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Optimisation of carbon fibres made from commercial polyacrylonitrile fibres using the screening design method

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Stabilization and carbonisation conditions are the main factors influencing the properties of carbon fibres manufactured from polyacrylonitrile (PAN) fibres. In this report, low-cost commercial PAN fibres (textile grade) were used as precursors and the effects of the two mentioned factors on the tensile strength of carbon fibres were evaluated. By using the well-known Plackett–Burman screening method in the design of experiments, the best conditions to produce an economical product were determined. The results showed that this method can improve carbon fibre tensile strength by more than 15.7%.

Key words: *carbon fibre; commercial polyacrylonitrile fibre; screening method; Plackett–Burman method*

1. Introduction

At present, three precursors, including polyacrylonitrile-based, rayon-based, and pitch-based fibres, are mainly used for the production of carbon fibres. Due to its high degree of molecular orientation, higher melting point, and greater yield of carbon fibres, polyacrylonitrile (PAN) fibre has been found to be the most suitable precursor for making carbon fibres [1]. PAN fibre is a form of acrylic fibre, composed of acrylonitrile (AN) units in at least 85% by weight. The remaining 15% consists of neutral and/or ionic co-monomers, used to improve the properties of the fibres [2, 3].

Carbon fibres are prepared by a controlled pyrolysis of special grade PAN fibres. The overall process for converting PAN to carbon fibres involves stabilization and

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carbonisation. The stabilization should be carried out in air at relatively low temperatures (180–300 °C). This step converts the precursor to a thermally stable structure capable of withstanding high temperature processing. Stabilization is a necessary and important step in achieving the desired product. The carbonisation involves rapid thermal pyrolysis in an inert environment (usually high purity nitrogen) at 1200–2000 °C, with an increase in carbon content to 85–99%. During this step, most of the non-carbon elements within the stabilized PAN fibres are volatilised in the form of H_2O, CH_4, NH_3, CO, HCN, CO_2, and N_2 [4, 5].

Carbon fibres have found several applications in modern technology. They have been utilized for advanced composites of plastics, metals, or ceramics based on their superior mechanical properties, such as high strength, high modulus, and low density. The main problem in this respect, however, is the high cost of carbon fibres. The high price of carbon fibres is mainly due to the high price of the precursor (i.e., special grade acrylic fibres) and high cost of processing. In order for this valuable material to become more popular in civilian applications, prices should definitely be lowered. One way of achieving this is through the use of cheap commercial acrylic fibres (textile grade PAN fibres). In recent years, there have been many attempts to use commercial acrylic fibres as precursors for the fabrication of carbon fibres, with the intention of producing lower priced carbon fibres [3, 6, 7].

Textile grade PAN fibres (commonly used in producing blankets, carpets, and clothes) have higher cross section areas and linear densities, smaller tensile strength, and different types and amounts of co-monomers compared to special PAN fibres. The modification of various parameters in these fibres (such as the types and amounts of co-monomers and linear density) is not easily possible and, if applicable, it causes their price to increase. On the other hand, producing carbon fibres with desirable properties using commercial PAN fibres through common processing routines is not possible. In recent years, however, some studies have been done using textile low price PAN fibres that led to the reduction of the price of carbon fibres, and these studies almost succeeded in this regard. In previous studies, carbon fibres with suitable mechanical properties were produced by using chemical and mechanical treatments before and after stabilization [6–8].

In this work, low-cost commercial PAN fibres were used as precursors in producing carbon fibres. The stabilization conditions and carbonisation temperature are the mainly affected factors in the properties of carbon fibres. In order to study the effects of these factors, a special screening experimental design method called the Plackett –Burman method [9] was applied, and the optimum factors were attained.

2. Experimental

Commercial PAN fibres used in this study, were produced by dry spinning. Table 1 shows the composition of these PAN fibres.

