Establishing the Conditions for Stable Extrusion of Melt Spun Polyacrylonitrile with Water Based Plasticizers

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Abstract

Polyacrylonitrile (PAN) fiber is one of the most important synthetic fibers in the world because it is a precursor to carbon fiber. Compared to the traditional solution spinning process, the melting spinning process of PAN is less costly and can further reduce the price of PAN fiber. This dissertation is concerned with the objective of establishment of conditions (temperature, plasticizer type, and plasticizer composition) that a PAN copolymer is able to be stable melt spun with water based plasticizers. More specifically, PAN/water/acetonitrile (70/15/15) mixture is considered as reference sample in this study because it was proposed in a BASF patent in which it was claimed it could be stably melt spun. We are looking for a more benign plasticizer so that the use of acetonitrile can be avoided and PAN can still be stably melt spun.

To achieve this objective, the first step is to measure the melting point (T_m) of PAN copolymer with various plasticizers and compositions by using differential scanning calorimetry (DSC). The results indicate the T_m of PAN copolymer can be reduced to around 160 ^{o}C with water only as a plasticizer, which is lower than the degradation temperature of PAN (180 ^{o}C). Moreover, using a water/ethanol mixture and

water/acetonitrile as plasticizers can further reduce the melting point of PAN to 150 ^{o}C and 135 ^{o}C, respectively.

The second step is conducting rheological measurements on the PAN/plasticizers mixture. A pressure chamber was designed and attached to the capillary rheometer in order to prevent the foaming and evaporation of plasticizers during the viscosity experiments. Both steady-shear and time-dependent viscosity measurements were conducted. The rheological measurement results indicate that PAN can keep stable for more than 120 minutes with all plasticizers under 170 ^{o}C, and it starts to degrade in 60 minutes at 180 ^{o}C, except samples plasticized with 30 wt% of water (which keep stable for 120 minutes as well). The steady-shear viscosity results indicate the shear-thinning behavior is observed for the PAN/plasticizer mixtures at a temperature ranging from 170 ^{o}C to 190 ^{o}C and provide the fundamental viscosity data which can be applied to the extrusion process. In conclusion, the rheological measurements show PAN/Water (70/30 wt%) at 180 ^{o}C and PAN/EtOH/Water (70/15/15) at 170 ^{o}C are two potential systems for carrying out the PAN melt spinning process.

Scanning electron microscopy (SEM) images were taken for the reference state and potential conditions. These images show that the copolymer strands have more and larger voids when plasticized with water only compared to those plasticized with water/acetonitrile and water/ethanol mixture. In this case, PAN/EtOH/Water (70/15/15) at 170 ^{o}C is considered to be the most benign system for that PAN melt spinning.

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GENERAL AUDIENCE ABSTRACT

The melt spinning process of polyacrylonitrile (PAN) has been studied in the past few decades. Compared to the traditional solution spinning process, it does not require toxic organic solvents. The major problem of the PAN melt spinning process is the melting point (T_m) of PAN is much higher than its degradation temperature. However, by adding plasticizers the T_m of PAN can be significantly reduced, which makes PAN melt spinning feasible. In this work we discuss the feasibility of the melt spinning process of polyacrylonitrile (PAN) copolymer plasticized with water based plasticizers by using differential scanning calorimetry (DSC) and rheological methods. The objective is to use water only as a plasticizer to melt spin PAN under specific conditions (composition, temperature etc). The melting point and rheological measurements have been conducted by DSC and a modified capillary rheometer, respectively, for this plasticized system. The DSC results show that the melting point of the PAN copolymer can be reduced below the degradation temperature of PAN, and the rheological results show that the PAN copolymer can be extruded with a reasonable viscosity at 15-20 ^{o}

above its melting point, and also the stability and viscosity are strongly dependent on temperature and the plasticizer type and content. Furthermore, the Scanning electron microscopy (SEM) images show the copolymer strands extruded from PAN/H_2O mixture have many more and larger voids than PAN/H_2O/EtOH mixture. In conclusion, the results indicate that the most appropriate condition for PAN melt spinning is PAN/H_2O/EtOH mixture of 70/15/15 wt% ratio at a temperature of 170 ^{o}C

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First of all, I would like to express my appreciation to Professor Donald G. Baird for his considerable guidance and support, both financially and professionally, through my PhD career. I would not be the researcher and person I am today without him. I would also like to thank Drs. Michael Bortner, Richey Davis and Judy Riffle for spending their time to serve as my advisory committee member. They provided me invaluable advice and have helped me understand my project and how I can be a qualified researcher.

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Original Contributions

The following are considered original contributions to the larger body of work on the polyacrylonitrile melting spinning process.

1. Establishment of a procedure that is appropriate for conducting rheological experiments of PAN with water based plasticizer. More specifically, the author determined an appropriate method to: a) mix PAN copolymer powder with liquid plasticizer (about 70~80 to 20~30 weight percentage ratio) homogenously, b) load the copolymer/plasticizer samples into the modified capillary rheometer without significant loss of plasticizers. The author also determined the conditions for conducting rheological measurements of PAN with water based plasticizers, such as temperature range, ambient pressure in pressure chamber, shear rate range and maximum experimental duration (for steady-shear rheological measurements)
2. Identification of a set of rheological data of PAN copolymer with various water-based plasticizers at various temperatures. More specifically, the author measured and reported both the time-dependent and steady-shear viscosity data of PAN/H_2O/Acetonitrile (the reference composition), PAN/H_2O (with various weight percentage ratios), PAN/H_2O/EtOH and PAN/Acetonitrile mixtures. Moreover, based on the rheological data and related SEM images, the author determined a more benign composition (PAN/H_2O/EtOH, 70/15/15 wt% at 170 ^{o}C) that can be

used for replacing the reference composition and potentially carrying out PAN melt spinning process.

3. Initiation of applying the rheological data of PAN melt to the single-screw extrusion process design. More specifically, the author identified: a) the residence time distribution curves in a single screw extruder of PAN/plasticizer mixtures based on their power-law indexes (which are obtained from steady-shear viscosity results). b) the maximum residence time of PAN in a specific condition (e.g. plasticizer type and composition, temperature) based on the time-dependent viscosity results. Based on these data, some extrusion parameters (e.g. throttle ratio and down-channel velocity) are able to be modeled and calculated.

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Chapter 1 Introduction

1.1 Research Background

Polyacrylonitrile (PAN) fiber is one of the most important fibers in the world as it is a precursor to carbon fiber. Approximately 90% percent of carbon fiber is produced from PAN fiber nowadays [1]. PAN fiber is considered as the most suitable precursor for generating high performance carbon fiber because the PAN-based carbon fiber has properties of low density, high strength and high thermal stability. PAN-based high performance carbon fiber is playing a significant role in many industrial areas, such as in aerospace and defense applications, as well as sporting goods and automotive applications [2-4].

Polyacrylonitrile is normally a copolymer of high content acrylonitrile (AN) and with a specific co-monomer, such as methyl acrylate (MA) or vinyl acetate (VA) which are used to improve the processability of PAN fiber [4]. The PAN copolymer that is used to generate carbon fiber is primarily AN/MA copolymer with more than 93 mol% AN content.

To produce PAN-based carbon fiber, there are three major steps: precursor fiber spinning, thermo-oxidative stabilization, and carbonization. For over 50 years, the major PAN fiber spinning method is traditional solution spinning, which is based on the use of a highly polar organic solvent to dissolve the PAN polymer during the spinning process. Some common organic solvents used during the PAN solution spinning process include N,N-dimethylformamide (DMF) and N-N dimethyl acetamide (DMAC). These organic solvents are normally used in the range of 70 to 93 wt % (7 to 30 wt % of polymer). In this case, a high proportion of the production costs are due to the usage and recovery of these solvents during the PAN fiber spinning process [5-8]. As a result, the price of PAN-based carbon fiber is still as high as around $11 per pound [9].

To reduce the cost of PAN-based carbon fiber, melt spinning is a potentially available option in the PAN-precursor fiber manufacturing industry. Compared to solution spinning, the melt spinning of PAN is less expensive and more environmentally friendly due to eliminating or reducing the usage of organic solvent. The cost of carbon fiber could be reduced to around \$5~\$7 if the PAN melt spinning technique is applied [9-10].

Due to the existence of polar nitrile groups, the polymer chains of PAN experience a very strong interaction, which also results in a high melting point of PAN at around 320℃ [10-13]. However, before reaching the melting point, PAN suffers exothermic reactions such as cyclization and crosslinking at around 180℃ to 220℃ [3,7,14]. That means, PAN starts to degrade before it is melted and will not reach a stable melted state [15]. These degradation reactions are very important during the thermo-oxidative stabilization process, but they are not desirable during the PAN melt spinning process [3, 16].

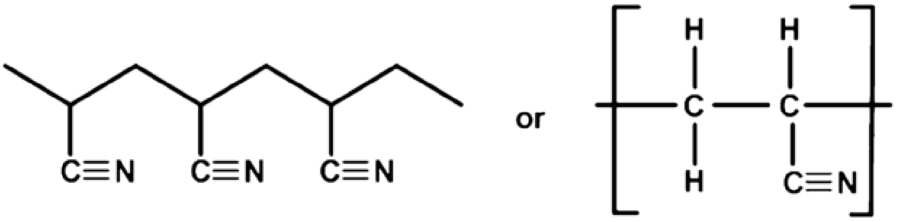

Figure 1.1, The molecular structure of polyacrylonitrile, Taken from [3]

Numerous research has been conducted during the past several decades to make the PAN melt spinning feasible. In 1952, Coxe [17] first discovered that water could be used as a plasticizer to hydrate the pendent nitrile groups of PAN, which remarkably reduce the melting point of PAN to below 200℃. This discovery allowed PAN to be melt extruded without significant degradation. However, Coxe failed to develop a complete melt spinning system due to an apparent foaming problem. In 1979, Porosoff [18] improved the melt spinning system based of Coxe's method by attaching a pressure chamber on the system and pressurizing the system during the spinning process. This innovation could sufficiently prevent water evaporating and foaming in the extruder, but the resulting fiber still contained voids. In 1992, Daumit et al [19] at BASF claimed in their patent that a mixture of water and acetonitrile (AC) could be used as a plasticizer for PAN melt spinning. With additional AC as plasticizer, the melting point of PAN could be further decrease to around 135℃. This process has been proved to be very effective and could produce decent quality PAN fiber. However, due to the toxicity and flammability of acetonitrile, the plasticizer still needed to be recovered, and so the cost was not adequately reduced. Due to the economical consideration and the change of the world carbon fiber market, this approach was not commercialized by BASF either [9].

Compared to the research and investigation related to the properties of PAN and the PAN melt spinning process, there are many fewer reports related to the rheological behavior of PAN. Rangarajan et al [20] reported the rheological data of an extrudable-grade PAN copolymer with only 65 mol % of acrylonitrile (Due to the low content of AN, the copolymer melting point was reduced below the degradation temperature without the use of plasticizers). Moreover, Bortner [21] and Wilding [22] performed some rheological investigations of AN/MA copolymer plasticized with supercritical carbon dioxide ($scCO_2$) at various temperature. In their work, not only viscosity data at different shear rate, but also the time-dependent rheological data were reported in their paper. However, very few reports had been published related to rheological data of melted PAN copolymer plasticized with water or water based plasticizers so far.

In addition to above, there are plenty of reports and investigations related to PAN and PAN melt spinning process effort. They will be further reviewed and discussed in the next chapter.

1.2 Research Objectives

The work in this dissertation seeks to determine the feasibility of PAN melt spinning with various water-based plasticizers and determine the most benign condition (i.e. temperature, plasticizer type and composition) based on the rheological and other experimental results. In sight of this goal, this work is guided by the following objectives:

1. **Establish a melt processing baseline by determining the melting point and rheological properties of PAN that is plasticized with 14 wt% of water and 14 wt% of acetonitrile. This plasticizer composition comes from the BASF patent, and it is the baseline and reference for this research.**
2. **Identify the melting point and rheological properties of PAN plasticized with other plasticizer types and compositions, such as water or water and alcohol or other substances, and compare them to the baseline system in objective 1 in an effort to identify more benign plasticizers.**
3. **To determine at what conditions, if any such as temperature, composition and residence time in processing, it is feasible to melt spin polyacrylonitrile with water only as the plasticizer.**

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Chapter 2 Literature Review

Many preliminary research related to polyacrylonitrile and its melt spinning process had been conducted and reported. These studies are briefly introduced in chapter 1, and in this chapter, a detailed literature review will be conducted. Section 2.1 will be concerned with the melting point of polyacrylonitrile with or without plasticizers; section 2.2 will be concerned with the degradation reactions of polyacrylonitrile; section 2.3 will be concerned with the preliminary effort of the polyacrylonitrile melt spinning process; section 2.4 will be concerned with the rheological research related to melted polyacrylonitrile.

2.1 The Melting point of Polyacrylonitrile

As mentioned in the previous chapter, the main challenging in the polyacrylonitrile (PAN) melting spinning process is the high melting point (T_m) of PAN at around 320℃. Plasticizers, especially water based plasticizers, are used to reduce the melting point of the PAN copolymer. In this case, the studies of PAN's melting point, with or without plasticizers, becomes very significant in this research project. In this section, some previous work related to this topic will be reviewed.

The research of melting point of polyacrylonitrile can be dated back to late 1950s. Krigbaum and Tokita [1] reported that the glass transition (T_g) and melting point (T_m) of pure polyacrylonitrile polymer is 104℃ and 317℃, respectively. They first used dimethylformamide and γ-butyrolactone as a solvent to make the PAN solution, then measured temperature where volume changes occurred for the solution samples (indicating phase change) at various compositions to determine the T_g and T_m by using a recording dilatometer. Finally, they plotted temperature data in terms of composition and calculated the T_m and T_g of pure PAN (Figure 2.1).

Meanwhile, in 1960, Schwenker and Beck [2] first used differential thermal analysis (DTA) to measure the melting points of pure PAN. They presented thermograms of pure PAN and found that a very strong exothermal peak occurred in the thermal spectra at around 308℃. Slade [3] reported a thermal spectrum that showed DTA melting points of a series of acrylonitrile-vinyl acetate (AN/VA) copolymers with various ratio of AN and VA (Figure 2.2). He suggested that with an increasing content of VA, the melting points of the copolymer decreased significantly.

Slade also suggested in his report that the Flory relationship for copolymer could be applied to estimate the melting point of PAN copolymers. The expression of the Flory relationship is shown in Equation 2.1:

$$\frac{1}{T_m} - \frac{1}{T_m^o} = -\left(\frac{R}{\triangle H_u}\right)\ln N_2 \qquad (2.1)$$

Where, in this particular case, T_m is the melting point of the PAN copolymer; T_m^o is the melting point of pure PAN; $\triangle H_u$ is the heat of fusion of the major component and N_2 is the mole fraction of AN. By plotting the $-\ln N_2$ vs $1/T_m$, $\frac{R}{\triangle H_u}$ can be determined from the slope. The melting point of pure PAN calculated from Flory relationship by Slade was 322℃, which is very close to the 317℃ found by Krigbaum and Tokita [1].

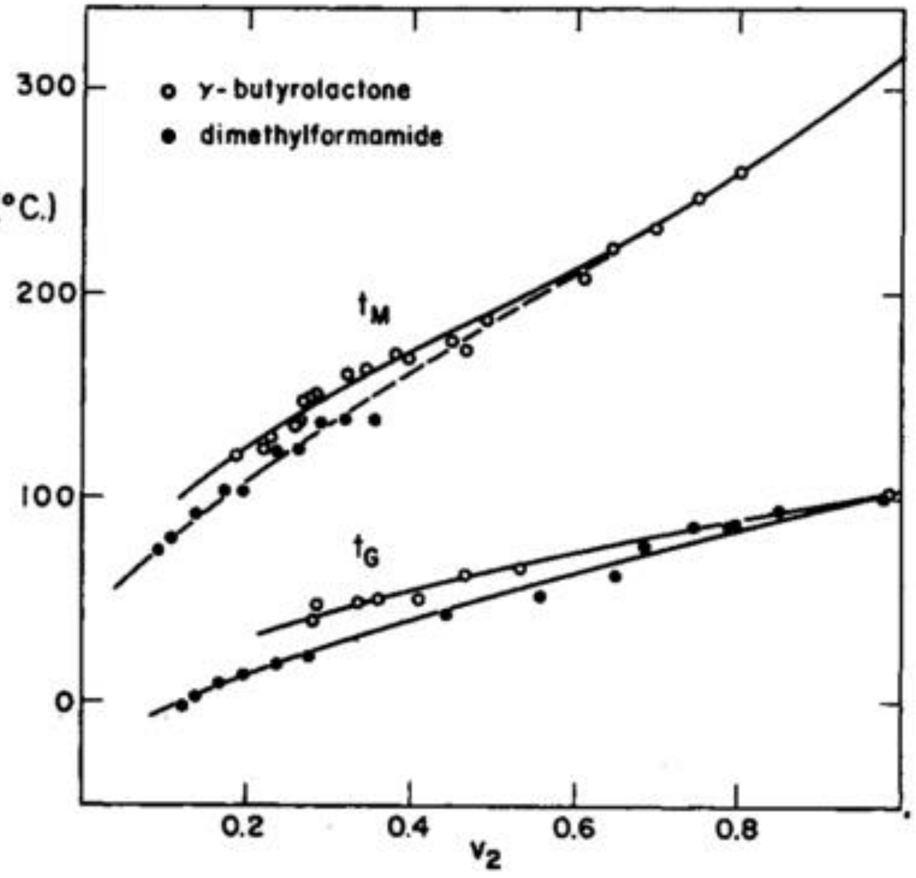
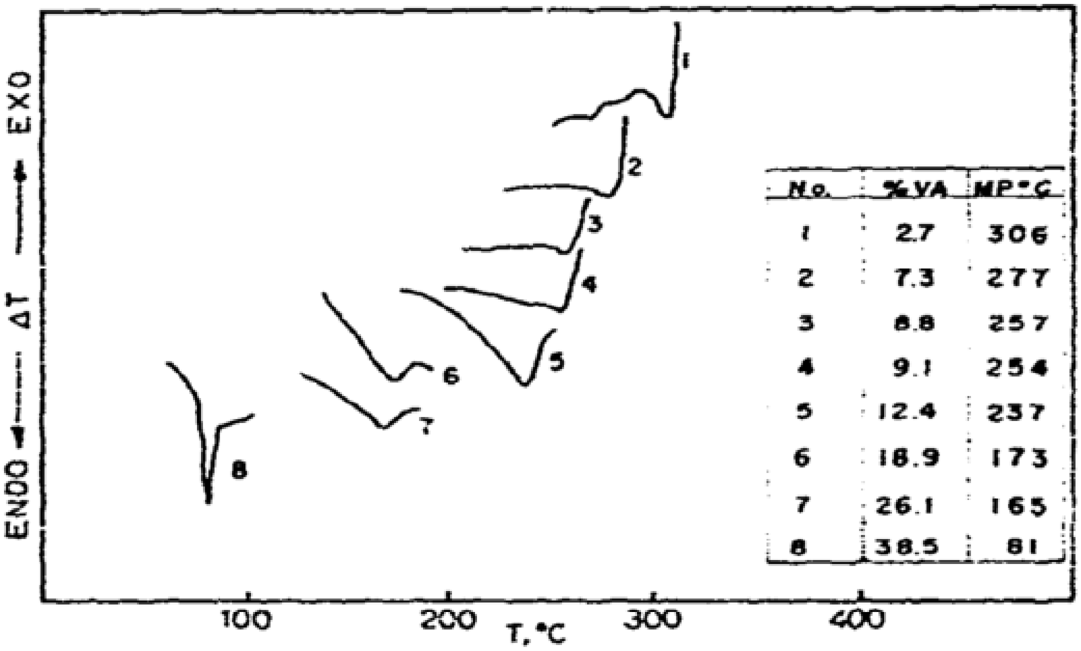


Figure 2.1, Melting and glass transition temperatures for dimethylformamide (filledcircles) and γ-butyrolactone (open circles) samples plotted against the volume fraction of polymer. Taken from [1]



No.	% VA	MP °C
1	2.7	306
2	7.3	277
3	8.8	257
4	9.1	254
5	12.4	237
6	18.9	173
7	26.1	165
8	38.5	81

Figure 2.2, DTA melting points of a series of acrylonitrile-vinyl acetate copolymer (in wt% basis) Taken from [3]

As mentioned in Chapter 1, the high melting point of PAN copolymer is the major barrier in the PAN melting spinning process. To solve this problem, Coxe [4] first found that the melting point of PAN can be significantly reduced by adding water as a plasticizer with PAN copolymer. After that, research concerning the melting point of PAN with various plasticizers has been widely conducted. Water, as one of the most effective plasticizer and most common chemical compound, was studied as the major plasticizer in PAN melting spinning process. In 1981, Frushour [5-7] developed a new scanning calorimetric technique for acrylic polymers and fibers that produced well-defined melting endotherms and crystallization exotherms of PAN-water mixtures. In his report, he claimed that polymer was placed in a special stainless steel capsule that fits in the differential scanning calorimetry (DSC) instrument he used. Water was added and the capsule was sealed. He used the new method to measure the melting points of PAN-water mixture and his results are demonstrated below (Figure 2.3)

Figure 2.3 describes the relationship between the melting point of PAN copolymer and both the water content and copolymer composition. It is very interesting that for each copolymer, there is a “plateau region” of water content where extra water would not affect the reduction of T_m of the copolymer. Frushour also described that once it reached the plateau region, a distinct water-polymer phase separation will occur so that extra water will not further plasticize PAN.

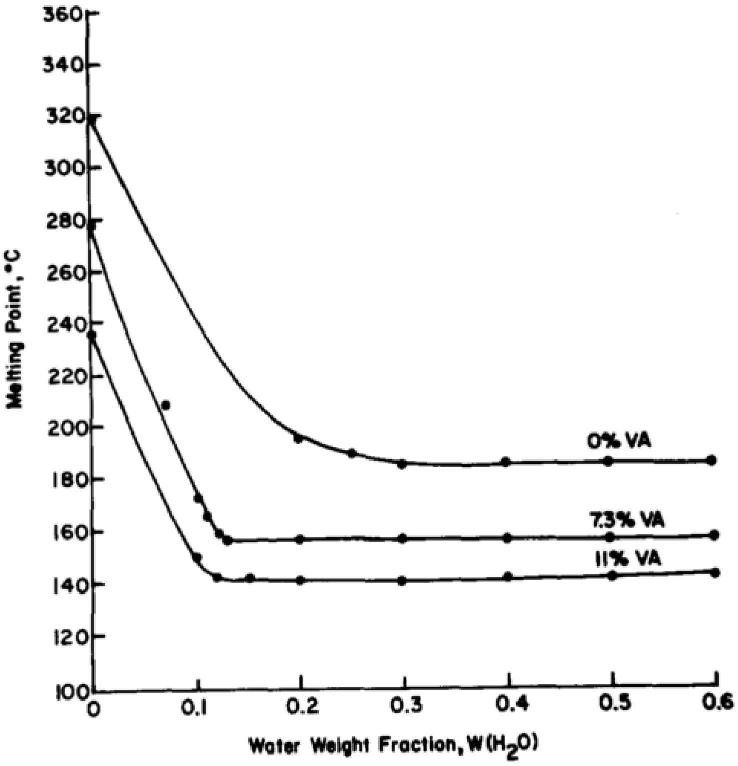


Figure 2.3, Dependence of polymer melting point on water content for different acrylic copolymer, Taken from [6]

Regarding why water can significantly reduce the melting point of PAN, Frushour [5-7] explained that the attractive interaction and dipolar bonding network among the nitrile groups on polyacrylonitrile were thought to stabilize the two-dimensional acrylic structure. By adding water, the water molecules were able to become associated with the nitrile group, therefore allowing the chemical potential of nitrile groups reduced [6]. He also explained that the critical value of the water content is the point at which all of the nitrile groups became complexed with the water instead of interacting with each other. Once all nitrile groups were complexed, extra water would not further interact with PAN, so the T_m of PAN will not decrease further.

A Korean group [8-9] also published their report related to the research of the T_m of PAN plasticized with water and water-ethylene carbonate (EC) mixture in early 1990s. They used the same method as Frushour that placed mixed PAN-plasticizer samples into a sealed stainless capsule to avoid the escape of steam. The PAN copolymer they used is an 88 wt% of AN, and 12 wt% of “unspecified comonomers”. Their results are presented in next two figures (Figure 2.4 and Figure 2.5).

The T_m results obtained from the Korean group agreed with Frushour’s results regarding to the T_m of PAN with different water content. The T_m of the copolymer reached a critical point at around 155℃ with around 23 wt% of water. They explained that the critical water content is equivalent to the theoretically predicted value calculated on the assumption that one nitrile group of PAN is combined with one water molecule. In this case, extra water will exist as a separate phase without participating in the hydration of the nitrile group and not help to further reduce the T_m of PAN.

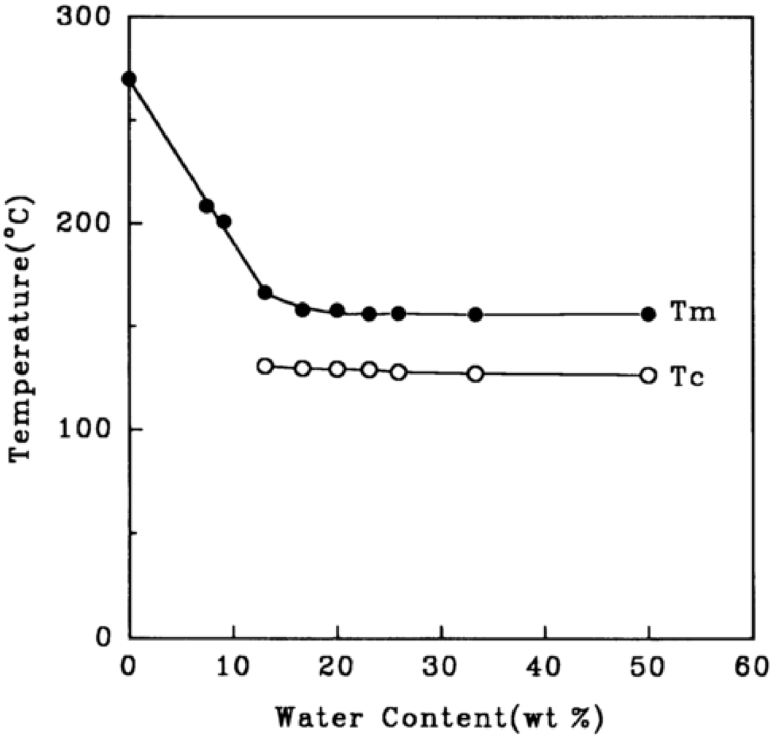


Figure 2.4, Variation of T_m and T_c of PAN (with 88 wt% of AN) with various water content, Taken from [8]

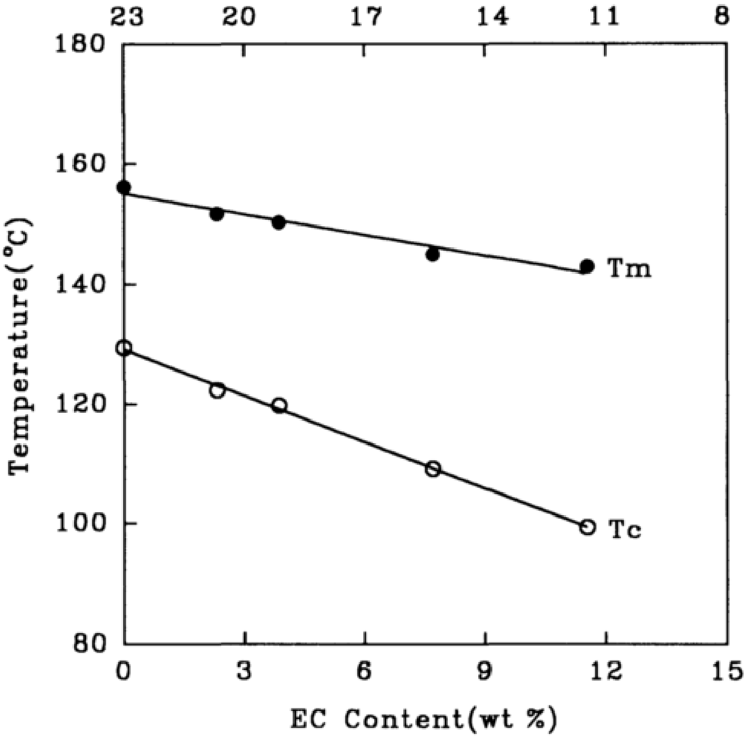


Figure 2.5, Variation of T_m and T_c of with the ethylene carbonate (EC) content showing the effect of replacing water with EC at a constant plasticizer content, 23 wt%, Taken from [8]

The T_m measurements of PAN-water-EC mixture is also helpful since this mixture will be used as a potential purge material in the PAN melting spinning process. Fig 2.6 shows that the additional ethylene carbonate could further decrease the T_m and T_c of PAN copolymer by several degrees, the combined use of water and EC produced a synergistic effect on the plasticization of PAN. However, there was no melting point data reported on PAN-EC mixtures, so it is still not clear if EC itself is a good plasticizer to reduce the T_m of PAN.

BASF had claimed in their patent that adding additional acetonitrile with water as a plasticizer could help to further lower the T_m of PAN [10]. However, they did not claim any T_m data in their patent or further documents. Huang [11] first measured and reported the melting point of PAN that is plasticized with water and acetonitrile by using DSC, the result diagram is shown below in Figure 2.6.

The DSC diagram indicates that with additional acetonitrile, the melting point of PAN (AN-VA copolymer) can drop to 132 °C. At this temperature, PAN could be melt spun without significant degradation.

Another plasticizer that is investigated for the PAN melt spinning process is supercritical carbon dioxide ($scCO_2$). Bortner and Wilding [12-16] have applied supercritical carbon dioxide in the study of the PAN melt spinning process. However, they did not report the T_m reduction of PAN as a function of the $scCO_2$ but reported the T_g reduction instead.

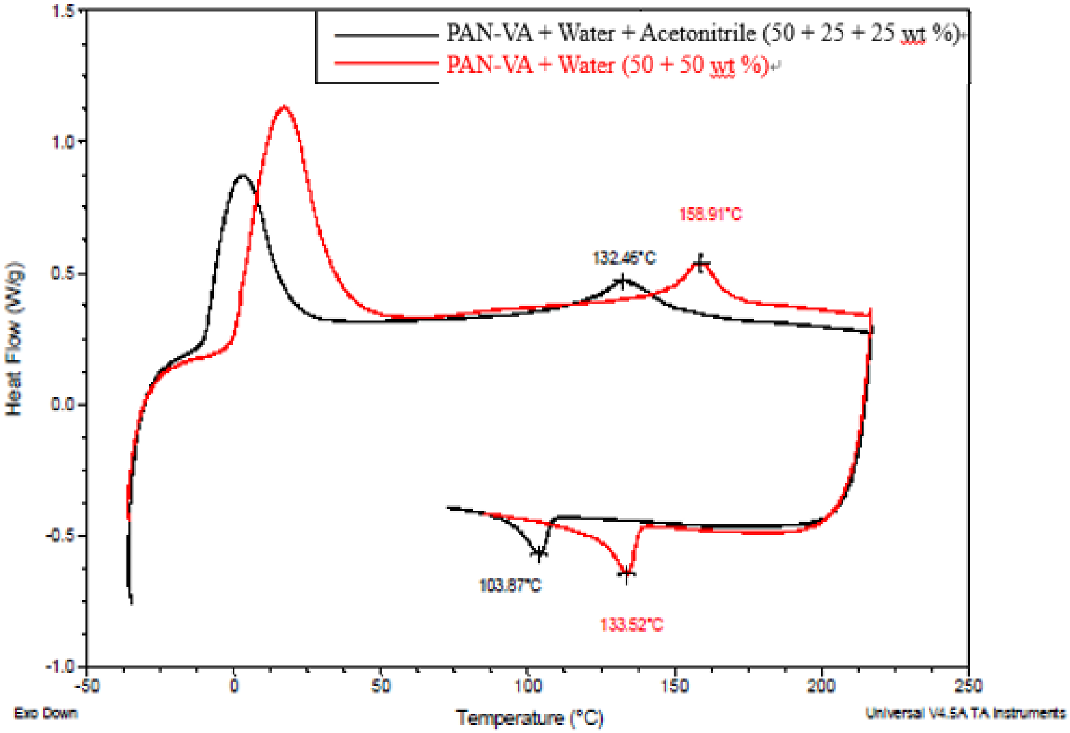


Figure 2.6, DSC scan of PAN/VA copolymer plasticized with water and water + acetonitrile, Taken from [11]

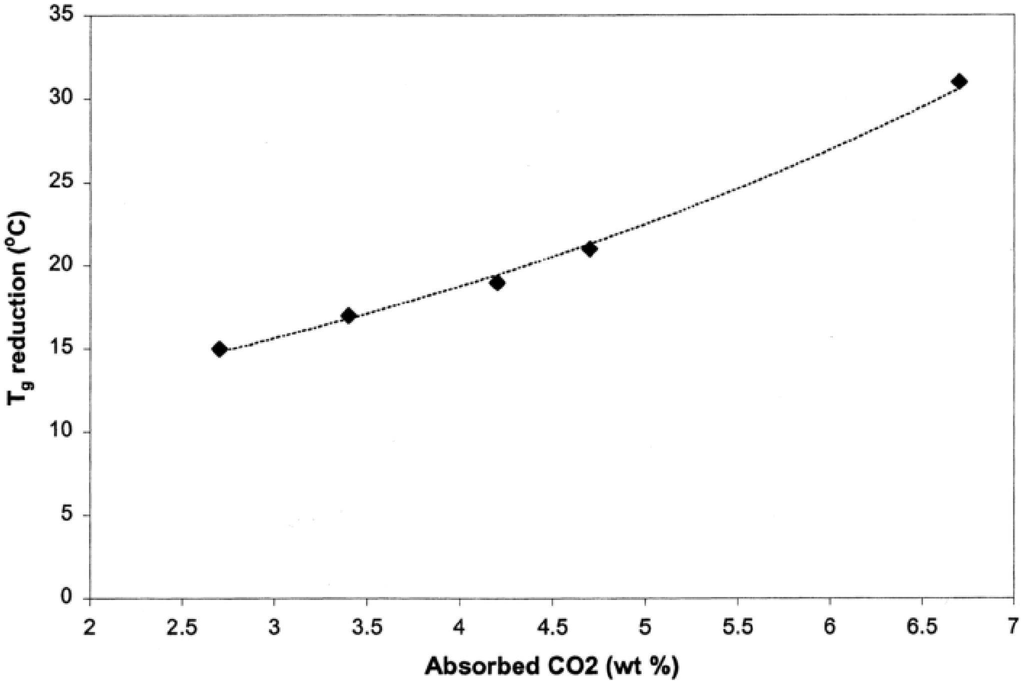


Figure 2.7, T_g reduction as a function of level of absorbed CO_2, Taken from [12]

Recall that the T_g for pure PAN is around 104℃, then CO_2 could lower the T_g of PAN to around 74℃. Besides, although the T_m is not reported in their paper, they performed the rheological tests at a temperature range from 180℃ to 240℃. In this case, we can assume the $scCO_2$ can at least lower the T_m of PAN to around 180℃.

In summary, following conclusions can be drawn based on the information above:

1. The melting point of pure PAN is around 320℃ and the glass transition temperature is around 104 ℃
2. Copolymer content will significantly influence the melting point of PAN. With a copolymer of AN-VA and AN-MA, the more content of AN, the higher T_m. The T_m for a specific sample can be obtained by applying Floyd relationship.
3. Water can significantly reduce the T_m of PAN as a plasticizer, but a critical point occurs at around 20 wt% of water. That means, the extrad water over 20 wt% could not further reduce the T_m of PAN. Normally, water only as plasticizer can reduce the melting point of PAN to around 160℃.
4. There are some other plasticizers investigated to decrease the T_m of PAN, such as acetonitrile, ethylene carbonate or $scCO_2$. They are all effective, especially the acetonitrile, which will also be focused in my research objectives.

2.2 Degradation of Polyacrylonitrile

As mentioned in the Chapter 1, PAN will suffer exothermic reactions such as cyclization and crosslinking at around 200℃[15, 17-18]. These reactions can be also called "thermal degradation reactions" of PAN. The thermal degradation reactions are not desirable during the melting spinning process because once the polymer start to degrade, it cannot be melted anymore and the viscosity of the molten polymer will significantly increase, which will result in difficulties in extrusion and spinning process. However, the degradation reactions are very important during the thermos-oxidative stabilization process, which is the step for converting the precursor fiber (PAN fiber) to carbon fiber [18].

Temperature plays a significant role in the degradation reactions. Gupta et al [18] reported that the cyclization generally began to occur at around 180℃, but became spontaneous and rapidly above 220℃. Moreover, violent exothermic reaction took place and resulted in a significant weight loss of the polymer by forming of “tarry” substance if the temperature is over 300 ℃ [17, 19].

There are many studies related to the reaction mechanics of the degradation reactions since it is also the “stabilization reactions” in the carbon fiber producing process. Figure 2.8 to 2.9 will describe the mechanism of the degradation reactions.

According to the schemes above, the degradation (stabilization) reactions contains two separated steps: dehydrogenation and cyclization. The dehydrogenation is a chain scission reaction that gives rise to volatile products, and also result in chain shrinkage [15, 19]. The cyclization reaction is condensing of the nitrile groups to form a ladder polymer (showing at Figure 2.2.1). These two reactions may occur at the same time; however, dehydrogenation is not desirable during the stabilization process of the precursor fiber, because the chain scission will result in a worse fiber orientation for producing carbon fiber, and reduce the strength of the carbon fiber. [15]. To avoid dehydrogenation reaction during the stabilization process, nitrogen may be introduced into the reaction system.

