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Synthesis of carbon cloth by controlled pyrolysis of rayon cloth for aerospace and advanced engineering applications

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Abstract

Carbon cloth was synthesized from rayon cloth by controlled carbonization process by impregnating it with $AlCl_3$. It was then subjected to acid, mechanical, and heat treatments respectively, in order to increase the breaking load and carbon content. Acid treatment was done using hydrochloric acid, which gave the low ash content that is required for aerospace applications. Further, mechanical flexing was done by keeping carbon cloth in between two rubber rollers to remove the adhering tar on it, to have high breaking load compared to non-fluxed carbon cloth. The carbon cloth was treated at different temperature viz 100 ºC, 1000ºC and 1200ºC; it was interesting to observe that by increasing the temperature, the carbon content also increased slightly. However, high ash content is observed at 1200ºC. So the optimum temperature of the carbon cloth is fixed at 100ºC. From the data resulted from different studies, it is concluded that impregnation of rayon cloth with $AlCl_3$ may be considered as an alternative and cost-effective method for the production of carbon cloth with good breaking load and improved carbon content that are required for aerospace engineering applications.

Keywords: Mechanical testing; mechanical properties; impact test

Introduction

Rayon fiber is one of the important raw materials for the manufacture of carbon fibers because of its abundant availability, low cost, and non-melting character. Rayon based carbon fibers have low thermal conductivity, low density and high break elongation characteristics, and have occupied a pioneer position in the aerospace industry as structural reinforcement for phenolic resin based ablative materials (Plaisantin *et al.*, 2001). Rayon based carbon cloths have been extensively used as a nozzle liner reinforcement material in the satellite launch vehicles due to its unique thermal, chemical and physical properties. These reinforcements impart improved strength and relatively uniform mechanical properties to the formed components that are relatively resistant to high temperatures, during use. The carbon cloth can be made by controlled pyrolysis of organic materials like rayon, polyacrylonitrile (PAN), polyvinyl alcohol (PVA), jute, pitch having desirable characters viz, non- toxic, improved mechanical, thermal and flame resistance. Most of the published procedures for carbonizing cellulosic or rayon cloth are lengthy and involve time consuming heating processes to produce the final product. Moreover the usual commercial methods of production of carbon cloth resulting in a recovery of only about 18 - 20 weight % of the carbon product, involves prolonged heating time, and low yield resulting in high production cost as well (Guigon & Oberlin 1986; Kobets & Deev 1997; Diefendorf & Tokarsky 1975).

All polymers yield a carbon end product after decomposition. However, for the production of fibers, the polymer must decompose with melting. Work was carried on poly vinyl alcohol by several researchers and it was found that it does not offer any exciting prospects for the manufacture of carbon cloth as it gave low yields in terms of final product's weight and required slow heating rates (Huang, 2009). The technique of converting pitch into carbon fibers is to melt spin the pitch into fibers, oxidizing it on the surface to provide hardening and prevent melting during subsequent heat treatment stages. Therefore is not chosen as the precursor. PAN is not indigenously available in India and is a costly precursor as well, besides exhibiting deficiency in insulating properties and chemical purity characteristics that are required for aerospace (Henrici-Olive & Olive,1983).

Viscous rayon is chosen as the precursor material for the present study, owing to its easy availability, low cost when compared to PAN and easy processability. Moreover, it also exhibits low toxicity and flammability. There are two methods of conversion of rayon precursor into carbon cloth: One is to convert rayon fibers into carbon fibers and then weave it into the fabric of the required weave pattern and specifications. The other method is to weave the rayon fibers into fabric of required specifications and then pyrolysing it to produce the carbon fabrics. It is easier to weave rayon fibers than carbon fibers into fabrics of required specifications. The weaving losses and the damage caused during weaving will be high in the case of carbon fibers compared to rayon fibers thereby elevating the cost of production of carbon fabric by the former method. Hence the latter method of using woven rayon fabrics as precursor is selected for this study.

Above all, carbon cloth has several advantages such as: High sublimation temperature, high strength to weight ratio, low density, low thermal expansion and resistance to oxidation (Goodhew *et al.*, 1975). Though carbon cloth can be obtained by controlled carbonization technique, it however results in poor yield, lot of time consumption and high production cost. Therefore production of carbon cloth through a modified carbonization technique is inevitable. It is reported in the literature that the pretreatment of the rayon cloth with appropriate inorganic salts or reagents could very well reduce the time required for the completion of the carbonization cycles and result in a higher carbon content and breaking load. Therefore, with all these ideas in mind, an attempt has been made in the present investigation to develop carbon cloth with improved carbon content and load bearing properties. In order to increase the above properties, the rayon cloth was impregnated in $AlCl_3$ solution and carbonized at various temperatures**.**

