OPTIMIZATION OF M5 FIBER HEAT TREATMENT CONDITIONS

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M5 FIBER CHEMICAL STRUCTURE

Chemical Structure of M5 Fiber: poly-pyridobisimidazole

Water – Polymer Interactions in M5 As-Spun Fiber

• M5 in the as-spun state may contain up to 20 wt% water
• At high annealing temperatures, the rate of water removal in a nearly-saturated fiber may lead to the formation of fiber defects

NON-ISOTHERMAL ANNEALING OF M5 FIBER

• The observed fiber damage opens the possibility of using variable temperatures during the annealing process: lower T during the initial stages, followed by higher T as the amount of water in the fiber diminishes
• Use of non-isothermal annealing conditions can:
  ✓ Maximize H-bond formation
  ✓ Minimize annealing time
  ✓ Prevent heat treatment-related fiber damage
• In order to establish optimal non-isothermal annealing conditions, non-isothermal kinetic and diffusion models need to be developed

NON-ISOTHERMAL KINETIC MODEL

Recalling the kinetic rate expression for hydrogen bond formation in M5 fiber:

\[
\frac{[A]}{[A]_k} = m_1 \exp(-k_1t) + m_2 \exp(-k_2t)
\]

We can define:

\[
e_1 = \exp(-k_1t), \quad \frac{[A]}{[A]_k} = m_1 e_1 + m_2 e_2
\]

The derivative of the expression is defined as

\[
\frac{d([A]/[A]_k)}{dt} = \frac{dm_1}{dt} e_1 + m_1 \frac{de_1}{dt} + \frac{dm_2}{dt} e_2 + m_2 \frac{de_2}{dt}
\]

Integration of the previous expression yields the dual mechanism, non-isothermal kinetic rate expression for hydrogen bond formation in M5 fiber during heat treatment:

\[
\frac{[A]}{[A]_k} = 1 + \int \left( \frac{dm_1}{dt} e_1 + m_1 \frac{de_1}{dt} + \frac{dm_2}{dt} e_2 + m_2 \frac{de_2}{dt} \right) dt
\]

NON-ISOTHERMAL KINETIC MODEL (cont’d)

EXPERIMENTAL VALIDATION OF NON-ISOTHERMAL KINETIC RATE EXPRESSION

Non-isothermal annealing of M5 fiber specimens has been performed using three different linear heating rates to Tfinal=150°C
NON-ISOTHERMAL DIFFUSION MODEL

The analytical expansion of the diffusion equation for non-isothermal annealing conditions is completely analogous to the analysis just described for the analytical expansion of the kinetic rate equation.

Recalling the diffusion equation for a solid, cylindrical fiber:

\[ \frac{M}{M_\infty} = 1 - \sum \frac{1}{\beta_n r} \exp\left(-D\beta_n^2 r^2 \right) \]

Where \( J_0(\beta_n r) = 0 \), and \( \beta_n s \) is the positive root of \( J_0 \), the Bessel function of the first kind of order zero, with \( s=r \), the fiber radius.

Defining:

\[ f_s = \exp\left(-D\beta_n^2 r^2 \right) \quad A_s = \frac{4}{\beta_n}, \left(\frac{\beta_n}{\beta_n s} \right), \left(\frac{\beta_n s}{\beta_n} \right) \]

The general diffusion equation from water desorption during M5 fiber annealing is obtained as:

\[ \frac{M}{M_\infty} = \int \left( \sum A_s \left(\frac{\beta_n}{\beta_n s} \right), \left(\frac{\beta_n s}{\beta_n} \right) \right) f_s \]

EXPERIMENTAL VALIDATION OF NON-ISOTHERMAL DIFFUSION EQUATION

- In order to validate the general diffusion equation, the weight loss values of the fiber specimens annealed according to the experimental heating rates used in the validation of the non-isothermal kinetic rate expression were measured once each of the heating rates reached 150°C.

- The general kinetic and diffusion models have been used to define heat treatment conditions that:
  1. Maximize hydrogen bond formation
  2. Minimize fiber residence time in the annealing process
  3. Minimize the risk of potential fiber damage due to accelerated water desorption

- The recommended two-step annealing procedure consists of:
  1. Annealing at 95°C for 3.75 Hr in order to perform most of the water desorption (\( M_{t=3.75Hr}/M_\infty = 0.9 \)), followed by
  2. Annealing at high (\( T_A=150 - 250 \)°C) temperature until the desired degree of intermolecular hydrogen bonding is reached

HEAT TREATMENT CONDITIONS FOR REDUCED CYCLE TIMES

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HYDROGEN BONDING & ANNEALING TIME

Output of the general kinetic model under the proposed two-step annealing procedure

CONCLUSIONS

1. Non-isothermal kinetic and diffusion models have been developed as aids in the optimization of the heat treatment process.
2. A two-step annealing process has been proposed in order to maximize hydrogen bond formation, minimize fiber residence time in the annealing process, and minimize potential fiber damage due to accelerated water desorption.

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