Table 1. Chemical analysis of commercial PAN fibres

Constituent	Weight (%)
Acrylonitrile (AN)	93
Methyl acrylate (MA)	6
Sodium methallyl sulphonate (SMS)	1

The PAN fibres were converted into carbon fibres through the following stages:

- Stabilization in a chamber furnace with air circulation at temperatures ranging from 180 to 280 ºC in discontinuous working conditions.
- Carbonisation of the stabilized PAN fibres in a horizontal tubular furnace with a ceramic tube under a high purity nitrogen atmosphere (99.999%) at temperatures ranging from 1350 to 1450 ºC for 10 minutes.

Tensile strength testing was done on single fibre samples by the ISO 11566 standard procedure. The test apparatus consisted of an Instron 5565 tensile tester equipped with a 2.5 N load cell and a crosshead speed of 2 $mm \cdot min^{-1}$. The gauge length was kept at 25 mm. At least 25 tensile tests were done on each sample and the average of the test results was reported.

3. Results and discussion

In this research, nine affecting variables and their influence on the properties of carbon fibres made from PAN fibres were examined and listed in Table 2. Accordingly, two main levels are considered for each variable, with 1 used for the low level of each factor and 2 for the high level.

Table 2. The most important factors (variables) influencing the properties of carbon fibres and their main levels

Variable		Main levels		Unit
No.	Name	Low	High	
1	1st step temperature of stabilization	180	200	°C
2	1st step maintaining time in stabilization	30	60	min
3	2nd step temperature of stabilization	210	220	°C
4	2nd step maintaining time in stabilization	30	60	min
5	3rd step of temperature stabilization	230	240	°C
6	3rd step maintaining time in stabilization	30	60	min
7	4th step temperature of stabilization	270	280	°C
8	4th step maintaining time in stabilization	30	60	min
9	Temperature of carbonisation	1350	1450	°C

In order to study 9 factors, the minimum necessary number of runs in the experiment would be $2^9 = 512$. Since each run is time-consuming, costly, and requires set-

ting and resetting the furnace, it is often not feasible to expect so many different production runs for the experiment. In these conditions, fractional factorials are used to "sacrifice" interaction effects so that the main effects may still be determined properly. A technical description of how fractional factorial designs are constructed is beyond the scope of this article. Detailed accounts of how to design $2^{(k-p)}$ experiments may be found, for example, in Refs. [10–12], to name just a few of many textbooks covering the subject.

The special screening design method called the Plackett–Burman method was used [9]. Screening designs are used to find the important factors of two-level factors. When the number of runs is 12, 20, 24, or 28, the Plackett–Burman design method is ordinarily used. By using STATISTICA Version6 software, a random design of the standard $\mathbf{L}_{12}$ orthogonal array [13] as tabulated by Taguchi [14] was constructed, which requires only 12 observation runs. The $\mathbf{L}_{12}$ vector allows the maximum number of main effects to be estimated in an unbiased (orthogonal) manner, with a minimum number of experiment runs. For 12 randomly designed experiments, average values of tensile strength for 25 filaments in the tow of carbon fibres measured are presented in the last column of Table 3.

Table 3. The arrangement of a $\mathbf{L}_{12}$ orthogonal random design and the experiment results (the low level of each variable denoted by 1 and its high level by 2)

Run No.	Variable No.									Average tensile strength
	1	2	3	4	5	6	7	8	9	
1	2	1	2	1	1	1	2	2	2	1684
2	2	2	1	2	1	1	1	2	2	1488
3	1	2	2	1	2	1	1	1	2	1420
4	2	1	2	2	1	2	1	1	1	1521
5	2	2	1	2	2	1	2	1	1	1619
6	2	2	2	1	2	2	1	2	1	1570
7	1	2	2	2	1	2	2	1	2	1477
8	1	1	2	2	2	1	2	2	1	1522
9	1	1	1	2	2	2	1	2	2	1418
10	2	1	1	1	2	2	2	1	2	1621
11	1	2	1	1	1	2	2	2	1	1426
12	1	1	1	1	1	1	1	1	1	1376

To determine significant variables, an analysis of variance is performed twice. The first step showed the first eight variables and the interactions between pairs of variables (1–2, 1–3, 1–4, and 1–7), all considered meaningful in 95%. Customarily, in order to obtain a more stable estimate of the error variance, small and non-significant effects are pooled into the error term. Table 4 shows the consequence of variance analysis after pooling factor No. 9 (temperature of carbonisation) into the error term.

