PAN based carbon fibre manufacturing

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Abstract: In Carbon Fibre (CF) production, generally Polyacrylonitrile (PAN) precursor is subjected to namely three process- polymerisation, carbonization, and heat treatment. Oxidation process is the first and foremost stage of the PAN fabrication, and subsequently it undergoes carbonization. Prior to carbonization, an important step-stabilization process is performed as part of the oxidation process. The stabilization is performed by ranging temperatures between 200°C-250°C. The carbon fiber manufactured has the density of 1.75-1.76 g/cc and tensile strength of 3.5-3.8 Gpa.

Key words: Inherent viscosity, carbonization, CSTR, elemental composition.

1. Introduction

Carbon fibre, alternatively graphite fibre or CF, is a material consisting of fibres about 5–10 μm in diameter and composed mostly of carbon atoms. To produce carbon fibre, the carbon atoms are bonded together in crystals that are more or less aligned parallel to the long axis of the fibre as the crystal alignment gives the fibre high strength-to-volume ratio. The unique properties of carbon fibres, such as high stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance, high specific strength and modulus, high thermal conductivity, good shock resistance and low thermal expansion make them highly popular hence they are extensively used as precursors for CF fabrication and has become predominant reinforcement in the fabrication of high performance composites in last decades. They have been extensively used in composites in the form of woven textiles, prepregs, continuous fibres/rovings, and chopped fibres. The composite parts can be produced through filament winding, tape winding, pultrusion, compression molding, vacuum bagging, liquid molding, and injection molding. In recent years, the carbon fibre industry has been growing steadily to meet the demand from different industries such as aerospace (aircraft and space systems), military, turbine blades, construction (non-structural and structural systems), light weight cylinders and pressure vessels, shore tethers and drilling risers, medical, automobile, sporting goods, etc. (Robert, 2006; Friedlander et al., 1968). For the automotive industry, fibre reinforced polymeric composites offer reduced weight and superior styling. Carbon fibres can find applications in body parts (doors, hoods, deck lids, front end, bumpers, etc.), chassis and suspension systems (e.g., leaf springs), drive shafts and so on. The estimated global carbon fibre consumption is increasing from 21000 tons in 2004 to 32400 tons in 2010 (Friedlander et al., 1968; Red, 2006) In fact, most of the carbon fibre manufacturers have plans for expansion to meet the market demand. However, the large-volume application of carbon fibre in automotive industry has been hindered due to the high fibre cost and the lack of high-speed composite fabrication techniques (NRC, 1992).
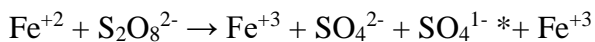
The current carbon fibre market is dominated by polyacrylonitrile (PAN) carbon fibres, while the rest is pitch carbon fibres and a very small amount of rayon carbon fibre textiles. Different precursors produce carbon fibres with different properties. Although producing carbon fibres from different precursors requires different processing conditions, the essential features are very similar. Due to low productivity of rayon-based CF, PAN and mesophase pitch have been more preferred. However, mesophase pitch-based CFs are inferior to PAN-based CF in tensile strength (Buckley and Edie, 1992). Furthermore, the difficulty of mesophase pitch synthesis with a high average molecular weight with no or small side groups required for melt spinning process is another drawback. Therefore, PAN has been most widely used materials for carbon fibre precursors for more than thirty years. Approximately 90% of CFs produced in the world is PAN-based CF (Buckley and Edie, 1992, Koganemars et al., 2004) Commercially, PAN precursors are polymerized with acidic co-monomers such as acrylic acid, methacrylic acid, and itaconic acid (Kim et al., 1993). Stabilization is one of the most important factors to determine mechanical strength of PAN based carbon fibres. Fitzer et al. reported optimization of stabilization of PAN fibres and effect of carbonization of resulting fibres on tensile strength (Fitzer et al., 1986). Even though stabilization of PAN fibres has been studied for more than thirty tears, the exact mechanism and the structure of stabilized PAN fibre are unknown.
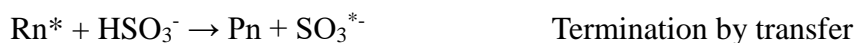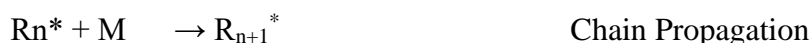
2. Materials and Methodology

The PAN copolymer can be synthesized using solution polymerization, bulk polymerization, emulsion polymerization and aqueous dispersion polymerization techniques. Here the continuous stirred tank reactor (CSTR) is adopted to prepare PAN copolymer using aqueous dispersion polymerization. In this polymerization technique de-ionized water is the continuous phase and the initiators dispersants are water soluble. A reaction system comprising of an oxidizer: Ammonium persulphate, a reducing agent/activator: Ammonium bisulphite/Sodium bisulphite and catalyst: Iron

containing compounds will generate free radicals effectively in water based system at temperatures of about 50-55°C and pH in the range of 2-3.