Table 1. Specifications of the rayon cloth

Yarn Specifications	
Filaments per yarn	720
Yarn Denier	1650
Filament Tenacity	
Warp direction (gpd)	5.0 ±0.2
Fill direction (gpd)	7.0 ±0.2
Oven-dry elongation %	10.5 ±2
Degree of polymerization	450±50
Finish and additives	Nil
Fabrics Strength	
Warp direction (kg/25.4mm)	145(min)
Fill direction (kg/25.4mm)	136(min)
Weight (g/m^2)	540±35
Style of weave	8 HS
Thickness (mm)	0.7
Thread count	
Warp direction (ends/25.4mm)	36±2
Fill direction (ends/25.4mm)	36±2

Experimental

The materials used are rayon purchased from Century Rayons Limited (Table 1), aluminum chloride and hydrochloric acid purchased from E.Merck India Pvt.Ltd.

Washing and drying of the rayon cloth

Sizing agents (eg. starch, lignin) are added to the rayon yarn (Table 1) to keep the filaments integrated and to avoid the mechanical damage during weaving. The precursor material should be free from foreign matter, which may disturb the desired carbonization. Hence the rayon cloth is washed thoroughly in hot water at about 50 to 60°C several times for 2-3 hours. The removal of sizing agents is indicated by no turbid formation in the washed water. Much care is taken while washing in order to prevent any damage to the rayon cloth due to handling. It was then air-dried. In our laboratory experiments, the weight loss in the rayon cloth due to water wash has been estimated to be around 3.0 to 5.0%. The sodium content in the rayon has to be reduced substantially, so as to have minimum thermal conductivity and improved purity required for ablative behavior. Hence to remove the metallic salts, the rayon cloth after washing and drying in hot water was treated with 0.1 M molar hydrochloric acid for 15 minutes. The cloth is then washed with water to remove the acid and then air dried. The sodium content of the rayon cloth is found to have reduced from 0.007 to 0.004% after hydrochloric acid wash.

Impregnation with anhydrous aluminum chloride

The washed and dried viscous rayon cloth is impregnated with 0.5 molar anhydrous aluminum chloride in aqueous medium. Thus sufficient amount of the catalytic salt solution is taken and the rayon cloth is kept immersed in it for 15 minutes. Then the cloth is again dried in air at room temperature for 2 hours.

First phase carbonization

The anhydrous aluminum chloride impregnated viscous rayon cloth is placed over a graphite boat and kept in the hot zone of a tubular furnace. The furnace is fitted with the digital temperature controller for monitoring the temperature. The carbonization is carried out in an atmosphere of ultra high purity nitrogen the first phase carbonization involves heating the rayon cloth from room temperature to a temperature of above 300ºC. One hour residence time is given at 100ºC to remove the adjourned moisture from the cloth. The heating rate is limited to 1.5ºC per minute in the temperature range between 100ºC and 300ºC. The carbonized rayon cloth is cooled to room temperature under the same atmosphere of ultra high purity nitrogen and taken out.

Post treatment after first phase carbonization (flexing)

During the heat treatment of the rayon cloth at 300ºC, the tar vapors are evolved and are flushed out with nitrogen gas flow. The cloth after first phase carbonization is fluxed mechanically in between two rubber rollers in order to remove the adhering tar if any, which would have re-deposited over the cloth during the first phase carbonization. Then the cloth is treated with 0.1 M hydrochloric acid for 15 minutes and then washed with water to remove the adhering acid. After washing it is dried in air and subsequently dried in air oven at 120 ºC for 2 hours.

Second phase carbonization

The carbon cloth after first phase carbonization and washing is heat treated in the hot zone of same tubular furnace to a temperature of 1000ºC. The second phase carbonization is also carried out under an atmosphere of ultra high purity nitrogen. The heating is carried out at the rate of 4ºC per minute from room temperature to a temperature of 100 ºC. The sample is held at 1000ºC for a period of 30 minutes and then cooled to room temperature under the same ultra high purity nitrogen atmosphere and taken out. The fully carbonized carbon cloth is then washed in 10% hydrochloric acid for a period of 15 minutes and then with distilled water. After the

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Table 2. Effect of HCl treatment on carbon cloth

Maximum heat treatment temperature	Acid used for treatment	Treatment time (hrs)	Before heat treatment				After Heat treatment			
			% Carbon	% Ash	% Aluminium	% Alumina	% Carbon	% Ash	% Aluminium	% Alumina
1000 ºC	HCl (36%)	24	87.1	5.2	1.5	2.82	81.5	3.86	1.7	3.2

washing the cloth is dried and then tested for breaking load and then for carbon content.

Post treatment after second phase carbonization

It is mainly carried out to have minimum thermal conductivity and improved content required for ablative application. The cloth is washed with 10% of hydrochloric acid for 24 hours followed by distilled water washing till the acid is removed completely. The complete removal of the solid is ensured by testing the washed water with pH paper. After the hydrochloric acid wash, the calcium content in the cloth is found to have reduced to 0.6%.

