

## **Temperature: Stabilization in Oxidation stage during Carbon Fibre production**

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**ABSTRACT :** In Carbon Fibre(CF) production, generally Polyacrylonitrile (PAN) precursor is subjected to namely three process- Oxidation, Carbonization, and Graphitization. Oxidation process is the first and foremost stage of the PAN fabricatio, 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 180°C- 400°C. However, various manufacturers perform study at various temperatures inside the Oxidation oven. This paper focuses on the temperatures set/recommended/literature review during the Stabilization process in an Oxidation oven during CF production.

**KEYWORDS** - Carbon fibre (CF), Polyacrylonitrile(PAN), Stabilization, Batch, Continuous.

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### **I. INTRODUCTION**

PAN fibers are extensively used as precursors for CF fabrication [1] A CF, carbon/carbon (C/C) composite avails numerous outstanding mechanical, electrical, magnetic properties [2]; and has become predominant reinforcement in the fabrication of high performance composites in last decades. The important property mainly includes high specific strength and modulus, low thermal expansion, high thermal conductivity and good shock resistance [3] [4]. Due to the exceptional mechanical properties of carbon fibre composites (CFC) has made interest in various applications, such as in Aerospace, Automotive, Wind power turbines and also in various other industrial applications. In the last decades, an increase in CF production has been noticed- from 15,000 metric tons (Mt) to 40,000 Mt. Mostly, an increased usage has been noticed in Aerospace industry to undercut the fuel bills caused due to reduction of weight than usual. The main reason is due to CFC weight basis is 2–5 times stronger (specific yield stress) and stiffer (specific modulus) than aluminum. The process of producing CFC's is well recognized by changing in different types or composition of precursor or processing conditions, and moreover CF can be made in different range of grades and with different properties. An approximate of 95% of all CF uses PAN as the precursor; the polymer comprises of a small amount of comonomer in-order to improve the solubility and facilitates the processing of the fibres. For resulting fibres with higher thermal and electrical conductivity, and higher elastic modulus along the fibre direction, pitch is also added as precursor material, which is extremely hard and non-flat provides a challenge [5] [6]. During the production of CF, it is oxidized from organic material by heating fibres, and continually through transporting systems- reciprocated, spaced rollers, over guides in order to prevent the shrinkage of fibres, the time spent between the guides is much longer than the time while the fibres are in contact with the guides [7].

While fabrication process, manufacturer sets unique temperature in Oxidation stage for transformation of fibre, which is known as Stabalization [1]. In Oxidation process the oven is preheated by regulating to the required temperature, next it is positioned to enclose the fibre loop by maintaining constant temperature in the oven. Continuously the oven is purged with the necessary atmosphere [8]. The heat treatment temperature during Stabilization ranges with a minimum temperature of 180°C - and to a maximum of 400°C. A PAN precursor; when heated to 180°C and above, it undergoes thermal degradation and causes cyclization of the structure. The cyclization reaction is exothermic in nature, which has to be regulated to obtain a better quality CF from PAN. Numerous studies were carried out particularly in this aspect to understand exothermic behavior of PAN during various temperatures during Oxidation process [9]. This exothermal reaction is observed in vacuum, air, oxygen, ozone, chlorine, and non-oxidizing inert gases such as nitrogen or argon, air and oxygen-containing atmospheres-depends on the treatment temperatures and on the nature of the polymers [1] [10]. It prevents polymer from decomposition throughout Carbonization process that occurs at high temperature [2]. The Oxidation Stabilization process is the least understood step during CF fabrication process, and is studied from many years. Therefore, Oxidative Stabilization process is relatively complex and strongly depends on the

temperature at which the PAN is cooked. Hence, for these reasons; this paper presents the temperatures at which various papers has either recommended from other research or performed.