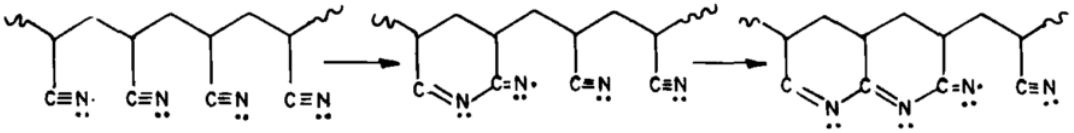


Figure 2.8, radical mechanism of the cyclization reaction, the product is called “ladder polymer”. Taken from [18]

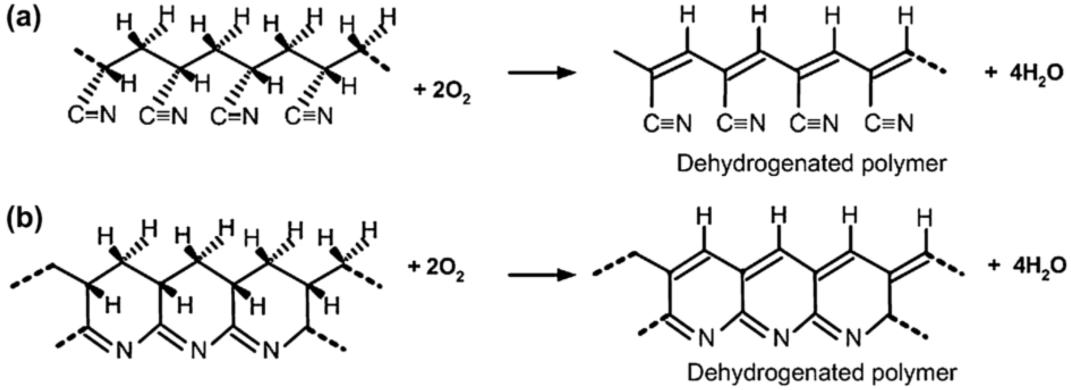


Figure 2.9, the dehydrogenation reaction during stabilization process: (a) PAN polymer; (b) cyclized PAN, Taken from [17]

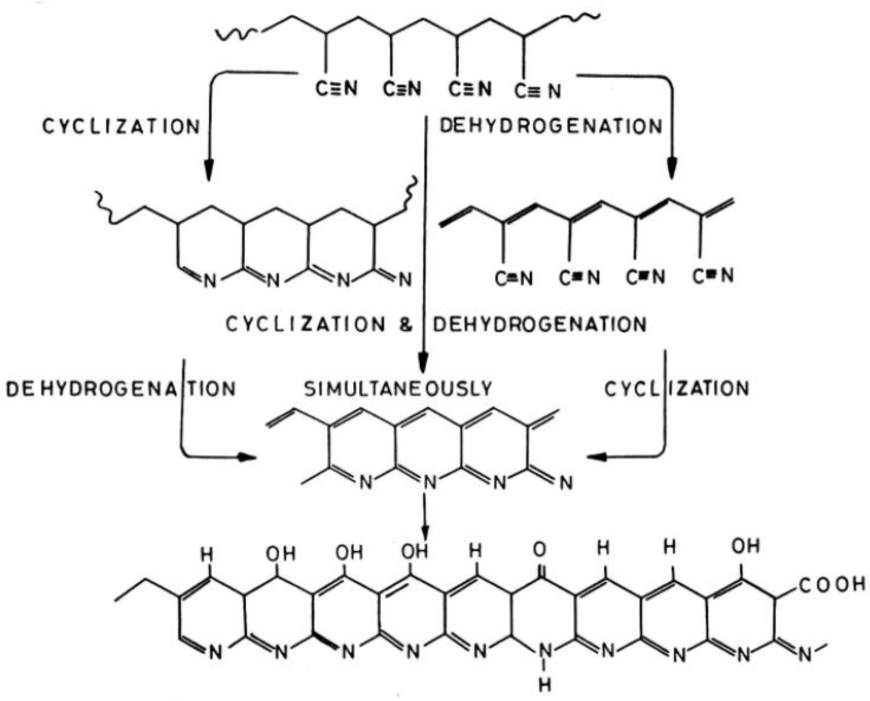


Figure 2.10, Sequence of reactions in thermos-oxidative stabilization of PAN precursors, Taken from [18]

2.3 Preliminary Effort of Melt Spinning of Polyacrylonitrile

Many preliminary attempts were performed to make PAN melt spinning feasible. Compared to the solution spinning, melting spinning can significantly reduce the production costs. This is because the traditional solution spinning requires some toxic solvents, such as N,N-dimethylformamide (DMF) and N-N dimethyl acetamide (DMAC) during the spinning process. These solvents have to be recovered and collected afterwards. For melt spinning, the use of solvents can be eliminated or significantly reduced, therefore, the costs of solvents and recovery can be significantly reduced as well [13, 20]. In this case, many scientists and inventors have conducted related research and experiments in this area.

In 1952, Coxe [4] is the first person who discovered that water can significantly decrease the melting point of PAN by hydrating the pendant nitrile groups and decoupling the nitrile-nitrile associations. His study confirmed that the T_m of PAN can be reduced to around 200℃ with 20 weight percent of water. However, Coxe failed to develop a PAN fiber melt spun process because he was not able to control the release of steam leaving the spinneret, which cause a severe foaming problem during the melt spin process [4, 8, 15]. After that, further studies were conducted to attempt to properly control the water evaporation and foaming problems. In 1979, Porosoff [21] improved the extruder and solved the foaming problem by placing the PAN and water into a “steam pressurized solidification zone” that could prevent rapid water evaporation. In his patent, he claimed that PAN fiber could be drawn with a steam pressure of 49 psig and at 147℃. However, the polymer he used was an 89.3 wt% acrylonitrile (AN) and 10.7 wt% of methyl methacrylate (MMA). This type of low-AN content PAN fiber is more likely to be used for textile applications instead of as precursor of carbon fiber (the AN content should be around 95 wt% to be the precursor of carbon fiber). Figure 2.11 below is the schematic of Porosoff’s invention.

Porosoff's invention was a big improvement in PAN melt spinning process since it completely eliminated the need of toxic solvents, and consequently, reduce the cost of the melt spinning process. Various studies followed with Porosoff's work to further determine the feasibility of his process and the mechanical properties of such melt spun PAN fibers. DeMaria et al [22] claim in their patent that wetting the fiber in the hot steam pressurized solidification zone could improve the fiber orientation and more easily facilitate the stretching of fibers. Grove et al [23] also reported that carbon fiber with a decent strength and modulus could be produced via the similar process of Porosoff. They also reported the detail mechanical properties of both the precursor fiber and stabilized fiber (for the detail experimental data, see the table 2.11 to 2.13 below). However, Grove et al also reported that the resultant fibers had numerous surface and internal flaws and micro-holes and broken filaments were observed as well. They used Scanning Electron Micrographs (SEM) to scan the fiber and observed voids are in the fiber (Figure 2.12), especially near the core. Meanwhile, Min et al [8-9] reported the similar results. They successfully melt spun PAN (88wt% of AN) fiber with 23 wt% of water but still observed a microporous structure at the spun fiber core from the SEM photographs. (see Figure 2.13). Here the fiber was melt spun at 150℃, the viscosity of the melt polymer was increase and the steam pressure was lowered. Min et al tried to use the combination to suppress foaming but it seemed there was still microholes exhibited in the fiber.

Daumit et al [10] at BASF also patented a method for producing melt spun PAN fibers. The schematic is presented below at Figure 2.14. A mixture of water, acetonitrile and C_1 to C_4 alcohol were used as plasticizers and the processing temperature was between 160℃ to 185℃ in the pressure chamber, which is pressurized by steam between 10 to 50 psig above the atmosphere. The pressure chamber was designed to prevent the loss of plasticizers at high temperature and minimize void formation during the melt spun process. After leaving the pressure chamber, the precursor fiber would enter an oven for removing the remaining plasticizers. Most of voids resulting from plasticizer removal are then collapsed during the spin drawing process in a steam bath at 18 psig.

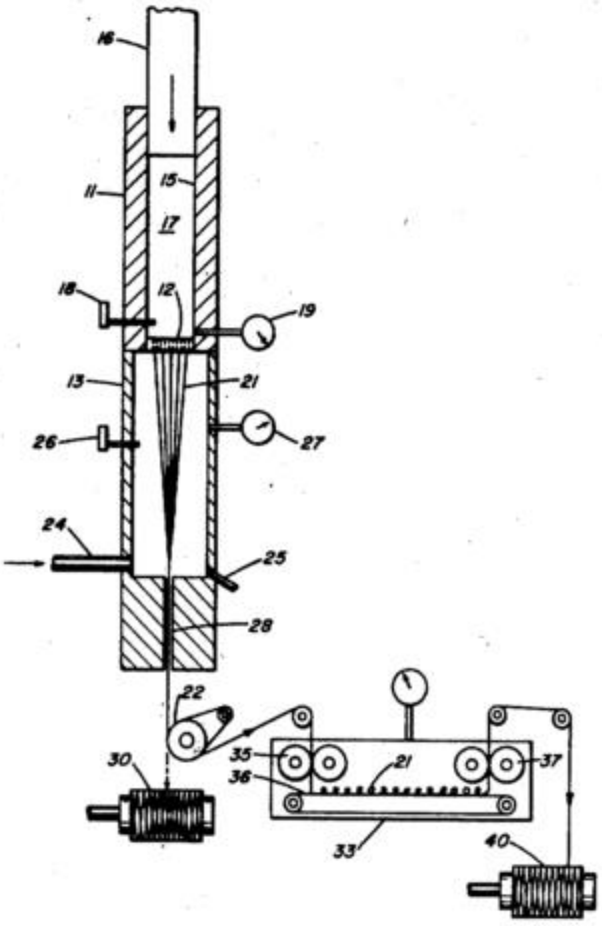
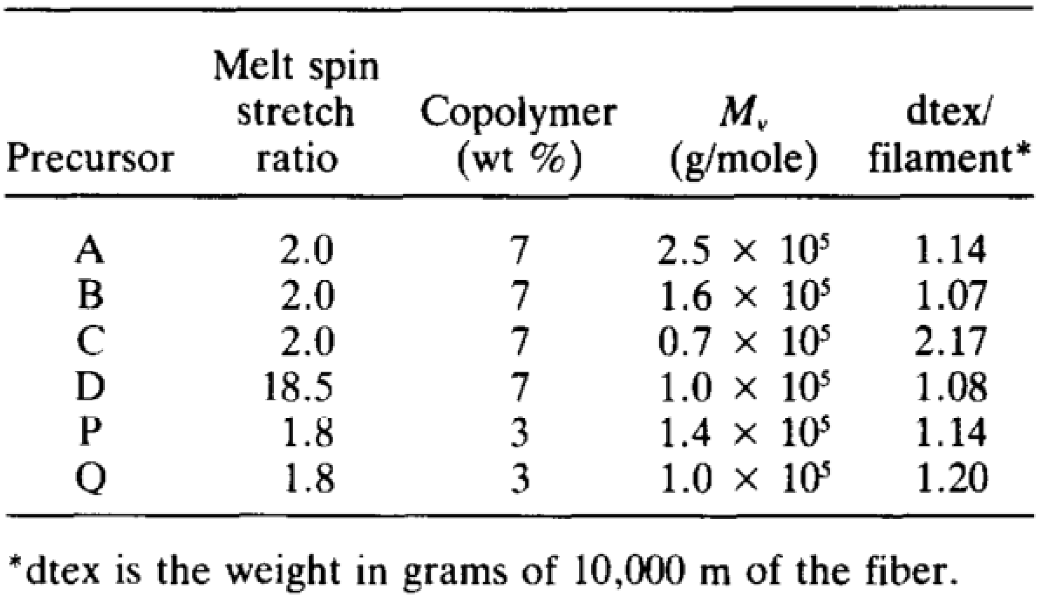


Figure 2.11, Process developed by Porosoff for melt extrusion of PAN. Taken from [21]

Table 2.1, Precursor fiber characteristic from Grove's report. Taken from [23]

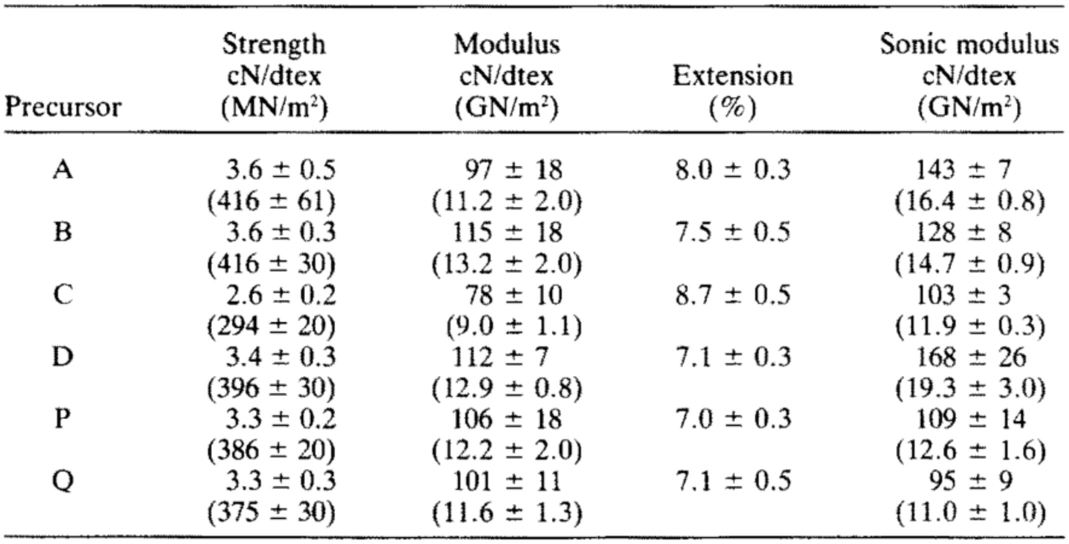


Precursor	Melt spin stretch ratio	Copolymer (wt %)	M_v (g/mole)	dtex/ filament*
A	2.0	7	2.5×10^5	1.14
B	2.0	7	1.6×10^5	1.07
C	2.0	7	0.7×10^5	2.17
D	18.5	7	1.0×10^5	1.08
P	1.8	3	1.4×10^5	1.14
Q	1.8	3	1.0×10^5	1.20

*dtex is the weight in grams of 10,000 m of the fiber.

Table 2.2, Mechanical properties of precursor fiber from Grove's report.

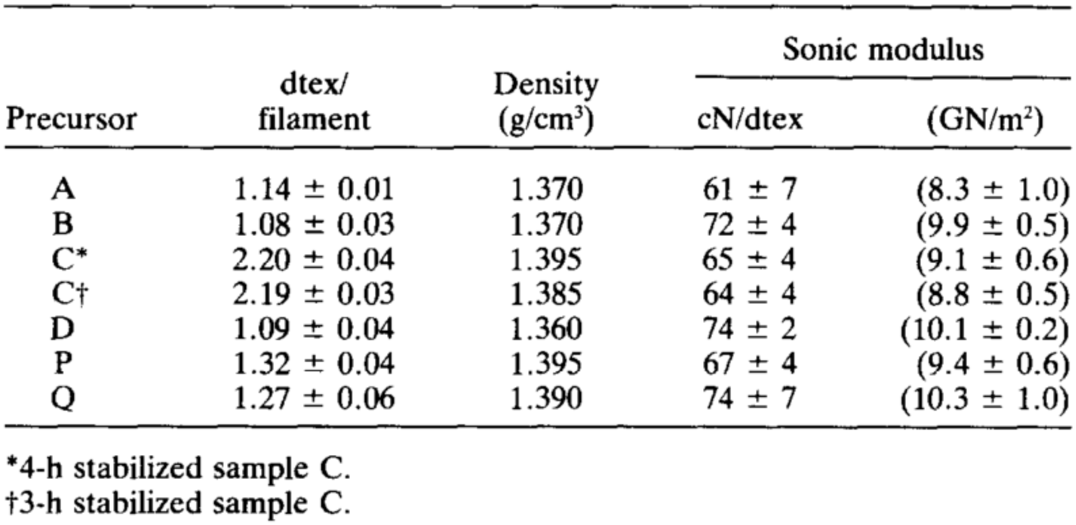
Taken from [23]



Precursor	Strength cN/dtex (MN/m^2)	Modulus cN/dtex (GN/m^2)	Extension (%)	Sonic modulus cN/dtex (GN/m^2)
A	3.6 ± 0.5 (416 ± 61)	97 ± 18 (11.2 ± 2.0)	8.0 ± 0.3	143 ± 7 (16.4 ± 0.8)
B	3.6 ± 0.3 (416 ± 30)	115 ± 18 (13.2 ± 2.0)	7.5 ± 0.5	128 ± 8 (14.7 ± 0.9)
C	2.6 ± 0.2 (294 ± 20)	78 ± 10 (9.0 ± 1.1)	8.7 ± 0.5	103 ± 3 (11.9 ± 0.3)
D	3.4 ± 0.3 (396 ± 30)	112 ± 7 (12.9 ± 0.8)	7.1 ± 0.3	168 ± 26 (19.3 ± 3.0)
P	3.3 ± 0.2 (386 ± 20)	106 ± 18 (12.2 ± 2.0)	7.0 ± 0.3	109 ± 14 (12.6 ± 1.6)
Q	3.3 ± 0.3 (375 ± 30)	101 ± 11 (11.6 ± 1.3)	7.1 ± 0.5	95 ± 9 (11.0 ± 1.0)

Table 2.3, Mechanical properties of stabilized fiber from Grove's report.

Taken from [23]



Precursor	dtex/ filament	Density (g/cm³)	Sonic modulus	
			cN/dtex	(GN/m²)
A	1.14 ± 0.01	1.370	61 ± 7	(8.3 ± 1.0)
B	1.08 ± 0.03	1.370	72 ± 4	(9.9 ± 0.5)
C*	2.20 ± 0.04	1.395	65 ± 4	(9.1 ± 0.6)
C†	2.19 ± 0.03	1.385	64 ± 4	(8.8 ± 0.5)
D	1.09 ± 0.04	1.360	74 ± 2	(10.1 ± 0.2)
P	1.32 ± 0.04	1.395	67 ± 4	(9.4 ± 0.6)
Q	1.27 ± 0.06	1.390	74 ± 7	(10.3 ± 1.0)

*4-h stabilized sample C.
†3-h stabilized sample C.

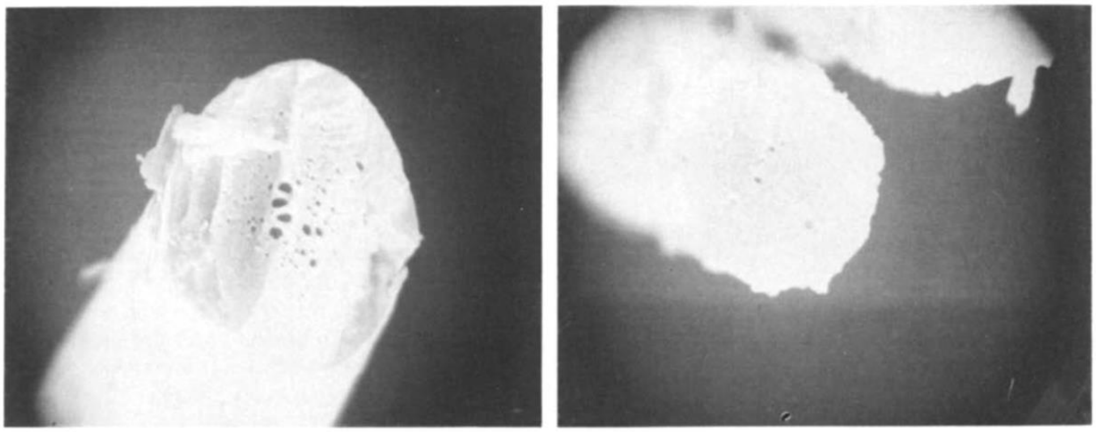


Figure 2.12, Scanning electron micrographs of microvoids in carbon fiber with different precursors from Groves report. Taken from [23]

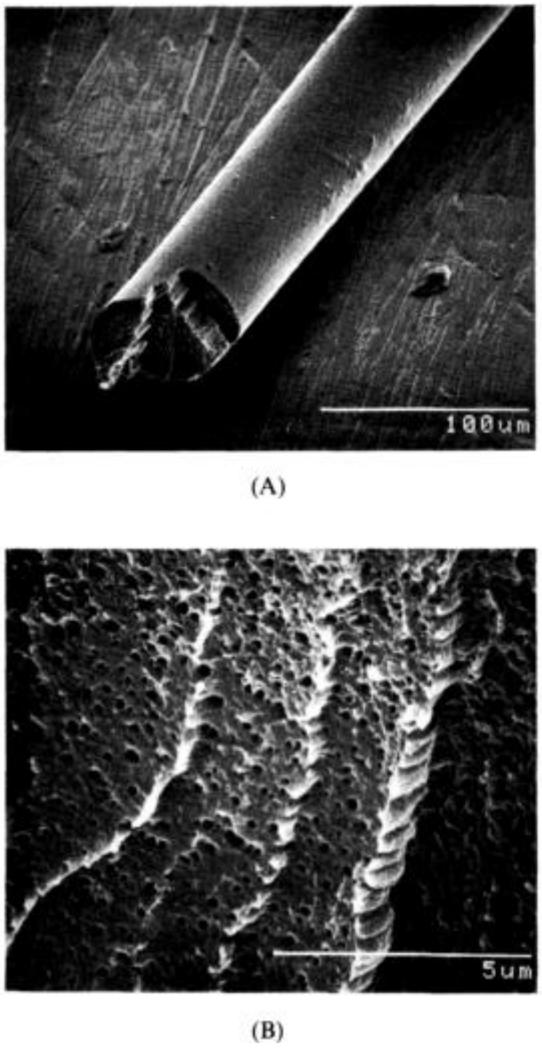


Figure 2.13, SEM microphotographs of melt-spun fiber form the supercooled melt of PAN-88 containing 23 wt% water at 150°C using a spinneret having 12 holes of 0.1 mm diameter. Photograph (B) is the magnified core cross-section of (A). Taken from [4]

Fig. 1

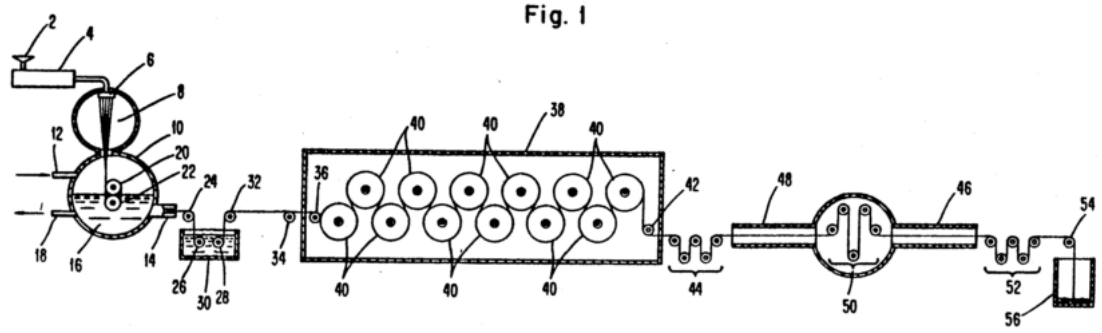


Figure 2.14, Process for melt extruder PAN precursor fibers by BASF. Taken from [10]

The BASF process was constructive since it introduced the second plasticizers that mix with water during the PAN melt spinning process. It also proved that PAN fiber can be obtained via a pseudo-melt spinning process. However, this process was never commercialized. The major reason was that this process required a high plasticizer content (24 to 50 wt%) so that the recovery must still be implemented. Moreover, the chemical compounds used as plasticizers were extremely toxic and required extra caution (for example, acetonitrile can degrade into cyanide at around the boiling point). The use of high content of plasticizer could potentially increase the cost of the melt spinning process, and reduced the environmental benefits. In fact, this process provided little economic benefit compared with the traditional solution spinning process of PAN. As a result of economic consideration, BASF decided not to commercialize this process.

Bortner and Wilding [12-16] attempted to use supercritical carbon dioxide as plasticizer to melt spun PAN. The equipment schematic is shown in Figure 2.15 below. In their study, copolymers with various acrylonitrile (AN)/methacrylate (MA) ratio (from 85/15 wt% to 98/2%) was used. Bortner and Wilding focused on the rheological measurements rather than the melt spinning process, they tried to use rheological data to prove the melt spinning was feasible. They performed the rheological test at around 200℃ and with a pressure of CO_2 of 17.2 MPa. The rheological data will be further discussed in the next section.

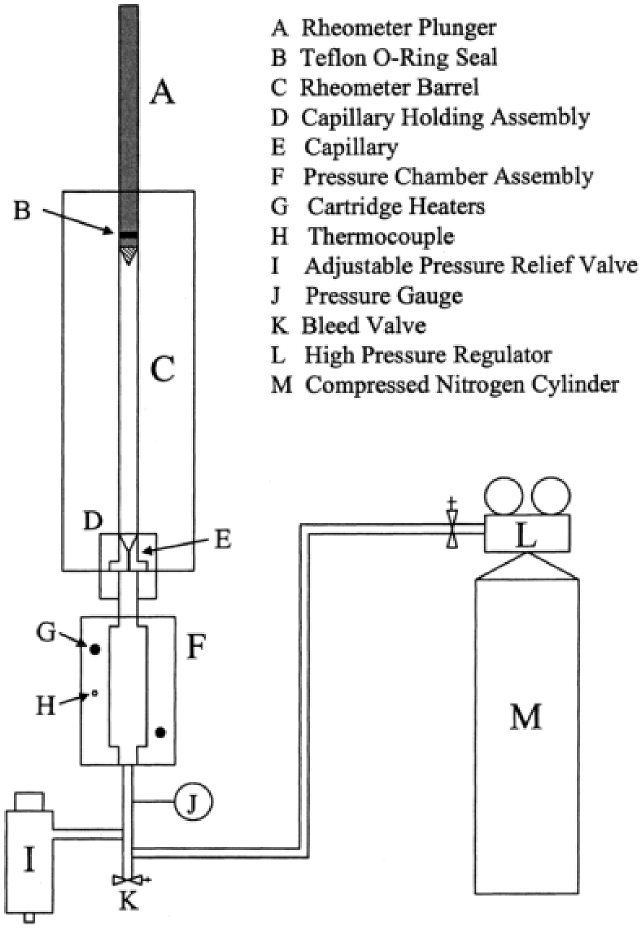


Figure 2.15, Schematic of the pressurized capillary rheometer for viscosity measurement of polymer containing absorbed CO_2. Taken from [14]

Huang [11] in 2014 also conducted some melt spinning PAN research. He followed with the processing procedure of the BASF patent and used water + acetonitrile mixture as the plasticizers. He reported both the melting point data and steady-shear viscosity data of PAN and the mechanical properties of the precursor fiber. Figure 2.16 is the schematic of his equipment. Specifically, he used a copolymer with 94 wt% of acrylonitrile and 6 wt% of vinyl acetate, plasticized with 20 wt% of water or 14 wt% water+ 14 wt% acetonitrile. The melt spinning process was performed at 185℃ and 165℃, for the polymer plasticized with water only and plasticized with water + acetonitrile, respectively. One thing he did differently from previous work was he used compressed nitrogen (150 to 200 psi) rather than steam to fill the pressure chamber. Also, the pressure chamber he used contains a “take-up” device, and that means the orifice was no longer needed. The filaments could be spun on the bobbin inside the pressure chamber. The advantage to using nitrogen was to minimize the dehydrogenation reactions during the spinning process since nitrogen did not react with neither PAN copolymer nor plasticizers. Spinning under pressure made the spinning process easier because the complication associated with the orifice (such as vibration and damage of the filaments caused by the turbulence of compressed gas and steam) can be completely eliminated.

Huang also posted comparison of the SEM images of the melt spun PAN fibers and commercial solutions pun PAN precursors (Figure 2.17) as well as the tensile property comparison (Figure 2.18). From the images, the melt spun PAN fiber is very similar to the commercial one for both morphological and mechanical properties.

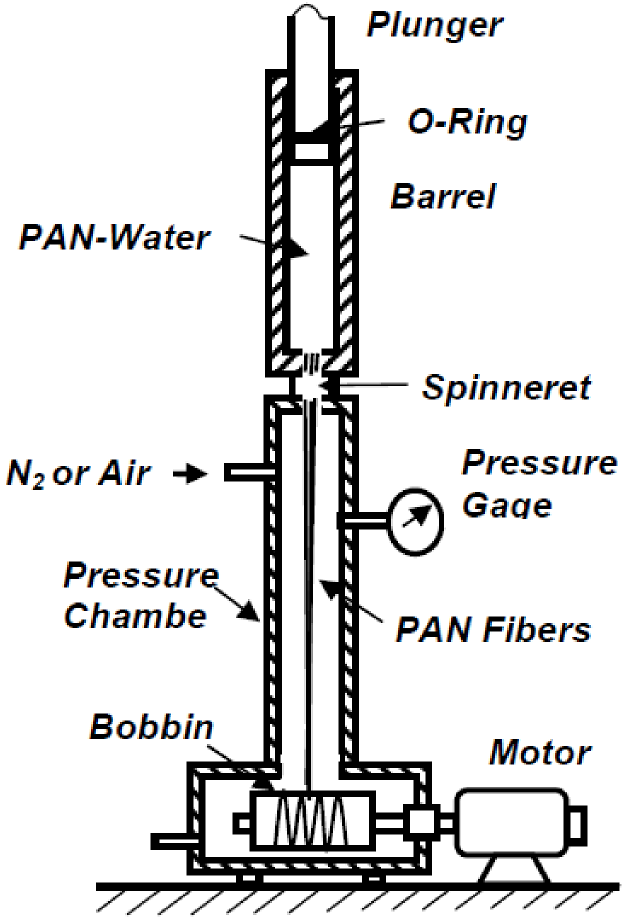


Figure 2.16, Schematic diagram of fiber spinning system with pressure chamber for Huang's research. Taken from [11]

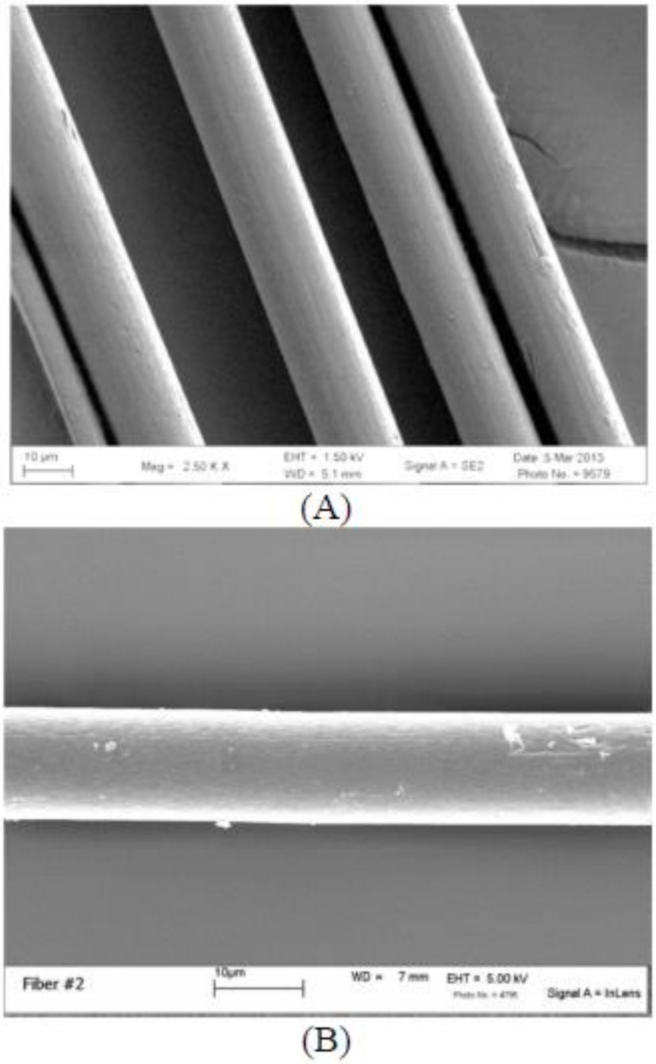


Figure 2.17, SEM images of melt spun PAN fibers (A) and commercial solution spun PAN precursors (B). Taken from [11]

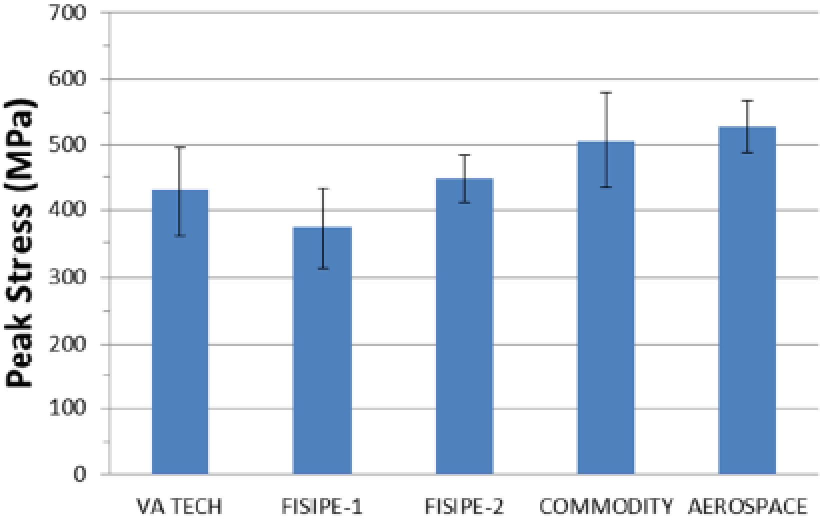


Figure 2.18, Comparison of tensile property (strength) of VA Tech melt spun precursor PAN fibers (generated by Huang) with commercial solution spun PAN fibers. Taken from [11]

2.4 Rheological Research of Melted Polyacrylonitrile

Compared to the melting point and degradation research of PAN, there are very few publications related to the rheological behavior of melt polyacrylonitrile. As mentioned above, Bortner and Wilding [12-16] had published some rheological data of PAN that was plasticized with $scCO_2$, and Huang [11] published rheological data of PAN that was plasticized with water and water-acetonitrile mixture.

Bortner used a modified capillary rheometer to measure the steady shear viscosity of PAN that plasticized with $scCO_2$. The capillary he used has a diameter of 0.69mm, with L/D=111. The experimental temperature was at 200°C (Figure 2.19) and 220°C (Figure 2.20). Results show that with an increasing number of the CO_2 absorption, the viscosity of melt PAN decrease significantly. It is important to note that the pure polymer without any plasticizer can also be melt at around 200°C. This is because the PAN sample Bortner used is an 85/15 weight ratio AN/MA copolymer (with such a low AN content it is possible to melt the polymer at around 200°C).