Reactions:

$Fe^{+2} + S_2O_8^{2-} \rightarrow Fe^{+3} + SO_4^{2-} + SO_4^{1-} * + Fe^{+3}$

$Fe^{+3} + HSO_3^{1-} \rightarrow Fe^{+2} + HSO_3 *$ bisulphite ion as reducing agent

The bisulphite ion takes dual role acting as a reducing agent and as chain transfer agent.

$SO_4^{1-} *$ or $HSO_3 * + M \rightarrow R_1 *$		Chain Initiation
$Rn* + M \rightarrow R_{n+1}^{*}$		Chain Propagation
$Rn* + HSO_3^- \rightarrow Pn + SO_3^{*-}$		Termination by transfer
$Rn* + Rm* \rightarrow Rm+n$		Termination by combination

The new free radicals produced combine sequentially to increase the chain length and transfer the free radicals site to the farther end of the chain, radical polymer chains get terminated through combination, disproportionation or chain transfer mechanisms. In acrylonitrile polymerization combination and chain transfer mechanism are predominant. Chain transfer mechanism may occur through the solvent, activator, initiator or monomer. The polymerization reaction can be terminated by adding terminators like ammonium bicarbonate/ammonium oxalate. The continuous stirred tank reactor (CSTR) is used to prepare PAN copolymer on a pilot plant scale as shown in Fig 1. The polymer is prepared at about 25-30 kg/hr.
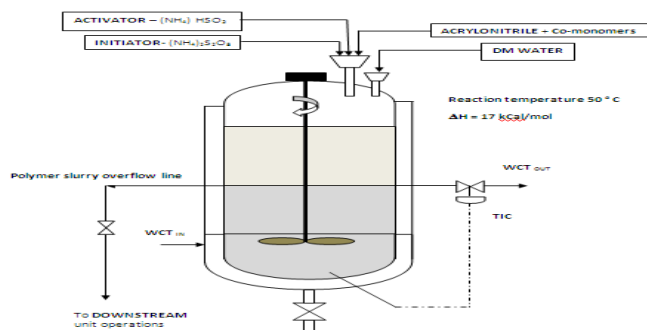

Fig. 1: A typical CSTR unit for carrying out polymerization reaction

A solution of PAN copolymer is dissolved in a suitable solvent, such as DMF, DMSO, NaSCN or $ZnCl_2$ under high shear to give a dope. When the dope has been made, it is de-aerated by heating under vacuum and then rigorously filtered in several stages before extrusion. Viscosity of the dope is measured using Brookfield viscometer. The porosity of the structure is controlled, initially by the coagulation conditions and is subsequently reduced by stretching and drying. Once the fibre has been spun and coagulated either in the wet or the dry jet process, the next steps of washing, stretching, finishing and drying are carried out.

The conversion of PAN based precursor to carbon fibre requires heat treatment of oxidation. In the oxidation stage, the PAN fibre density increases from 1.18 g/cm^3 to about 1.36–1.38 g/cm^3 and is called as oxidized PAN fibre (OPF). During pre-carbonization reaction about 30-35% of mass loss takes place and usually the gases evolved are HCN, ammonia, CO_2 etc. which are further treated in an incinerator at about 750-850°C. The carbonization reactions are carried out in high temperature furnaces where the pre-carbonized fibre is heated up to 1300-1500°C under inert (N_2) atmosphere. The temperature of carbonization is usually determined by the end application requirement. The carbon content of the fibre at this stage increases to > 92% and during this process stage small amount of nitrogen and hydrogen are evolved. After the high temperature treatment during carbonization, the surfaces are treated by anodic oxidation to improve their adhesion with resin matrix thereby increasing the inter laminar shear strength of the fibre. Next the sizing is carried out. The sizing is an aqueous dispersion of an epoxy based compound which is applied on the carbon fibre tows as an emulsion in water. In order to control the size pick up it is necessary to dry the fibre tows. After all these processes the carbon fibre is wound in form of bobbins on the winding machine.

