Iranian Polymer Journal (2018) 27:395–404
https://doi.org/10.1007/s13726-018-0617-6

ORIGINAL RESEARCH

The cyclization index and toughness of gel spun polyacrylonitrile (PAN) proportionality with its heat of stabilization

Mahmoud Heydari[1] · **Naser Mohammadi**[1]

Received: 4 November 2017 / Accepted: 12 April 2018 / Published online: 25 April 2018

Abstract

The spun tapes of synthesized PAN, its copolymer with 1 wt% itaconic acid, and doped version with 1 wt% sodium dodecyl sulfate (SDS) all showed stripy, even, and compact cross-sections as the hallmark of gel forming products. PAN doping with SDS and acrylonitrile copolymerization with itaconic acid reduced its dimethylformamide (DMF) solution structural viscosity index ($\Delta\eta$) by 50% and 30%, respectively, at 675 s^{-1}. In addition, the modification of synthesized PAN through doping and acrylonitrile copolymerization with itaconic acid led to severe and mild gelation temperature decrease, respectively. The stabilization peak of the synthesized PAN tape was enhanced as much as 25 °C by 900% hot drawing, decreased by about 10 °C through copolymerization, while experienced small temperature changes through doping. The *second derivative* of Fourier transform infrared and Gaussian fitting was used to analyze the tapes cyclization due to stabilization treatment through introducing I_{sd} index. 10 min I_{sd} index was raised as much as 430% and 800% in comparison with the synthesized PAN through its doping or acrylonitrile copolymerization with itaconic acid, respectively. Further 180 min of I_{sd} index, however, showed the same proportional increase as toughness of the drawn tapes versus their heat of stabilization through their physical and chemical modifications.

Keywords Cyclization index · Structural viscosity · Toughness · Heat of stabilization · Gel

Introduction

Nowadays, the application of carbon fibers has been widespread not only in military and aerospace industries, but also in many composite-made products such as cars, roads, buildings, and innovative energy generators. Enhancing of spinning or heat treatment process during carbon fiber manufacturing is very important research topics by various and novel solutions like nanoparticle inclusion [1–3], melting point modifier for copolymers [4], or even blending with bio-based material [5]. The main raw material of carbon fiber is polyacrylonitrile and its acidic or neutral copolymers. The comonomers improve the precursor spinnability and stretchability along with its stabilization process outcome by optimization of the interchain interactions. Analysis of carbon–nitrogen double bond and cyanide peaks plus E_s as the first-to-second peak of stabilization ratio at 220 °C for PAN and its itaconic acid copolymer confirmed the role of facilitated oxygen diffusion and ionically initiated reaction in lowering the stabilization temperature of the latter [6]. To enhance the resolution of the assessed overlapping peaks of acrylonitrile–itaconic acid copolymer during stabilization, the second derivative of infrared spectra was evaluated [7]. The cyclization reaction rate constant of acrylonitrile/methyl acrylate/dimethyl itaconate (AN/MA/DMI) was found five-to-seven times higher than AN/MA copolymer, with 20 to 40 kJ/mol lower activation energy [8]. Accordingly, a five-member ring structure formation was proposed as the initial conversion step induced by dimethyl itaconate. Using solid-state NMR spectroscopy, Miyoshi and his colleagues [9] introduced dehydrogenation and cyclization under oxygen and nitrogen atmospheres as the main mechanisms of polyacrylonitrile stabilization, respectively. Overall, 66% cyclization was estimated during PAN stabilization using DSC [10]. Analysis of three-functional comonomers, i.e., methyl hydrogen itaconate (MHI), aminocarbonyl butenoic methyl ester (ABM), and aminocarboxylate butenoic

✉ Naser Mohammadi
mohamadi@aut.ac.ir

[1] Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, PO Box 15875-4413, Tehran, Iran