Table 4. The analysis of the variance table after pooling the meaningful variable into the error term

Parameter	*SS*	*df*	*MS*	*F*	*P* value
(1) 1st step temperature	62208.0	1	62208.00	7776.000	0.007219
(2) 1st step time	1814.1	1	1814.07	226.759	0.042214
(3) 2nd step temperature	35392.2	1	35392.16	4424.020	0.009571
(4) 2nd step time	1236.2	1	1236.20	154.526	0.051103
(5) 3rd step temperature	2612.6	1	2612.56	326.570	0.035192
(6) 3rd step time	12222.9	1	12222.87	1527.858	0.016283
(7) 4th step temperature	38384.2	1	38384.20	4798.025	0.009190
(8) 4th step time	8557.0	1	8557.04	1069.630	0.019459
1 by 2	10069.4	1	10069.41	1258.677	0.017939
1 by 3	4182.5	1	4182.50	522.813	0.027825
1 by 4	9188.7	1	9188.70	1148.587	0.018779
1 by 7	23918.2	1	23918.22	2989.778	0.011642
Error	8.0	1	8.00		
Total *SS*	359756.9	13			

The effects of statistically meaningful variables being present in the regression model, with their coefficient estimates based on the original factor values, are shown in Table 5.

Table 5. The point estimation of coefficients in the coded value regression model

Parameter	Regression coefficient	Standard error	*t*	*P* value
Mean/Interc.	1861.333	17.39732	106.9897	0.005950
(1) 1st step temperature	–613.000	10.89342	–56.2725	0.011312
(2) 1st step time	–391.556	11.29405	–34.6692	0.018358
(3) 2nd step temperature	457.333	14.78738	30.9273	0.020577
(4) 2nd step time	–301.889	9.59166	–31.4741	0.020220
(5) 3rd step temperature	–57.778	3.19722	–18.0712	0.035192
(6) 3rd step time	137.889	3.52767	39.0878	0.016283
(7) 4th step temperature	–305.444	8.74325	–34.9349	0.018218
(8) 4th step time	84.444	2.58199	32.7052	0.019459
1 by 2	235.333	6.63325	35.4778	0.017939
1 by 3	–199.333	8.71780	–22.8651	0.027825
1 by 4	179.333	5.29150	33.8908	0.018779
1 by 7	289.333	5.29150	54.6789	0.011642

On this basis, the average tensile strength of the produced fibre $\overline{Y}$ can be introduced by following regression model:

$$\begin{aligned}\overline{Y} = {} & 1861.333 - 613X_1 - 391.556X_2 + 457.333X_3 - 301.889X_4 - 57.778X_5 \\ & +137.889X_6 - 305.444X_7 + 84.444X_8 + 235.333X_1X_2 - 199.333X_1X_3 \\ & +179.333X_1X_4 + 289.33X_1X_7\end{aligned} \tag{1}$$

Here, X_1 through X_8 stand for the 8 statistically meaningful factors in the analysis. The effects shown earlier also contain these parameter estimates. Regarding the given model coefficients, the error terms of the model are close to zero, which is an appropriate reason to verify the model. One of the most important results is to predict the tensile strength of carbon fibres for different procedure conditions. It is obvious that the more variables of procedural settings should be around its high and low values.

4. Model verification

In order to verify the models, error analysis followed based on the experimented results. The achieved regression model exhibits the smallest error possible. By substituting the experiment run results in the model, no errors were obtained. Figure 1 illustrates the observed value of carbon fibre tensile strength versus the strength predicted by the model, which presents a perfect fit.

