

# PHOTO-INDUCED CROSSLINKING AND CYCLIZATION OF SOLUTION-SPUN POLYACRYLONITRILE COPOLYMER

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## Introduction

High strength carbon fibers used in structural composite applications are derived from solution-spun PAN precursor fibers. Post-drawing of fibers must be performed to collapse the voids and to increase molecular orientation. However, this orientation is partly lost due to molecular relaxation processes that occur when the PAN precursor fibers are heated to  $\sim 300^{\circ}\text{C}$  during oxidative stabilization. Additional stresses must be applied during stabilization and carbonization steps in an attempt to regain the molecular orientation. This strategy results in carbon fibers with high strength, but the limited molecular orientation prevents the fibers from developing an ultra high modulus. Also, thermal stabilization process is the rate-limiting step in the production of PAN-based carbon fibers. During thermo-oxidative stabilization, heat is produced by exothermic reactions and a temperature gradient is generated within the fiber due to the low thermal conductivity of PAN precursors ( $\sim 0.26 \text{ W m}^{-1} \text{ K}^{-1}$  [1]). The overall goal of this research is to investigate an alternative stabilization route for PAN precursors to significantly reduce the processing time, keeping the properties of resulting fibers. The fundamental study reported here specifically investigates the crosslinking and cyclization reactions induced by the addition of photo-initiators to solution-cast PAN samples.

## Experimental

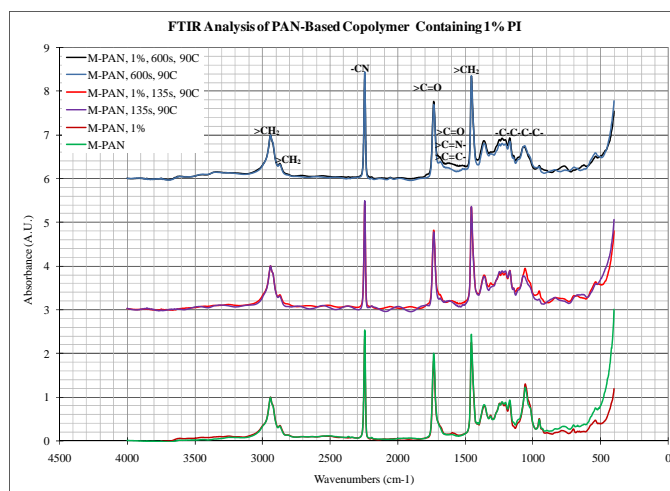
The materials employed in the present study were commercial grade Mitsubishi fibers with a nominal acrylonitrile (AN)/ methyl acrylate (MA) ratio of 94:6, with a glass transition temperature of  $\sim 82^{\circ}\text{C}$ . In addition, 1-hydroxycyclohexyl phenyl ketone (PI) and dimethyl sulfoxide (DMSO) were used; both were obtained from Sigma-Aldrich. All the materials were used as received.

PAN-based fibers and PI were dissolved in DMSO at  $70^{\circ}\text{C}$ . The amount of solids in solution was kept at  $\sim 20\%$ . Films were cast from solution and dried at  $70^{\circ}\text{C}$  for  $\sim 24$  hours. The final thicknesses of the films were  $\sim 20\mu\text{m}$ . In addition, by changing the amounts of PI added to the mixture, films with a 0%, 0.3%, 1%, and 3% content of PI were produced. The films were irradiated with a Nordson 4.5kW mercury high-power UV lamp for 135 and 600 seconds. The distance of the samples from source was  $\sim 20\text{cm}$ . The temperatures employed during the UV-treatment were  $65^{\circ}\text{C}$ ,  $80^{\circ}\text{C}$ , and  $90^{\circ}\text{C}$ . The irradiated samples were subsequently immersed in DMSO at  $70^{\circ}\text{C}$  for over 24 hours to determine the sol versus gel (crosslinked) fractions. DSC and FTIR analysis were

conducted on the films with and without UV-treatment using a Pyris 1 DSC (Perkin Elmer Instruments) and Nexus 870 FT-IR ESP (Nicolet) respectively.

## Results and Discussion

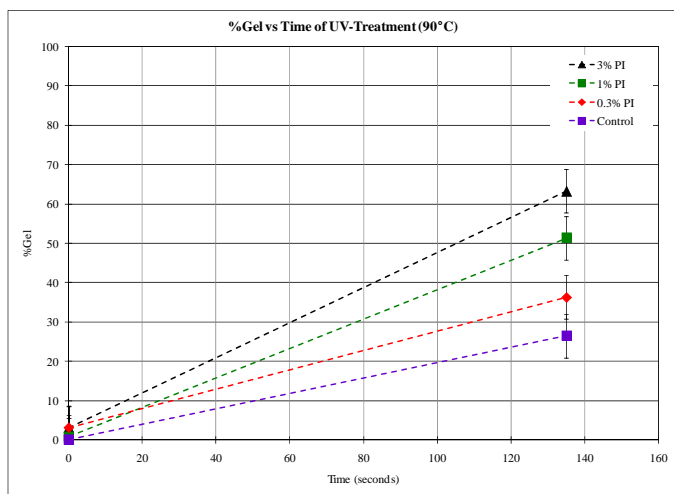
As presented in Figure 1, FTIR spectra indicate that  $2242 \text{ cm}^{-1}$  stretching absorbance is lowered after high power UV irradiation while broad overlapped peaks appear in the frequency range  $1500 - 1700 \text{ cm}^{-1}$ . FTIR results show the reduction of carbon-nitrogen triple bonds and the formation of carbon-nitrogen double bonds as a function of time, which is attributed to cyclization reactions taking place during the UV-treatment of the samples [2-4]. This suggests that the UV-assisted reactions can lead to incipient cyclization.