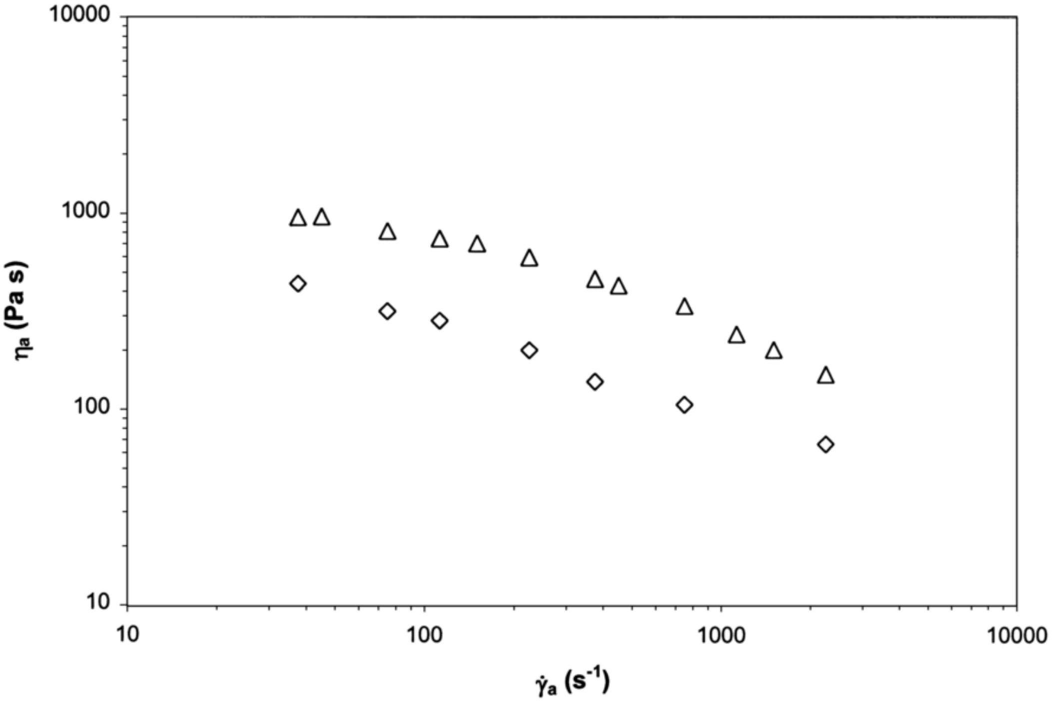


Figure 2.19, Apparent viscosity vs. shear rate for the 85/15 AN/MA copolymer. (△) pure and (◊) plasticized copolymer containing 5.6 wt% absorbed CO2. Test temperature 200 °C. D = 0.69 mm. L/D = 111. Taken from [12]

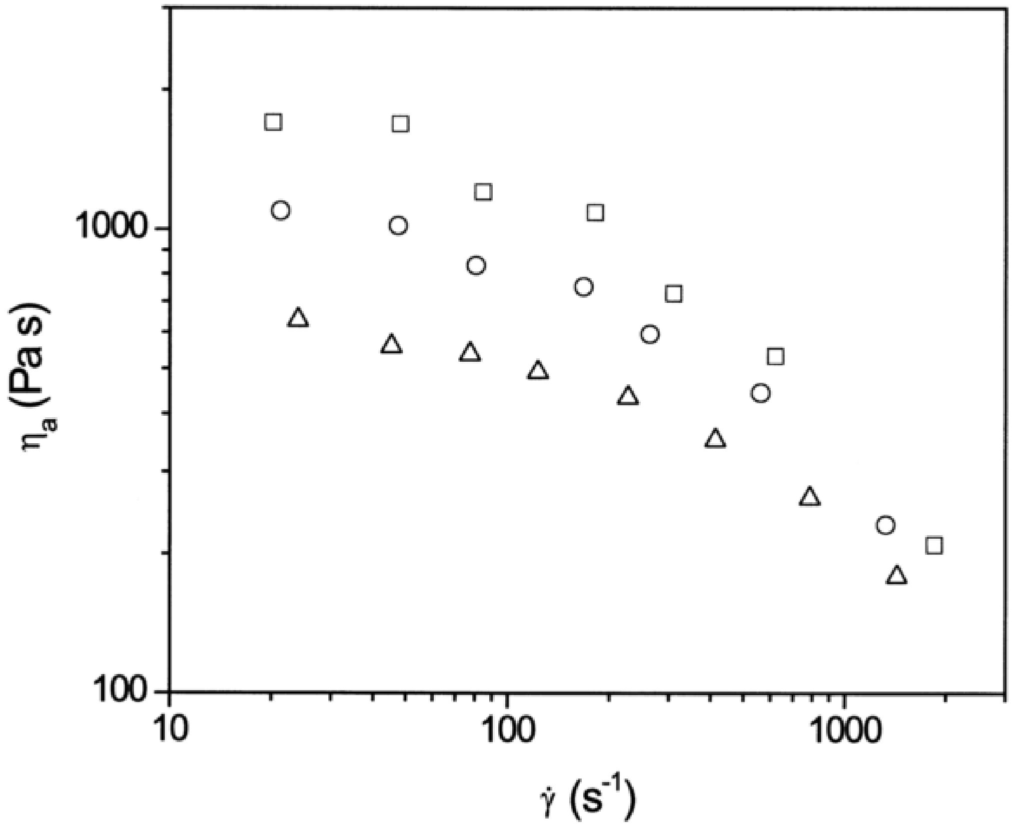


Figure 2.20, Apparent viscosity vs. shear rate for the 90/10 AN/MA copolymer. Data are shown for the (□) pure copolymer and plasticized copolymer containing (○) 2.0 and (Δ) 3.0 wt% absorbed CO2. Test temperature 220 °C. D = 0.69 mm. L/D= 111. Taken from [12]

Another rheological experiment Bortner conducted was the time-dependent viscosity measurement [13]. That was, keeping the shear rate and temperature as constants, track the viscosity change in the function of time. The reason to perform this measurement was to track the stability of the PAN copolymer, because once the PAN copolymer started to degrade, it cross-linked and cyclized, which lead to an increasing in viscosity. In this case, the duration of PAN processing without significant degradation at a certain temperature could be tracked [25]. The polymer sample he used for time-dependent viscosity measurement is the 85/15 wt ratio AN/MA copolymer, which could be melt without any plasticizer above 200℃. Bortner performed the time-dependent rheological measurements at shear rate of $0.1s^{-1}$ and temperature range from 200℃ to 260℃, the results are present below (Figure 2.21 to 2.22)

The viscosity of PAN was very stable when the temperature was below 220℃, these results indicated that PAN did not suffer any significant degradation within 30 minutes in such a temperature range. However, once the temperature rose over 220℃, the viscosity increased rapidly in the function of time, indicating the degradation of the copolymer. These results were similar to the Gupta’s work which he indicated that PAN starts to degrade at 180℃ and the degradation start rapid and spontaneous at 220℃ [18]

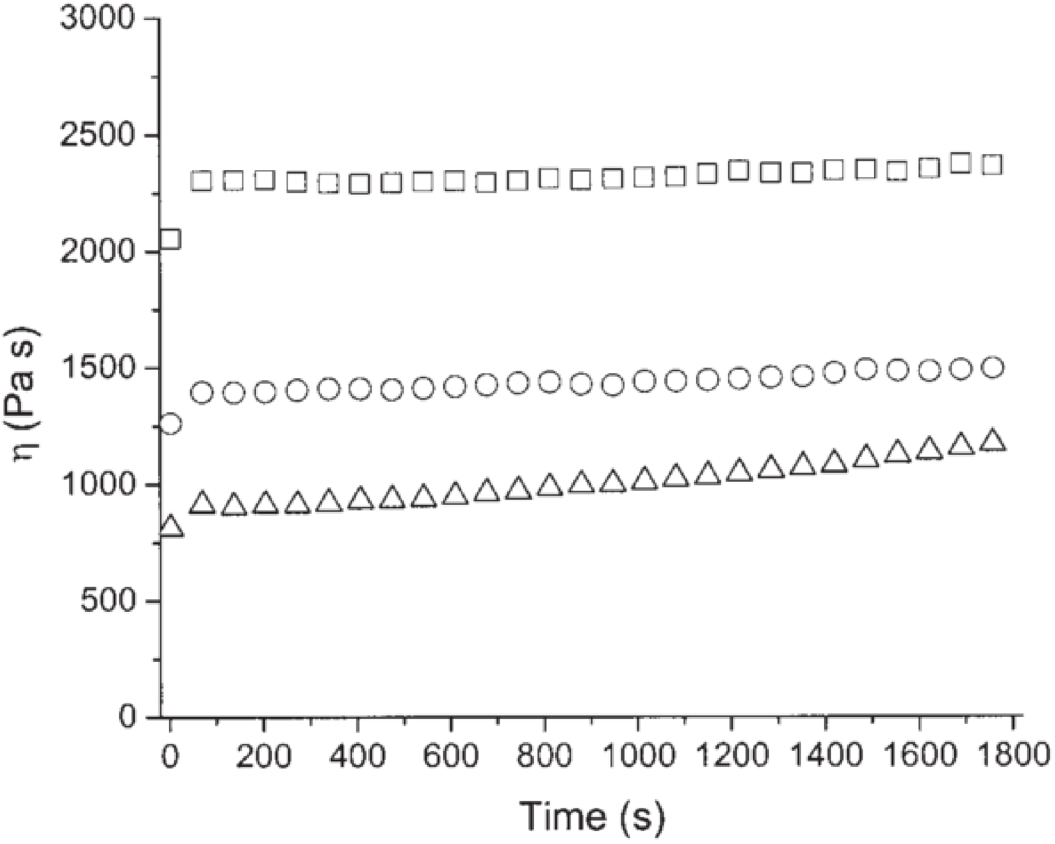


Figure 2.21, Time-dependent viscosity data for the AN/MA copolymer at shear rate = 0.1 s^{-1} and (□) 200°C (○) 210°C (Δ) 220°C. Taken from [13]

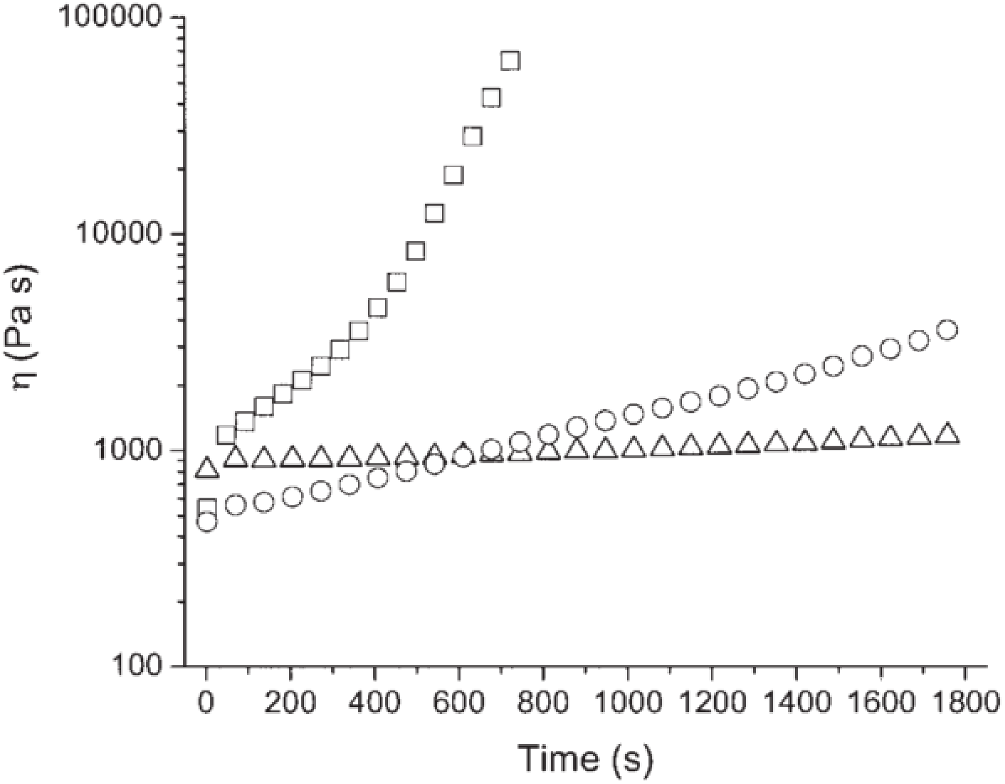


Figure 2.22, Time-dependent viscosity data for the AN/MA copolymer at shear rate = 0.1 s^{-1} and (□) 260°C (○) 240°C (Δ) 220°C. Taken from [13]

Huang [11] published viscosity data of melt PAN that was plasticized with water and water + acetonitrile (Figure 2.23). His work showed that additional acetonitrile could reduce the processing temperature significantly. The polymer material he used was a high AN content AN/VA copolymer (94 wt% of AN) which could not be directly melted without plasticizers. From his results, the viscosity of melt PAN with acetonitrile at 155℃ was similar to the viscosity of the same material without acetonitrile at 190℃, indicating that the processing temperature could be reduced by around 30℃. His discovery also indicated that one may process PAN at around 160℃ with water + acetonitrile as plasticizers. At such a low temperature, the degradation reaction could be negligible. However, he did not report any stability data for PAN that plasticized with water and water + acetonitrile, so it is still unknown how the acetonitrile could influence the stability of PAN.

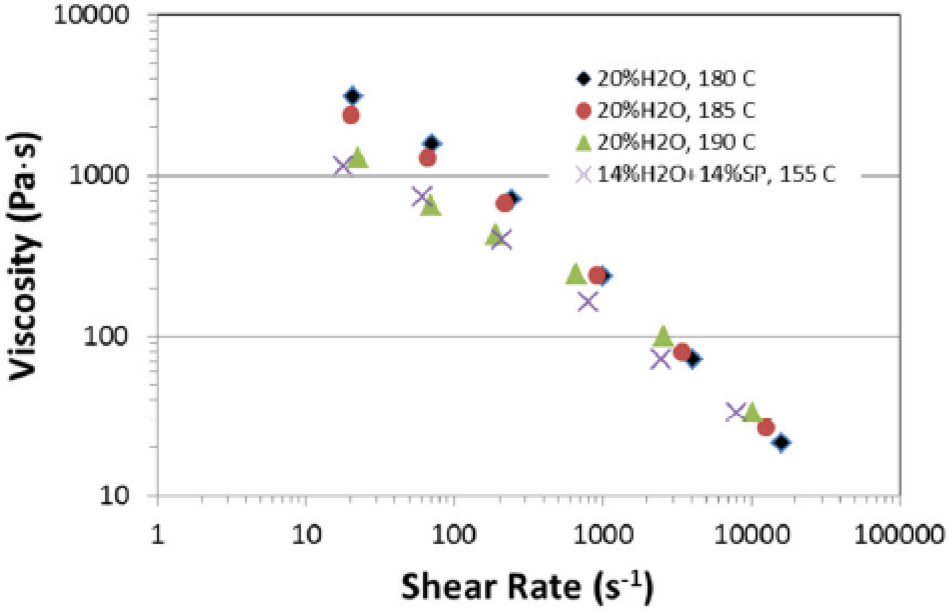


Figure 2.23, Viscosity of AN/VA with plasticizers, SP = acetonitrile. Taken from [11]

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Chapter 3 Identifying Melt Processing Conditions for a Polyacrylonitrile Copolymer Plasticized with Water, Acetonitrile and their Mixtures

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3.1 Abstract

This paper discusses the feasibility of the melt spinning process of polyacrylonitrile (PAN) copolymer (acrylonitrile/methylacrylate 95.6/4.4 mol% ratio) plasticized with H_2O acetonitrile (ACN) and their mixture. The objective is to use water only as a plasticizer to melt spin PAN under specific conditions (composition, temperature etc). The melting point and rheological measurements have been conducted by differential scanning calorimetry (DSC) and a modified capillary rheometer, respectively, for this plasticized system. The DSC results show that the melting point of the PAN copolymer can be reduced from over 300 °C to below 180 °C, which is the temperature for the onset of degradation (cyclization and crosslinking) of PAN. Rheological results show that the PAN copolymer can be extruded with a reasonable viscosity at 15-20 °C above its melting point, and also the stability and viscosity are strongly dependent on temperature and the plasticizer type and content. Furthermore, the results indicate that the most appropriate condition for PAN melt spinning is for the PAN/H_2O mixture of 70/30 wt% ratio at a temperature of 180 °C for which the copolymer sample can remain stable without significant degradation for around 120 minutes and maintain its viscosity in the range of around 600 Pa*s.

3.2 Introduction

Polyacrylonitrile (PAN) fiber is one of the most important fibers in the world as it is a precursor to carbon fiber. In 2013, approximately 90% percent of carbon fiber was produced from PAN fiber. PAN fiber is considered as the most suitable precursor for generating high performance carbon fiber because the PAN-based carbon fiber has properties of low density, high strength and high thermal stability. PAN-based high performance carbon fiber is playing a significant role in many industrial areas, such as in aerospace and defense applications, as well as sporting goods and automotive applications(Cato & Edie, 2003; Frank, Hermanutz, & Buchmeiser, 2012; Odian, 2004; Rahaman, Ismail, & Mustafa, 2007).

Polyacrylonitrile is normally a copolymer of high content acrylonitrile (AN) and a specific co-monomer, such as methyl acrylate (MA) or vinyl acetate (VA) which are used to improve the processability of the PAN fiber(Frank et al., 2012). The PAN copolymer that is used to generate carbon fiber is primarily AN/MA copolymer with more than 93 mol% AN content(Daumit, Ko, Slater, Venner, & Young, 1990, 1992).

There are three major steps in producing the PAN-based carbon fiber: precursor fiber spinning, thermo-oxidative stabilization, and carbonization. As a precursor of carbon fiber, PAN fiber spinning is the first major step in the manufacturing process. For over 50 years, the major PAN fiber spinning method is traditional solution spinning, which is based on the use of a highly polar organic solvent to dissolve the PAN polymer during the spinning process. Some common organic solvents used during the PAN solution spinning process include N,N-dimethylformamide (DMF) and N-N dimethyl acetamide (DMAC). These organic solvents are normally used in the range of 70 to 93 wt % (7 to 30 wt % of polymer material). In this case, a high proportion of the production costs are due to the usage and recovery of these solvents during the PAN fiber spinning process (M. Bortner, 2004; Henrici-Olivé & Olivé, 1979; Morgan, 2005; Ribeiro, Pardini, Alves, & Brito Júnior, 2015). As a result, the price of PAN-based carbon fiber is still as high as around $11 per pound (Paulauskas, 2012).

Melt spinning is an alternative technique to produce PAN fiber. The advantage is that toxic organic solvents, such as DMF and DMAC mentioned above, are not required in the PAN melt spinning process, and it further reduces the cost of the spinning process because nothing needs to be collected and recovered afterwards. However, due to the existence of polar nitrile groups, the polymer chains of PAN experience very strong interactions, which also result in a high melting point of PAN of around 320 ^{o}C (M. J. Bortner, Bhanu, McGrath, & Baird, 2004; Frushour, 1981; Da, 1960). Before reaching the melting point, PAN will suffer exothermic reactions such as cyclization and crosslinking at around 180 ^{o}C (M. Bortner, 2004; Rahaman et al., 2007; Xue, McKinney, & Wilkie, 1997). That means PAN will degrade and never reach a stable melt state.

Numerous preliminary works have been conducted in this field. Coxe (1952) first discovered that by adding water as a plasticizer, the melting point of PAN could be significantly reduced to below 200 ^{o}C. However, he failed to melt spin PAN fiber due to the foaming problem. Porosoff (1979) improved the melt spinning process based on Coxe's work by adding a pressure chamber to the spinning system. This innovation could potentially prevent water evaporation and the foaming problem. Daumit et al. (1992) at BASF claimed in their patent that the mixture of water and acetonitrile (ACN) was a more efficient plasticizer compared to water alone. With approximately 14 wt% of water and 14 wt% of acetonitrile (ACN) one could further decrease the melting point of PAN to around 135 ^{o}C. However, due to the economic considerations and the change of the world carbon fiber market, this approach was never commercialized by BASF either (Paulauskas, 2012).

Although plenty of studies have been reported regarding polyacrylonitrile and its spinning (both solution spinning and melt spinning) process, there has been very little research conducted on the rheological behavior of PAN. Rangarajan et al. (2002) reported the rheological data of a PAN copolymer with only 65 mol% of acrylonitrile. With such a low content of acrylonitrile, this copolymer sample could be melted below the degradation temperature of PAN without the presence of plasticizers, however, it was too time consuming at the stabilization process. M. J. Bortner et al (2004) and M. D.Wilding (2009) reported work on the rheological investigation of AN/MA copolymer plasticized with supercritical carbon dioxide ($scCO_2$). In addition, Huang and Baird (2014) reported their work on melt spinning of AN/VA copolymer using water/acetonitrile mixture as plasticizers. They successfully obtained PAN fibers and reported their mechanical properties and microstructures using SEM photos and there were no voids observed. However, they did not spin AN/MA copolymer with the same method and procedure nor did they use pure water as a plasticizer.

Miller et al. (2017) published some preliminary results. In the previous paper the chemical and thermal analysis of an AN/MA copolymer was reported and this information is referred to in this paper along with some of the rheological data of the AN/MA-water-acetonitrile and AN/MA-water-adiponitrile systems. This paper will further report the rheological properties and stability of the AN/MA copolymer with water and acetonitrile as plasticizers. These rheological results may not only provide fundamental understanding of molten polyacrylonitrile with plasticizers but also be of use for extruder design of PAN melt spinning. Furthermore, although acetonitrile was still used in this paper, it was used as baseline to study its behavior as a plasticizer. Our ultimate goal for this project is to establish whether pure water can reduce the processing temperature to a point competitive with that of a water/acetonitrile mixture as this would eliminate the need to use an organic plasticizer such as acetonitrile in the melt spinning process.

3.3 Experimental

3.3.1 Materials

The chemical properties of the polyacrylonitrile copolymer used in this study were analyzed and reported in our previous paper(Miller et al., 2017). The polymer sample used in this study is poly (acrylonitrile-ran-methyl acrylate) which is composed of 95.6 mol% of acrylonitrile and 4.4 mol% of methyl acrylate. This material can be identified as an appropriate PAN copolymer to be used in carbon fiber industry due to its high content of acrylonitrile(Daumit et al., 1990; Rangarajan et al., 2002). Our previous paper also reported the molecular weight of the copolymer with M_n = 123.1 kDa and M_w = 238.2 kDa. This copolymer material was provided by Fisipe and used as received. The acetonitrile (ACN) was purchased from Spectrum Chemicals and used as received. The entanglement molecular weight (M_e) was reported at 3100 g/mol (polymer database, 2016)

3.3.2 Sample Preparation

The PAN copolymer sample needed to be mixed with plasticizers before being loaded into the capillary rheometer. Specifically, the PAN sample was weighed and mixed with plasticizers in a desired ratio first. (for example, if a 70/15/15 wt% of PAN/ACN/H_2O sample needed to be prepared, 1.2 gram of ACN, 1.2 gram of H_2O and 5.6 gram of copolymer powder were placed into a sealed container). Then the container was placed into a convection oven and heated at 60 °C for around 2 hours. This heating process helped the plasticizers to be dispersed in the polymer powder. Finally, the mixture of copolymer and plasticizers was held in the sealed container at room temperature over-night.

3.3.3 Differential Scanning Calorimetry (DSC)

DSC tests were used to determine the melting point (T_m) of the plasticized PAN in this study. The experimental method and instruments were the same as described in the previous paper (Miller et al., 2017). Specifically, the PAN/plasticizer mixtures are placed in special high volume pans with an O-ring for sealing and preventing the volatilization of the plasticizers. A TA Instruments DSC Q200 was used to conduct the measurements. The copolymer-plasticizer mixtures were heated in nitrogen from room temperature to 200℃ at a rate of 10 ^{o}C /min and then cooled at a rate of 10 ^{o}C /min to 0 ^{o}C and heated again to 240 ^{o}C at the same rate.

3.3.4 Rheological Measurements

The rheological measurements were conducted on an Instron model 3211 capillary rheometer. The capillary rheometer was modified with a pressurized system which was similar to that reported by Bortner and Baird (M. J. Bortner & Baird, 2004; M. J. Bortner et al., 2004). A schematic of the modified system is shown in Figure 3.1. As shown, the system was modified with an additional pressure chamber that attached to the exit of the capillary die. During the rheological tests, the entire system, including the rheometer barrel and pressure chamber, were pressurized to around 1.38MPa (200psi) by nitrogen. This pressure was reported by Huang and Baird (J. Huang & Baird, 2014) and because it was higher than the vapor pressure of water at 190℃ (182psi) so that plasticizers should not evaporate during the rheological tests. O-rings were used on the plunger

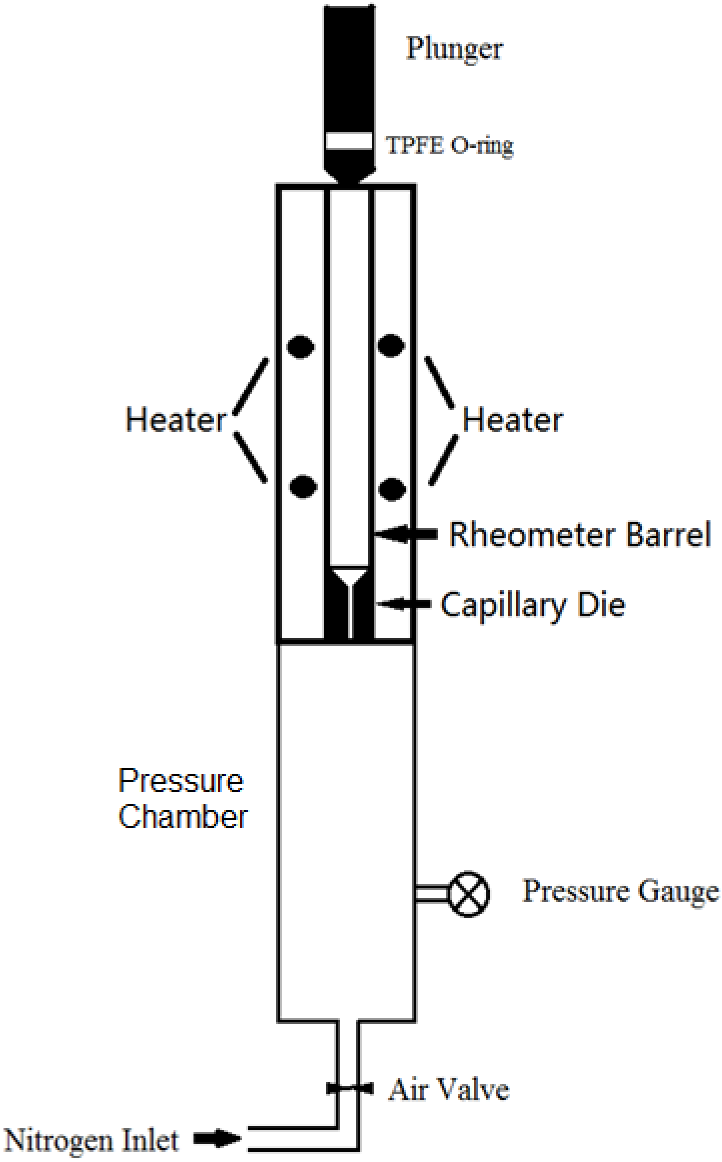

Figure 3.1, Schematic of the Modified Capillary Rheometer

and capillaries for sealing the system. The system held the pressure until the end of the experiments.

To start the rheological measurements, the prepared PAN sample that was described in the previous section was directly loaded into the barrel of the rheometer. The plunger (with O-rings attached) was then inserted into the chamber and the air valve was turned on to start the pressurization of the system, and the temperature was set to the target temperature. Then there was a 25 to 30 minutes holding time to ensure the entire system reached the experimental temperature and the polymer sample inside the rheometer was completely melted.

Customized capillary dies were used for the rheological measurements with length of 25.6mm, diameter of 0.35mm and entrance angle of 90 degrees. This made the L/D ratio of the dies around 73, which allowed the entrance effect to be neglected at such a high L/D ratio. An O-ring could be placed onto these dies as well to prevent leaking and losing plasticizers from the bottom of the rheometer. Moreover, the diameter of the rheometer barrel was 9.53mm. The speed of plunger could be controlled and adjusted at various values from 0.03 cm/min to 6 cm/min. Shear rates could be easily calculated with these parameters.

There were two types of rheological measurements that were conducted in this study, and the experimental procedure for each type was different. The first type of measurement was the steady-shear viscosity measurement. For this measurement, the viscosity of the polymer sample was measured at 7-8 different shear rate values which ranged from 50 to 10000 s^{-1}, and the temperature was held constant during the measurements. The Rabinowitsch correction was applied in steady-shear viscosity measurements in order to obtain the true shear-rate from apparent shear-rate (which normally influence the shear-rate by around 10 percent). The second type of measurement was the time-dependent viscosity measurement. For this measurement, the viscosity of polymer sample was measured at a constant temperature and shear rate ($135s^{-1}$ in this study). The time-dependent viscosity measurement was terminated if the polymer sample was run out (normally 2 hours from the beginning of the measurement) or the pressure was too high to reach the upper limit of the rheometer. The time-dependent viscosity measurements were conducted prior to the steady-shear viscosity measurement in order to obtain the maximum measurement duration to avoid significant degradation of polymer samples.

3.4 Results and Discussion

3.4.1 Melting Point Results

Melting points for the PAN with plasticizers are significant in this study because they provide information of the lowest possible temperature to melt spin PAN. The melting point of each sample is shown in Table 3.1.

The letter “a” in the table indicates the data had been reported in our previous paper(Miller et al., 2017), and the letter “b” indicates the data is obtained recently. The data in Table 1 show that the melting point of PAN can be significantly reduced to below 180°C with plasticizers. Hence, it is feasible to melt process PAN without significant degradation. This data also match the results from Min et al’s report(Min, Son, Kim, Lee, & Jo, 1994) that the T_m of PAN will not be further reduced by addition of water if the content of water is over 20 wt%. Hence there is no significant difference between the copolymer samples with 20wt% and 30 wt% of water. Also, acetonitrile (ACN) appears to be a more effective plasticizer compared to water because PAN plasticized with ACN has even a lower melting point at around 135°C. This is much lower than the degradation temperature reported in literature and so degradation can be prevented if PAN is processed at this temperature.

Table 3.1, Melting Point of PAN/ACN/H_2O Compositions

PAN:ACN: H_2O (wt% ratio)	Tm °C
70:15:15[a]	134
70:0:30[b]	160
80:20:0[b]	146
80:0:20[a]	156

3.4.2 Time-Dependent Viscosity Results

It is very difficult to track and quantify the degradation of polyacrylonitrile with plasticizers by using a chemical analytical method, such as NMR, due to two major reasons. First, the degraded PAN copolymer cannot be dissolved in any organic solvent which is normally required in most chemical analysis. Second, most chemical analytical instruments are not designed for a pressurized environment, which could cause the loss of plasticizers during the measurement. In this case, time-dependent viscosity measurements are considered as an effective method to track the extent of degradation of PAN copolymer. In this study, time-dependent viscosity measurements were used to determine how long the PAN copolymer could stay at a certain temperature without degradation. Specifically, the viscosity of PAN significantly increases once it starts to degrade because the copolymer cannot be melted when the degradation occurs. Hence, how long the viscosity can be held stable is considered as the length of time the copolymer is stable without degradation. The experimental conditions and methods were explained in the previous section (The experimental shear rate was 130 s^{-1} for all time dependent measurements).

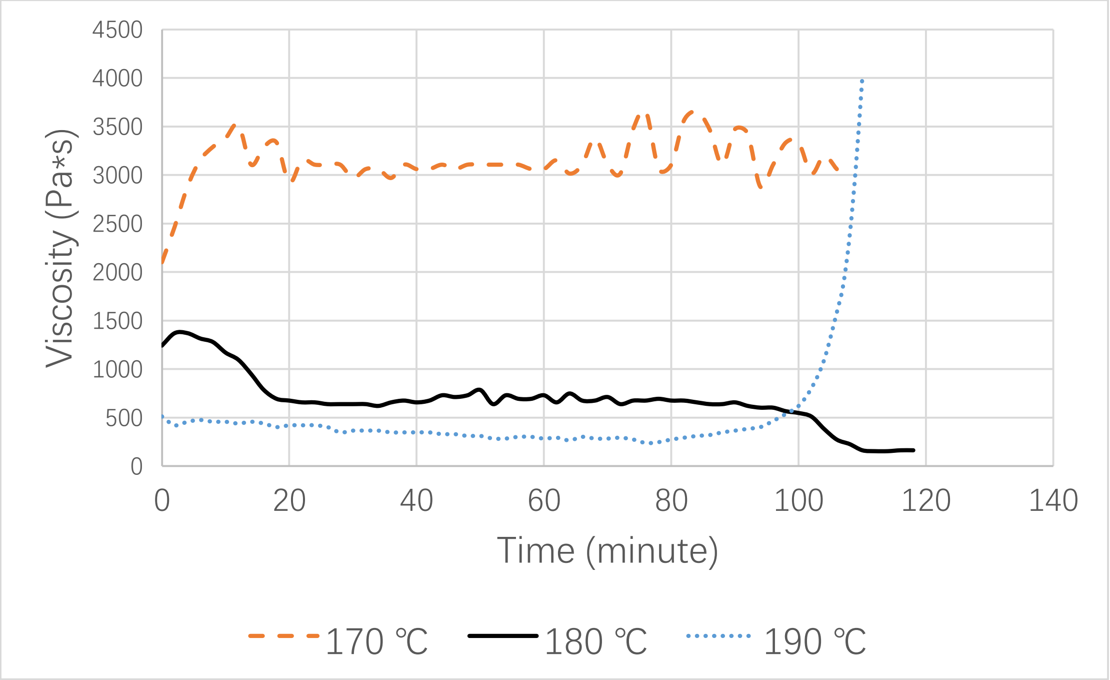

Figure 3.2, Time-Dependent Viscosity Data for AN/MA-H_2O (70/30 wt%)

In Figure 3.2 it is presented the time-dependent viscosity results of the PAN copolymer melt plasticized with 30 wt% of water from 170 ºC to 190 ºC. The magnitude of viscosity decreases with an increase of processing temperature. The viscosities are close when the samples are processed at 180°C and 190°C, which range from 300 to 700 Pa*s when they are stable. On the other hand, the viscosity of PAN melt is much higher when it was processed at 170°C, which is around 3,000 Pa*s. This is because it is only 10°C above the T_m of this sample and PAN copolymer does not completely melt. Furthermore, the viscosity of the PAN melt increases after 100 minutes at 190°C, which indicates the degradation of the PAN copolymer. There is no significant viscosity increase at 170°C and 180°C, which means this sample can be kept stable for around at least 100 minutes and 120 minutes, respectively, at 170°C and 180°C without significant degradation. However, the magnitude of viscosity is very high at 170°C. This is because it is too close to the melting point of this sample (160°C). Also the viscosity is not stable at this temperature and the oscillation of viscosity is possibly due to the incomplete melting of polymer.

In Figure 3.3 is presented the time-dependent viscosity results of the PAN copolymer melt plasticized with 20 wt% of water from 170°C to 190°C. Compared to the 30 wt% water sample presented at Figure 3.2, it is similar in that the viscosity of the PAN melt decreases with an increase of temperature, and the viscosity of this sample at 170°C is much higher than at 180°C and 190°C. However, this sample degrades at both 180°C and 190°C, and the copolymer can only remain stable for around 70 minutes at 180°C and around 30 minutes at 190°C.

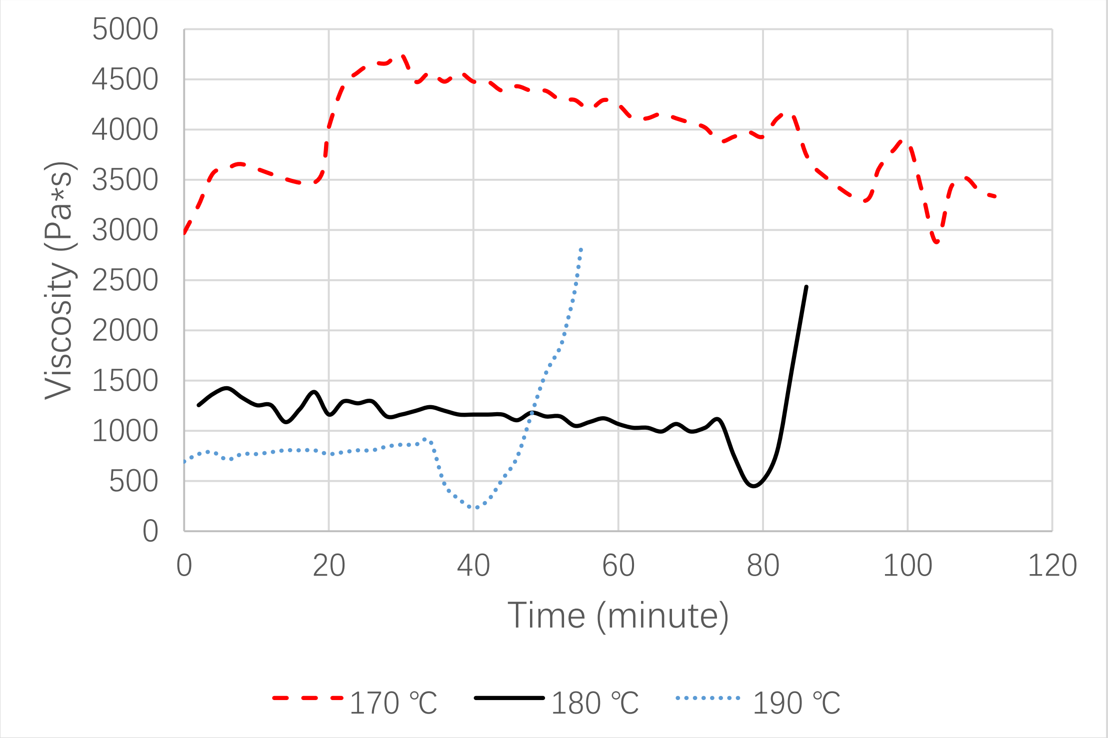

Figure 3.3, Time-Dependent Viscosity Data for AN/MA-H_2O (80/20 wt%)

In Figure 3.4 is presented the time-dependent viscosity results of the PAN copolymer melt plasticized with 20 wt% of acetonitrile (ACN) from 160°C to 190°C. This sample starts to degrade at 175°C, and it degrades much faster than the samples plasticized with water. Also the magnitude of the viscosity does not follow the temperature. At 190°C. The viscosity is very high and increase sharply in 30 minutes, which indicates that the PAN copolymer may already start to degrade during the 15 minutes of melting time in the barrel.

As mentioned in the previous section, the experimental temperature of the rheological tests should be at least 10 to 15 °C above the melting point of the copolymer sample, otherwise the viscosity will be too high to melt process the copolymer. This explains why the PAN-ACN-H_2O (70/15/15 wt%) system can be tested at 160°C (T_m=146 °C) and the PAN-H_2O (80/20 wt%) sample can only be tested at 170 °C as the lowest experimental temperature (T_m=156 °C).

