

MECHANICAL PROPERTIES OF STABILIZED ITACONIC ACID MODIFIED POLYACRYLONITRILE

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Introduction

To produce PAN-based CFs, three stages are required: wet spinning, stabilization, and carbonization. Stabilization of PAN is performed by heating from 200 to 300°C in air under tension, leading to cyclization, dehydrogenation, and oxidation. PAN molecules are cyclized to transform into a non-meltable ladder structure, which is critical to avoid melting during carbonization [1]. It is known that nitrile groups in PAN are initiated thermally through a free radical mechanism, leading to cyclized network of hexagonal carbon-nitrogen rings [2]. Further, the nitrile groups in PAN with a large dipole provide high cohesive energy density and chain stiffness, which result in excellent tensile strength [3]. Stabilization is one of the most important factors to determine mechanical strength of PAN based carbon fibers. Fitzer et al., reported optimization of stabilization PAN fibers and effect of carbonization of resulting fibers on tensile strength [1].

In this study, a systematic study on the stabilization of itaconic acid-modified PAN was reported. The itaconic acid-modified PAN fibers were stabilized for various duration times. Evolution of the extent of stabilization was observed using Fourier Transform Infrared spectroscopy (FT-IR). Further, the effect of stabilization on tensile properties was studied.

Experimental

Commercial itaconic acid-modified PAN fibers were obtained from Sinosteel Jilin Carbon Co., Ltd. (Jilin, China). As-received fibers are in tows of 3000 with a diameter of $9.7 \pm 0.4 \mu\text{m}$. NMR showed that a content of itaconic acid was ~1 wt%. Molecular weight of as-received fibers was found to be $\sim 140,000 \text{ g}^{-1}$ by HLC8320GPC (TOSOH, Japan). Stabilization of fibers was performed in a convection oven at 250°C for various duration times (5-180 min). A constant tension was applied to fiber tows. FT-IR spectra were obtained using a Nicolet iS10 FTIR spectrometer (Thermo Scientific, USA) in a range of 400-4000 cm^{-1} with an Attenuated Total Reflectance (ATR) mode. For mechanical testing, a single fiber was loaded to a paper tab with a 25 mm gauge length. An epoxy resin was applied to both ends of fibers, and cured for 24 hrs at 50°C. Fiber diameters were measured by an optical microscope (Olympus BX51, Japan). The tensile properties were determined using an Instron Universal Tester 5567 (Instron, USA) at 25°C. The crosshead speed was 5 mm/min for all specimens, and twenty replicates were tested at each condition.

Results and Discussion

FTIR analysis of stabilized itaconic acid-modified PAN fibers

Figure 1 show FTIR spectra of itaconic acid-modified PAN fibers before and after stabilization in a convection oven at 250°C with various times. Before stabilization, distinct absorption bands appeared at 2939, 2243, 1720, 1454, 1360, and 785 cm^{-1} assigned to $\nu_{\text{C-H}}$ in CH_2 , $\nu_{\text{C}\equiv\text{N}}$ in CN, $\nu_{\text{C=O}}$ in COOH, $\delta_{\text{C-H}}$ in CH_2 , $\delta_{\text{C-H}}$ in CH, and $\delta_{\text{C-C}}$ in C-CN, respectively (Figure 1a). The band at 1454 cm^{-1} is due to itaconic acid modified in PAN as a comonomer, while other bands are associated with PAN. Stabilized fibers for 5 min showed an appearance at 1595 cm^{-1} assigned to conjugated C=N stretching with a little intensity. After stabilization for 10 min, a band at 1595 cm^{-1} became bigger, but intensities of bands at 2939, 2243, 1720, and 1454 cm^{-1} decreased, resulting from the cyclization and dehydrogenation of fibers (Figure 1c). Such a change is significant with the fibers stabilized for 30 min. It was observed that the band at 1720 cm^{-1} disappeared, which indicates that most itaconic acids participated in cyclization reaction through an ionic mechanism in Figure 1d. Further, two shoulders appeared at 1710 and 1660 cm^{-1} . Shimada and Takahagi reported that these shoulders are assigned to the free ketones in hydronaphthyridine rings and the conjugated ketones in acridone rings, resulting from the oxygen uptake reaction [4,5]. A new distinct band at 2200 cm^{-1} was observed with fibers stabilized for 120 min Figure 1f. It is reported that the band is assigned to the α,β -unsaturated nitrile groups due to hydrogenation, or tautomerization and isomerisation of the ladder polymer [2]. The C=O stretching band at 1454 cm^{-1} became a small shoulder in the spectrum, indicating the main chains of PAN transform into cyclized network. The C \equiv N stretching band at 2243 cm^{-1} is still observed. In Figure 1g, it is interesting that the band and shoulder at 2243 and 1454, respectively, are noticeable. This reveals that all PAN are not cyclized even after stabilization for 180 min 250°C.