Testing methods

Determination of breaking strength: The specimens of size 6” X 12” are prepared from carbonized cloth for determining the breaking strength. The specimens are mounted on a paper backing such that 3” gauge length is available for the tensile test. 1.5” of the sample on each end placed with the paper backing using quick fix as adhesive. The widths of the samples are trimmed to 1” from 1.5” by taking cut carbon filament from both sides uniformly. The specimen is then tested in an INSTRON D638, USA machine keeping the crosshead speed at 10 mm/min. The breaking load, time for breaking and percentage elongation were determined.

Determination of ash content: In the determination of ash content, muffle furnace, capable of sustained operation up to 1000ºC is employed, platinum crucibles , analytical balance, 200 g capacity and 0.1 mg accuracy are utilized, Oven is used to maintain the temperature up to 150 ± 2ºC. The ash content is determined using the formula: $Z = (W_3 - W_1).* 100/ (W_2 - W_1)$, where W_1 = weight of platinum crucible in g,W_2 = weight of platinum crucible + sample in g,W_3 = weight of crucible + ash in g.

Determination of carbon content: The analytical method is based on the complete and instantaneous oxidation of the sample by “Flash combustion” which converts the sample into combustion products; the resulting combustion gases pass through a reduction furnace and are swept into the chromatographic column by carrier gas. The gases are separated in the column and detected by the thermal conductivity detector. The output signal is proportional to the concentration of the individual components of the mixture.

Results and discussion

Effect of impregnation in $AlCl_3$

The main purpose of impregnating the rayon cloth into $AlCl_3$ solution is to achieve higher breaking strength of the carbon cloth. The effect of impregnation on the breaking load was studied. It observed that the values of tensile load increases after impregnating with $AlCl_3$. The breaking load was increased to 16.7 kg/inch for the $AlCl_3$ impregnated carbon cloth whereas in imported cloth the maximum load is 8.67 Kg/inch. This is because the tar vapor evolution from the rayon molecule is very slow, because of that damage on the cloth is less, and therefore breaking load is increased.

Effect of acid treatment

The rayon cloth is kept in 0.1 M hydrochloric acid for 24 hours mainly to reduce the thermal conductivity and ash content. The values of the ash content for the carbon cloth after treatment are tabulated in Table.2. From the Table it is evident that after the acid treatment the ash content is reduced from 5.22% to 3.86%. However there is no significant change in carbon content.

Effect of flexing on mechanical strength

The effect of flexing on the tensile properties of carbon cloth was carried out. During this flexing process the deposited tar vapor over the cloth is removed successfully by passing the cloth in between two rollers. Apparently the tar vapors were getting detached from the carbon cloth, thereby enhancing the tensile load bearing properties. It was noted that the breaking load non-flexed carbon cloth is 10.2 kg/inch and the maximum breaking load of the flexed carbon cloth is 16.7 kg/inch. The enhancement in breaking load values for the carbon cloth after flexing may be due to uniform heat distribution over the cloth.

Table 3. Effect of temperature on carbon cloth

Maximum heat treatment T (ºC)	% Carbon	% Ash	% Aluminium	% Alumina
1000	87.1	3.86	1.5	2.82
1200	87.2	9.34	3.8	7.14

Effect of temperature on carbon cloth

The carbon cloth after first phase carbonization is heated to 1200 ºC at a rate of 4ºC/min. During this process, the cloth was initially kept at 100ºC for one hour, in order to remove any moisture present in it. Furthermore the temperature of the cloth was raised to 1000ºC and subsequently to 1200 °C at a similar rate of heating. It was interesting to observe that there was a slight increase in carbon content, with an increase in temperature till 1200 ºC. However the ash content was also found to be increasing from 3.86 wt % to 9.9 wt %. as shown in Table 3. From this we concluded that the optimum temperature is found to be 1000ºC, where the ash content is minimum.

Summary and conclusion

Carbon cloth was synthesized by controlled carbonization from rayon cloth with impregnation of $AlCl_3$. It was then subjected to acid, mechanical, and heat treatments respectively. In order to increase the breaking load and carbon content of the rayon cloth, acid treatment was done using hydrochloric acid. We found that HCl gave the low ash content which is required for aerospace applications. Further, mechanical flexing was done by taking carbon cloth in between two rubber rollers to remove the adhering tar on the carbon cloth, which gave high breaking load compared to non fluxed carbon cloth. The carbon cloth was treated at different temperature viz 100 ºC, 1000ºC and 1200ºC; it was found that by increasing the temperature, the carbon content also increased slightly. However, ash content also increased at 1200ºC. So, optimum temperature of the carbon cloth is fixed at 100ºC. From the data resulted from different studies, it is concluded that impregnation of rayon cloth with $AlCl_3$ may be considered as an alternative and cost-effective method for the production of carbon cloth with adequate breaking load and improved carbon content that are required for aerospace engineering applications.

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