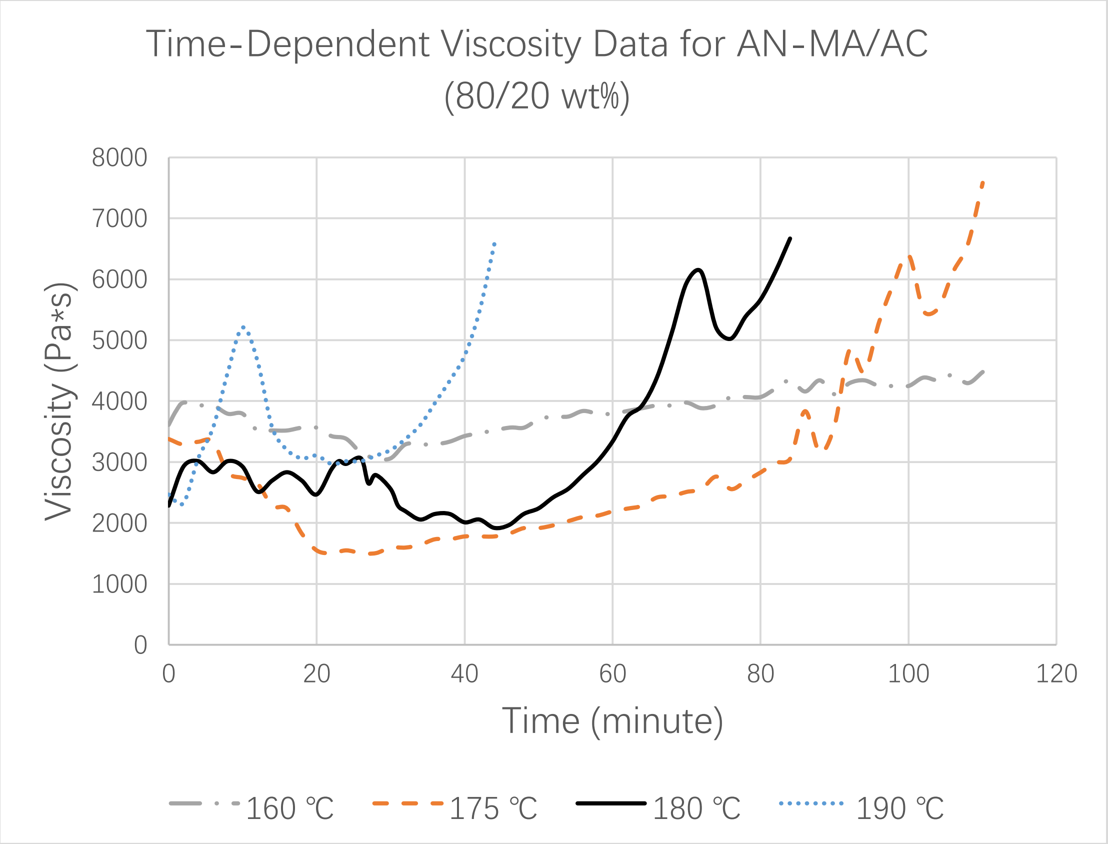

Figure 3.4, Time-Dependent Viscosity Data for AN/MA-ACN (80/20 wt%)

The major purpose of the time-dependent viscosity measurements is to track the degradation of the PAN copolymer samples. The polymer does not melt while it starts to degrade. In this case, a sharp increase of viscosity can be considered as a signal indicating degradation of PAN. The time-dependent viscosity results indicate that PAN will suffer degradation if the processing temperature is over 180℃, The only exception is for PAN-H_2O with 70-30 wt% ratio at 180℃, where the viscosity of this sample does not significantly increase in 120 minutes, which indicates it did not degrade in this period. Also, the data show that the PAN copolymer always degrades faster at a higher temperature. For example, with 20 wt% of water, PAN started to degrade after around 40 minute at 190℃ and 80 minutes at 180℃.

Figure 3.5 contains the time dependent viscosity results of the PAN copolymer with different plasticizers at 180℃. This plot directly shows how the variety and content of plasticizers influence the stability of PAN. There are two major indications in this figure. First, the presence of water can postpone the degradation of PAN. The PAN copolymer started to degrade after 40- 45 minutes without any water (ACN only 80/20). It started to degrade after around 70-80 minutes with 15 to 20 wt% of water and did not degrade after 120 minutes with 30 wt% of water. Second, the presence of water lowered the viscosity of the PAN melt. For example, with 20 wt% of water, the viscosity of the PAN melt was around 1,200 Pa*s. However, with 30 wt% of water, the viscosity is significantly reduced to around 600 Pa*s. Also, ACN could not decrease the viscosity of the PAN melt as much as water. With 20 wt% of ACN, the viscosity of the PAN melt is around 2,500 Pa*s.

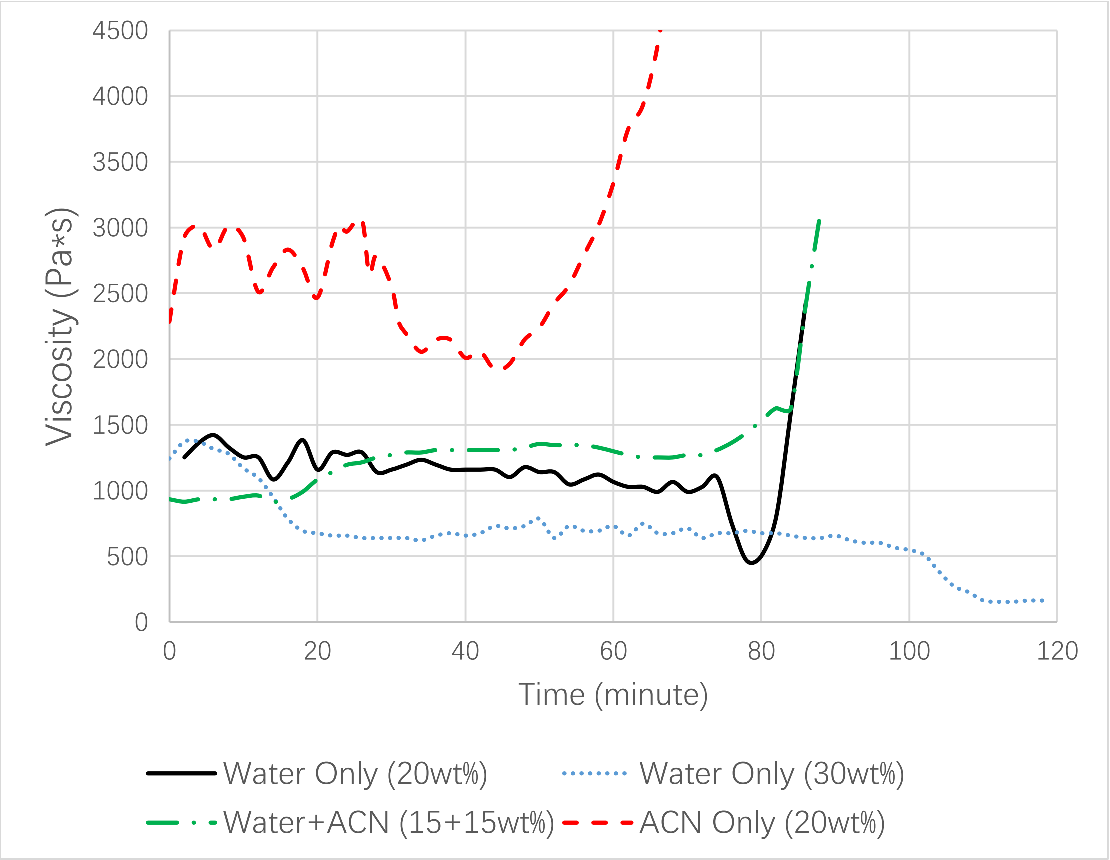

Figure 3.5, Time-Dependent Viscosity Data for Comparison at 180°C

It may be noticed that the viscosity slightly decreased before it degraded for most cases. The reason is still unclear. One possible explanation is while the copolymer sample started to degrade, the polymer and plasticizer may separate and divide into several different phase layers inside the rheometer (plasticizer fluid phase, polymer fluid phase and degraded polymer phase). In this case, the plasticizer layer, which has a relatively low viscosity, is the bottom layer and can be extruded through the capillary. The viscosity was actually measured on this layer, which caused the reduction of the viscosity.

The time-dependent viscosity curves sometimes oscillated in a small viscosity range especially at relatively low temperature. These instabilities are due to two reasons. First, the time-dependent viscosity measurements were conducted at a relatively low shear rate ($131s^{-1}$), in which the capillary system tend to become less stable with such a low shear rate. Second, the copolymer sample might not completely melt if the processing temperature is close to the melting point. In this case, the fluid is not homogeneous, which also lead to the viscosity instability.

In general, the time dependent viscosity results indicate that degradation will start at 175°C to 180°C, which agrees with results in the literature (M. Bortner, 2004; Rahaman et al., 2007; Xue et al., 1997). On the other hand, the viscosity of the material will be too high for melt processing at 170°C if water only is used as the plasticizer. In future extrusion work, one potential option is to use 30 wt% of water at the processing temperature of 180°C, in which the PAN copolymer is stable for over 120 minutes with an acceptable viscosity magnitude and without significant degradation.

3.4.3 Steady Shear Viscosity Results

The steady shear viscosity experiments are the traditional rheological measurements in which the viscosity is measured in terms of shear rate. This measurement is also essential in the PAN melt spinning process. In the real extrusion and spinning processes, the shear rate is around 1000 s^{-1} rather than the low shear rate that was used in the time-dependent viscosity measurements. The steady shear viscosity results could also provide information to help further calculate the residence time distribution, which is a key factor in the extrusion process.

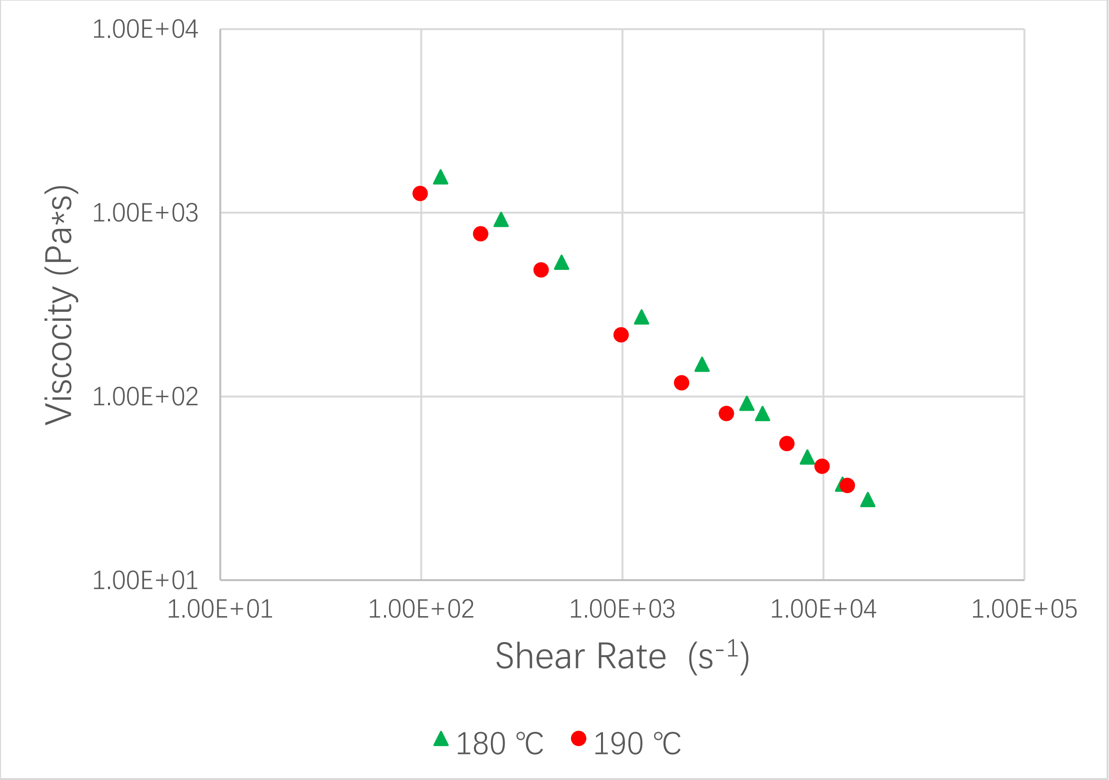

Figure 3.6, Steady Shear Viscosity Data for AN/MA-H_2O (80/20 wt%)

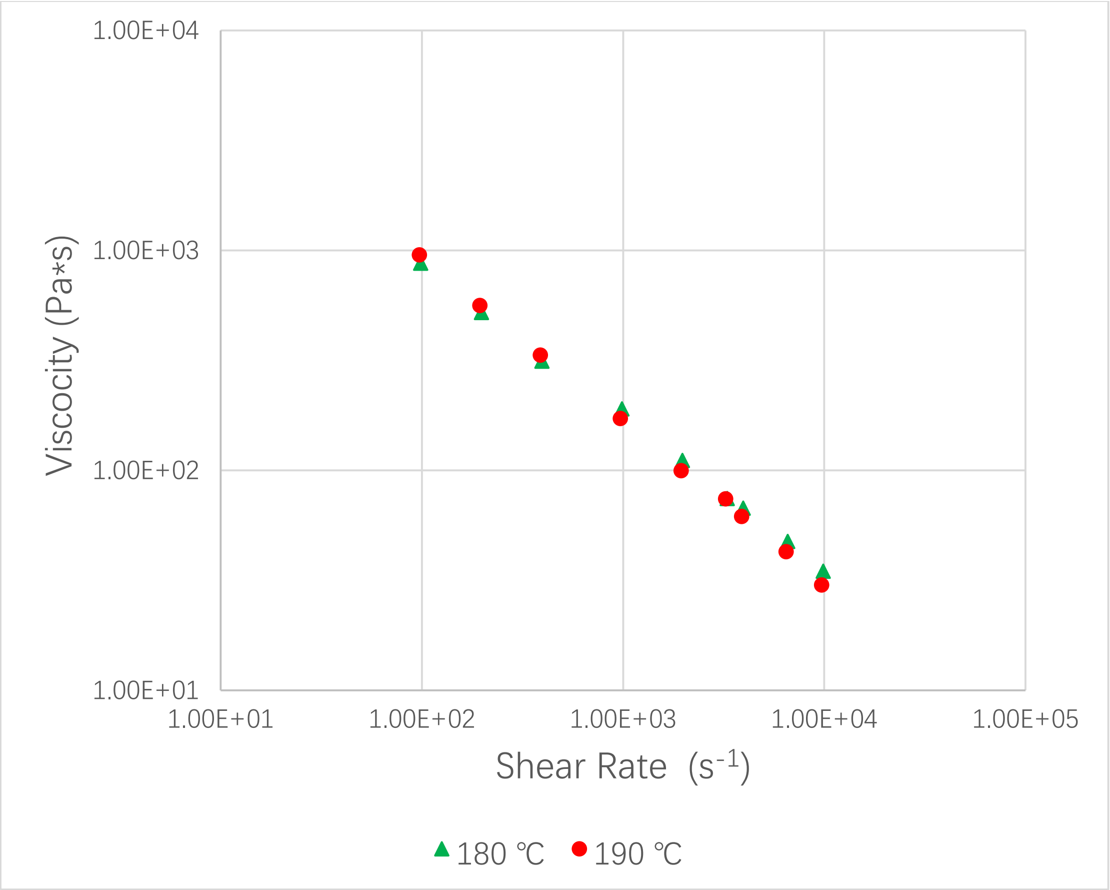

Figure 3.7, Steady Shear Viscosity Data for AN/MA-H_2O (70/30 wt%)

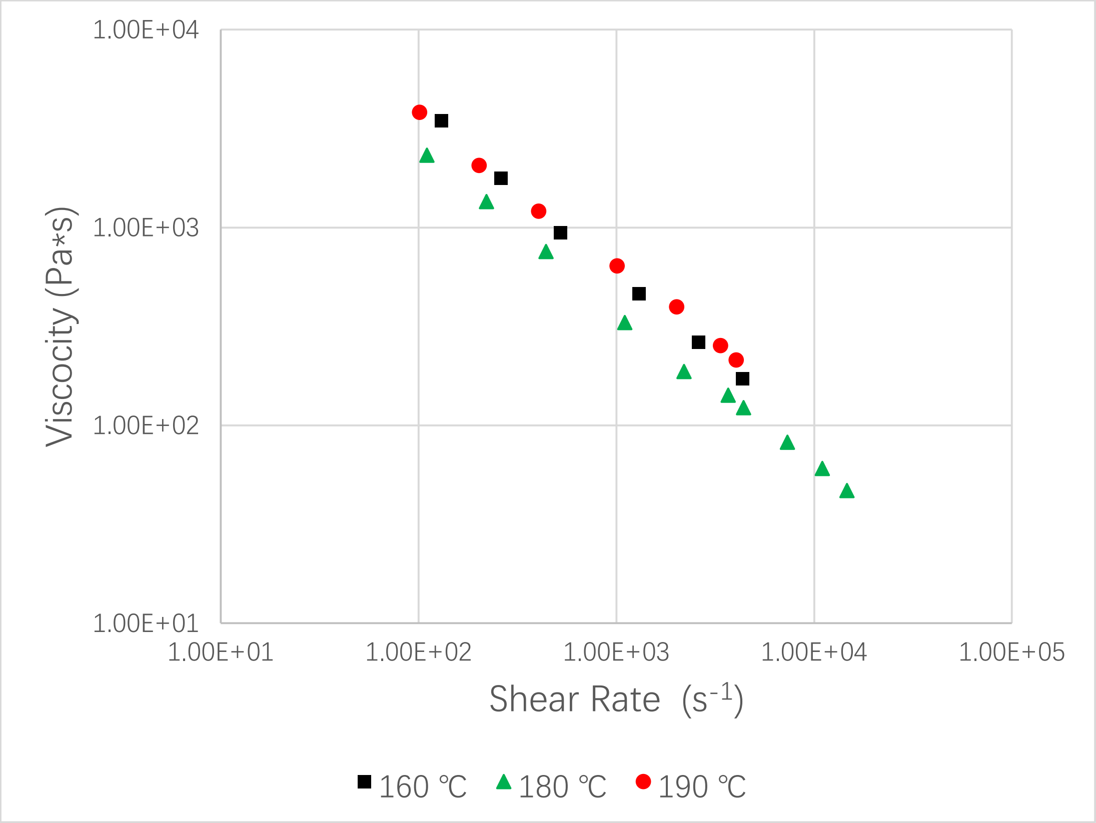

Figure 3.8, Steady Shear Viscosity Data for AN/MA-ACN (80/20 wt%)

Figure 3.6 and 3.7 present the steady shear viscosity data for PAN-H_2O system with two different weight ratios and Figure 3.8 presents the steady shear viscosity data for PAN-ACN mixture. The experimental temperature is determined from both melting point results and time-dependent viscosity results. These results indicate the shear-thinning behavior of the polymer samples, and all data curves can be fitted in a linear regression in the natural log base, which indicate the curves can be described by the power law model.

Once PAN had been melted completely, the viscosity did not decrease with the increase of temperature. For example, there is no significant difference in viscosity between 180°C and 190°C for the PAN-H_2O as the temperature was at least 20°C higher than the melting point (where the polymer is considered as "completely melted") On the other hand, at Figure 3.8, the viscosity of PAN-ACN at 160°C is much higher than at 180°C, in which the polymer is too close to its melting point of 160°C. One thing needs to be noticed here and that is the viscosity at 190°C is also higher than at 180°C as shown in Figure 3.8. It actually matched the time-dependent viscosity data displayed in Figure 3.4 As we discussed in section 3.2, the reason of a relative high viscosity of this sample (PAN-ACN) at 190°C was possibly due to the low stability. That means, the polymer may start to degrade even within the 25-30 minutes heating and melting period and cause the relatively high viscosity.

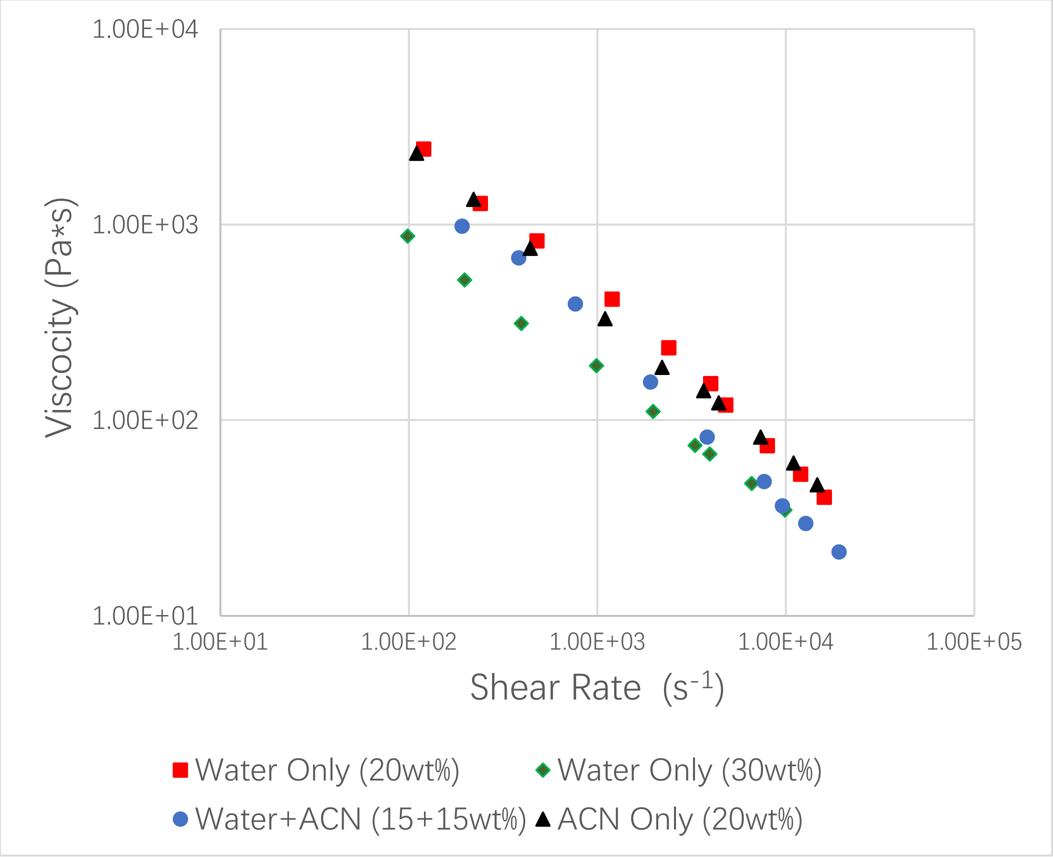

Figure 3.9, Steady Shear Viscosity Data for Comparison at 180℃

Figure 3.9 shows the steady shear viscosity data of PAN-plasticizer mixtures at the same temperature. This plot indicates that the higher percentage of plasticizer in the system may cause the lower viscosity of the PAN copolymer melt. Furthermore, the viscosity difference is more significant and obvious at the low shear rate range as these viscosity curves tend to merge with the shear rate increase. As we mentioned in the previous section, the normal wall shear rate for the extrusion process is around several thousand reciprocal seconds, where the viscosity is around 100 Pa*s with appropriate plasticizers.

Power-law constants were calculated based on the steady-shear viscosity data. The values ranged from 0.15-0.25. Because the constant values were greater than zero, so there should no slip during the rheological measurements.

In general, the steady-shear viscosity results provided information of how the viscosity curves are influenced by various plasticizers and composition. It also provides basic rheological data of the PAN melt, which no one has reported before. These results could be used to design the extruder and the PAN melt spinning system.

3.5 Conclusions

The melting point results indicate that the melting point of polyacrylonitrile can be reduced to below 180°C with proper plasticizers and provide the potential condition by which PAN may be melt spun without significant degradation. The time-dependent viscosity results show that the PAN copolymer will start to degrade around 180°C, and the degradation rate is highly depending on the plasticizer types and compositions. Also, the processing temperature should be at least 15 to 20°C above the melting point of the sample to ensure the polymer is completely melted. The steady–shear viscosity results provide the basic rheological data for the processing of the PAN melt. It indicates the shear-thinning behavior of the copolymer mixture. Furthermore, it shows the viscosity would decrease with a higher plasticizer content.

By taking all the data presented in this paper into consideration, AN-MA/H_2O (70/30 wt%) as plasticizers at 180°C is considered the most appropriate material and composition for use in the PAN melt spinning process. This is due to three reasons. First, it does not contain any other plasticizers except water, and, hence recovery and collecting systems are not needed. This could reduce spinning costs significantly. Second, the time-dependent viscosity data indicates this sample can be spun for over 120 minutes without significant degradation with a reasonable viscosity. Third, the viscosity of this sample is lower than that of the other samples due to the presence of the extra water, which is desired in the extrusion process. Overall, we believe with the appropriate material and composition described above, water only is potentially able to be used as plasticizer to melt spin PAN fibers. In this case, acetonitrile can be eliminated from the PAN fiber spinning process and the cost of the process can be significantly reduced.

3.6 Acknowledgement

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Chapter 4 Study of Melt Spinning Processing Conditions for a Polyacrylonitrile Copolymer with a Water/Ethanol Mixture as a Plasticizer

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4.1 Abstract

This paper is concerned with the feasibility of melt spinning of polyacrylonitrile (PAN) copolymer (acrylonitrile/methylacrylate 95.6/4.4 mol% ratio) plasticized with water-ethanol (EtOH) mixtures. The melting point and rheological and stability behaviors of PAN/water/ethanol mixture are reported. The objective is to determine whether this mixture is appropriate for allowing the PAN to be melt spun. The melting point results from differential scanning calorimetry show the T_m of PAN/water/ethanol (70/15/15 wt%) mixture can be reduced to 150 ^{o}C from 300 ^{o}C. The time-dependent viscosity results showed that this mixture can be processed at 170 ^{o}C for more than 100 minutes without degradation. The steady-shear viscosity results indicated the shear-thinning behavior is observed for this mixture at a temperature ranging from 170 ^{o}C to 190 ^{o}C. These rheological data are also highly similar to the reference condition and other potential conditions reported in our previous paper, which indicates PAN/water/ethanol (70/15/15 wt%) at 170 ^{o}C is a

potential condition for PAN melt spinning. The scanning electron microscopy diagrams show the copolymer strand melt extruded from PAN/water (70/30 wt%) mixture contains many more voids and bubbles than the PAN/water/ethanol (70/15/15 wt%) system. In conclusion, PAN/water/ethanol (70/15/15 wt%) at 170 ^{o}C is the most benign set of condition (i.e. the composition and temperature) for carrying out the PAN melt spinning process.

4.2 Introduction

Polyacrylonitrile (PAN) fiber is one of the most important synthetic fibers as it is a precursor to carbon fiber. Approximately 90% of carbon fiber is generated from PAN fiber. These PAN-based carbon fibers are widely used in aerospace, automotive and sporting-goods industries. Comparing to other common materials like aluminum and steel, PAN-based carbon fiber has advantages such as low density, high strength and high thermal stability. Normally, polyacrylonitrile is a copolymer of high acrylonitrile (AN) content and a second monomer, such as methyl acrylate (MA) or vinyl acetate (VA). AN/VA copolymer is commonly used in the textile industry and AN/MA copolymer is used to generate carbon fiber. The AN/MA copolymer for generating carbon fiber needs to contain at least 93 wt% of AN. (Cato & Edie, 2003; Frank, Hermanutz, & Buchmeiser, 2012; Odian, 2004; Rahaman, Ismail, & Mustafa, 2007, Daumit, Ko, Slater, Venner, & Young, 1990, 1992).

The PAN fiber spinning process is essential during the production of carbon fiber. Solution spinning is the major process and it requires the use of a large amount of organic solvents, such as N,N-dimethylformamide (DMF) or N-N dimethyl acetamide (DMAC), which need to be collected after the spinning process, which leads to a high cost of the process. Melt spinning, however, does not require these organic solvents be involved in the process. According to a report from Oak

Ridge National Lab, using the melt spinning process instead of solution spinning can reduce the price of carbon fiber from \$11 per pound to \$7 per pound (Paulauskas, 2012).

The main challenge in the use of PAN melt spinning is the high melting point (T_m) of PAN. Krigbaum and Tokita (1960) reported the melting point of pure PAN is around 320 °C. However, PAN starts to suffer exothermic reactions such as cyclization and crosslinking reactions at 180 °C. These reactions are also considered as “degradation reactions” of PAN copolymer. Once PAN copolymer starts to degrade, it is not able to melt nor dissolve in any solvent. In this case, in order to melt PAN before its degradation, the melting point of PAN needs to be reduced. (M. Bortner, 2004; Rahaman et al., 2007; Xue, McKinney, & Wilkie, 1997)

Plasticizers are normally used to reduce the melting point of polymers. Some studies have been conducted on the use of plasticizers for PAN and their use in the PAN melting spinning process. Coxe (1952) is the pioneer of using water as a plasticizer for melt spinning PAN. He successfully reduced the melting point of PAN to below 200 °C. However, he failed to melt spin PAN due to the foaming problem. Porosoff (1979) improved the process from Coxe’s work by attaching a pressure chamber to the spinning system. His innovation efficiently prevented the evaporation and foaming of the plasticizers during the spinning process. Daumit et al. (1992) at BASF claimed in their patent that using acetonitrile (ACN) as a second plasticizer (in addition of water) can further decrease the melting point of PAN to around 135 °C. They also designed a pressurized system and claimed they successfully melt spun PAN fiber. However, because acetonitrile is not environmentally-friendly and carcinogenic, acetonitrile is required to be collected after the melt spinning process. This collection process is as costly as collecting DMF and DMAC. Therefore, due to the economic considerations and the change of world’s demand of carbon fiber, this innovation was never commercialized. (Paulauskas, 2012)

We have already published two preliminary ariticles in this study. Miller et al. (2017) reported the chemical and thermal analysis of AN/MA copolymer along with some of the rheological data of AN/MA-water-acetonitrile and AN/MA-water-adiponitrile systems. Yu et al. (2019) further reported melting points, rheological behavior and stability behaivior of AN/MA with various water-based plasticizers. We also proposed several conditions that are potentially appropriate for PAN melt spinning based on these data. This paper is concerned with efforts to develop a plasticizer system that will allow the economical melt spinning of PAN.

In this paper, we focus on the study of AN/MA-water-ethanol mixture. We are trying to determine the possbility of using ethanol as the second plasticizer instead of acetonitrile. Ethanol is seletced mainly because of two reasons, The first is that it has some properties similar to acetonitrile. Both of them have a lower boiling point than water, both of them are polar and both form an azeotrope with water. The second is to compare its behavior to acetonitrile as ethanol is much cheaper and safer than acetonitrile. Acetonitrile is carcinogenic and needs to be treated with extrame caution. So the use of ethanol instead of acetonitrile could reduce the cost of the process.

4.3 Experimental

4.3.1 Material and Sample Preparation

The same copolymer material was used as described in our previous paper (Yu et al., 2019). Specifically, the polymer sample used was poly (acrylonitrile-ran-methyl acrylate) (AN/MA) which is composed of 95.6 mol% of acrylonitrile and 4.4 mol% of methyl acrylate (AN/MA). The molecular weight values of the copolymer sample are M_n = 123.1 kDa and M_w = 238.2 kDa. This copolymer material was provided by Fisipe and used as received. The ethanol (EtOH) used in this study was anhydrous and was purchased from Fisher Scientific.

The same sample preparation method was used as described in our previous paper as well (Yu et al., 2019). The PAN copolymer was mixed with plasticizers in a desired ratio before being placed into a conventional oven and heated at 50-60 ^{o}C for around 2 hours in a sealed container. Then the container was held at room temperature over-night to homogeneously disperse the plasticizers into the copolymer powder.

4.3.2 Rheological Measurements

Basically, the same instruments and techniques which were reported in our previous paper were used (J. Huang & Baird, 2014; Yu et al., 2019). Two types of rheological measurements were conducted: time-dependent viscosity and steady-shear viscosity measurements. In the time-dependent viscosity measurements both the temperature and shear rate were kept constant and the viscosity was measured in terms of time. In steady shear viscosity measurements, temperature was kept constant and the viscosity was measured in terms of several shear rates. The temperature range of these rheological measurements was from 170 ^{o}C to 190 ^{o}C. The shear rate was kept at 135s^{-1} during the time-dependent viscosity measurements and ranged from 100s^{-1} to 15,000s^{-1}.

Both types of rheological measurements were conducted on a modified Instron model 3211 capillary rheometer with a pressure chamber attached. The pressure chamber provided 1.38MPa (200 psi) of nitrogen to the exit of the capillary rheometer during all rheological measurements in order to prevent the evaporation and foaming of the plasticizers. The capillary die used had a length of 25.6mm, diameter of 0.35mm (L/D=73) and entrance angel of 90^{o}. With such a large L/D value, the entrance effect could be neglected. The diameter of the rheometer barrel was 9.53mm and the speed of the plunger could be varied from 0.06 mm/min to 6 mm/min. Shear rate could be obtained from these parameters and the Rabinowitch correction was applied to the calculation of the viscosity.

The copolymer samples were in “powder” form when loaded into the capillary rheometer at room temperature. Then the entire system was sealed and pressurized before being heated to the target temperature. This process could prevent the loss of plasticizers during the loading. The heating to the desired experimental temperature took around 25 to 30 minutes.

4.3.3 Differential Scanning Calorimetry and Scanning Electron Microscopy

The experimental method and instrument for differential scanning calorimetry (DSC) was the same as described in the previous paper as well (Miller et al., 2017; Yu et al., 2019). Specifically, the copolymer samples were placed in high volume pans with O-rings in order to seal and prevent loss of plasticizers. The copolymer samples were heated in a nitrogen environment from room temperature to 200℃ at a rate of 10 ^{o}C /min and then cooled at a rate of 10 ^{o}C /min to 0 ^{o}C and heated again to 240 ^{o}C at the same rate. The instrument used for the DSC tests was a TA Instruments DSC Q200.

The scanning electron microscopy (SEM) images were obtained from a LEO (Zeiss) 1550 field-emission device. The copolymer strands were obtained from the capillary device during the time-dependent viscosity measurements. The copolymer strands were in the diameter range of 1 to 1.5mm and were cryofractured in liquid nitrogen before being cut into small pieces. The cross sections of the strands then were scanned in multiple magnification ranges from 250X to 50,000X.

4.4 Results and Discussion

4.4.1 Melting Point Results

The melting points, T_m, of the polyacrylonitrile copolymer-plasticizers compositions were significant because they were able to provide the minimum temperature of the rheological tests and melt spinning process. They also provided the temperature range of the rheological tests. The values of T_m for various compositions are summarized in Table 1. The DSC data in Table 1 indicates that the combination of ethanol and water as a plasticizer can further reduce the melting point of PAN compared to pure water by 5-10^{o}C, which makes PAN capable of being melt spun and processed at a lower temperature and thus reduce the degree of degradation. However, the ethanol itself was not considered as a plasticizer for PAN, because it did not efficiently reduce the melting point of PAN. Sample 3 in Table 1 was not considered as an appropriate combination either because its melting point was very close to the degradation temperature of PAN (around 180 ^{o}C). In this case, only Sample 1 is an appropriate combination for carrying out further rheological experiments and assessing the possibility of melt spinning.

Table 4.1, Melting Point of the Polyacrylonitrile Copolymer-Plasticizers Compositions

Sample Number	PAN:EtOH: H_2O (wt% ratio)	T_m °C
1[a]	70:15:15	150
2[a]	70:30:0	>190
3[a]	80:10:10	168
4[b]	80:0:20	156
5[b]	70:0:30	160

The letter "a" in the table indicates that the data is obtained in this work, and the letter "b" indicates the data is from our previous work (Miller et al., 2017; Yu et al., 2019).

In our previous paper it was reported that the melting point of PAN/ACN/H_2O with 70/15/15 wt% ratio is 134 °C (Miller et al., 2017). Comparing to those results, the ethanol-water combination is not as efficient as the acetonitrile-water combination as a plasticizer for PAN. This is because acetonitrile itself is considered as a good plasticizer and is able to reduce the T_m of PAN (to around 135 °C), but ethanol itself is not able to reduce the T_m of PAN. Based on that, we believe water is the key component in the plasticizer composition and ethanol is the "supplement" component that further reduce the T_m of PAN. The detailed chemical mechanism is still unclear, but it is believed that it could relate to the polarity of ethanol or the azeotropic property of water and ethanol.

4.4.2 Rheological Results of the PAN/EtOH/H_2O Composition

As described in the previous section, two types of rheological experiments were conducted in the capillary rheometer. The first one was the time dependent viscosity measurement, in which the viscosity measurement at a constant shear rate under various temperatures was carried out to times of over 100 minutes. The data are displayed in Figure 4.1. The time-dependent viscosity measurements were conducted at a constant apparent shear rate of 131 s^{-1}. At this shear rate, the magnitude of viscosity is relatively high. Data in Figure 4.1 show the viscosity of the PAN copolymer ranges from 700-1700 Pa*s before degradation. The magnitude of viscosity is very close at 170 °C and 180 °C, but it is significantly lower at 190°C compared to the other two other temperatures.