3. Results and discussion

3.1. Inherent viscosity of polymer

A dilute solution of polymer (concentration= 0.1, 0.2 and 0.4 % w/v %) in dimethylformamide (DMF) were prepared. The inherent viscosity was measured using Ubbelohde viscometer. The inherent viscosity Vs concentrations were plotted and extrapolated to zero concentration to get intrinsic viscosity. The inherent viscosity of polymer is 1.484 and the viscosity average molecular weight of polymer was calculated from Mark-Houwink equation as 1.13lakhs K and values of the Polymer in DMF are 2.4×10^{-4} and 0.75 at room temperature.
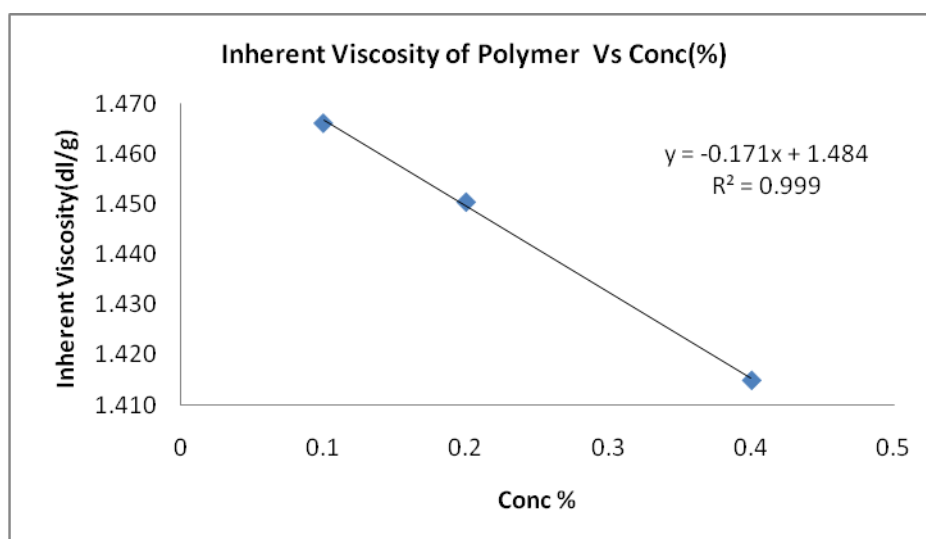

Fig. 2: Inherent viscosity of polymer Vs Concentration (%)

3.2. Concentrated Polymer solution (dope) viscosity measurement by Brookfield viscometer

A concentrated solution (20 % w/w) of polymer was prepared in dimethyl acetamide (DMAc) and its viscosity at different spindle rpm are measured using Brookfield viscometer. It is observed from the graph that the viscosity of dope decreases with rpm. This type of a behavior is typical of non Newtonian liquid and the dope is a shear thinning liquid i.e, as the shear rate increases viscosity comes down.
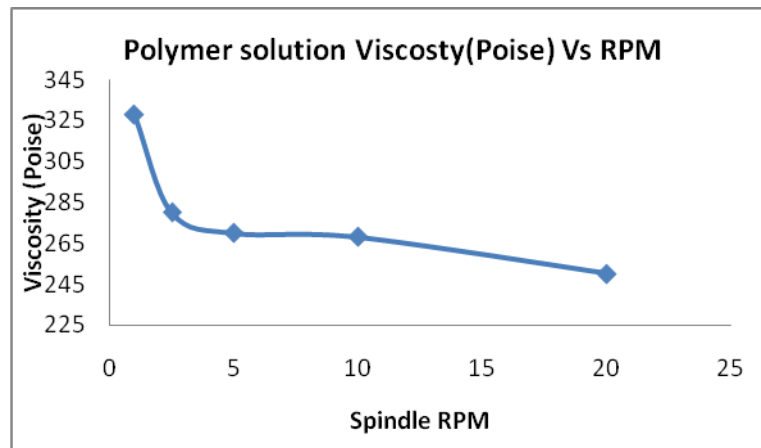
Fig. 3: Viscosity of 20 % polymer in DMAc versus Spindle rpm