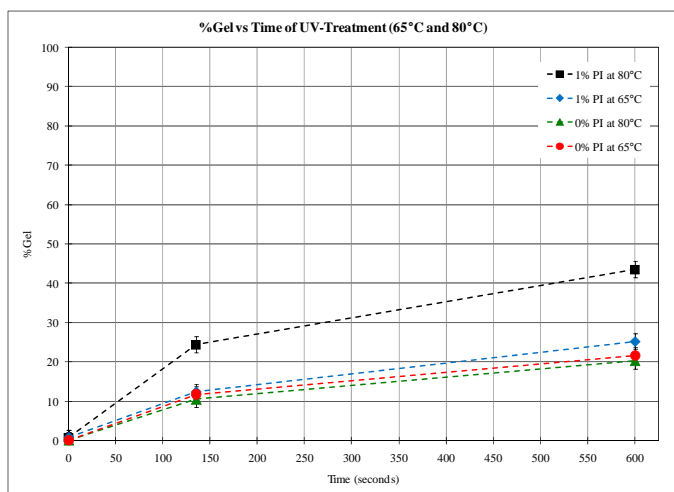
**Fig. 1** Fourier Transform Infrared Spectroscopy (FTIR) analysis of PAN-based samples with 1wt% and without photo-initiator UV-treated at  $90^{\circ}\text{C}$  for 0, 135 and 600 seconds (Number of Scans: 32, Resolution: 4)

Figure 2 and 3 display gel contents as a function of UV-irradiation times. Increasing amounts of photo-initiator and/or UV-treatment temperature increase the rate of cyclization and cross-linking leading to a higher conversion of the precursor that is confirmed by the higher gel fractions shown in Figures 2 and 3. These results are consistent with prior studies that show that PAN precursors can be cross-linked by high-intensity UV radiation [5-7]. The cross-linked polymer can subsequently be thermally stabilized for successful conversion into carbon fibers [6].

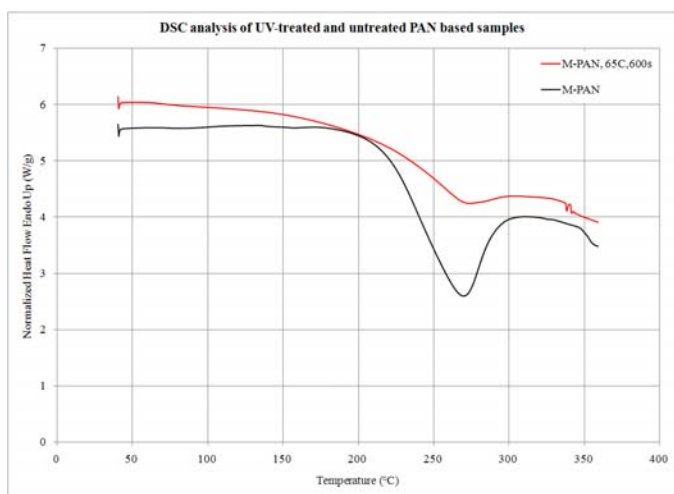
Figure 4 shows DSC results of UV-treated PAN-based precursor for 600 seconds at  $\sim 65^{\circ}\text{C}$  compared with non-treated precursor (control). The heats of cyclization reaction are approximately  $1000 \text{ J/g}$  and  $300 \text{ J/g}$  for the control and UV-treated precursor respectively. This significant reduction can be possible attributed to three phenomena undergoing during the UV-treatment of the precursor: cyclization, crosslinking, and scission of the polymer chains [5-7]. Polymer chain scission is not desired because reduces the mechanical properties of the final carbon fiber produced [4].



**Fig. 2** Gel content of crosslinked PAN as a function of UV irradiation time at various PI concentrations



**Fig. 3** Gel content of crosslinked PAN as a function of UV irradiation time at various temperatures and PI concentrations



**Fig. 4** DSC analysis of UV-treated and untreated PAN-based samples with a heating rate of 5°C/min

## Conclusions

FTIR results show the reduction of carbon-nitrogen triple bonds and the formation of carbon-oxygen, carbon-nitrogen, and carbon-carbon double bonds as a function of time, which is attributed to cyclization reactions taking place during the UV-treatment of the sample. Increasing amounts of photo-initiator accelerate the rate of cyclization and cross-linking leading to a higher conversion of the precursor that is confirmed by the higher gel fractions. Films UV-treated for 600 seconds at 65°C (below  $T_g$ ) undergo a significant reduction on the heat of cyclization which can be possible attributed to three phenomena undergoing during the UV-treatment of the precursor: cyclization, crosslinking, and scission of the polymer chains

Future studies will involve the production of PAN fibers containing photo-initiator; carbonization of the stabilized fibers; and the measurement of mechanical properties of the resulting carbon fibers

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## References

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