## II. STABILIZATION

Stabilization process is predecessor to Carbonization process, and it varies widely from one precursor to other. The chief aim of Stabilization is to form a thermally stable ladder polymer that it will avoid the precursor from deforming or melting at Carbonization temperatures, for few materials, such as thermo-chemical, a polyethylene, Stabilization stage in fuming sulfuric acid or chlorosulfonic acid to sulfonate the fibre prior to Carbonization, which is essential. Sulfonation is also necessary to boost up the yield potential of the fibre varying from less than 1% up to 70% or further. While for other materials, such as PAN and PAN/carbon nanotube, and lignin, a thermo-oxidative Stabilization stage; the atmospheric air is introduced prior to Carbonization. The chief input parameters of stabilization steps are [11].

- 1) Time
- 2) Quantity of available precursor
- 3) Desire to control either tension or strain.

The most important step of Stabilization is to bond as-spun structure, and to insure that both the molecular and the fibrillar orientation are not lost during final heat treatment. To attain this, either the molecules must be tied together or the inherent stiffness of the PAN molecules must be increased in order to eliminate/limit, relaxation, and chain scission during the final Carbonization step. Mostly in commercial process PAN precursor fiber is Stabilized by exposing to the air, most of them would agree that both dehydrogenation and cyclization can take place during Stabilization step. Particularly cyclization is a highly exothermic, but in fact while PAN copolymer precursors are employed exotherm is reduced. Evidently, during Stabilization reaction comonomer acts as an initiator. Various studies indicated that the rate (time), temperature, and applied tension, all together (TTT- Time, Temperature, Tension) of oxidative Stabilization is affected by copolymer composition of PAN precursor fiber, even though many researchers agree upon that during this process a ladder polymer forms, and its structure is still a doubt. In cyclization reaction may be stereo specific would occur preferentially in isotactic sequences. However, the syndiotactic sequences were equally capable of cyclization, whereas the problem may be due to the polymer chains within the fibril form an irregular rod-like helix formed due to the intramolecular repulsion of nitrile groups. In turn the fibrils consists together both crystalline and amorphous regions [12].

### 2.1. BATCH

For applications where the load size or production volumes vary substantially, batch processing is a good approach. Batch ovens are also ideal for situations that require a high degree of flexibility in terms of process; variables such as temperature or dwell (soak) time. [13]. In batch ovens; a constant tension is maintained and not constant strain, and usually represented for a larger scale equipment temperature/time. During the process the material is held in a static, and with a constant force (constant tension) applied versus variable force (constant strain). In batch Stabilization, parameters such as temperature control and uniformity within reaction volume are most important. While designing a batch oven, it is always advantageous to provide change of temperatures within the volume to maintain a similar zone to zone temperature variation and travelling time between zones on a continuous line, this is especially necessarily recommended for research and development purposes [11].

### 2.2. CONTINUOUS

In continuous, similar products with large quantities are processed, continuous operation is the optimal approach. A continuous oven assists with the consistent of thermal processing time for each specific part during high volume technology. Furthermore, this oven type allows several discrete process than can be combined, reducing material handling and increasing throughput. [13]. In this process the material moving all through the system and has more elaborate equipment have need of a large amount of more mass of precursor while compared to batch processing, but has the benefit of controlled strain. The rate of reaction tends to be greatly sensitive to temperature, if not controlled suitably, it can attribute to exothermic process in the material, as similar to batch process. Besides, for implementing flexibility in research, a wide range of temperature is also beneficial. Continuous processing exerts large samples as well. For a very small scale continuous Stabilization, a typically small oven design is used by using a air through approach with single tubes individually for each pass. Thereby provides a clean environment, reduced build up toxic emission in the interior of the process chamber, minimize the exothermic reaction causing air and discards the necessity of water suppression system for the fibre. The design limits by allowing a very quick changes with the temperature, uniformity of the temperature within each pass, and excellent accuracy [11].

2.3. TEMPERATURES OF STABILIZATION PROCESS IN OXIDATION OVENS

The studies conducted by various researchers during the Stabilization process in the Oxidation stage are listed in Table.1; temperature ranges between 180°C - 400°C. However, in most of the cases the temperature is maintained no more than 300°C. In contrast, few of the researchers determined that ranging temperature less than 300°C is not at all thermally stabilized and complete. Alternatively it was recommended that temperature ranging 350°C as minimum and 400°C as maximum seems to be necessary for proper and complete stabilization [11].