3.3.   Tensile properties of SAF

The tensile properties of the fibre are obtained by testing the fibre yarn or the single filament in Universal test equipment. In CF pilot plant, Hounsfield H10KS Universal Testing Machine was used for this purpose. SAF single filament of 20mm gauge length and a loading rate of 25 mm/min were used. The breaking load in Newton, Initial Slope (N/mm) and maximum extension (mm) were noted down from the load Vs Extension plot. A typical plot of load vs extension for SAF single filament is as shown in fig 4.
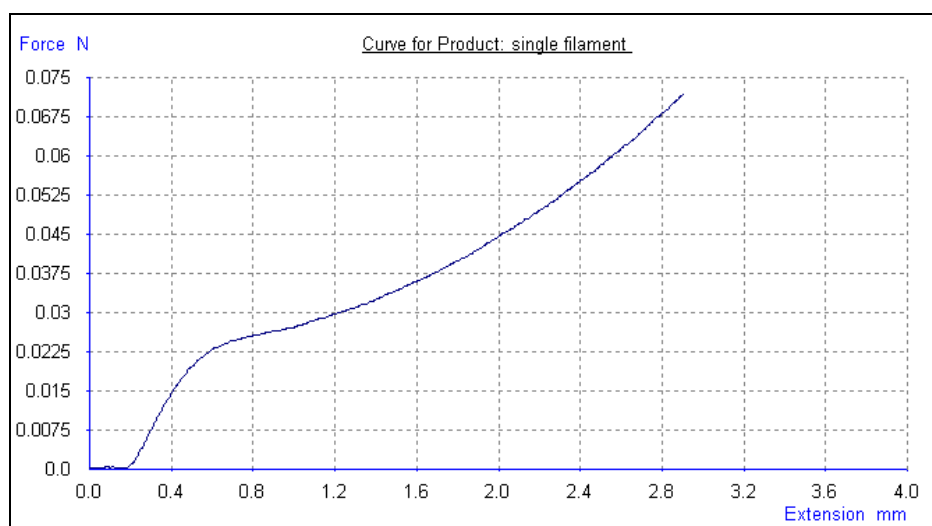

Fig. 4: Load Vs extension for SAF single filament

3.4. Elemental analysis

CHNS elemental analyzers provide a means for the rapid determination of carbon, hydrogen, nitrogen and sulphur in organic matrices and other types of materials. They are capable of handling a wide variety of sample types, including solids, liquids, volatile and viscous samples, in the fields of pharmaceuticals, polymers, chemicals, environment, food and energy. Elementar Vario micro cube Elemental analyser with GC column and thermal conductivity detector was used and all the fibre samples are weighed in tin capsule in a high resolution Mettler balance. Helium is used as carrier gas and high purity oxygen as the oxidizing gas. The results of density and elemental composition of SAF, oxidized fibre and CF are given in Table 1.

Table 1: Density and Elemental Composition of different fibres

Sample Id	Nitrogen %	Carbon %	Hydrogen %	Oxygen %	Density (g /cc)
SAF	23-24	65-66	5-6	5.5	1.185-1.190
Oxidised SAF	21-22	60-61	4-5	13.5	1.36-1.37
CF	4-5	94-95	0.2-0.3	0	1.75-1.76

The PANOX fibres are precarbonised and carbonized in a series of high temperature furnaces to carbon fibre and the carbon fibre (CF) will be characterized for mass per unit length (mpul), density, sizing content, elemental composition and tensile properties. The typical results of carbon fibre (CF) is given in Table 2.

Table 2: Test results of carbon fibre (CF)

Mpul (g /m)	Density (g /cc)	Tensile strength (GPa)	Tensile modulus (GPa)	Sizing content (%)
0.400	1.75-1.76	3.5-3.8	230-250	1.0-1.2

4. Conclusion

PAN based Carbon Fibre manufacturing process and the characterization involved in various stages of processing and developing are polymer synthesis, wet spinning facility and heat treatment. The PAN copolymer characterization studies included inherent viscosity, molecular weight of the polymer and rheological behavior of spin dope at various shear rates. The PAN precursor and oxidized PAN cross sectional shape and the area were studied using optical microscope. The tensile properties of the fibres were analyzed. The change in elemental composition during the conversion of PAN copolymer to carbon fibre was evaluated using elemental analyzer and compared with the corresponding fibre densities.

Acknowledgment

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