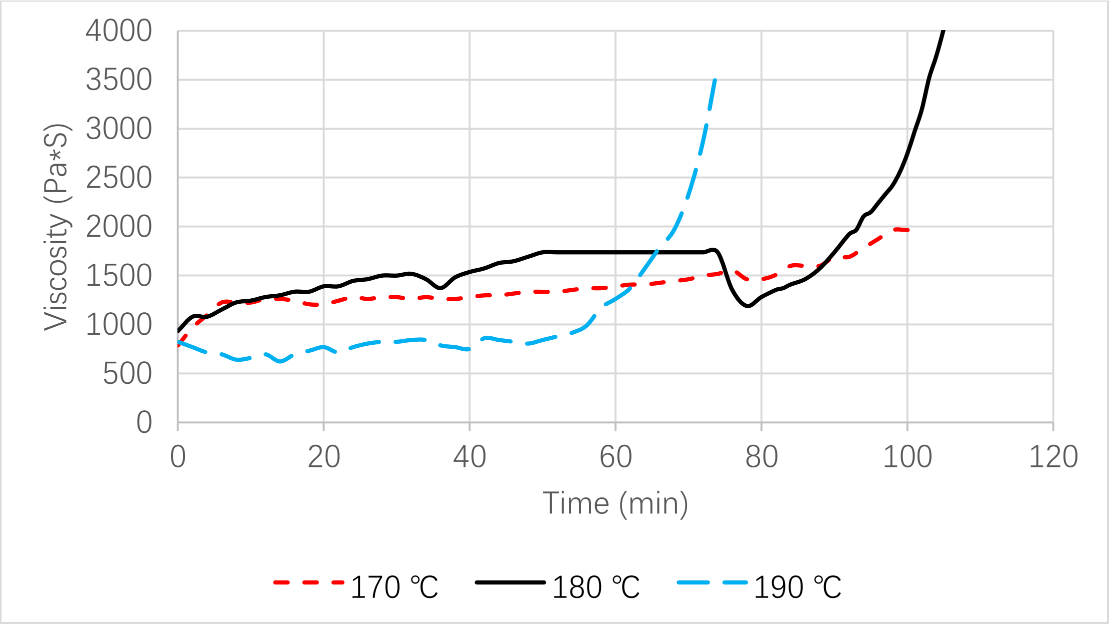


Figure 4.1, Time-dependent viscosity data for PAN/EtOH/H_2O (70/15/15 wt%)

The main purpose of conducting time-dependent viscosity measurements is to track the degradation of the PAN copolymer at a certain temperature. PAN is not able to melt once it started degrading, which leads to a rapid increment of the viscosity of PAN. In Figure 4.1 it presents the time-dependent viscosity data of PAN/EtOH/H_2O (70/15/15 wt%) composition at a temperature range from 170 ^oC to 190 ^oC. The data indicate the copolymer can maintain its stability without significant degradation for more than 100 minutes below temperatures of 170 ^oC, and it starts to degrade after 75 minutes and 55 minutes at temperature of 180 ^oC and 190 ^oC, respectively. This agrees with the theory that the degradation reaction occurs more rapidly with increasing temperature.

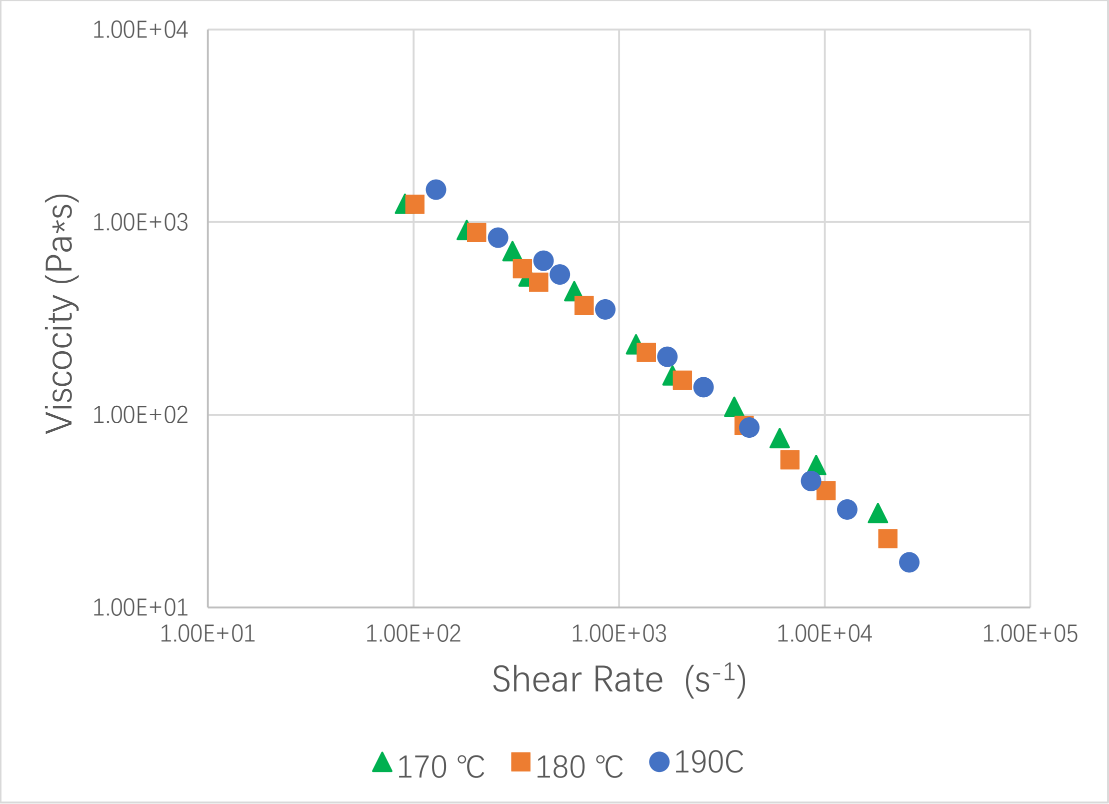


Figure 4.2, Steady shear viscosity data of PAN/EtOH/H_2O (70/15/15 wt%)

The second type of rheological measurement is the steady shear viscosity measurement. This is the classical rheological test in which the viscosity of the polymer melt is measured at various shear rates. By using a capillary rheometer, the shear rate can be varied from 10 to 50,000 s^{-1}. In this study, the shear rate ranged from $100s^{-1}$ to $15,000s^{-1}$. In Figure 4.2 it is shown the steady shear viscosity data of PAN/EtOH/H_2O (70/15/15 wt%) composition under temperatures ranging from 170^oC to 190^oC. The data indicate the rheological properties of this copolymer are not significantly affected by temperature, especially in the high shear rate range. In addition, the data indicate shear-thinning behavior is observed for this copolymer in this temperature range, and all data curves can be fitted to a linear regression curves, which means these curve can be modeled and described by Non-Newtonian models such as the power law empiricism.

Moreover, these rheological data can be used for the extrusion process design as well. For example, the steady-shear viscosity data can be used to calculate the residence time distribution (RTD) of the extrusion process. The time-dependent viscosity data provided the basic information of the stability of the copolymer, and the maximum allowed residence time during the extrusion. With this information, a benign melt spinning extrusion process can be designed.

4.4.3 Comparison of Rheological Results

The rheological results in Section 3.2 above indicate that using an ethanol-water mixture as a plasticizer at 170 ^oC (Composition 1) can be considered as a potential composition to achieve the PAN melt spinning process. In this section, the mixture is compared to two other compositions. PAN/H_2O 70/30 wt% at 180 ^oC (Composition 2) was proposed in our previous paper as a possible system to be used in PAN melt spinning (Yu et al., 2019). PAN/ACN/H_2O 70/15/15 wt% at 170 ^oC (Composition 3) is considered as the reference composition, and its rheological data were reported in another of our previous papers (Miller et al., 2017). The reason it is selected as a reference composition is because this composition was reported in BASF's patents ((Daumit, Ko, Slater, Venner, & Young, 1990, 1992) and BASF claimed that PAN could be successfully melt spun under this condition.

The comparison of the time-dependent viscosity data of these compositions is presented in Figure. 3. The trends of the data curves of these three compositions are very similar. All the three compositions are able to maintain their stability for at least 100 minutes, and the magnitudes of viscosity are in a reasonable range (under 2000 Pa*s). However, we notice that the viscosity of Composition 2 is lower than the other two compositions. One possible reason is that the presence of additional water in the composition makes the polymer melt less viscous.

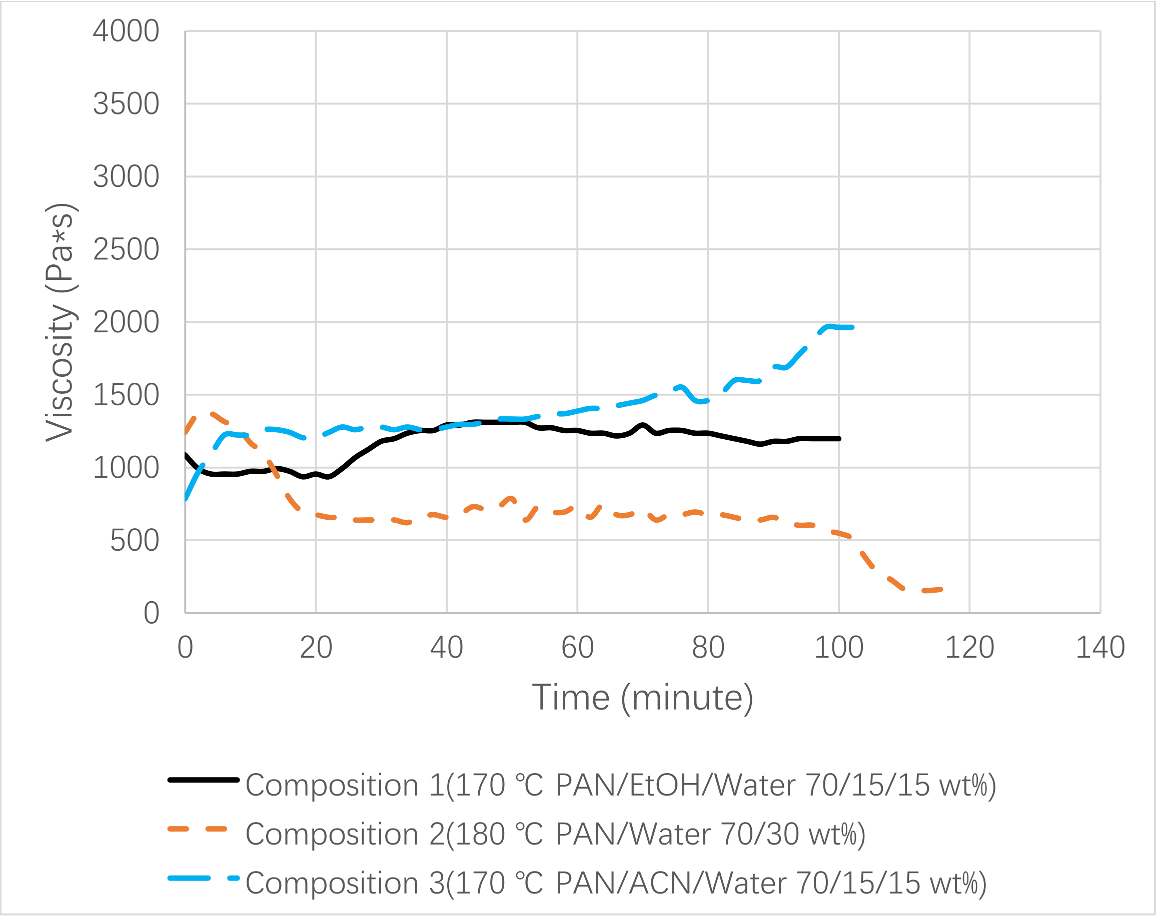


Figure 4.3, Comparison of the time-dependent viscosity data

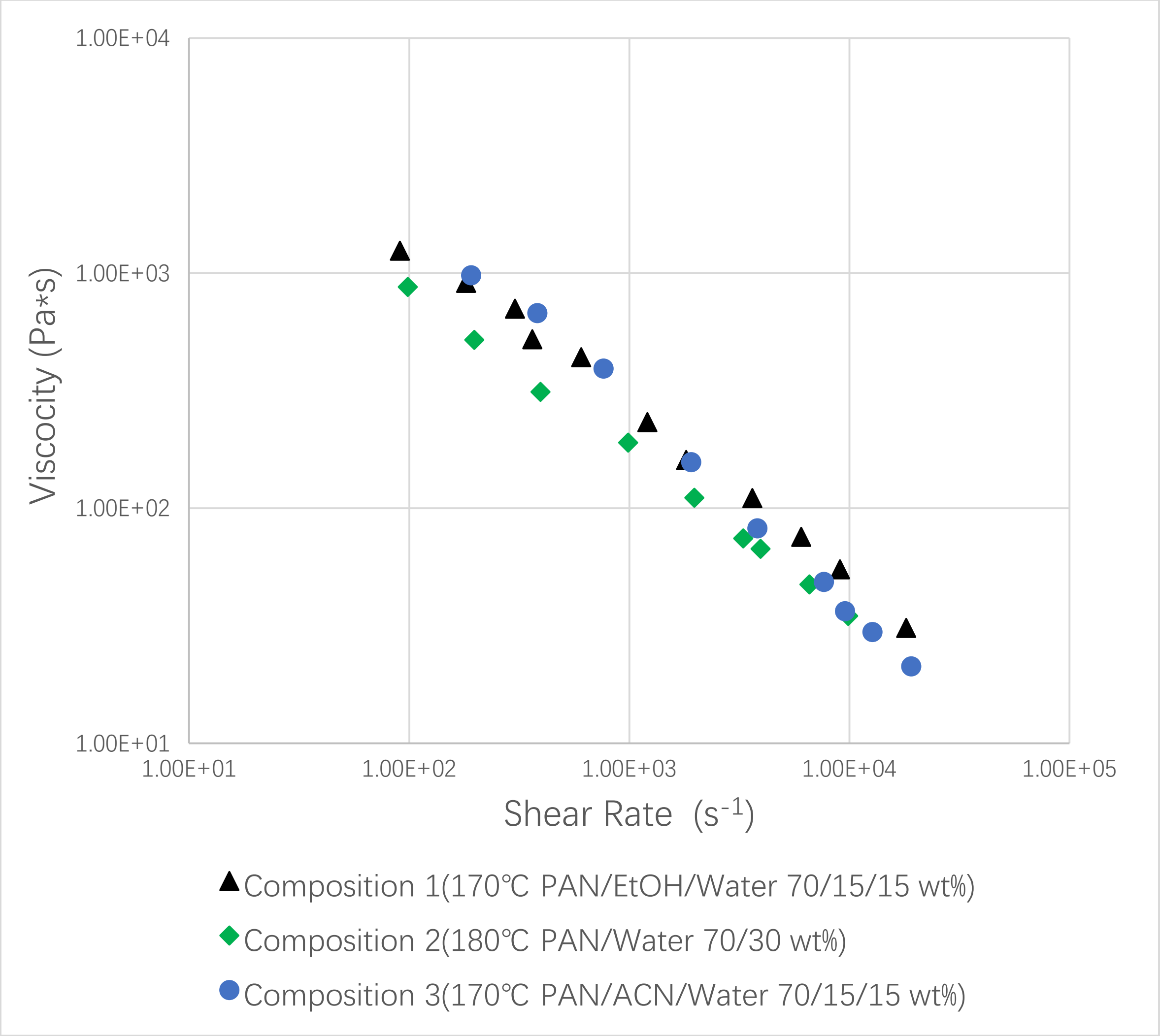


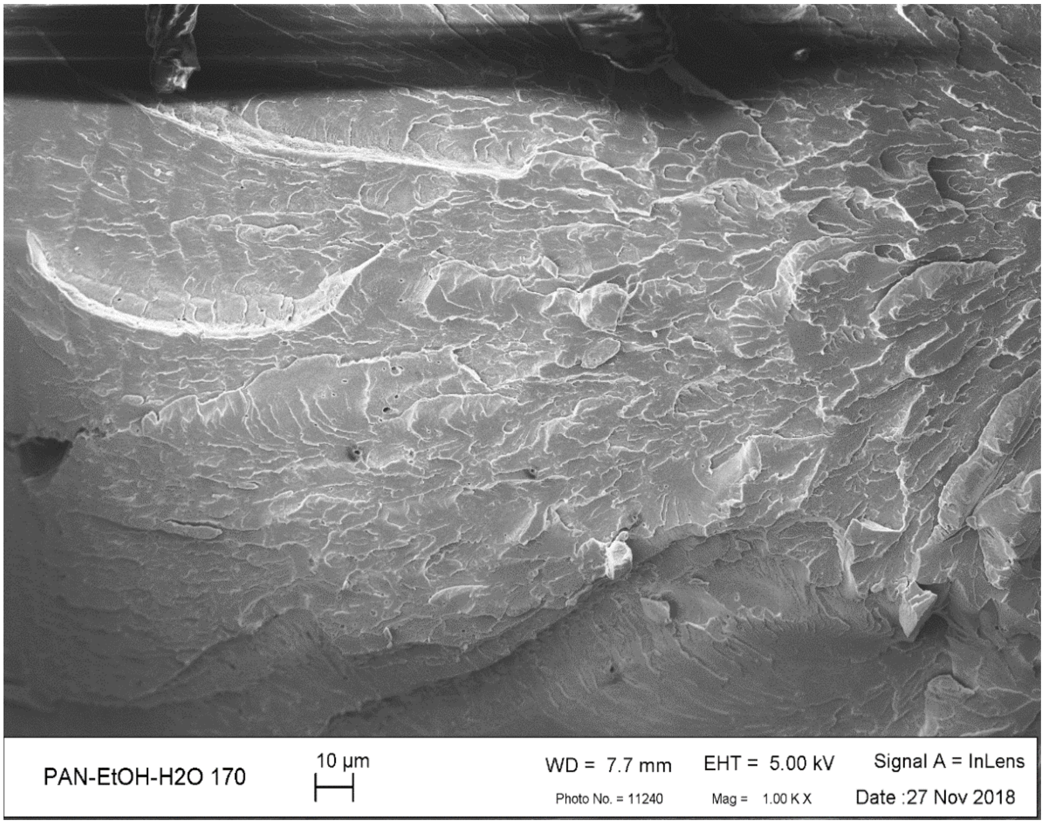
Figure 4.4, Comparison of the steady-shear viscosity data

In Figure 4.4 is shown the comparison of the steady-shear viscosity data for three compositions, which are similar to those described previously in Figure 4.2. The viscosity curves of Composition 1 and Composition 3 basically overlap, especially in the shear rate range of around 1,000 s^{-1}. This means Composition 1 and Composition 3 have very close rheological behavior.

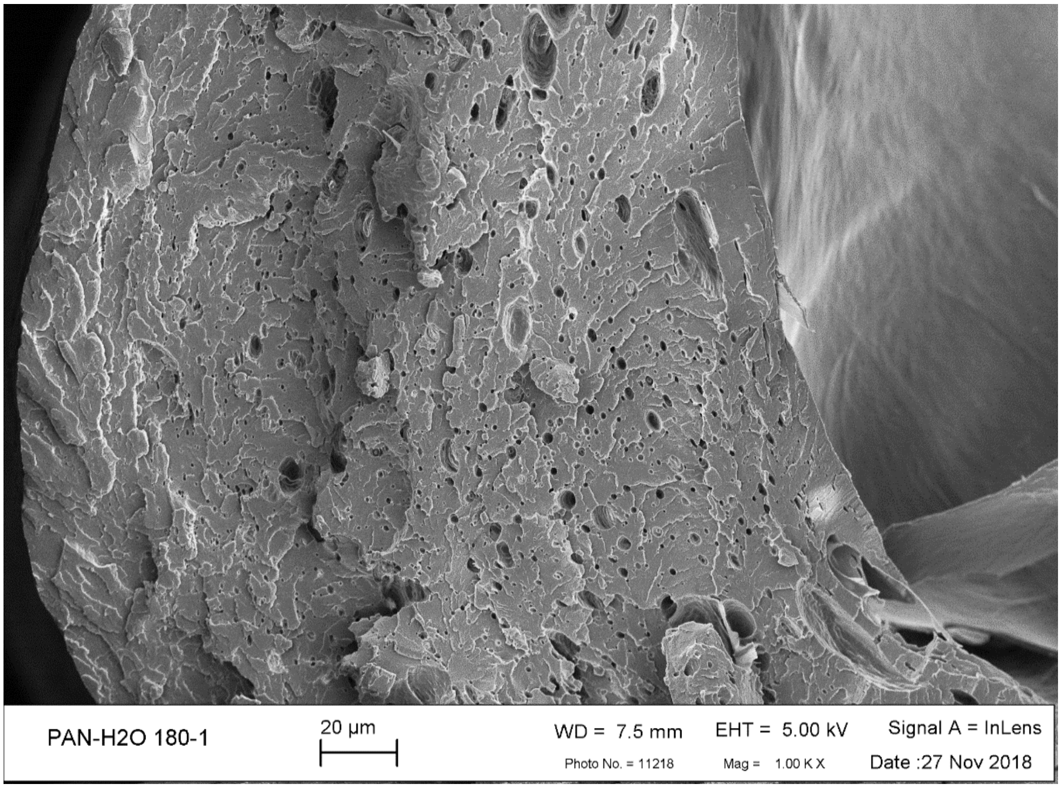
In conclusion, Composition 1 is promising for being considered as a potential composition of PAN for the use in the melt spinning process. Both types of viscosity data of this composition are very similar to the reference composition. Ethanol can be used to replace acetonitrile as a second plasticizer without significantly influence the rheological properties of PAN. In this case, it is worth conducting further studies on Composition 1.

4.4.4 Scanning Electron Microscope Results

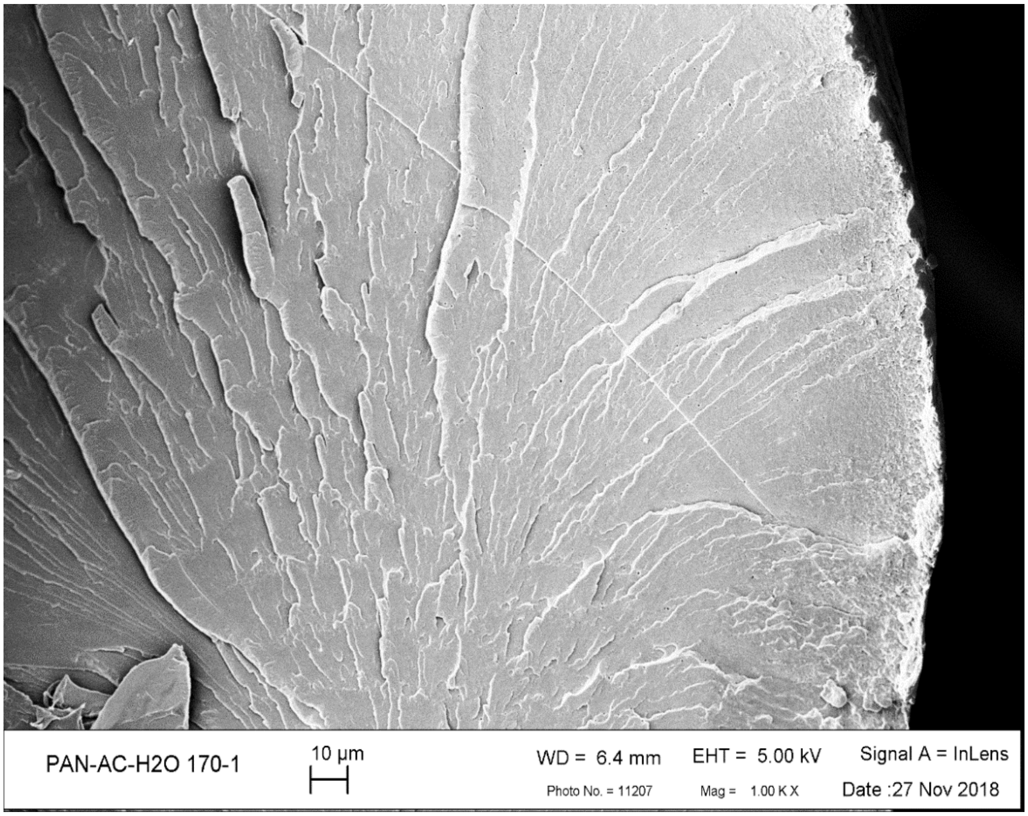
Scanning Electron Microscopy (SEM) is a technique that allows one to scan and take images of small surface, such as the cross-sectional area of a fiber. In this project, SEM was used to scan the cross-sectional surface of the copolymer strands that were extruded from a capillary rheometer into a pressure chamber of 200 psi, which was above the vapor pressure of the plasticizers. These copolymer strands were generated from the three compositions described in Section 4.4.3.


PAN-EtOH-H2O 170
10 µm
WD = 7.7 mm
EHT = 5.00 kV
Signal A = InLens
Photo No. = 11240
Mag = 1.00 K X
Date :27 Nov 2018

(a)

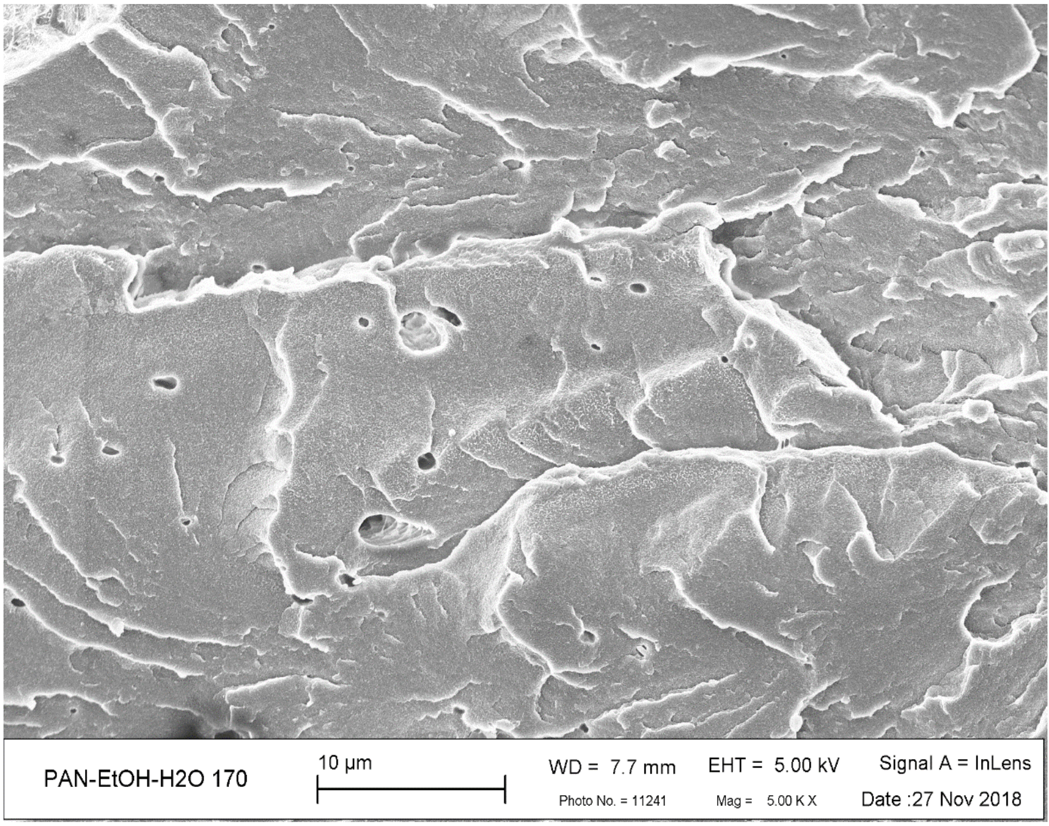

PAN-H2O 180-1
20 µm
WD = 7.5 mm
EHT = 5.00 kV
Signal A = InLens
Photo No. = 11218
Mag = 1.00 K X
Date :27 Nov 2018

(b)

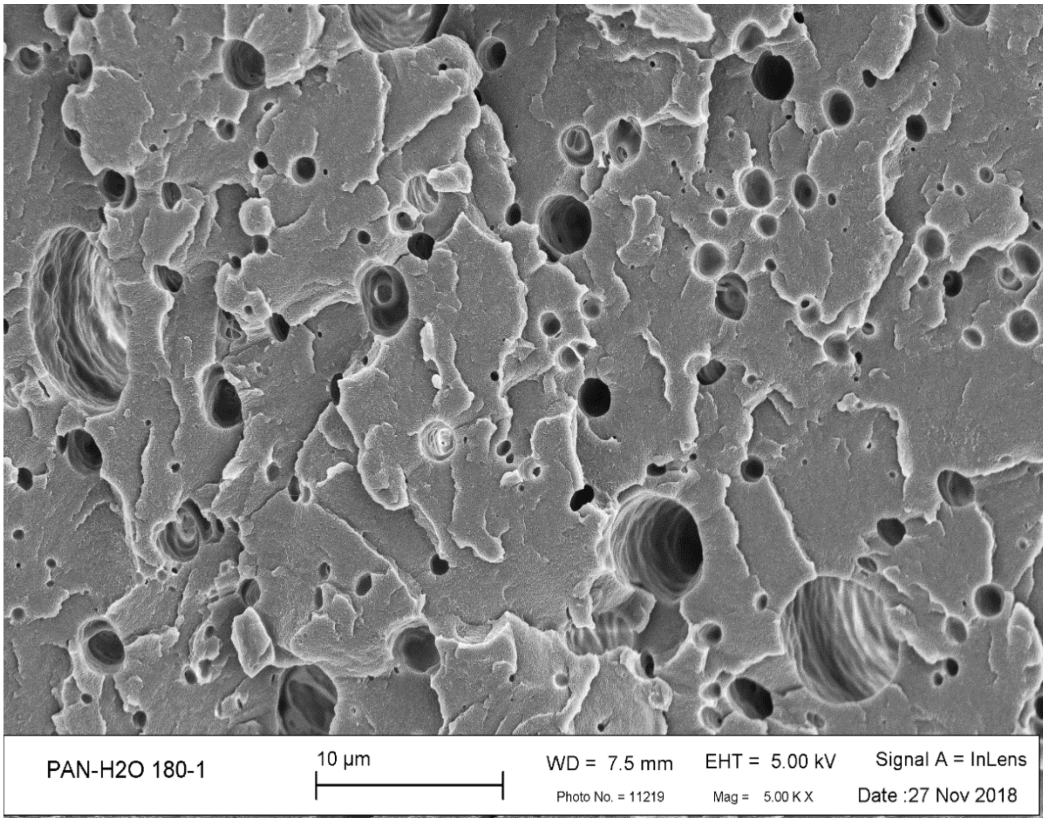


(c)

Figure 4.5, SEM images of the copolymer strands with 1,000X magnification extruded under three compositions: (a) PAN/EtOH/H_2O 70/15/15 wt% at 170 °C; (b) PAN/ H_2O 70/30 wt% at 180 °C; (c) PAN/ACN/H_2O 70/15/15 wt% at 170 °C


PAN-EtOH-H2O 170
10 µm
WD = 7.7 mm
EHT = 5.00 kV
Signal A = InLens
Photo No. = 11241
Mag = 5.00 K X
Date :27 Nov 2018

(a)


PAN-H2O 180-1
10 µm
WD = 7.5 mm
EHT = 5.00 kV
Signal A = InLens
Photo No. = 11219
Mag = 5.00 K X
Date :27 Nov 2018

(b)

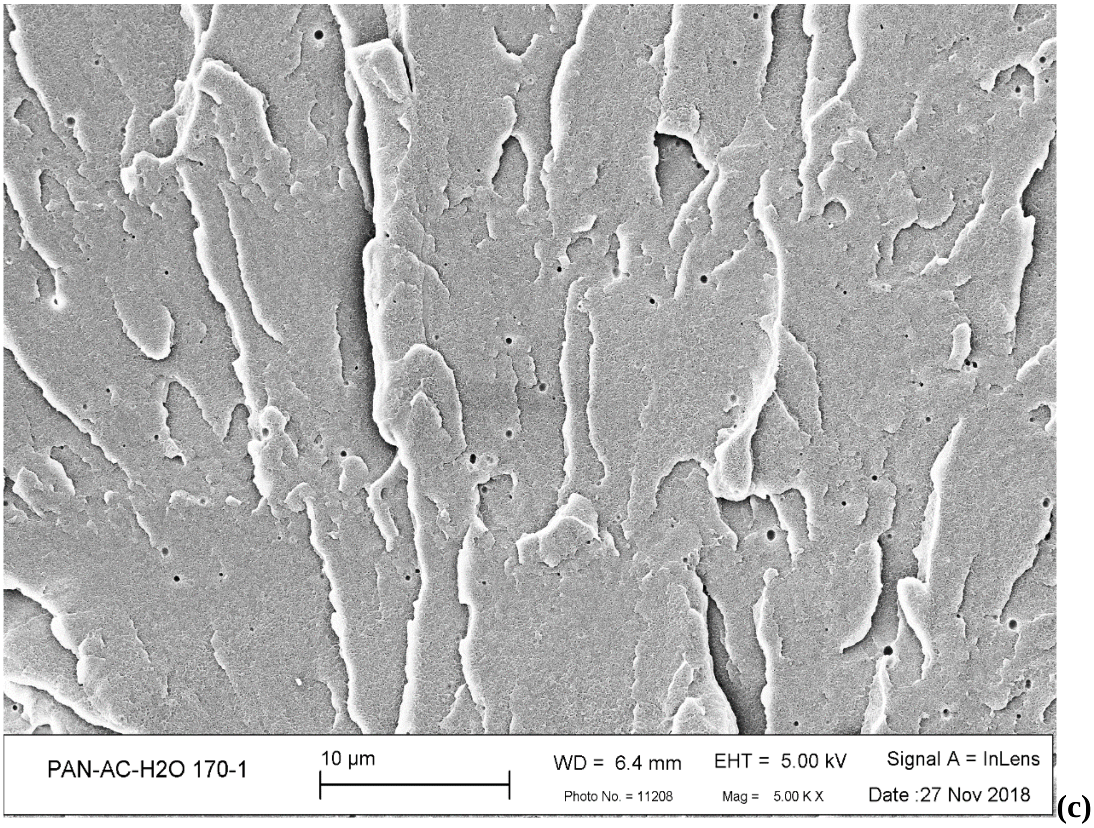
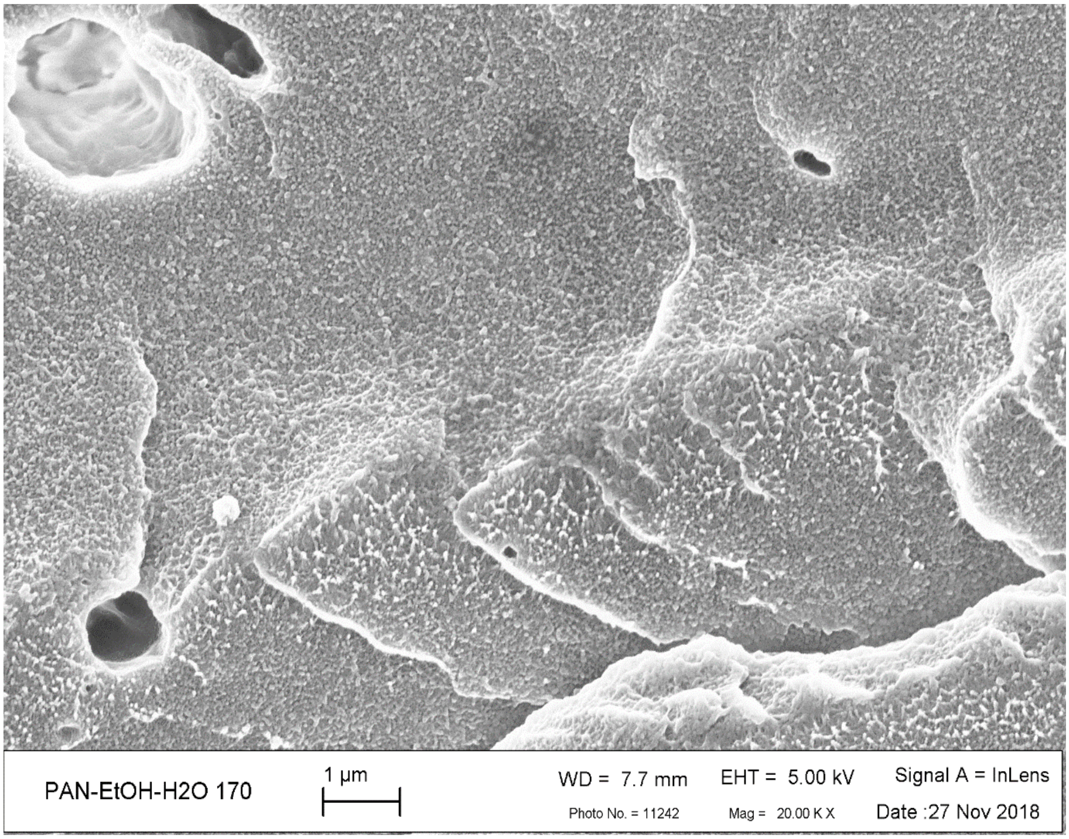
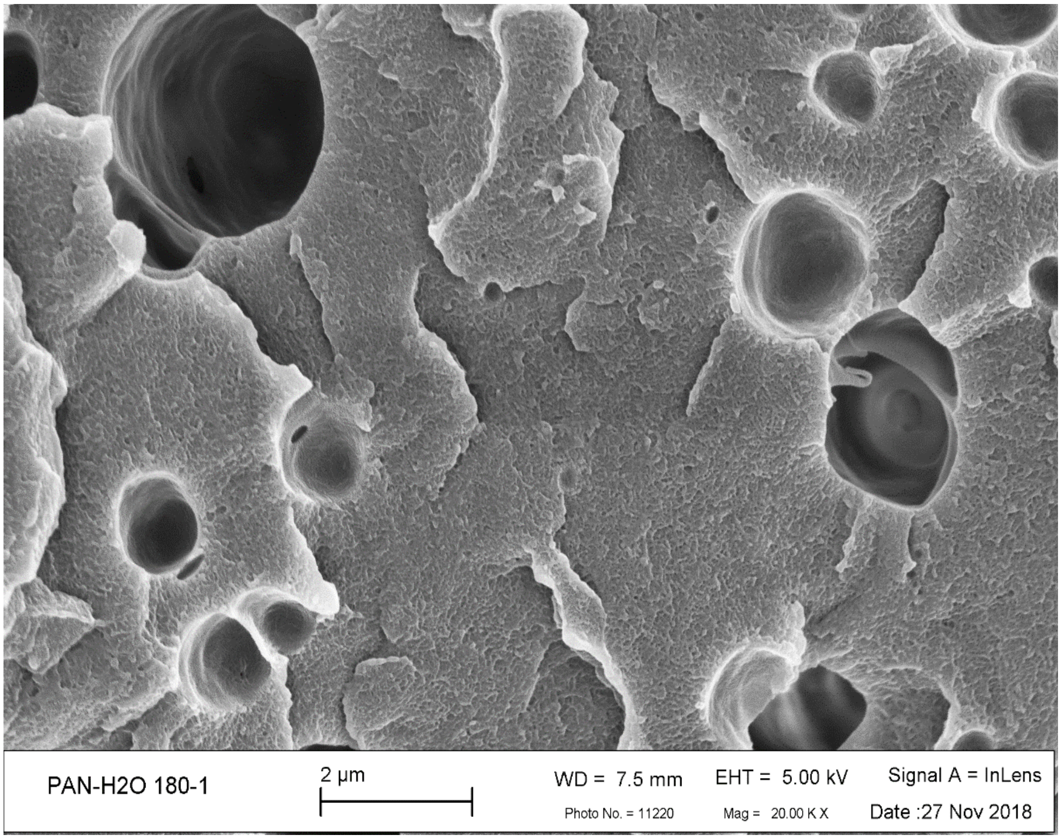


Figure 4.6, SEM images of the copolymer strands with 5,000X magnification extruded under three compositions: (a) PAN/EtOH/H_2O 70/15/15 wt% at 170 °C; (b) PAN/ H_2O 70/30 wt% at 180 °C; (c) PAN/ACN/H_2O 70/15/15 wt% at 170 °C


PAN-EtOH-H2O 170
1 µm
WD = 7.7 mm
EHT = 5.00 kV
Signal A = InLens
Photo No. = 11242
Mag = 20.00 K X
Date :27 Nov 2018

(a)


PAN-H2O 180-1
2 µm
WD = 7.5 mm
EHT = 5.00 kV
Signal A = InLens
Photo No. = 11220
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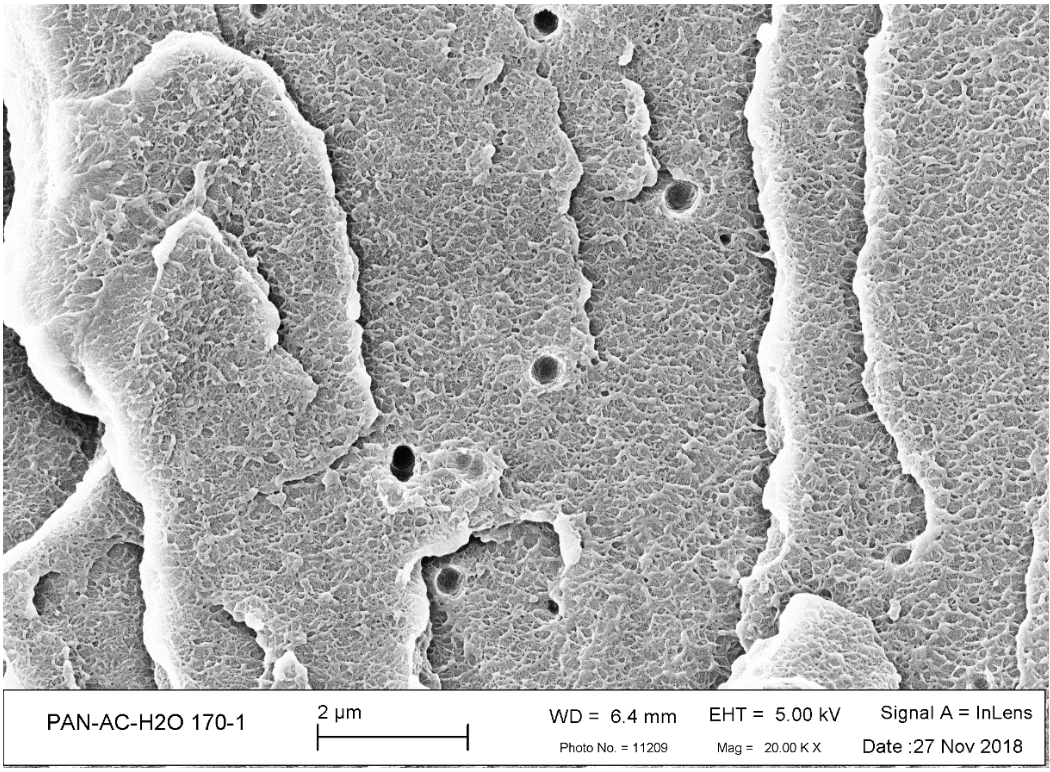
Date :27 Nov 2018

(b)



(c)

Figure 4.7, SEM images of the copolymer strands with 20,000X magnification extruded under three compositions: (a) PAN/EtOH/H_2O 70/15/15 wt% at 170 ^oC; (b) PAN/ H_2O 70/30 wt% at 180 ^oC; (c) PAN/ACN/H_2O 70/15/15 wt% at 170 ^oC

Figure 4.5, 4.6 and 4.7 are the SEM images of the cross sectional area of PAN strands at different magnifications. Comparing to the other two compositions, Composition 2 (PAN/H_2O 70/30 wt% at 180 ^oC) has more and large voids in the copolymer strands. The diameter of these voids ranges from several micrometers to hundreds of micrometers. For example, in Figure 4.5 (b), the right part of the image exhibits a huge void with a diameter of hundreds of micrometers, and these huge voids are not observed in any other samples. Composition 1 (PAN/EtOH/H_2O 70/15/15 wt% at 170 ^oC) has significantly less voids than composition 2 but slightly more voids than composition 3 (PAN/ACN/H_2O 70/15/15 wt% at 170 ^oC), and the size of these voids from Composition 1 are around 1μm. The polymer strands from composition 3 have the least and smallest voids in the SEM photos, and the size of voids are around 0.3 μm.