Table.1. Temperatures maintained by various studies during stabilization during oxidation stage.

Study	Temperature recommended/performed	Description
Yaodong lin, and Satish Kumar [16]	180°C - 300°C	Literature Review
US Patent [17]	1st- 220°C to 250°C, 260°C, 2nd-300°C	The oxidation is splitted in two sates
AVILÉS et al. [18]	200°C to 300° C	Precursor is heated in air or oxygen containing process
D. D. Edie [12]	230°C to 280°C.	In most commercial processes, the PAN precursor fibre is stabilized by exposing it to air at temperatures ranging from
J. Zhu et al. [19]	220°C, 250°C, 280°C and 300°C	Different temperatures considered during study
Chen and Harrison [20]	230°C	Batch process
Wangxi et al. [20]	200°C -400°C	Batch process
Hou et al. [20]	300°C	Batch process
Yu et al. [20]	195°C –280°C	Continuous process – 10 separated zones, 6 min for each zone
Gupta and Harrison [20]	200°C –500°C, optimum temperature at 380 °C , 200°C –280°C	Batch process
Hou et al. [20]	200°C –280°C	Batch process
Wu et al. [20]	160°C -280°C	Performed study
Mathur et al. [20]	230°C	Batch process
Ge et al [20]	190°C -275°C	Continuous process
He et al. [20]	190°C -270°C	Continuous process
Fazlitdinova et al. [20]	240°C -290°C	Batch process,
Renee M. Bagwell [11]	350°C up to 400°C	Outlining the parameters considering
Anna Biedunkiewicz [21]	180 °C – 289 °C	Outlining the parameters considering
Otakar Franks [22]	225°C, 245 °C, 270°C	Outlining the parameters considering
Study [15]	300°C -400°C	Weight changes in case of pure PAN-derived fibers occur largely around 300°C, and stabilize for temperature region above 400°C
E. Fiizer et al. [23]	260°C and 290°C, and <350	Temperatures considered
Ylva Nordström [24]	200°C -280°C	PAN homopolymer ,Stabilization oxygen atmosphere
Cheung	180°C -300°C	A comprehensive study [25]
Kelly	300°C	
Ullmann's	200°C -300°C	
Morgan	220°C -270°C	
CEH	190°C -280°C	
Kirk Othmer	200°C -300°C	
Minus and Kumar	200°C -300°C	
L. Lin et al. [26]	250°C	Linin Based Carbon Nano fiber Heating the fibre in air
Bajaj & Dhawan [14]	180°C -400°C	PAN based activated carbon fibre
M. G. Dunham and D. D. Ediet [27]	200°C to 300°C	PAN based CF stabilized in air at 200°C to 300°C to lock the orientation in place and make them infusible.
D. Esrafilzadeh et al. [28]	180°C –300 °C	special polyacrylonitrile nano fibers as carbon or activated carbon nano fiber precursor
R.B.Mathura,O.P.Bahl, J.mittal [29]	250°C	PAN fibres

S. Dalton et al. [30]	200°C, 225°C, 250°C, 275°C and 300°C	Different temperatures considered during study
A.Gupta and I.R.Hakrison [31]	200°C and 300°C	Batch Process-in the presence of oxygen and for extended periods of time, varying from 1 to 24 hours.
M.C. Paiva et al. [32]	180°C to 300°C	polyacrylonitrile fibers in the air
S. Bkazewicz [33]	200°C to 300°C	PAN fibres preliminarily oxidized with SO <sub>2</sub> to carbon fibres.
E. Fkzer and D. J.Miller [1]	200°C and 300°C	Homopolymer and copolymer PAN fibers
G. S. Bhat et al. [8]	230°C and 260 °C	Batch mode
B.G. Min et al. [34]	200°C –300°C	PAN/SWNT composite fiber composites at 250°C

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