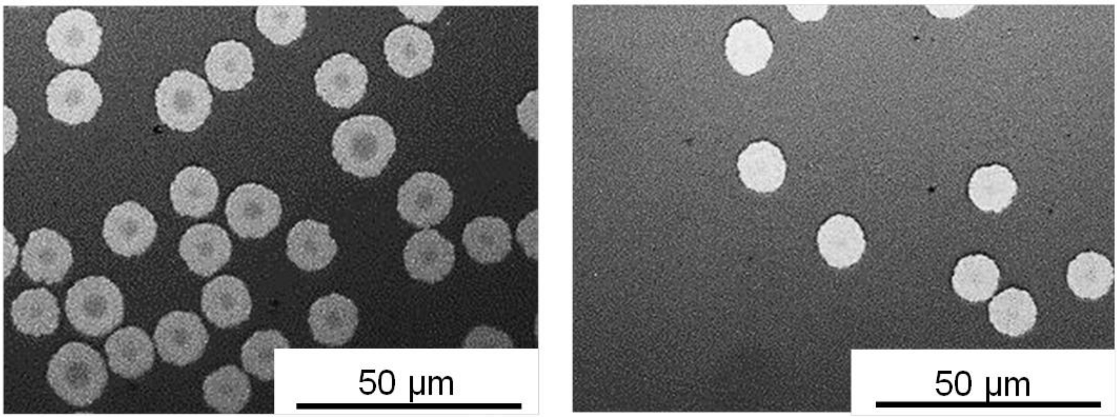

Figure 6. Core-skin structure of stabilized fibres with a draw ratio of 1.00 (left) and a draw ratio of 1.10 (right)

It can be seen, that with the application of a proper drawing profile, the formation of a core skin-structure can be minimized. This indicates that through application of drawing profiles during stabilization the formation of a core-skin structure can be minimized. Based on these results stabilization profiles for a continuous stabilization are developed.

A majority of stabilization reaction is going on in the last zones at higher temperatures. Chemical shrinkage should be allowed, but with the application of a drawing force the formation of core-skin structures can be hindered. Furthermore, the residence time in the first zones is reduced. Based on these assumptions, the following stabilization profiles are tested (Table 2).

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Table 2. Tested stabilization profiles

Number	Unit	Zone 1	Zone 2	Zone 3	Zone 4	Total
1	[min]	25	25	25	25	100
2	[min]	17	17	21	21	76
3	[min]	17	17	17	17	68
4	[min]	13	13	17	17	60
Draw ratio	[-]	1.04	1.03	1.02	1.01	1.10

Based on these 4 stabilization profiles, 12k precursor fibres are stabilized in a technical scale continuous stabilization oven. The stabilized samples are tested on their oxidation degree, based on Belyaevas formula (Table 3) [5].

Table 3. Oxidation degree of the stabilized samples

	Unit	Profile 1	Profile 2	Profile 3	Profile 4
Oxidation degree	[-]	1.00	0.97	0.90	0.81

As expected the oxidation degree decreases with shorter residence times. Profile 1 with a residence time of 100 minutes has an oxidation degree of 1.00. This indicates, that the stabilization reaction is finished and the fibre is fully prepared for LT carbonization. For profile 4, the oxidation degree is with 0.81 very low. This indicates that the stabilization reaction is not completed. Parts of the stabilization reaction are therefore going on during LT carbonization. In the next step the stabilized samples are carbonized and tested on their mechanical properties my single filament strength tests. Figure 7 shows the strength of the carbonized samples.

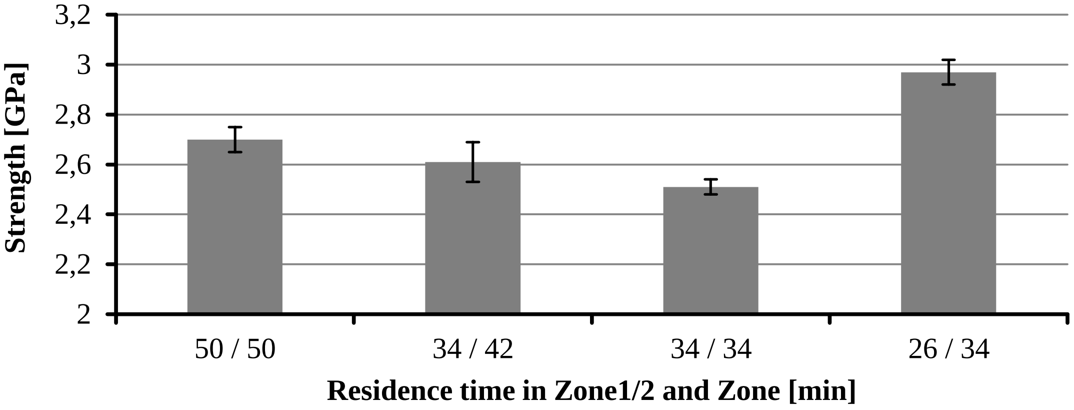

Figure 7. Single filament strength of the carbonized samples

As a result, the strength of the produced fibres (2.97 GPa) is 10 % higher compared to fibres produced by the traditional stabilization profile (2.7 GPa). For short residence times, the benefit of a reduced oxidation degree and therefore reduced destruction of pyridine rings overbalances the disadvantage of non-finished stabilization reactions. The strength of the fibres is comparable to a Toray T300 fibre (single filament strength test).

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4. Conclusion

A huge cost saving potential lies in the development of new stabilization profiles, which are adapted to the chemical behavior of the precursor material. It was shown, that drawing has a positive influence on the formation of core-skin structures. With the application of proper drawing profiles during stabilization, carbon fibre strength can be improved. Furthermore, the stabilization time was reduced by 40 % with no loss in mechanical strength. By this method, the energy consumption, process time and consequently the costs of carbon fibres can be drastically reduced.

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