It is still unclear why different types of plasticizer make such a huge difference in the PAN copolymer strands in terms of the quantity and size of voids. There are several potential assumptions that can explain this observation. First, the azeotropic properties between water and the second plasticizers (ethanol/acetonitrile) help the extraction of plasticizers from the copolymer strands at lower temperature. Second, the boiling point of water/ethanol and water/acetonitrile mixture are close to or lower than the glass transition temperature (T_g) of PAN (around 90^oC) (Howard, 1961), but the boiling point of water is higher than the T_g of PAN. So without the second plasticizer, water can only be extracted from the polymer strands above the T_g of PAN, and this helps the formation of bubbles and voids when water is extracted.

The quantity and size of voids in the polymer strands and fibers can directly influence their strength and quality. Voids should be avoided during the PAN melt spinning process as it leads to a reduction in strength of the fibers. Based on the SEM photos, the voids in copolymer strands from composition 2 significantly exceed the other two compositions. So composition 2 is not considered as an appropriate composition and condition for fiber spinning.

4.5 Conclusion

The melting point results indicate that with the 15/15 wt% of water/ethanol mixture as the plasticizer, the T_m of PAN can be reduced to around 150^{o}C, which is lower than the T_m of PAN/water system. However, ethanol itself is not a plasticizer for PAN, and it is not able to sufficiently reduce the T_m of PAN. The rheological results indicate that PAN/water/EtOH can be melted and extruded at 170^{o}C without significant degradation for at least 100 minutes, and the magnitude of viscosity is still in a reasonable range. These results indicate that PAN/water/EtOH (70/15/15 wt%) at 170^{o}C can be taken as a potential composition and condition for the PAN melt spinning process.

The rheological properties, both time-dependent and steady-shear, of the PAN/water/EtOH (70/15/15 wt%) mixture at 170^{o}C are very similar to the reference composition (PAN/ACN/H_2O 70/15/15 wt% at 170 ^{o}C) and another potential composition **(**PAN/ H_2O 70/30 wt% at 180 ^{o}C) proposed in our previous paper (Miller et al., 2017; Yu et al., 2019). However, the SEM photos show that the extruded polymer strands of PAN/water/EtOH (70/15/15 wt%) mixture have less and smaller voids and bubbles than PAN/Water (70/30 wt%) mixture. In this case, water/EtOH (15/15 wt%) is considered as a more benign plasticizer for PAN rather than water only. Ethanol is able to be used as a second plasticizer and replace acetonitrile during the PAN melt spinning process. PAN/water/EtOH (70/15/15 wt%) at 170^{o}C is an appropriate composition and temperature for PAN melt spinning.

4.6 Acknowledgement

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Chapter 5 Applications of Rheological Data of Polyacrylonitrile

The rheological data of polyacrylonitrile (PAN) has been reported and discussed in the previous two chapters. In this chapter, further discussion of applications of the rheological data to estimating the degradation of the PAN during extrusion will be discussed. In Section 5.1 the power law parameters of PAN copolymer melts under different conditions will be discussed and in Section 5.2 an estimate of the residence time distribution of PAN copolymer in the metering section of a single screw extruder will be carried out.

5.1 Power law parameters of polyacrylonitrile melt at different conditions

The power law model is a simple model used to describe melt viscosity as a function of shear rate for non-Newtonian fluids[1]. The power law model is:

$$\eta = m \left| \frac{dv_x}{dy} \right|^{n-1} \tag{5.1}$$

where η is viscosity, $\frac{dv_x}{dy}$ is the velocity gradient, m and n are two parameters in the power law model. n, which is a unitless parameter, is called the power law index. m, which has the unit of Pa*s^n, is called the consistency[2]. For n=1, the flow is Newtonian. For n<1, the fluid is pseudoplastic and for n>1 the fluid is dilatant. Most polymer melts including the PAN/plasticizer mixture in this study, has the n value smaller than 1.

In Chapters 3 and 4, the steady-shear viscosity results of the PAN melts were reported. Based on these results, the power law parameters can be calculated. The results are presented in Table 5.1.

Table 5.1, Power law parameters of polyacrylonitrile melt under different conditions

Plasticizers Type	Composition (PAN/P1/P2 wt%)	Temperature (°C)	n	m(Pa*s^n)
Water/Acetonitrile	70/15/15	170	0.17	115202
Water/Acetonitrile	70/15/15	180	0.15	113611
Water/Acetonitrile	70/15/15	190	0.15	112769
Water	80/20	180	0.16	95829
Water	80/20	190	0.25	40682
Water	70/30	180	0.3	20611
Water	70/30	190	0.26	28041
Water/Ethanol	70/15/15	170	0.29	36458
Water/Ethanol	70/15/15	180	0.23	49306
Water/Ethanol	70/15/15	190	0.15	100624

In Table 5.1 is shown the two power law parameters of PAN melts under various conditions (temperature, plasticizer types and compositions). The n values range from 0.15 to 0.3, which shows a strong shear-thinning behavior of this material. This indicates that the viscosity of PAN is strongly related to the shear rate, that is, with a higher shear-rate, the viscosity of the PAN melt is lower. There is no significant correlation between the power law parameters and the plasticizer type and composition. However, it shows the n values are normally decreasing with increasing temperature. This indicates that the polymer melt is more "shear thinning" at higher temperatures.

Based on the results and conclusions from Chapter 3 and 4, the two potential conditions of conducting PAN melt spinning are PAN/Water/Ethanol (70/15/15 wt%) at 170 oC and PAN/Water (70/30 wt%) at 180 oC, plus the reference condition (PAN/Water/Acetonitrile 70/15/15 wt%). These three conditions will be further studied in the next sections.

5.2 Residence time distribution (RTD) analysis of PAN melt in a single screw extruder

5.2.1 Background and model description

The residence time distribution (RTD) is significant during the extrusion process. It was first introduced by Danckwerts in 1953[3], and it is defined as the fraction of the exit stream , *f(t)dt,* with residence time between *t* and *t+dt*. The cumulative RTD faction, *F(t)* is defined as

$$\mathrm{F(t)} = \int_{t_0}^{t} f(t')dt \tag{5.2a}$$

$$\mathrm{f(t)dt} = \frac{dQ}{Q} \tag{5.2b}$$

where t_0 is the minimum residence time, Q is the volumetric flow rate at the exit and dQ is the fraction of the volumetric exit flow rate with residence time between t and t+dt [2].

There are two methods that have been used to characterize RTD. The first method is to establish a flow model which can represent the main features of the physical flow pattern. In this method, the single screw system is modeled to a combination of a plug flow reactor (PFR) and continuous stirred tank reactor (CSTR), CSTRs in series, CSTRs with dead volume and laminar pipe flow. Based on this method, Wolf & Resnick [5] and Yeh [4] developed their RTD models and their models have been widely applied to the food extruder[6-8] and long fiber reinforced thermoplastics[9].

The second method, which is used in this project, is to derive the RTD from the fundamental analysis of velocity profiles, which the screw geometry, thermal and rheological properties of the materials will be required. Tadmor & Pinto[10] have introduced the analysis by this method and reported the RTD curves for Newtonian fluids and Bigg & Middleman[11, 12] extended the work to non-Newtonian fluids with the power law model. In this chapter, the author's work and analysis is based on the model introduced in Bigg's PhD dissertation[12].

Here is a brief introduction of the Bigg's model. A rectangular channel model is used to describe the screw channel as shown in Figure 5.1. With assumptions of isothermal flow, negligible end effect and leakage flow, the dynamic equations of motion for this model can be written as:

$$\frac{\partial p}{\partial x} = \frac{\partial \tau_{yx}}{\partial y} \tag{5.3a}$$

$$\frac{\partial p}{\partial z} = \frac{\partial \tau_{yz}}{\partial y} \tag{5.3b}$$

With the power law model, the constitutive equation then can be written as:

$$\mu = m\left[\left(\frac{\partial v_x}{\partial y}\right)^2 + \left(\frac{\partial v_z}{\partial y}\right)^2\right]^{\frac{n-1}{2}} \tag{5.4}$$

The shear stress components are then related to the velocity gradient by:

$$\tau_{yx} = -m\left|\frac{\partial v_x}{\partial y}\right|^{n-1}\frac{\partial v_x}{\partial y} \quad ; \quad \tau_{yz} = -m\left|\frac{\partial v_z}{\partial y}\right|^{n-1}\frac{\partial v_z}{\partial y} \tag{5.5}$$

The two velocity components, $v_x(y)$ and $v_z(y)$ then can be calculated by numerical methods. Once the velocity components are obtained, the down-channel velocity, V_L, (which is parallel to the to the helixes path along the screw channel) can be calculated. Then the volumetric flowrate, Q, can be obtained. Finally, the F(t) curve can be calculated by applying Eq 5.2a and 5.2b. The detailed derivations are introduced in Bigg's PhD dissertation[12]. In this study, the author regenerated Bigg's method by using Python for the numerical calculations. The related Python code is attached in the Appendix B.

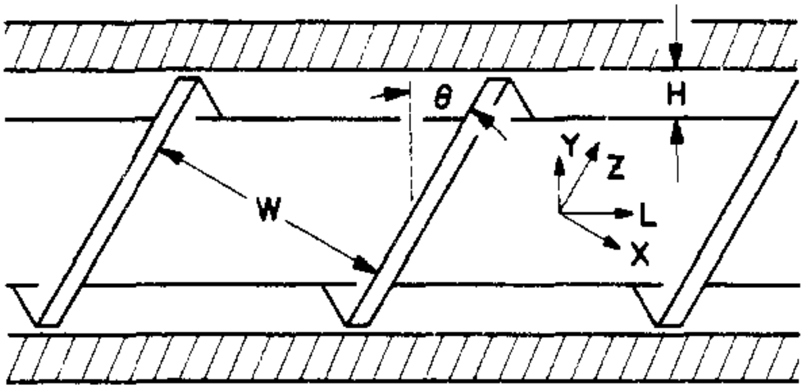

Figure 5.1, Model of extruder geometry, Taken from [11]

The throttle ratio (Q_P/Q_D) is extremely important in the RTD calculation. it is defined as the ratio of pressure to drag flow rates. The expression of Q_P/Q_D is:

$$Q_P/Q_D = -\left(\frac{\partial p}{\partial z}\right)\frac{H^2}{6\mu \mathrm{V}_L} \tag{5.6}$$

In Bigg's method, he used another parameter, Q^*, to represent the same concept [12]. Bigg define Q^* as a dimensionless total flow rate. The equation of Q^* is:

$$Q^* = \frac{Q}{WH\mathrm{V}_L} \tag{5.7}$$

Where the Q is the total volumetric flow rate for the system. Moreover, the general relation between Q_P/Q_D in Baird's book [2] and Q^* in Bigg's method is:

$$Q_P/Q_D = Q^* - 1 \tag{5.8}$$

And in this chapter, Q_P/Q_D is used as a reference instead of Q^*.

The unit of x-axis of the RTD curves is defined as t/t_B**,** where *t* is the time. t_B, is defined as the mean residence time, which is equal to:

$$t_B = \int_{t_0}^{\infty} t f(t) dt = \frac{V}{Q} = \frac{L}{\mathrm{V}_L * \sin\theta * Q^*} \tag{5.9}$$

Where V is the channel volume ($V = WHL/\sin\theta$ and L is the length of screw)

5.2.2 RTD diagrams of PAN melts

Based on the Bigg's model described above, RTD curves are generated with various Q_P/Q_D and *n* values. According to the data reported in Table 5.1, *n=0.17 and 0.29* are selected because they represent the reference condition and the most benign condition to carry out PAN melt spinning, respectively. They are also close to the upper and lower boundaries of *n* values in Table 5.1. One thing needed to be noticed here is the range of Q_P/Q_D values is varied based on the value of *n*. More specifically, the smaller value of *n*, the narrower the range of Q_P/Q_D. The largest possible Q_P/Q_D values are -0.59 and -0.63 and the smallest possible Q_P/Q_D values are -0.99 and -0.93for *n*=0.29 and 0.17, respectively. The two RTD diagrams are shown below in Figure 5.2 and 5.3.

Based on Figures 5.2 and 5.3, the minimum residence time, t_0, (which is defined as when the first particle exits from the extruder), are normally around a range of 0.7-0.8 of t/ t_B. Also, the minimum t_0 is at Q_P/Q_D = -0.77 and -0.85, for *n*=0.29 and 0.17, respectively, and either an increase or decrease in Q_P/Q_D leads to a higher t_0. For *n*=0.29, more than 60% of the material will exit the extruder when $t=t_B$ and this percentage increases to more than 90% when $t = 1.5t_B$. And for *n*=0.17, it shows the similarity of the curves except Q_P/Q_D = -0.93, which has only 50% of material exit the extruder when $t=t_B$. There is no significant difference between the curves when the value of *n* changes from 0.29 to 0.17. This is probably because the variation of *n* value is too small. It is also very difficult to find the optimized Q_P/Q_D value because the trend of F(t) curves are very close to each other.

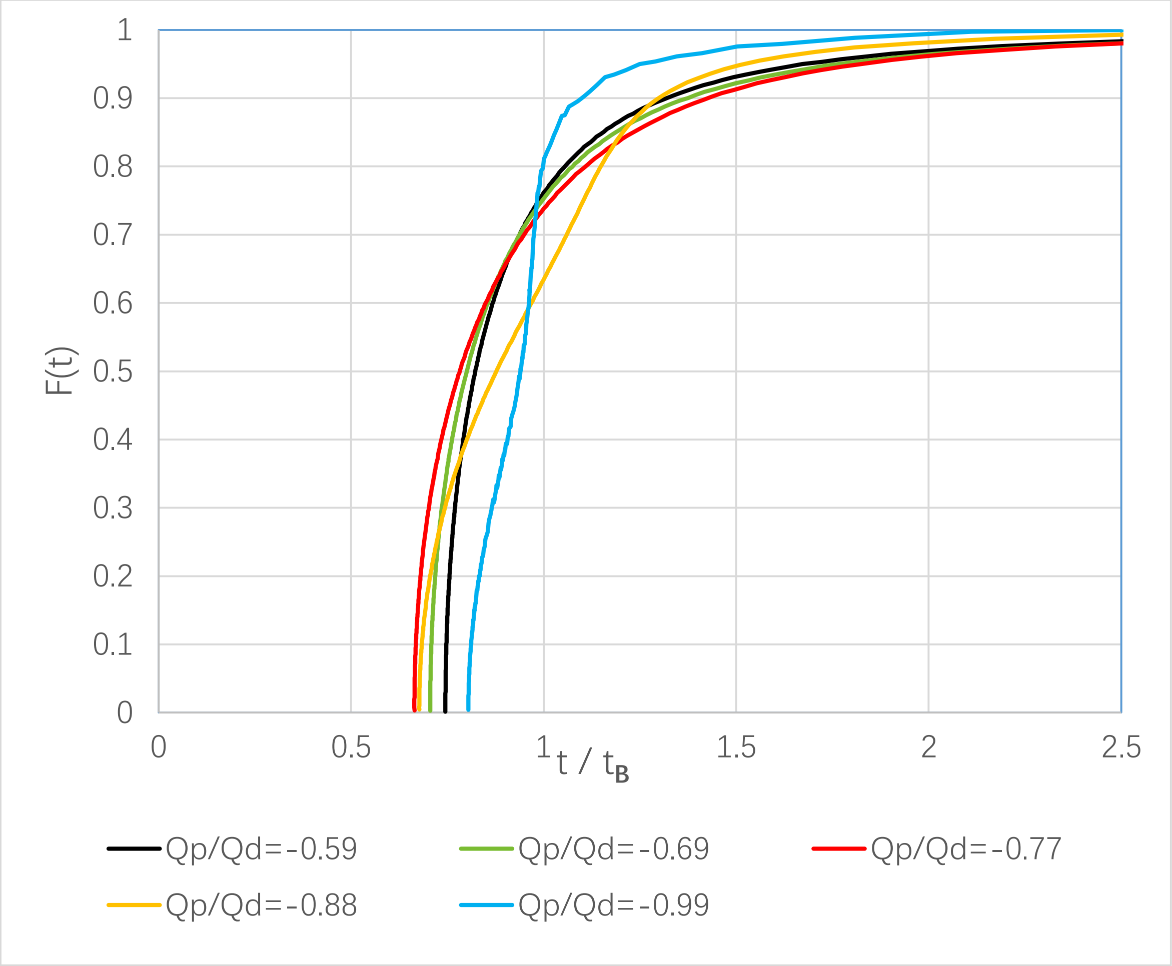

Figure 5.2, RTD Diagram of PAN, n=0.29

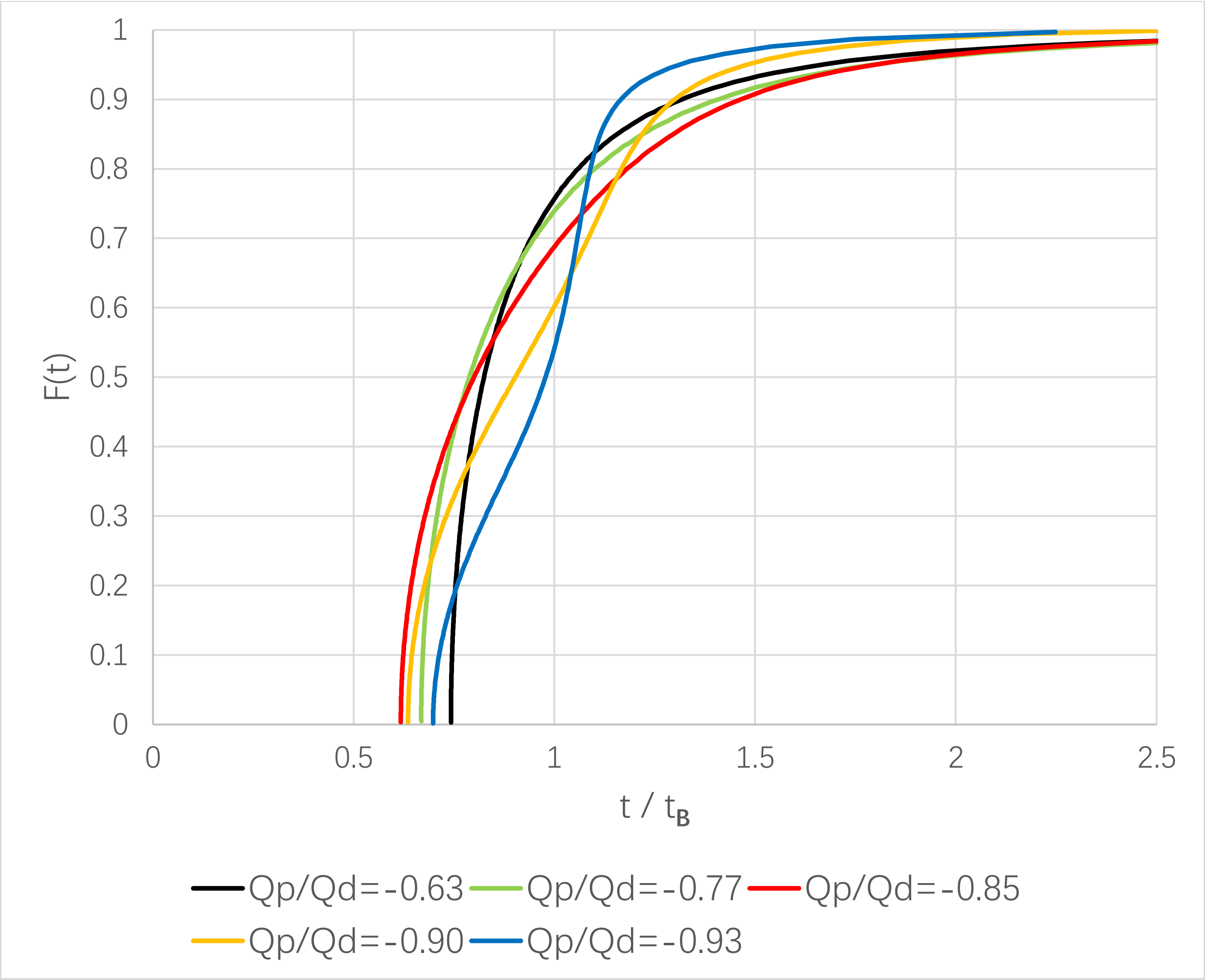

Figure 5.3, RTD Diagram of PAN, n=0.17

It is very important to know what the value of t_B is if it is to be applied to the RTD analysis in the PAN extrusion process. As discussed in Chapter 3 and 4, PAN starts to degrade after 60 minutes when it is at 180°C. In order for at least 90% of material to leave the extruder before it degrades, the t/t_B must be smaller than 1.5 and t_B must be shorter than 40 minutes. Here is a sample calculation, for a simple single screw extruder, with the $\theta = 17.74^o$, the length of screw (L) = 75cm, the average channel depth (H) = 0.286 cm, the channel width (W) = 1.512cm and $Q_P/Q_D = -0.77$. By using Equation 5.9, the expression of t_B can be re-written as

$$t_B = \frac{75\ cm}{V_L * 0.07} \tag{5.10}$$

In order to ensure $t_B < 40$ minutes, the down channel velocity, v_L must be greater than 26.8 cm/min, a relatively slow speed in the real extrusion process and easy to be achieved.

5.3 Conclusion

The two power law parameters, *n* and *m*, of PAN melt at various conditions, has been reported. The values of *n* range from 0.15 to 0.3. The RTD diagrams of PAN show more than 50% of PAN can pass the extruder when $t=t_B$ and this percentage increases to 90% when $t=1.5*t_B$. A sample calculation shows that with a simple single screw extrusion system, 90% of PAN can exit the extruder without degradation at 180°C if the down-channel velocity is greater than 26.8cm/minutes.

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Chapter 6 Summary, Conclusion and Recommendation

6.1 Summary and conclusion

- The melting point (T_m) of polyacrylonitrile (PAN) can be reduced from 320°C to below 180°C when plasticized with water-based plasticizers. More specifically, water only as plasticizer is able to reduce the T_m of PAN to around 156°C; water/acetonitrile as plasticizer is able to reduce the T_m of PAN to around 134°C; and water/ethanol as plasticizer is able to reduce the T_m of PAN to around 150°C. Moreover, acetonitrile only as a plasticizer can reduce the T_m of PAN to around 145°C, and ethanol only as a plasticizer fails to reduce T_m of PAN to below 190 °C, which indicates that ethanol is not a plasticizer of PAN.
- The time-dependent viscosity results show that the degradation of PAN starts at 180 °C. A higher temperature leads to a rapid degradation. The content of water can affect the stability of PAN as well. More specifically, with 0 wt% water as a plasticizer, PAN can be stably melt processed for at least 42 minutes. With 15-20 wt% water as a plasticizer, PAN can be stably melt processed for at least 75-80 minutes. With 30 wt% water as a plasticizer, PAN can be stably melt processed for more than 120 minutes. For a temperature equal to or lower than 170 °C, PAN can be stably melt processed for more than 120 minutes with any plasticizers. However, a PAN/water mixture cannot be processed at 170 °C due to the extremely high viscosity. The reason PAN cannot be stably melt processed after a certain time is because the rapid and significant viscosity increasing, which is probably caused by the degradation (crosslinking and cyclization) of PAN copolymer
- The steady-shear viscosity results show the strong shear-thinning behavior of the plasticized

PAN melt. The data can be fit by the power-law model and the power-law parameter, *n*, is in the range from 0.15 to 0.3 for the plasticized PAN melt. The shear-rate viscosity curves of PAN have no strong correlation with temperature, but they are significantly influenced by the type and composition of plasticizers. More specifically, the more water content in the plasticizer, the lower the magnitude of viscosity of the PAN melt. At a shear rate of 1000 s^{-1}, the viscosity of the PAN melt is around 150-300 Pa*s.

- Based on the melting point and rheological results, there are two potential compositions that are appropriate for PAN melt spinning. PAN/water (70/30 wt%) at 180 ^{o}C and PAN/water/ethanol (70/15/15 wt%) at 170 ^{o}C. However, the SEM images show the polymer strand of PAN/water (70/30 wt%) has many more and larger voids than PAN/water/ethanol (70/15/15 wt%), which could significantly reduce the quality and strength of PAN fiber.
- In conclusion, ethanol is able to replace acetonitrile as a second plasticizer, which is safer and cheaper. PAN/water/ethanol (70/15/15 wt%) is the most benign composition for carrying out PAN melt spinning at 170 ^{o}C. However, further spinning and extrusion experiments need to be conducted in order to determine if PAN copolymer can be stably spun with this plasticizer composition.

6.2 Recommendation

- Due to the limitation of instruments and shortage of PAN material, no extrusion experiments of PAN melt spinning has been conducted in this study. The extrusion experiment can provide a better understanding of the fundamentals of PAN melt spinning. Also the experimental data can be compared to the residence time distribution (RTD) analysis introduced in Chapter 5.

The challenge is that it is very difficult to seal and pressurize the entire extruder. One possible solution is to design and build up a new extruder that can be divided into several zones. The feeding zone (hopper) needs to be separate from other part of the extruder. A large pressure chamber needs to be attached to the end of the extruder and the take-up devices need to be placed into the pressure chamber.

- Identifying the glass transition temperature (T_g) of PAN with plasticizers is also an essential part to the spinning process. This is because the T_g of PAN with plasticizers may be directly related to the foaming problem, and lowering T_g of the PAN mixture may help to prevent bubble nucleation during the drawing step. However, measuring T_g of PAN with plasticizers is very challenging. First, the relevant instruments (differential scanning calorimetry, DSC or dynamic mechanical analysis, DMA) need to be modified so that they can be sealed and pressurized in order to prevent the evaporation and loss of plasticizers. Second, the T_g of PAN is very close to the range of boiling points of the plasticizers, which makes it is difficult to distinguish and identify the peaks from DSC or DMA images
- There are some other chemicals that may be used as plasticizers in the PAN melt spinning process as well, such as methanol and acetone (which was also mentioned in BASF's patent). These organic compounds have some similar properties as acetonitrile and ethanol (e.g. low boiling point). The melting point studies need to be conducted in order to determine if these chemicals and their mixtures with water can sufficiently reduce the melting point of PAN copolymer. If so, further rheological studies need to be conducted and the results can be compared to the reference composition to determine if the plasticizer can be used in PAN melt spinning process.

Appendix A

The appendix part A contains two articles. The first one is a journal manuscript that the author is a co-author. This manuscript focus on the chemical characteristics of polyacrylonitrile (PAN) copolymer and the rheological data of the PAN/acetonitrile & PAN/adiponitrile mixture. The second one is an ANTEC preprint wrote by the author. This preprint focus on some early stage work of this study and the rheological data of PAN/VA copolymer with various plasticizers.

Melt-spinnable Polyacrylonitrile Copolymer Precursors for Carbon Fibers

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1. Introduction

Polyacrylonitrile (PAN) is an acrylic polymer with a very high crystalline melting point (317°C) and limited solubility in most common solvents with the exception of ethylene carbonate [1], propylene carbonate [2, 3], concentrated aqueous solutions of inorganic salts [4], and some dipolar aprotic solvents including dimethylformamide (DMF), dimethylsulfoxide (DMSO), and dimethylacetamide (DMAc) [5]. The high melting point of PAN has been attributed to dipolar forces among polar nitrile groups adjacent to one another along the polymer backbone that restrict bond rotation leading to a stiff rod-like polymer [4, 6]. Strong repulsive dipole-dipole intramolecular interactions between parallel nitrile neighbors along the polymer backbone lead to an irregular helical conformation, and attractive dipole-dipole intermolecular interactions between anti-parallel nitrile groups of neighboring chains lead to a parallel orientation of the helices relative to one another [7].

Carbon fibers are exceptional materials due to their high strength, chemical inertness, and low density relative to glass. More than 50% of the carbon fibers produced are utilized in air and spacecraft applications to save on weight and fuel without sacrificing structural integrity, but carbon fibers are increasingly finding applications in shipping, sporting and medical fields [8, 9]. The structural unit of a carbon fiber is a planar network of connected benzene rings, similar to the planar hexagonal honeycomb arrays found in graphite [8, 10]. The two most common precursor sources for the commercial production of carbon fibers are a mesophase pitch produced by the destructive distillation of coal and synthetic polymeric fibers [11]. Most carbon fibers are of the latter variety and are produced from a polyacrylonitrile (PAN) copolymer-based precursor [9] in a multi-step method. First, the precursor fiber is subjected to a thermo-oxidative so-called stabilization procedure in which the fiber is heated to 200-350°C under tension in air for long times (~5-10 hours). This stabilization process results in crosslinking and cyclization reactions that form a ladder-type structure. The process most likely occurs via a combination of intra- and inter-molecular reactions between pendant CN groups. Next, in a process known as carbonization, the fiber is heated to ~1300°C in an unstressed state and inert atmosphere to yield a fiber with at least 97% carbon content. Finally, in the graphitization step, the filament is further heated to ~3000°C to increase the modulus of the carbon fiber [10-15].

More than 300 million pounds of acrylic PAN-based fibers are produced annually [16]. Polyacrylonitrile fibers are generally spun in a wet-spinning process that includes drawing in such a way that the polymer chains become oriented parallel to the fiber axis. Comonomers such as methyl acrylate and vinyl acetate are often incorporated into PAN to increase the solubility of the polymer in solvents that are used in the spinning process as well as to mediate the kinetics of crosslinking during the exothermic thermo-oxidative step [8, 11, 14]. High production costs associated with the organic solvent and its recovery are inherent in all of the current carbon fiber production processes [14]. It would be desirable to melt-spin the PAN copolymer fibers for both economic and environmental reasons. However, the polymer undergoes a thermal crosslinking reaction prior to reaching the melting temperature [9, 17-19].

Research into melt-spinning processes for PAN involve two general approaches: internal and external modification. Several examples of internal modification exist. This is generally achieved by adding one or more comonomers during the free radical polymerization [9, 14, 15, 20-22]. In 1952, Coxe [23] pioneered the field of external PAN modification when he observed that high pressure mixtures of PAN with water could be melt-extruded. However, foaming of the fibers as they exited the spinneret and the water evaporated prevented this method from being widely adopted. Much research has been conducted building on Coxe's initial findings including exploring different techniques involving pressurized mixtures of PAN and water [18, 24, 25], pressurized mixtures of PAN, ethylene carbonate, and water [17], pressurized mixtures of PAN, dimethylformamide and water [19], pressurized mixtures of PAN, acetonitrile and water [26], pressurized mixtures of PAN and carbon dioxide [27], and mixtures of PAN with ionic liquids [28]. It has been shown that the modification effect of water on a poly(acrylonitrile-*ran*-vinyl acetate) copolymer comprised of 88 wt % of acrylonitrile with a M_v = 82,000 g/mole reached a maximum potential at 23% water, and additional water past this critical concentration had no added benefit [17]. Min et al. [19] found that by adding DMF in addition to the critical 23 wt % of water, both the melting point and the crystallization temperature of a PAN-VA copolymer (88 wt% AN, 12wt% VA) could be decreased further, even achieving melting points as low as 140°C.

This paper details effects of mixing polar additives as modifiers on the melting temperatures of PAN-MA copolymers with well-defined compositions and molecular weights. The melt rheological behavior of the modified PAN-MA copolymer is described both as a function of time and shear-rate.

2. Experimental

2.1. Materials

Poly(acrylonitrile-*ran*-methyl acrylate) (PAN-MA) was purchased from Fisipe and used as received. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and acetonitrile were purchased from Spectrum Chemicals and used as received. 1,6-Hexanedinitrile (adiponitrile) and 2-ethyl-2-oxazoline were purchased from Sigma-Aldrich and used as received.

2.2. Mixing of PAN copolymers and plasticizers

DMF (0.5 g), polymer powder (3.5 g) and DI water (1 g) were mixed thoroughly to produce 5 g of a copolymer mixture containing 10 wt % of DMF and 20 wt % of water [70:10:20]. This process was repeated for each copolymer/melting point modifier composition. Melting point modifiers used in this study included deionized water, NMP, DMF, 2-ethyl-2-oxazoline, acetonitrile, and hexanedinitrile (commonly referred to as adiponitrile).

