UNIVERSITY OF DELAWARE

OPTIMIZATION OF M5 FIBER HEAT TREATMENT CONDITIONS

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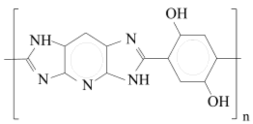
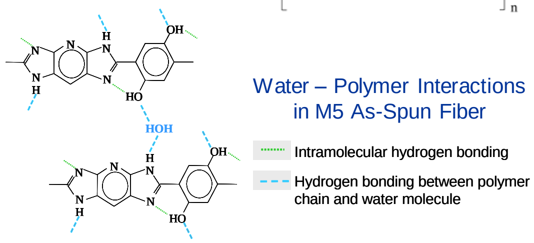
M5 FIBER CHEMICAL STRUCTURE

Chemical Structure of M5 Fiber: poly-pyridobisimidazole





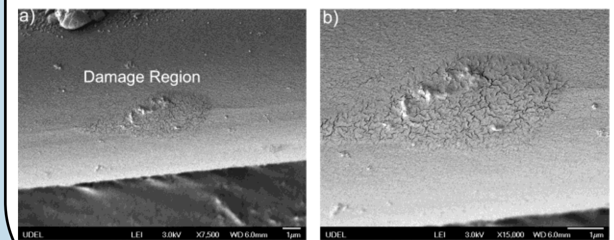
Water – Polymer Interactions in M5 As-Spun Fiber

- 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

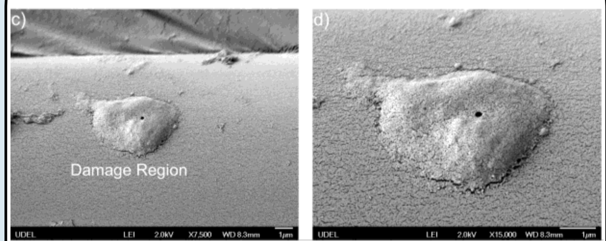
FIBER DEFECTS INDUCED BY HEAT TREATMENT

Extreme Case: M5 As Spun fiber saturated by immersion in water

In order to illustrate the potential of fiber damage during heat treatment, M5 in the as spun state was saturated by immersion in water for 12 Hr, followed by immediate placement in an oven at 200°C (Residence Time 1 Hr)



FIBER DEFECTS INDUCED BY HEAT TREATMENT



Mechanical Properties of M5 fibers annealed at 200°C for 1 hour

Fiber	Weight Loss	E_{1t} (GPa)	E_{1c} (GPa)	σ_{1c} (GPa)	σ_{1t} (GPa)
M5 Annealed *As Received*	18.61 %	126 ± 6	117.2	1.27 ± 0.08	2.2 ± 0.4
M5Annealed *after Saturation in Water*	49.83 %	97 ± 6	90.2	0.50 ± 0.10	2.1 ± 0.6

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:

$$\frac{[A_1]_t}{[A_1]_0} = m_1 * \exp(-k_1 t) + m_2 * \exp\left(-k_2 t^{0.36}\right)$$

$$m_1 + m_2 = 1$$

We can define:

$$e_1 = \exp(-k_1 t)$$

$$e_2 = \exp\left(-k_2 t^{0.36}\right)$$

And express the kinetic rate expression as:

$$\frac{[A_1]_t}{[A_1]_0} = m_1 * \mathrm{e}_1 + m_2 * \mathrm{e}_2$$

The derivative of the expression is defined as

$$\frac{d\left([A_1]_t/[A_1]_0\right)}{dt} = \frac{dm_1}{dt} * e_1 + m_1 * \frac{de_1}{dt} + \frac{dm_2}{dt} * e_2 + m_2 * \frac{de_2}{dt}$$

NON-ISOTHERMAL KINETIC MODEL (…cont'd…)

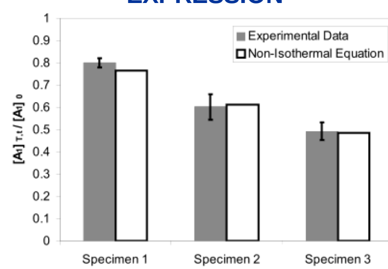
$$\frac{d\alpha_{t,T(t)}}{dt} = \left(\frac{\partial \alpha}{\partial T}\right)_t * \frac{dT}{dt} + \left(\frac{\partial \alpha}{\partial t}\right)_T$$

$$\frac{d\left([A_1]_t/[A_1]_0\right)}{dt} = \sum_{i=1}^{2}\left(\frac{dT}{dt}\left[e_i\left(\frac{\partial m_i}{\partial T}\right)_t + m_i\left(\frac{\partial e_i}{\partial T}\right)_t\right] + \left[e_i\left(\frac{\partial m_i}{\partial t}\right)_T + m_i\left(\frac{\partial e_i}{\partial t}\right)_T\right]\right)$$