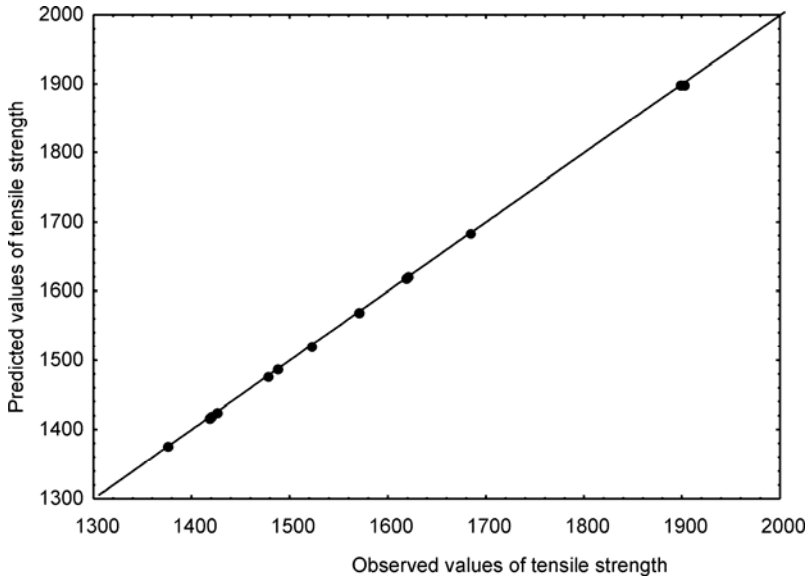

Fig. 1. Observed values of carbon fibre tensile strength versus the strength predicted by the regression model

In order to obtain an estimate of any run result, it is possible to substitute an arrangement of the model through coded units. For example, to estimate the tensile strength at the conditions 180 °C, 30 min, 220 °C, 60 min, 230 °C, 60 min, 280 °C, 60 min, and 1450 °C for X_1–X_9, respectively, the relevant coded value (1, 1, 2, 2, 1, 2, 2, 2, 2) can be applied to obtain the expected tensile strength. Table 6 shows the results of predicted (later abbreviated by Pre.) versus observed (Obs.) values for some experimental arrangements.

Table 6. The observed model values versus predicted ones
for the tensile strength of carbon fibres in a couple extra pilot experiments

Experimental arrangement								Pre. value	Obs. value
2	2	1	2	2	1	1	2	1430	1433
2	2	2	2	2	2	2	2	1900	1897
1	1	2	2	1	2	2	2	1953	1948

According to the model, the maximum value of carbon fibre tensile strength that could be deduced mathematically was 1953 MPa at the arrangement showed in detail in Table 7. This arrangement was experimentally investigated and the observed value of 1948 MPa deviates less than 0.3% from the expected value. This shows the way to optimise the desired quality characteristics from 1684 MPa (the best previously observed value) to 1948 MPa, improving it by more than 15.7%. Such a value contains reasonably appropriate quality characteristic when raw material cost is near the ground.

Table 7. Optimum levels of the main variables and maximum tensile strength of carbon fibres

Variable No.	1	2	3	4	5	6	7	8	Tensile strength (MPa) 1953
Optimum level code	1	1	2	2	1	2	2	2	
Optimum process arrangements and value	180 (°C)	30 (min)	220 (°C)	60 (min)	230 (°C)	60 (min)	280 (°C)	60 (min)	

5. Conclusions

In this article, using local textile grade PAN fibres, which seem to be a suitable alternative for producing low price carbon fibres, was surveyed. In order to achieve a mathematical model for evaluating the effect of the 9 variables of stabilization conditions and carbonisation temperature on tensile strength, a well-known experimental analysis method (Plackett–Burman) was used and a non-linear mathematical function attained. The optimisation procedure was conducted using the STATISTICA version 6 package. By analysing this model, an optimum set of process arrangements was obtained. According to the model, it is possible to predict the tensile strength of carbon fibres for different stabilization and carbonisation conditions. The optimum process arrangement showed the possibility of increasing the tensile strength of carbon by more than 15.7% with a maximum 0.3% error.

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