Tensile properties of stabilized itaconic acid-modified PAN fibers

Figure 2 displays tensile properties of PAN fibers and stabilized fibers. Tensile strength of PAN fibers without stabilization was 1 GPa (Figure 2a). However, PAN fibers stabilized for only 5 min showed a significant decrease of tensile strength (0.6 GPa). A further increase of stabilization time led to a monotonous decrease of tensile strength. A similar result was observed with Young's modulus. In Figure 2b, Young's modulus was 26 GPa and 15 GPa for PAN fibers and fibers stabilized for 5 min, respectively. As stabilization time increased, a change of Young's modulus was not significant (13 GPa with stabilized fibers for 180 min). Based on these results, we suggest that tensile strength and Young's modulus of cyclized PAN are lower than those of uncyclized PAN. Gupta and Harrison reported a decrease of tensile strength and Young's modulus as a function of stabilization temperature [6]. They suggested that cyclization reaction

resulted in the loss of inter-chain cohesive energy, leading to a decrease of tensile properties of PAN fibers. It is recalled that FT-IR spectra of fibers stabilized for 5 min showed the low degree of cyclization). It is likely that mechanical properties such as tensile strength and Young's modulus were determined with an initial stabilization stage where cyclization is not significant.

Strain-to-failure of PAN fibers in Figure 2c was found to be 11%, but fibers stabilized for 5 min showed strain-to-failure of 15%. Stabilized fiber for 30 min was found to be the highest value of 18%. Up to stabilization time of 180 min, strain-to-failure decreased down to 13%, and a similar value was observed with a further increase of stabilization time. This is consistent to the result by Gupta and Harrison [6]. They reported that a decrease of strain-to-failure was attributed to intermolecular cross-linking reactions to lead to a network formation. It is recalled that there was not a significant difference between fibers stabilized for 120 and 180 min in FT-IR spectra.

Conclusions

Itaconic acid modified PAN fibers were stabilized with various times at 250°C. As expected, FT-IR spectra of stabilized fibers indicated cyclization of PAN fibers to form network structure. Tensile strength and Young's modulus of PAN and stabilized fibers suggested that cyclized structure affect mechanical properties of stabilized PAN fibers significantly.

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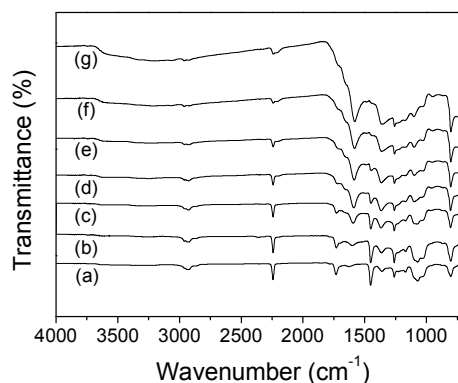


Fig. 1 FT-IR spectra of (a) PAN fiber and its stabilized fibers at 250°C for: (b) 5 min, (c) 10 min, (d) 30 min, (e) 60 min, (f) 120 min, and (g) 180 min.

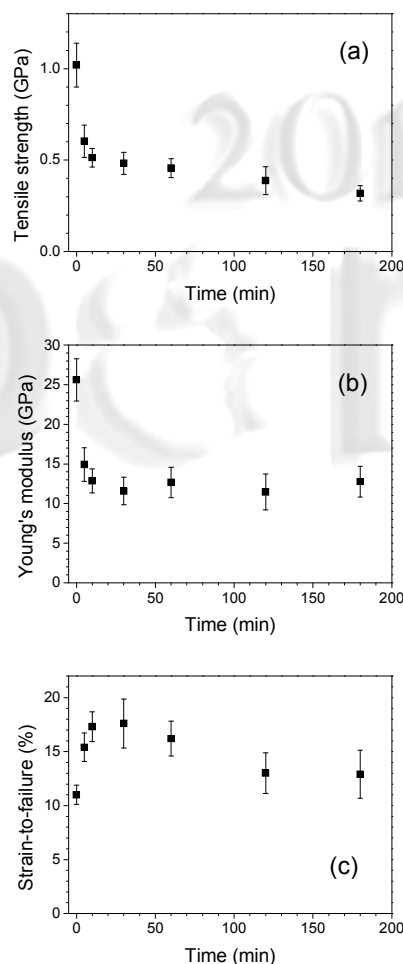


Fig. 2 Tensile properties of PAN fiber and its stabilized fibers: (a) tensile strength, (b) Young's modulus, and (c) strain-to-failure.