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

$$\frac{[A_1]_{T,t}}{[A_1]_0} = 1 + \int_0^t \left(\frac{dT}{dt}\left[e_1\left(\frac{\partial m_1}{\partial T}\right)_t + m_1\left(\frac{\partial e_1}{\partial T}\right)_t + e_2\left(\frac{\partial m_2}{\partial T}\right)_t + m_2\left(\frac{\partial e_2}{\partial T}\right)_t\right] + m_1\left(\frac{\partial e_1}{\partial t}\right)_T + m_2\left(\frac{\partial e_2}{\partial t}\right)_T\right) dt$$

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 T_{final}=150°C

OPTIMIZATION OF M5 FIBER HEAT TREATMENT CONDITIONS

(Continued)

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:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{r^2 \beta_n^2} \exp\left(-D\beta_n^2 t\right)$$

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:

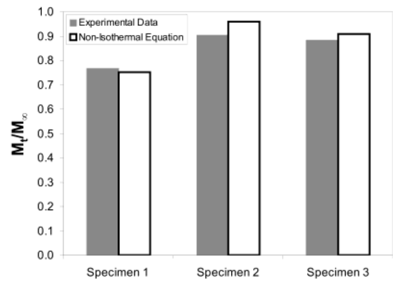
$$f_n = \exp\left(-D\frac{(\beta_n s)^2}{r^2} t\right) \qquad A_n = \frac{4}{r^2\left(\frac{(\beta_n s)^2}{r^2}\right)} = \frac{4}{(\beta_n s)^2}$$

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

$$\left(\frac{M_t}{M_\infty}\right)_{T,t} = \int_0^t \left(-\sum_{n=1}^{30} A_n * \left(\frac{dT}{dt} * \left(\frac{\partial f_n}{\partial T}\right)_t + \left(\frac{\partial f_n}{\partial t}\right)_T\right)\right) dt$$

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

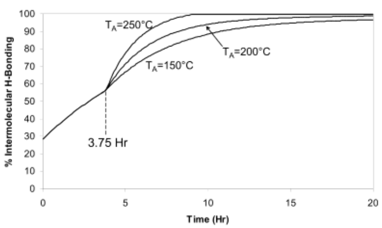


Non-isothermal annealing of M5 fiber specimens has been performed using three different linear heating rates to T_{final}=150°C

HEAT TREATMENT CONDITIONS FOR REDUCED CYCLE TIMES

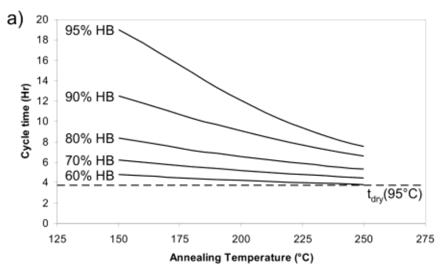
- The general kinetic and diffusion models have been used to define heat treatment conditions that
  - ✓ Maximize hydrogen bond formation
  - ✓ Minimize fiber residence time in the annealing process
  - ✓ Minimize the risk of potential fiber damage due to accelerated water desorption
- The recommended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

HYDROGEN BONDING & ANNEALING TIME



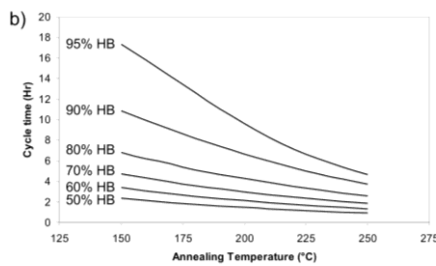
Output of the general kinetic model under the proposed two-step annealing procedure

DESIGN CHART – SATURATED FIBER



Annealing conditions necessary to achieve different degrees of intermolecular hydrogen bonding (HB) in M5 as-spun fiber saturated at 93% R. H. The fiber is dried for 3.75 Hr at 95°C before increasing annealing temperature

DESIGN CHART – DRY FIBER



Annealing conditions necessary to achieve different degrees of intermolecular hydrogen bonding (HB) in M5 as-spun fiber with no initial moisture

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

ACKNOWLEDGEMENTS

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