2.4. Structural characterization

Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy was performed on an Agilent MR4 spectrometer operating at 400 MHz. All ^{1}H spectra were obtained from 15% (w/v) 1-mL solutions in deuterated dimethylsulfoxide (DMSO-d_6) using a 30° pulse angle, 5s relaxation delay, and 64 scans and was performed in triplicate to obtain quantitative results. Molecular weights of the copolymer were obtained by size exclusion chromatography (SEC). The SEC system consisted of an isocratic pump (Agilent 1260 infinity, Agilent Technologies, Santa Clara, CA) with an online degasser (Agilent 1260, Agilent Technologies, Santa Clara, CA), autosampler and column oven used for mobile phase delivery and sample injection, and three Agilent PLgel 10-μm Mixed B-LS columns 300 x 7.5 mm (polystyrene/divinylbenzene) connected in series with a guard column as the stationary phase. A system of multiple detectors connected in series was used for the analysis. The columns and detectors were maintained at 50°C. A multi-angle laser light scattering (MALS) detector (DAWN-HELEOS II, Wyatt Technology Corporation, Goleta, CA), operating at a wavelength of 658 nm, and a refractive index detector operating at a wavelength of 658 nm (Optilab T-rEX, Wyatt Technology Corporation, Goleta, CA) provided online results. The system was corrected for interdetector delay, band broadening, and the MALS signals were normalized using a 21,720 g/mole polystyrene standard obtained from Agilent Technologies or Varian. Data acquisition and analysis were conducted using Astra 6 software (Wyatt Technology Corporation, Goleta, CA). The mobile phase was DMAc, which was vacuum distilled over CaH_2 before use. A solution of 0.1 M LiCl, dried at 120°C *in vacuo* for 2 h, in DMAc was prepared, and the solvent solution was degassed and filtered before use. The sample solutions were prepared in a concentration range of 2~3 mg/mL and were filtered to remove any dust or insoluble particles using 0.22-μm PTFE filters. Molecular weights were calculated from the light scattering data.

Differential refractive index increment (dn/dc) measurements of the PAN-MA copolymer were made using an Agilent 1260 infinity multidetector SEC equipped with a Wyatt T-rex differential RI detector at 30°C and with a flow rate of 0.3 mL/min. The following representative procedure was used: 400 mg of the sample was weighed into a vial and dissolved in 20 mL of DMAc containing 0.1 M LiCl (dried as described previously). This solution was stirred for approximately 12 h. The sample solution was then diluted to 50 mL in a volumetric flask. This stock solution was used to make 7 new dilutions that were filtered through a 1-μm PTFE filter. The refractive index for each of 8 concentrations was measured and the data points were fitted to a straight line. The dn/dc was determined to be the slope of the line.

2.7. Differential scanning calorimetry (DSC)

The glass transitions, melting temperatures and the relative stabilities of the copolymer/modifier mixtures were investigated with a TA Instruments DSC Q200 using high volume DSC pans with O-rings. For determining the copolymer T_m's, the copolymer/modifier mixtures were heated under nitrogen at a rate of 10°C min^{-1} to 200°C, cooled at a rate of 10°C min^{-1} to 0°C, and heated again at a rate of 10°C min^{-1} to 240°C. For determining the T_g's of the copolymer/modifier mixtures containing acetonitrile, a modified experimental procedure was developed. The mixtures were heated at a rate of 10°C min^{-1} to 200°C, cooled at a rate of 20°C min^{-1} to 0°C, then heated again at a rate of 5°C to 240°C. The reported DSC transitions were from the second heating scans. For determining the relative stabilities of the copolymer/modifier mixtures, an isothermal DSC experiment was employed in which the mixtures were heated under nitrogen at a rate of 10°C min^{-1} to 110°C, cooled at a rate of 10°C min^{-1} to 40°C, heated to ~10°C below the target temperature, equilibrated at the target temperature, then held isothermally for 4 h at the desired temperature.

2.8. Preparation of polymer/modifier pellets for rheology measurements

The copolymer powder was first mixed thoroughly with the modifer(s) to obtain the desired composition, then the mixture was press molded at room temperature with a hydraulic press into a metal die to obtain a cylindrical pellet with a uniform diameter of 9.5 mm. The copolymer pellet helped to prevent voids in the samples as well as make it easier to load the copolymer/modifier mixture into the capillary rheometer with minimal solvent loss. For mixtures containing acetonitrile, an additional heating step was necessary for suitable pellet pressing. For this heating step, the mixture was heated in a sealed resin kettle for ~1 h above the mixture's T_g (42 °C), then it was allowed to cool overnight before preparing the pellets. It is the belief of the author that heating the copolymer mixture above it's T_g allowed better incorporation of the solvent mixture into the copolymer due to the increased chain motion and free volume at the elevated temperature. It is anticipated that this treatment will be necessary to prepare PAN-MA/ACN/H_2O samples for melt-extrusion as well. A sample pellet of approximately 10 grams was required for each rheology measurement experiment.

2.9. Pressurized capillary rheometry

Viscosity measurements were conducted on an Instron model 3211 capillary rheometer with modifications and using a procedure similar to that reported by Bortner and Baird [27]. The rheometer was modified with the addition of a sealed chamber at the capillary exit to create a static pressure that maintained a homogeneous single melt phase and minimized macrophase separation or volatilization of the modifiers from the copolymer. The pressure assembly also enabled collection of the extrudate during the viscosity measurements for subsequent analysis. Nitrogen was used with a constant pressure of 1.38 MPa to apply a static pressure to the capillary exit. This pressure is above the calculated saturation pressure for the additives at test temperatures. Nitrogen was used because prior work has verified that nitrogen does not have a plasticizing effect on PAN polymers [27]. Teflon O-rings were employed on the plunger and Teflon spacers were used between the pressure chamber assembly and the capillary to seal the pressurized system. A detailed schematic diagram of the modified capillary rheometer is provided in Figure 1.

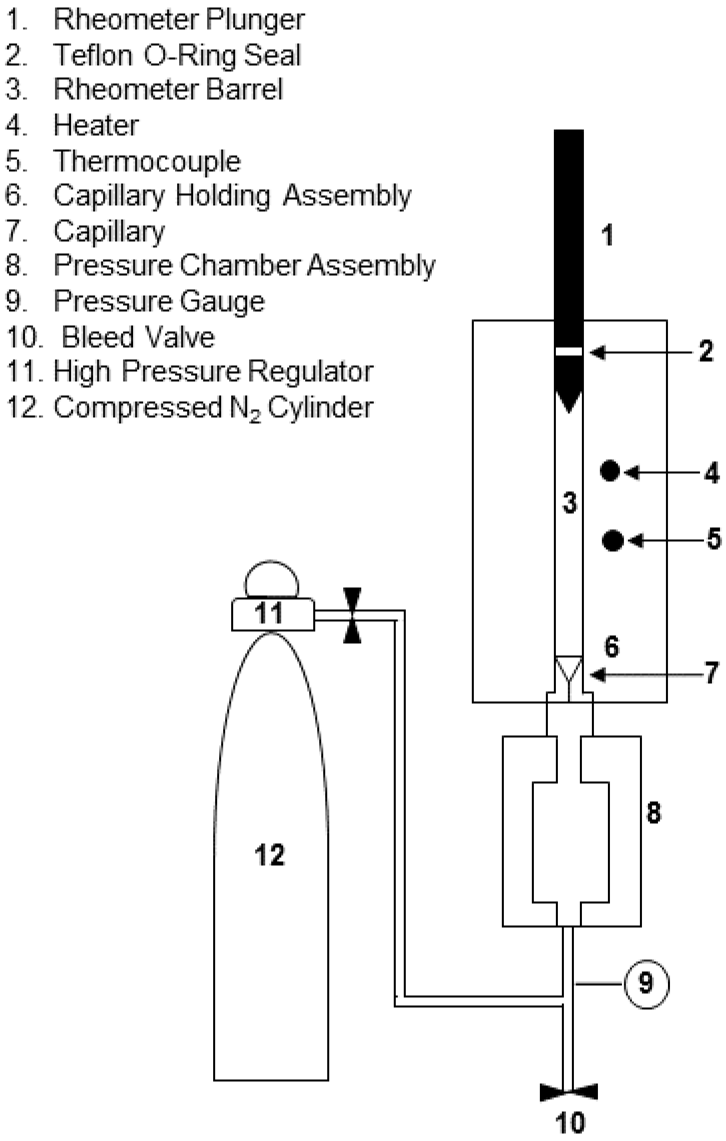

Figure 1. Schematic diagram of modified capillary rheometer

The following procedure was implemented to prevent the loss of melting point modifiers that would normally occur if loaded into a preheated rheometer. Copolymer/modifier pellets were loaded into the rheometer at room temperature with a chamber diameter of 9.53 mm, a capillary diameter of 0.0356 mm, and an entry angle of 180°. The system was sealed with a piston and static pressure was applied to the capillary exit. With the system pressurized, the rheometer was heated to the experimental temperature. The copolymer pellet was initially held at the experimental temperature for 10-12 min to allow complete melting of the pellet in the rheometer prior to performing the rheological tests. To quickly compact the sample following heating, a high plunger speed of 2 cm/min was used until a quasi- steady state force was reached, at which time the plunger speed was decreased to 0.06 cm/min and the melt was allowed to relax to steady-state. The pressure gradient was calculated using the force measured by the load cell at the top of the plunger. Corrections were made by subtracting the contribution of applied static pressure at the capillary exit (1.38 MPa) and the frictional force from the Teflon O-rings used to seal the space between the plunger and barrel. A capillary with L/D of 88 was used to minimize the impact of entry effects.

Steady shear viscosity measurements were performed at a constant apparent shear rate of 161.3 s^{-1} to analyze the time dependence of viscosity. Further measurements were performed at apparent shear rates ranging from 80-10,755 s^{-1} until a steady-state viscosity was achieved for each shear rate. Viscosities were calculated by known methods from plunger speeds and force measurements [29]. The apparent shear rate, $\dot{\gamma}_a$, was calculated based on the volumetric flow rate of the polymer through the capillary, Q, and the radius of the capillary, R, as defined by Eq. (1):

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \qquad (1)$$

The wall shear stress, τ_R, was calculated using Eq. (2):

$$\tau_R = \frac{\Delta P R}{2L} \tag{2}$$

where ΔP is the pressure gradient, R is the radius of the capillary, and L is the length of the capillary. The apparent viscosity was calculated from Eq. (3).

$$\eta_a = \frac{\tau_R}{\dot{\gamma}_a} \tag{3}$$

The power law fluid model was used for comparing the relative shear thinning behavior between samples according to Eq. (4):

$$\log \eta_a = \log K + (n-1) \log \dot{\gamma}_a \tag{4}$$

where K is the flow consistency index and n is the flow behavior index.

3. Results and Discussion

The feasibility of melt extrusion of a PAN-MA copolymer relies upon melting of the copolymer, a sufficiently low viscosity of the resulting melt, as well as the stability of the melt against competing cyclization and crosslinking reactions under the extrusion conditions. During melt extrusion, the viscosity is expected to increase as a result of crosslinking in addition to cyclization, which depends on the processing temperature and residence time in the extruder [14]. It is prudent to describe, quantitatively, the changes in viscosity as a function of temperature, time, and shear rate so that proper melt-extrusion parameters can be identified.

3.1 Composition and stability of PAN-based copolymers

From prior literature [9], it is known that PAN-MA copolymers containing more than 10 mole % of MA have improved melt processability, but this comes at the expense of lower carbon content and compromised mechanical properties in the resulting carbon fibers after conversion. Therefore, the copolymer used to make a precursor fiber for a carbon fiber should ideally contain less of the comonomer to achieve carbon fibers with good mechanical properties. The composition of the copolymer used for this investigation was determined by ^{1}H-NMR. The spectrum had well-resolved peaks that confirmed that the copolymer consisted of methyl acrylate and acrylonitrile repeat units. Methyl acrylate is a desirable comonomer for PAN-based carbon fiber precursors because the reactivity ratios of AN with MA in DMF at 62°C have previously been found to be 1.29 and 0.96, respectively. Therefore, the copolymer that is produced is a predominately random copolymer [30]. A representative spectrum is shown in Figure 2. The signal at 3.2 ppm (b,d) corresponds to the backbone methine (CH) protons from acrylonitrile and methyl acrylate. The signal at 2.1 ppm (a,c) corresponds to the backbone methylene (CH_2) protons from both acrylonitrile and methyl acrylate. The signal at 3.7 ppm (e) corresponds to the methyl (CH_3) protons of the methyl acrylate units. The copolymer composition was calculated from the integral values of the methylene protons according to the following equations:

$$Moles\ \ MA\ \ \alpha\ \ \left(\frac{\int CH_3}{3}\right)$$

$$(Moles\ \ MA)\ \times\ \left(86.04\ \ \frac{g}{mole}\right) = relative\ \ weight\ \ MA$$

$$Moles\ \ AN\ \ \alpha\ \ \left[\left(\frac{\int X}{2}\right) - \left(\frac{\int CH_3}{3}\right)\right]$$

$$(Moles\ \ AN)\ \times\ \left(53.06\ \ \frac{g}{mole}\right) = relative\ \ weight\ \ of\ \ AN$$

$$Weight\ \ Percent\ \ AN = \frac{relative\ \ weight\ \ AN}{relative\ \ weight\ \ AN\ \ + relative\ \ weight\ \ MA}\ \times 100$$

$$Weight\ \ Percent\ \ MA = 100 - weight\ \ percent\ \ AN$$

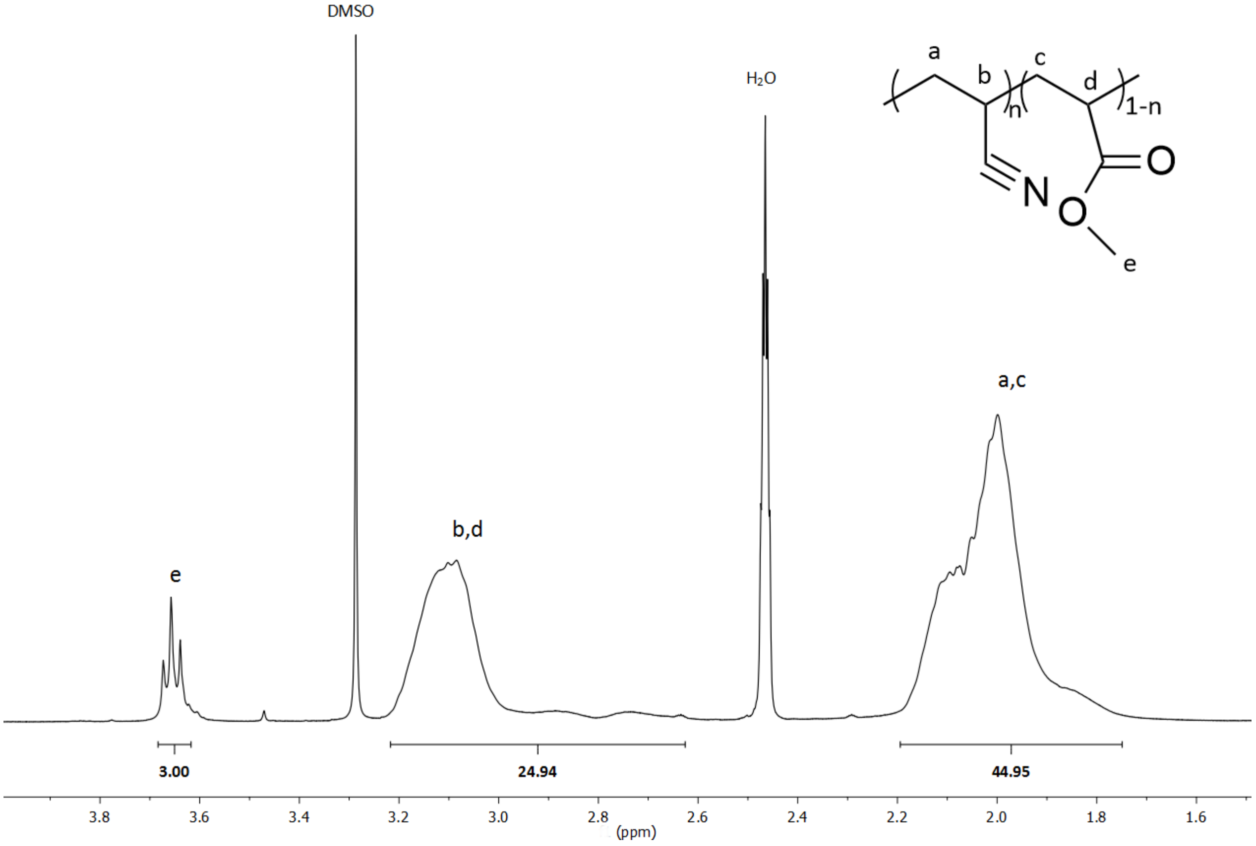

Figure 2. ^{1}H-NMR Spectrum of PAN-MA

From analysis of the ^{1}H-NMR spectra, the copolymer was found to be 95.6 ± 0.13 mole % acrylonitrile and 4.40 ± 0.13 mole % methyl acrylate.

3.2 Molecular weight of the PAN-MA copolymer

Molecular weight of the PAN-MA precursor copolymer has been shown to exert an effect on the mechanical properties of the resulting carbon fiber produced from solution-spun precursor fibers. Very high molecular weight copolymers yield carbon fibers with higher tensile strengths, elastic moduli, and ultimate elongations than carbon fibers produced from lower molecular weight copolymers [31, 32]. The precursor fiber produced from a high molecular weight PAN-MA produced filaments of smaller diameter than filaments produced from low molecular weight PAN-MA due to lower solids content in the spinning dope and higher drawability. It is hypothesized that the smaller diameter of the precursor filaments allows better diffusion of oxygen throughout the carbon fiber as it forms, thus resulting in a homogeneous microstructure across the diameter of the carbon fibers and that this contributes to significantly higher moduli and tensile strengths [32].

Size exclusion chromatography (SEC) was used to analyze the molecular weight and molecular weight distribution of the PAN-MA copolymer in this study. The light scattering and refractive index curves are shown in Figure 3. The results show a smooth light scattering curve, without any high or low molecular weight shoulders, indicative of a normal Gaussian distribution. The dn/dc value for this copolymer composition was measured offline and used to calculate the molecular weights. This is necessary since the molecular weights calculated from the light scattering data depend on the square of the refractive index increment, and thus, this provides confidence in the molecular weight values.

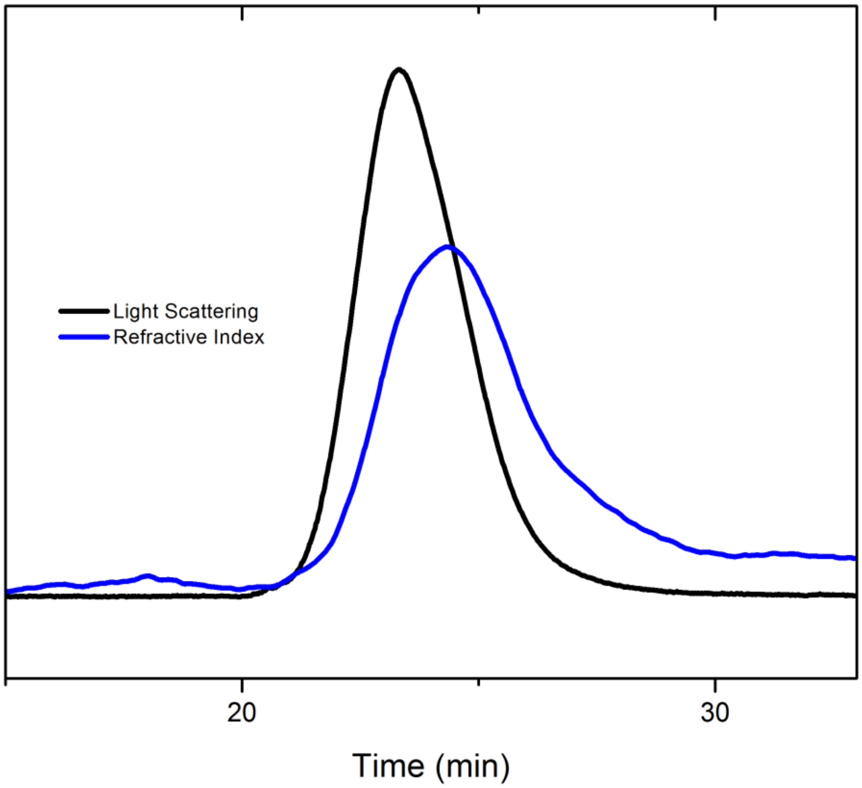

Figure 3. Size Exclusion Chromatograms for PAN-MA Copolymer where the M_n = 123.1 kDa, M_w = 238.2 kDa, polydispersity = 1.9, and dn/dc = 0.0855 mL/g.

3.3 Thermal transitions of polymer/modifier blends

DSC was used to determine the melting points of PAN-MA compounded with a binary mixture consisting of H_2O and various plasticizing melting point modifiers. Analysis of the DSC experiments was performed using TA Universal Analysis software. The T_m of each composition was assigned as the peak of the endotherm of the second heat of each experiment. Prior literature has shown that the maximum melting point depression of a PAN-vinyl acetate copolymer (88 wt% AN and 12 wt% vinyl acetate) solely from modification with H_2O occurs at 20 wt % of H_2O. This yielded a melting point of ~155°C [17], and additional modifiers had to be added into the mixture to depress the melting point further [19]. The melting point depression effect of H_2O is not well understood, but it is thought that the water molecules are able to interact with the pendant nitrile groups of the copolymer in a hydrogen bonding motif. This is most likely in the amorphous component of the copolymer, and weakly shields the nitrile from the repulsive dipole-dipole interactions which give the copolymer its characteristic rigid helical morphology [2, 3, 33, 34]. For the data depicted in Figure 4, all compositions included 20 wt % of H_2O with increasing amounts of a second melting modifier. The ratio of water molecules relative to nitrile substituents on the copolymer at 20 wt% of water is approximately 0.87:1. Figure 4 shows a curve of T_m vs percentage of the second modifier. It shows that the two nitrile containing modifiers, acetonitrile (ACN) and adiponitrile (ADPN), are more efficient at depressing the melting points relative to the other modifiers when used in combination with the water.

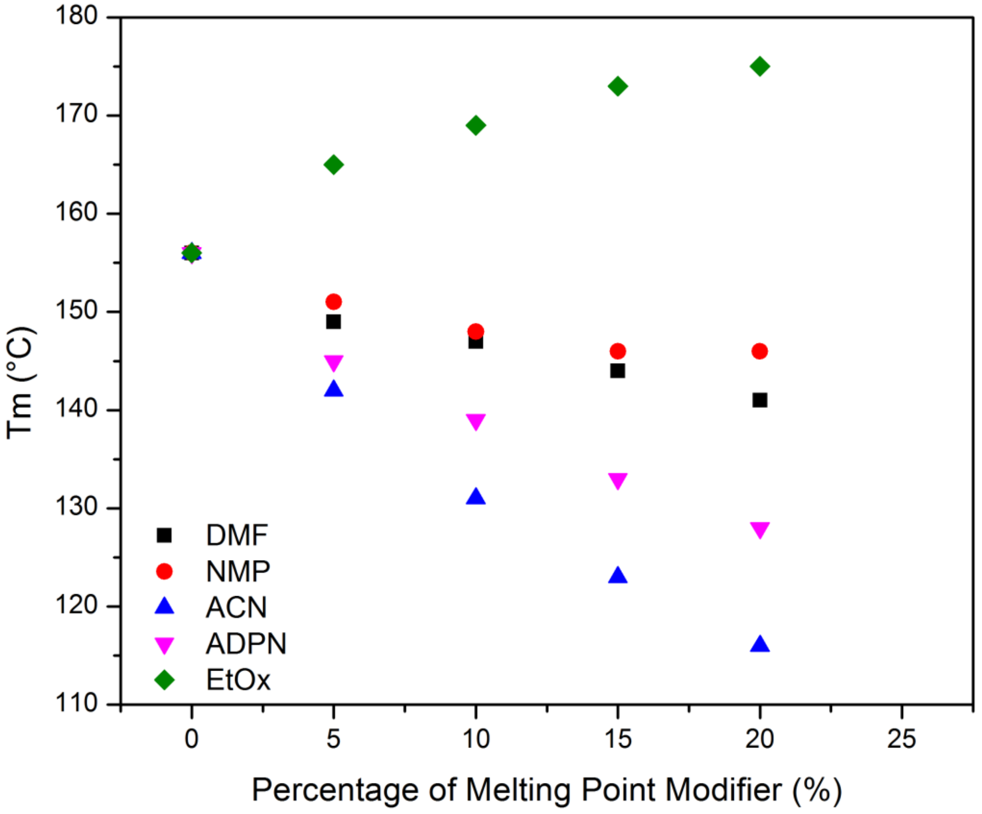

Figure 4. Melting points vs percentage of modifier in the PAN-MA mixtures. Each composition contains 20 wt % of water in addition to the denoted modifiers.

It is hypothesized that the mechanism for this pronounced effect of the nitrile-containing modifiers arises from the modifier nitrile group maintaining complementary dipole interactions with the nitrile groups along the PAN-MA backbone, thereby disrupting some of the interchain nitrile-nitrile interactions between neighboring PAN-MA chains. This may penetrate somewhat into the crystalline domains, thereby allowing the ingress of water into those regions which may have otherwise been inaccessible. Complementary interchain nitrile-nitrile polar interactions are thought to be the mechanism by which acrylonitrile based polymers form lamellae for crystallization [3, 33-37]. One composition, PAN-MA/ACN/H_2O 55:25:20 wt:wt:wt, showed a depressed melting point of 116°C, which is a depression of over 200°C from the neat copolymer. DMF and NMP also have a synergistic effect with H_2O to depress the melting point of PAN-MA. Unlike ACN and ADPN, DMF and NMP are good solvents for the copolymer at room temperature. It is hypothesized that these two materials depress the melting point of the copolymer by a similar mechanism as the one in which they dissolve the copolymer. We postulate that such modifiers are able to disrupt the crystallinity of the polymer and allow the H_2O to penetrate into these domains, thereby lowering the melting point. In contrast to all of the other materials used in this study, EtOx had an antagonistic effect in combination with H_2O on the melting point of the copolymer. As more EtOx was added to the PAN-MA/ 20 wt % H_2O blends, the melting point of the system increased systematically. This was a somewhat surprising result, since EtOx is an isomer of NMP. This affords some insight into the mechanism by which these modifiers mediate the melting points, and strongly supports the assertion that the water is necessary to achieve the desired melting point depression. EtOx is a monomer for a very hydrophilic polymer [38], and is quite hydrophilic itself. Some melting point depression is achieved just by the addition of 20 wt % of H_2O, but as EtOx is added to the system, it is believed that a competition results between the polymer and EtOx for interaction with the H_2O molecules, thereby reducing the efficacy of the effect of H_2O hydrogen bonded to the copolymer.

Since the two nitrile-functional melting point modifiers used in this study yielded the best melting point depressant properties when used in combination with H_2O, these two materials were chosen for a further study in which the wt % of water was varied and the resulting T_m's were determined by DSC. The results are tabulated in Table 1, and indicate that many compositions of PAN-MA mixed with water and a nitrile-containing melting point modifier show promise as potential melt-processable carbon fiber precursor materials.

Table 1. T_m of PAN-MA/CAN/H_2O or PAN-MA/ADPN/H_2O compositions.

MP Mod.	PAN-MA (%/wt.)	MP Mod. (%/wt.)	H_2O (%/wt.)	T_m (°C)
ACN	55	25	20	116
	60	20	20	123
	65	15	20	131
	70	10	20	142
	70	15	15	134
	70	20	10	135
	70	25	5	146
	70	30	0	165
	75	10	15	139
	80	10	10	150
	85	10	5	168
ADPN	55	25	20	128
	60	20	20	133
	65	15	20	139
	70	10	20	145
	70	15	15	136
	70	20	10	136
	70	25	5	161
	70	30	0	185
	75	10	15	148
	80	10	10	158
	85	10	5	181

3.3 Thermal stability of polymer/modifier blends against crosslinking

PAN-based polymers are known to undergo crosslinking reactions in the presence of oxygen and at elevated temperatures. This results in the desired ladder polymer formation during carbon fiber production. However, it is important for the carbon fiber precursor to undergo this reaction at the appropriate time in the stabilization process. Therefore, it was judicious to determine whether the melts that resulted from mixing PAN-MA with water and the synergistic melting point modifiers resisted crosslinking for an amount of time that was adequate to extrude precursor fibers. An isothermal DSC experiment was designed to probe the relative stabilities of melts of PAN-MA compounded with a binary mixture consisting of H_2O and various melting point modifiers. Each experiment was performed at a temperature above the melting point of the mixture. During the isothermal DSC experiment, the evolution of an exotherm was attributed to crosslinking reactions, and the time required for the exotherm to begin was recorded. Some of the most promising candidates from Figure 4 were chosen for this experiment.

Conventional wisdom dictates that a melt should remain stable against crosslinking for at least an hour to be a suitable candidate for melt extrusion. Figure 5 shows the times for onset of an exotherm vs temperature for various PAN-MA/melting point modifier/H_2O mixtures. It was observed that all of the compositions studied were stable for at least an hour at temperatures $\leq 200°C$. The general trend from Figure 5 is that the stability of PAN-MA/melting point modifier/H_2O compositions are as follows: ADPN>ACN>DMF with the nitrile-containing melting point modifiers producing mixtures that were significantly more stable than when using DMF. This is most likely due to the fact that the nitrile modifiers are better able to disrupt the nitrile-nitrile interchain forces which are necessary for the crosslinking reaction. It is also worth noting that there was little difference in stability between the two ACN containing mixtures that were studied.

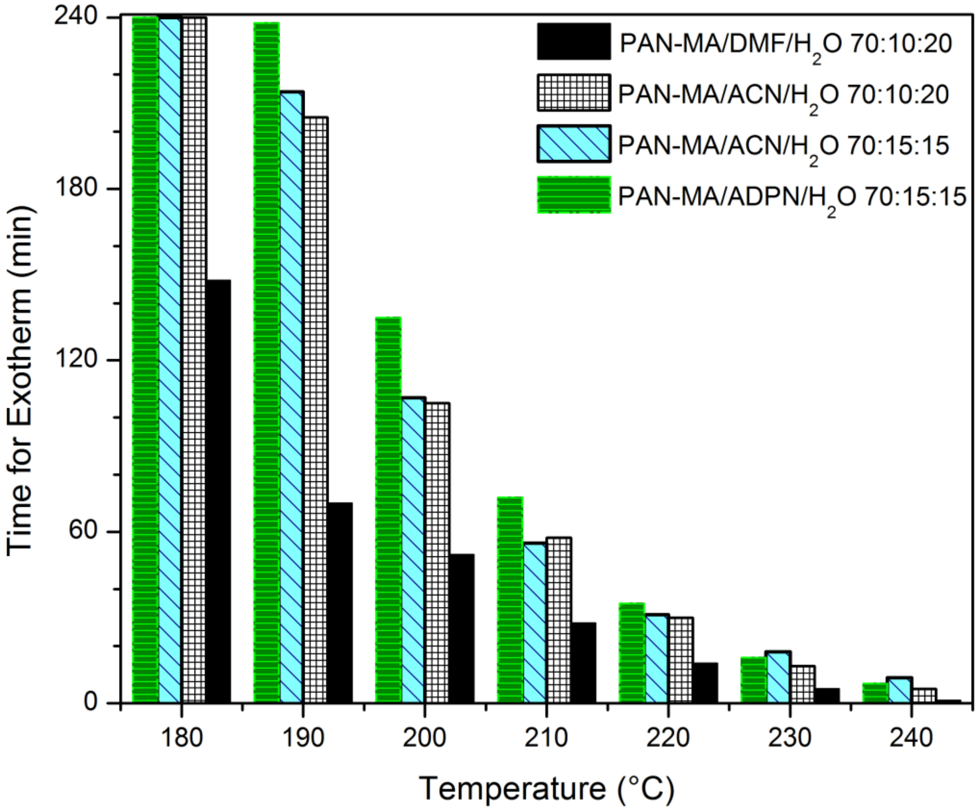

Figure 5. Times for onset of an exotherm vs temperature in isothermal DSC experiments.

3.4 Time and shear dependent melt rheology

Melt viscosities are key to understanding potential melt extrusion conditions that are suitable for melt processing of copolymer/melting point modifier mixtures. Specifically, we wish to understand the relationship between melt viscosity and shear rate as a function of time and temperature to establish practical limitations on extrusion flow rate, die geometry, and residence time. Temperatures were chosen above the melting points of the mixtures. Steady shear viscosity was measured as a complementary experiment to analyze the thermal stability of the copolymer/modifier mixtures under shear, and for comparison to the static thermal stability analysis performed using isothermal DSC.

Results of the time-dependent steady shear measurements are illustrated in Figure 6. A low apparent shear rate of 161.3 s^{-1} was used in all measurements to enable the longest possible measurement time at a low volumetric flow rate. Figure 6A shows the apparent viscosity for a PAN-MA/ACN/H_2O 70:15:15 wt:wt:wt blend at temperatures ranging from 170-190°C. The data show an increase in the viscosity at 170 and 180°C that occurs at different times during the experiment. Following the pre-conditioning step at high plunger speed that was employed to compress the sample at the beginning of the experiment, the copolymer mixtures require time to relax to steady-state viscosity. At the higher temperature of 190°C, the sample quickly relaxes to steady-state viscosity. As temperature is decreased to 180 and then to 170°C, the relaxation time increases as expected, as less thermal energy and corresponding thermal motion increase the characteristic relaxation time [39]. However, in all cases, the polymer mixture relaxes to a steady state viscosity plateau prior to observation of significant crosslinking, which is typically observed as a sharp increase in viscosity from the steady state plateau.

The results in Figure 6A suggest that the activation energy for flow is relatively small for the copolymer mixtures, with relatively small differences in viscosity observed as a function of temperature at the measured shear rate [39]. However, the thermal stability is drastically impacted by changes in measurement temperature. At 170°C, the composition maintained a stable viscosity of approximately 2000 Pa*s for 116 minutes under shear. The times that are reported are limited by the amount of sample that can be loaded into the rheometer, but the sample was stable during the whole course of the experiment. At 180°C, the mixture reached a stable viscosity of approximately 2000 Pa*s, which it maintained for approximately 87 minutes, after which the viscosity increased at a moderate rate. The viscosity at 190°C showed a mixture that maintained a stable viscosity of approximately 1300 Pa*s for approximately 47 minutes, after which the viscosity sharply decreased and then quickly increased. It is hypothesized that the crosslinking kinetics increase substantially as temperature increases. As the kinetics increase, the contraction of the system during the crosslinking step occurs faster than the rheometer can push the material through the capillary. As a result, there is a period of time before the plunger completely compacts the contracted copolymer prior to observation of the very sharp, almost discontinuous increase in viscosity that is indicative of a highly crosslinked system.

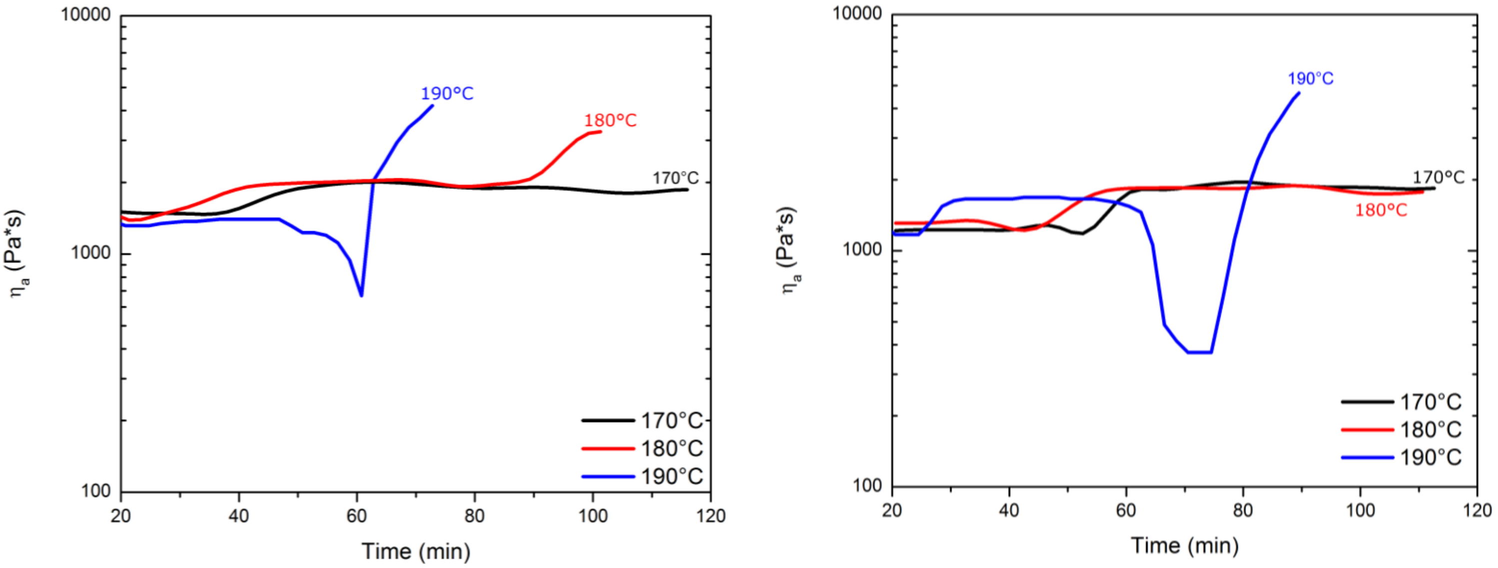

Figure 6. (A) Log Viscosity as a function of Time for PAN-MA/ACN/H_2O 70:15:15 wt:wt:wt mixtures. **(B)** Log Viscosity as a function of Time for PAN-MA/ADPN/H_2O 70:15:15 wt:wt:wt mixtures

Figure 6B shows the analogous time dependent apparent viscosity results for PAN-MA/ADPN/H_2O 70:15:15 wt:wt:wt blends at temperatures ranging from 170-190°C. This mixture exhibits similar trends in response to the PAN-MA/ACN/H_2O 70:15:15, except that the relaxation to steady state requires a longer time to reach a viscosity plateau. Additionally, the mixture exhibits a comparable stable time relative to the ACN mixture at 170°C, and a longer stable time than the ACN mixture at both 180 and 190°C. This result confirms the results from isothermal DSC measurements that indicate that PAN-MA mixtures containing ADPN are more stable against thermally induced crosslinking than mixtures that contain ACN. However, the times observed via capillary viscosity measurements are substantially shorter than isothermal DSC results. DSC measures thermal stability under static flow conditions, while rheometry imposes a constant shear and high pressures. The combined effects of shear and pressure assist in introducing thermally metastable functionalities during the crosslinking reaction, effectively increasing the rate at which the reaction takes place and resulting in an equivalent reduction in stable time.

Overall, time-dependent capillary rheometry indicated that mixtures of PAN-MA, ACN or ADPN, and H_2O can maintain a stable viscosity for over an hour at both 170°C and 180°C. Mixtures containing ADPN prove to be slightly more stable than their ACN counterparts. At 190°C, PAN-MA mixtures containing either ACN or ADPN are thermally metastable and have limited potential extrusion residence time prior to crosslinking. The stability times can be found in Table 2.

In order to process polymer melts, one needs knowledge of the shear rate dependence of viscosity to analyze multiple potential processing conditions. Figure 7 illustrates the shear rate dependence of viscosity for mixtures of PAN-MA/H_2O with ACN and ADPN at temperatures ranging from 170-190°C. Residence time was limited based on the results in Figure 6 to ensure that minimal thermally induced crosslinking occurred during the course of the measurements.

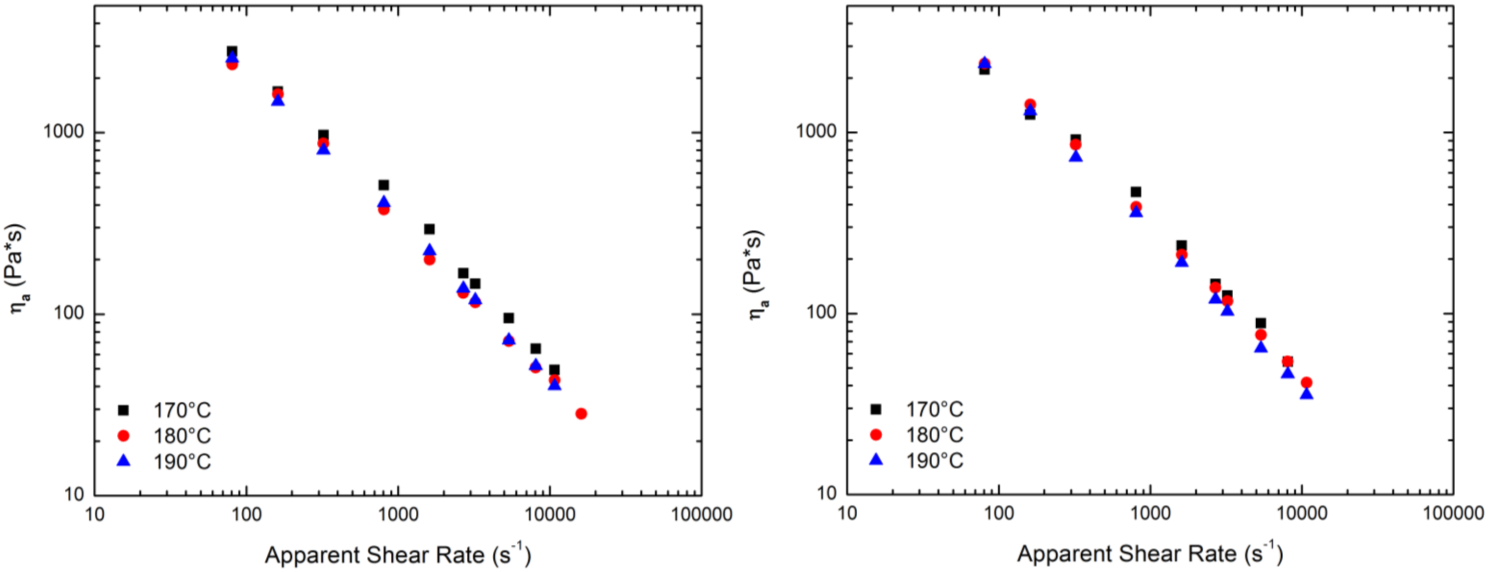

Figure 7 (A). Viscosity as a function of Apparent Shear Rate for PAN-MA/ACN/H_2O 70:15:15 wt:wt:wt mixtures. **(B)** Viscosity as a function of Apparent Shear Rate for PAN-MA/ADPN/H_2O 75:10:15 wt:wt:wt mixtures.

For both materials, the data in Figure 7 indicate shear-thinning behavior for these copolymer mixtures at all of the measurement temperatures. Furthermore, in all cases, the data can be fitted by a linear regression with excellent fit; R-squared values are all >0.99. The flow consistency index, K, and the flow behavior index, n, were calculated for both mixtures at all three temperatures using a power law fluid model (equation 5) for comparison of the effect of the additives on viscosity at multiple shear rates and temperatures (Table 2). The results indicate that the ADPN modifier/H_2O mixture induces more change in the degree of shear thinning as temperature is increased, which is desirable and advantageous for extrusion and increased throughput compared to the ACN modifier/H_2O mixture. However, at 180°C, the ACN/H_2O mixture has a higher degree of shear thinning. Thus the benefit of the temperature-dependent shear response of ADPN/H_2O is not realized until the mixture is processed above 180°C.

Table 2. Stability Times of Melts and Power Law Model Parameters

Copolymer Mixture	Temperature	Stability Time (min)	K	n
PAN-MA/ACN/H_2O 70:15:15	170°C	≥116	115202	0.17
	180°C	87	113611	0.15
	190°C	47	112769	0.15
PAN-MA/ADPN/H_2O 70:15:15	170°C	≥113	81072	0.20
	180°C	≥111	100249	0.16
	190°C	63	106064	0.14

Conclusion

Properties of blends of multiple small molecule melting point modifiers with a high molecular weight, high acrylonitrile content PAN-MA copolymer have been investigated to assess the potential for melt spinning. Melting point modifiers that contain nitrile functionality, when used synergistically with water, showed the most promise as they lower the T_m of the copolymer most effectively. The resulting melt is stable for ample time to allow melt extrusion as confirmed by isothermal DSC and time-dependent capillary rheometry. Copolymer mixtures containing nitrile melting point modifiers, in combination with water, show a strong time dependence for remaining stable, but do not show a strong temperature dependence on shear-dependent melt viscosity. By fitting the shear-dependent viscosity results to a power law fluid model, the flow consistency index and flow behavior index were determined at temperatures ranging from 170-190°C to compare the impact of the different compositions on rheology and enable estimation of viscosity at shear rates above those measured via pressurized capillary rheometry. The model results indicate that the ADPN/H_2O mixture has a stronger influence on the temperature dependence of shear thinning, but that the benefit is not realized unless the mixture is processed above 180°C. However, the stability times may be marginal above 180°C and thus, both the ACN/H_2O and ADPN/H_2O mixtures are likely good candidates for further investigations of melt-spinning. The results overall suggest that multiple compositions of the PAN-MA copolymer mixed with water and nitrile-containing melting point modifiers are potentially suitable for melt spinning to produce precursor fibers for carbon fiber production.

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THERMAL AND TIME-DEPENDENT RHEOLOGICAL STABILITY BEHAVIOR OF POLYACRYLONITRILE WITH VARIOUS PLASTICIZERS

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Abstract

The feasibility of melt spinning polyacrylonitrile (PAN) with plasticizers has been investigated for decades but it is still not been commercialized yet. In this paper, the thermal and time-dependent rheological stability behavior of PAN with various plasticizers is reported. The thermal behavior experiments show that the plasticizers are able to sufficiently decrease the melt temperature of PAN which make the melt spinning process feasible. The time-dependent rheological stability experiments show that PAN could hold its viscosity stable without significant degradation and crosslinking for a sufficient period of time below 180°C.

Introduction

Polyacrylonitrile (PAN) fiber is currently one of the most important synthetic fibers and approximately 90% of carbon fiber is made from PAN fibers as a precursor [1]. PAN-based carbon fiber plays a significant role in many modern industries, such as the aerospace and automobile industries, because it has low density, high thermal stability, high tensile strength and high tensile modulus. However, due to the limitations of the current PAN spinning processes (solution spinning), the cost is relatively high and the relevant solvents are environmental unfriendly. The development of PAN melt spinning has the potential to significantly reduce the cost of carbon fiber.

The melting point of PAN polymer is as high as 320°C, but PAN starts to suffer a cyclization reaction around 180°C (the reaction becomes rapid and spontaneous at 220°C) [2]. This degradation reaction is undesirable in the spinning process (but desirable in the carbon fiber conversion process). The major challenge of PAN melt spinning is to find a plasticizer to reduce the melting point of PAN and entirely remove the plasticizer after the spinning.

In 1952, Coxe [3] first discovered that water could be used as plasticizer to hydrate the pendant nitrile groups of PAN, which would significantly reduce the melting point of PAN to below 200 °C. It allows PAN to be melt extruded without significant degradation. However, he failed to develop a complete melt spinning system due to the steam foaming problems. After that, some other substances have been mixed with water in order to further decrease the melting point of PAN. These substances are normally polar and able to form an azeotrope with water. BASF [4] claims in their patent that a mixture of water and acetonitrile(AC) could be used as plasticizer for the PAN melt spinning. This process has been proved to be very effective and it can produce a decent quality fiber. However, AC is carcinogenic and needs to be recovered, so the spinning cost is not adequately reduced. Also, the mixture of water and AC cannot be removed completely after the spinning process, which could cause problems in further processing steps, such as carbonation and stabilization.

In this study, two potential plasticizers, water and ethanol, are considered. We first investigate the thermal behavior of the plasticized polyacrylonitrile (PAN) by using Differential Scanning Calorimetry (DSC), which provides the melting temperature of the PAN and plasticizers mixture. Time-dependent rheological tests are followed to obtain the basic viscosity data and test the stability of PAN. The preliminary results of this study will be presented in this paper.

Experimental

Materials

Polyacrylonitrile copolymer was kindly provided by FISIPE of Portugal. The copolymer sample contains 93 mol% of acrylonitrile (AN) and 7 mol% vinyl acetate (VA) and has an intrinsic viscosity (IV) of 1.27. Deionized water and 200-proof ethanol (Fisher Scientific, used as received) are used as plasticizers in this study.

DSC Analysis

The glass transition temperature, Tg, and the melting temperature, Tm, values were obtained from Differential Scanning Calorimetry (DSC) measured by a Thermal Analysis (TA) Q1000. A 10 ℃/min heating rate was used to determine the Tg and Tm of all the plasticizer blends. High volume pans with O-ring seals were used to prevent volatilization of the plasticizer. A heat/cool/heat cycle was performed. The pans were heated from 0 to 200 ℃, cooled to 0 ℃ and then heated to 250 ℃.

Viscosity Measurement

Viscosity measurements were performed on a Gottfert Rheograph 2001 capillary rheometer. A pressure chamber is additionally attached to the rheometer to pressurize the entire system with nitrogen. Extra teflon O-rings are also applied on the plunger to help sealing the entire pressurized system. The detailed schematic diagram of the modified capillary rheometer is provided below.

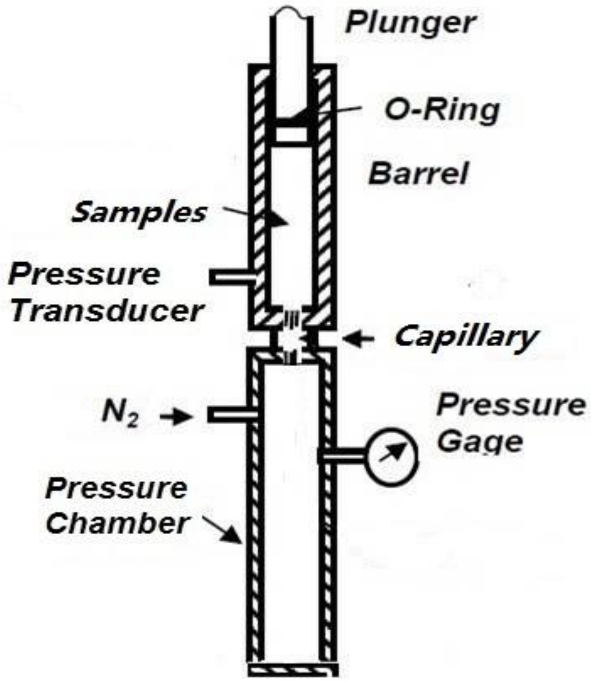

Figure 1. the schematicof capillary rheometer

The copolymer powder was first mixed with a certain amount of the plasticizers, then it was press molded to a rod-shaped sample. The copolymer rods had a diameter of 13.5 mm, which is slightly smaller than the diameter of the rheometer barrel, which is 15 mm. The rod-shaped copolymer sample was easier to load to the capillary rheometer since the rheometer was preheated before loading the samples. This also avoided voids in the samples. For one test, approximately 10 grams of mixed sample was used. The system was sealed and pressurized immediately after the copolymer rods had been loaded. The copolymer rods were placed in the rheometer barrel under pressurized conditions for 8 minutes, which was called the “melting time” to ensure the copolymer rods completely melted in the rheometer before the rheological tests.

A capillary with a diameter of 0.6 mm and length of 30mm and entry angle of 180 °was used. The pressure gradient was measured from both the pressure transducer above the capillary and the pressure gage below the capillary. For viscosity measurements, the pressure below the capillary was provided by a nitrogen tank with values ranging from 10.34 bar (150 psi) to 12.41bar (180 psi). Viscosity values were calculated from the pressure gradient from the equations below [5],

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \tag{1}$$

$$\tau_R = \frac{\Delta PR}{2L} \tag{2}$$

$$\eta_a = \frac{\tau_R}{\dot{\gamma}_a} \tag{3}$$

Here $\dot{\gamma}_a$ is the apparent shear rate, which is determined from the plunger speed, and the value of shear rate for all the time-dependent viscosity experiments was fixed at 72 s^{-1}. τ_R is the wall shear stress calculated from the pressure gradient. η_a is the apparent viscosity value that could be calculated from both shear rate and shear stress.

There was a limitation for this capillary rheometer while performing time-dependent viscosity measurements. This rheometer was designed in shear-rate basis. That is, before the test, up to 18 apparent shear rate values were able to be input, and the system would automatically record data and switch the apparent shear rate in sequence while the pressure transducer reading was stable. Therefore, the more stable the viscosity tendency, the shorter the experimental length. This limitation would cause the inconsistency of the length of each time-dependent rheological test.

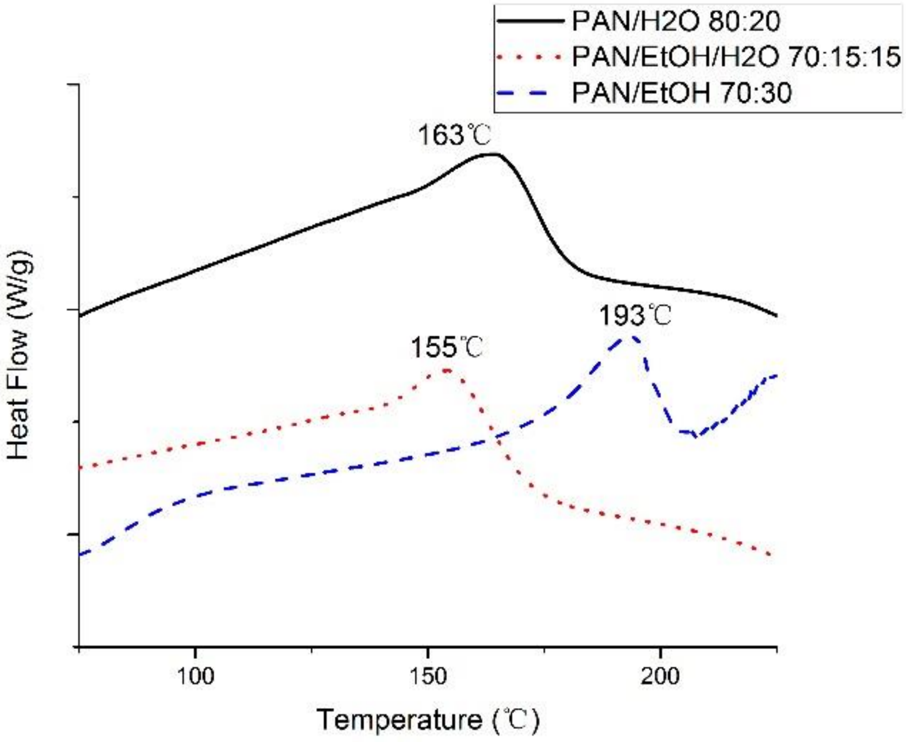

Figure 2. DSC scan of PAN/VA copolymer plasticized with various plasticizers, ratio in weight basis

Results and Discussion

Thermal Behaviors of Plasticized PAN Polymer

Figure 2 presents the DSC curves for PAN/VA copolymer plasticized with the two different potential plasticizers, water (PAN/H_2O, contains 20 weight percent of water), ethanol (PAN/EtOH, contains 30 weight percent of ethanol) and their mixture (PAN/EtOH/H_2O, contains 15 weight percent of water and 15 weight percent of ethanol). The solid curve shows that the melting temperature of PAN/H_2O decreases to 163℃, and the dot curve indicates that with additional of ethanol, the melting temperature of the PAN copolymer is further decreased to 155℃. However, by plasticizing with ethanol only, the melting point of PAN copolymer only decreased to 193℃, which is much higher than when plasticized by water and the water/ethanol mixture.

The thermal analysis indicates that water plays an essential role in lowering the melting temperature of PAN copolymer. To avoid severe degradation and crosslinking during the PAN melt spinning process, the processing temperature has to below 185℃. Obviously, although plasticization by ethanol only was not adequate in lowering the melting temperature, the water/ethanol mixture as plasticizers made PAN/VA copolymer melt spinning theoretically feasible. From the DSC data, it shows that the water/ethanol mixture is more effective in decreasing the melting temperature of PAN/VA copolymer than water only. This discovery allows water/ethanol mixture to become a remarkable potential plasticizer for future PAN melt spinning studies.

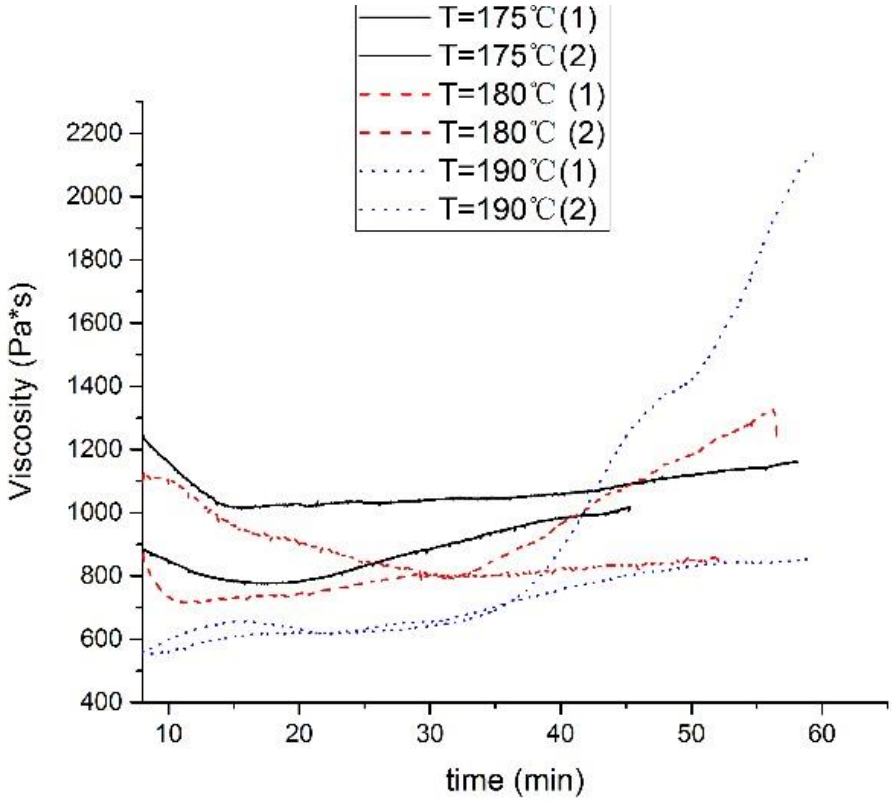

Figure 3. Time dependent apparent viscosity data for PAN/VA copolymer plasticized with water/ethanol (weight percentage: 70/15/15)

Time-Dependent Rheological Behaviors

Investigation of the time-dependent rheological behaviors of plasticized PAN copolymer is not only able to test the stability of the polymer under a certain temperature as the apparent viscosity data could be an indication of degradation, but also provide related data for designing melt spinning extruder in future studies. Due to the high melting temperature, further study of the time-dependent rheological behavior for PAN/EtOH was discontinued. In this section, the time-dependent viscosity changes of PAN/EtOH/H_2O and PAN/H_2O are the major focus.

Figure 3 presents the time-dependent viscosity curves of PAN/EtOH/H_2O for three different temperatures. As mentioned in the previous section, there were 8 minutes of “melting time” before the starting of the rheological measurements to ensure the copolymer sample were completely melted. Two experimental runs were performed for each temperature and the numbers in the parentheses just represent different trials at the same temperature. Due to the limitation of the capillary rheometer described in the previous section, the experimental time duration length was slightly different for each test.

From the results presented in Figure 3, the viscosity is stable at 175°C (Solid lines), which indicates that the PAN copolymer barely suffers degradation in such a relatively low temperature. Besides, slight degradation may occur after 30 minutes under 180 °C since one dash line is gradually increased after 30 minutes. The dot lines shows a rapid and significant viscosity rise under 190°C after 35 minutes, which indicates obvious degradation of the PAN copolymer. These results matched the literature [2] and our expectation that the PAN copolymer starts to degrade at 180°C. As the temperature increased, the degradation will become more rapidly. The results also suggest that PAN polymer could be melt spun below 180 °C without significant degradation.

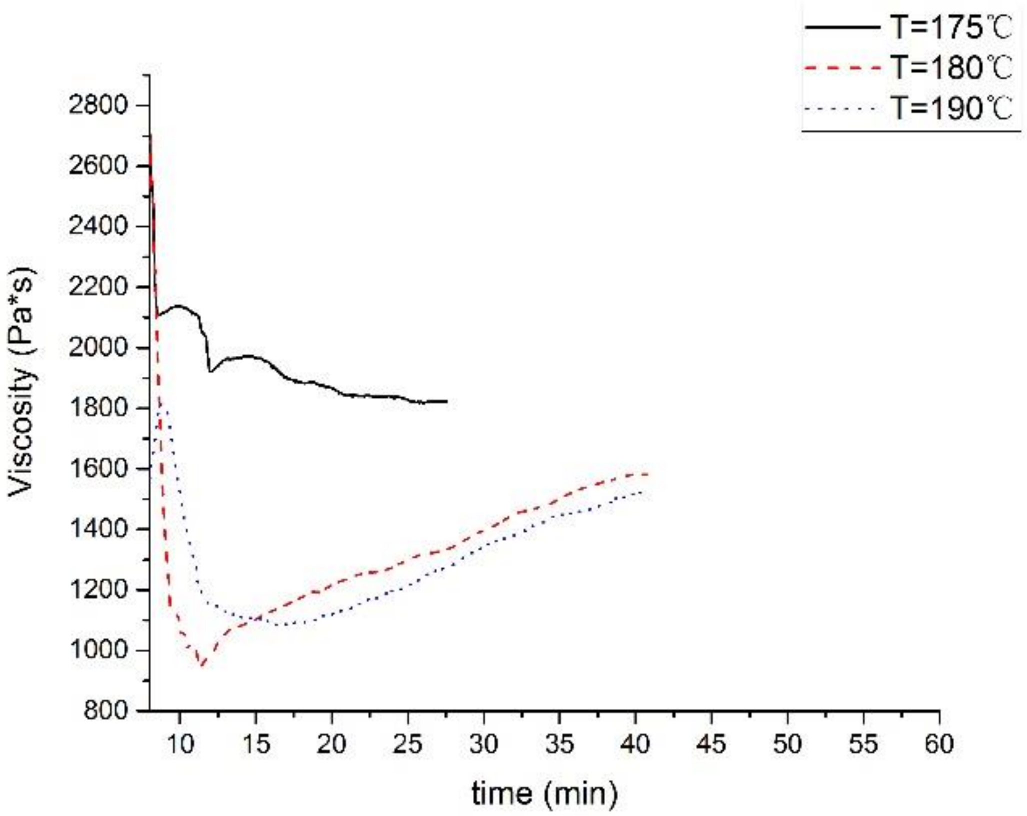

Figure 4. Time dependent apparent viscosity data for PAN/VA copolymer plasticized with water only (20 weight percent water)

Figure 4 presents the time-dependent apparent viscosity data of PAN/H_2O over the same temperature range as above. The viscosity curves trend is similar to the PAN copolymer plasticized with water/ethanol. The viscosity is stable under 175°C, but gradually increases at 180°C and 190°C.

Compared to the PAN/EtOH/H_2O, the viscosity of PAN/H_2O is higher than that of PAN/EtOH/H_2O under the same condition. This is because, **a)**, the total weight percentage of plasticizers for PAN/EtOH/H_2O was 30% compared to 20 wt% for PAN/H_2O. The additional liquid plasticizers may influence the viscosity of the melted PAN copolymer. **b)** According to the DSC data, the melting temperature of PAN/EtOH/H_2O is lower than PAN/H_2O. So under the same temperature, the PAN/H_2O may not be as completely melted as the PAN/EtOH/H_2O. At 175℃, the DSC curves show that PAN/H_2O is still in its melting range, and hence incomplete melting of the PAN copolymer may have caused such a high viscosity.

It is still not completely clear why the viscosity decreased in the first several minutes for several data curves. One possibility is the copolymer sample was still relaxing after passing from the plunger. Further investigation will be carried out to address this problem.

Conclusions

The melting and time-dependent rheological behavior for PAN/VA copolymer with various plasticizers was studied. Water and water/ethanol are appropriate plasticizers which are able to significantly lower the melting point of the PAN copolymer. The time-dependent viscosity data shows that the PAN copolymer with plasticizer was possibly melted and processed for at least 30 minutes without significantly degradation.

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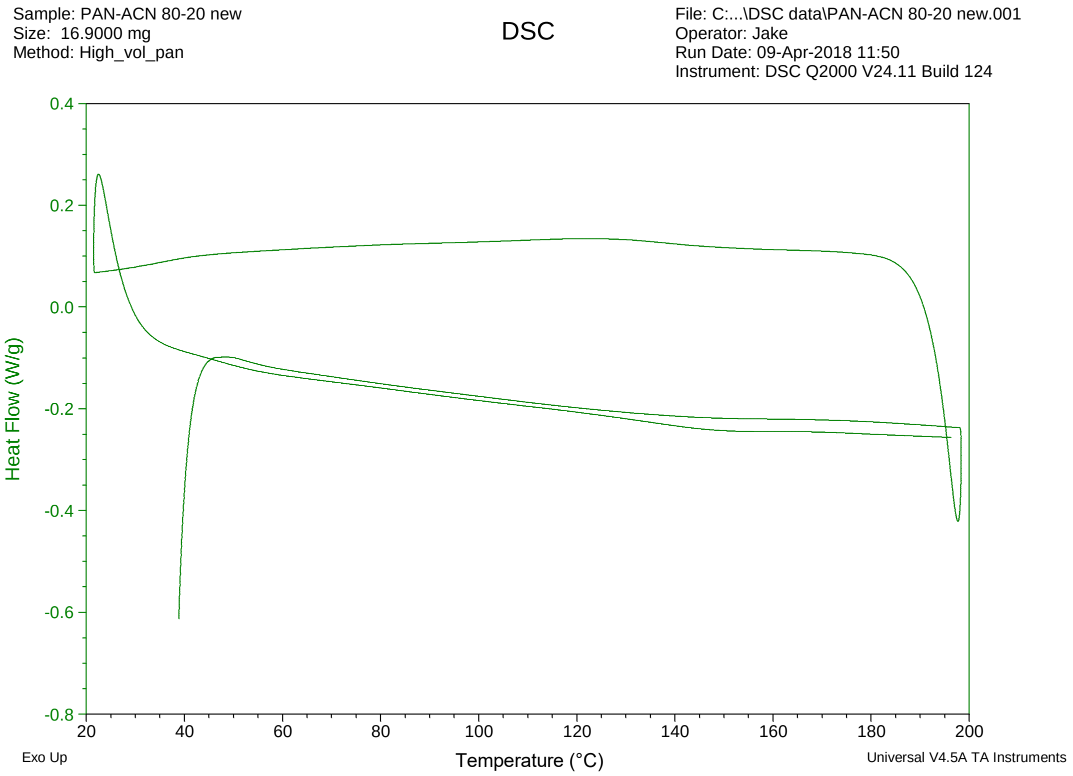
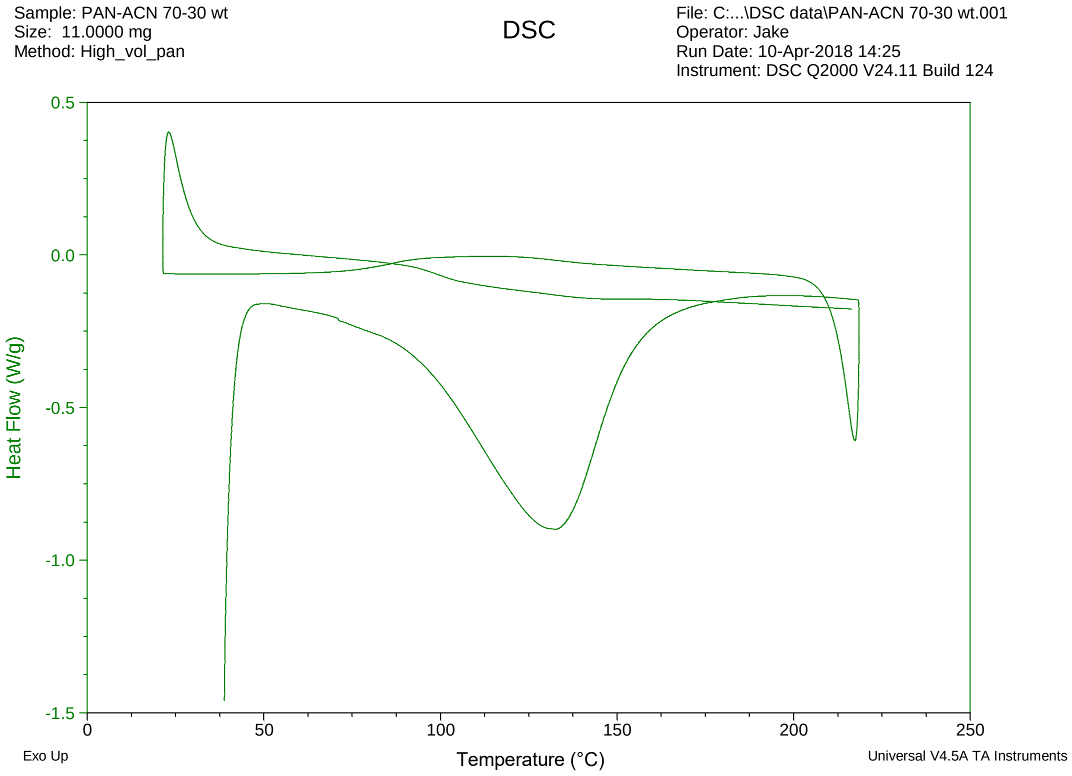
Appendix B

The appendix part B contains three part, the first part is the original DSC diagrams of PAN/plasticizers mixture, the second part is the original rheological data table and the third part is the Python code of RTD analysis.

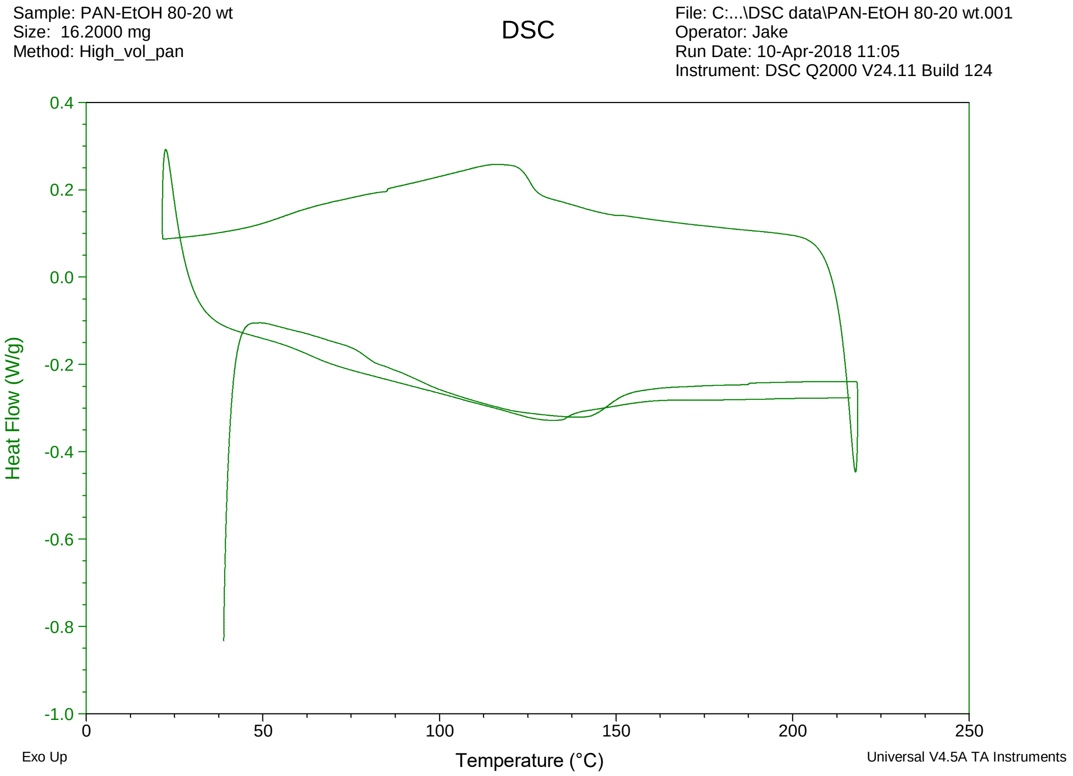
Original DSC Diagram of PAN/plasticizers mixture



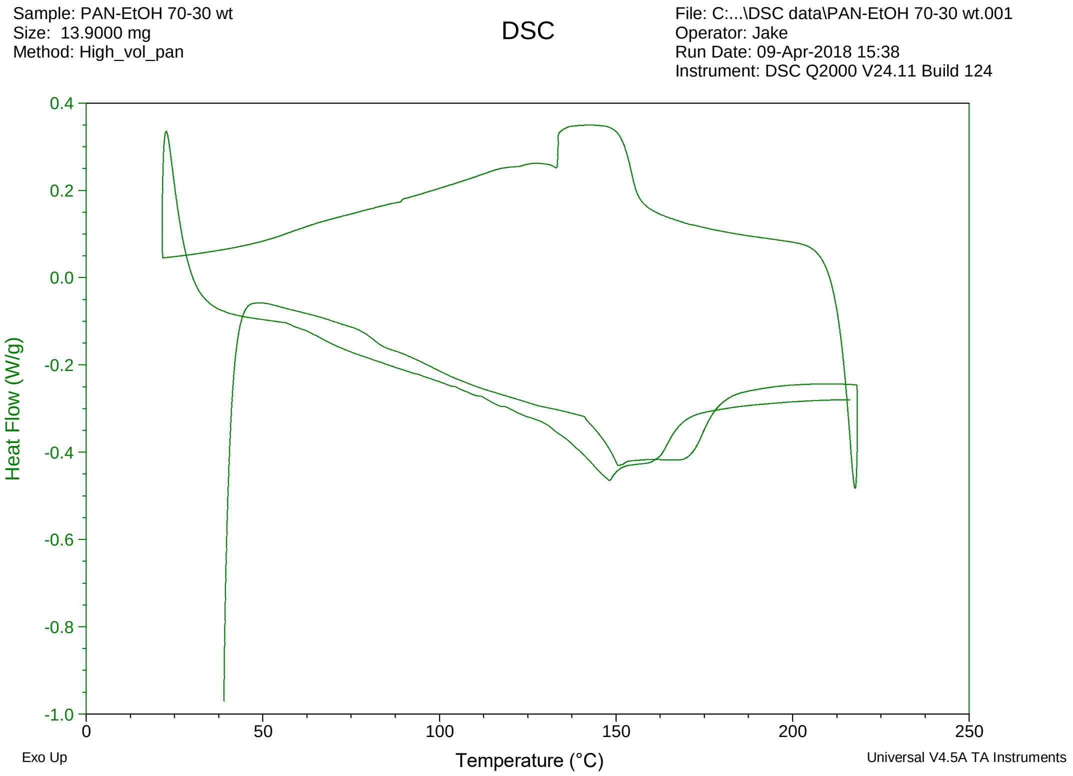
DSC Diagram for PAN/Acetonitrile with 80/20 wt% ratio



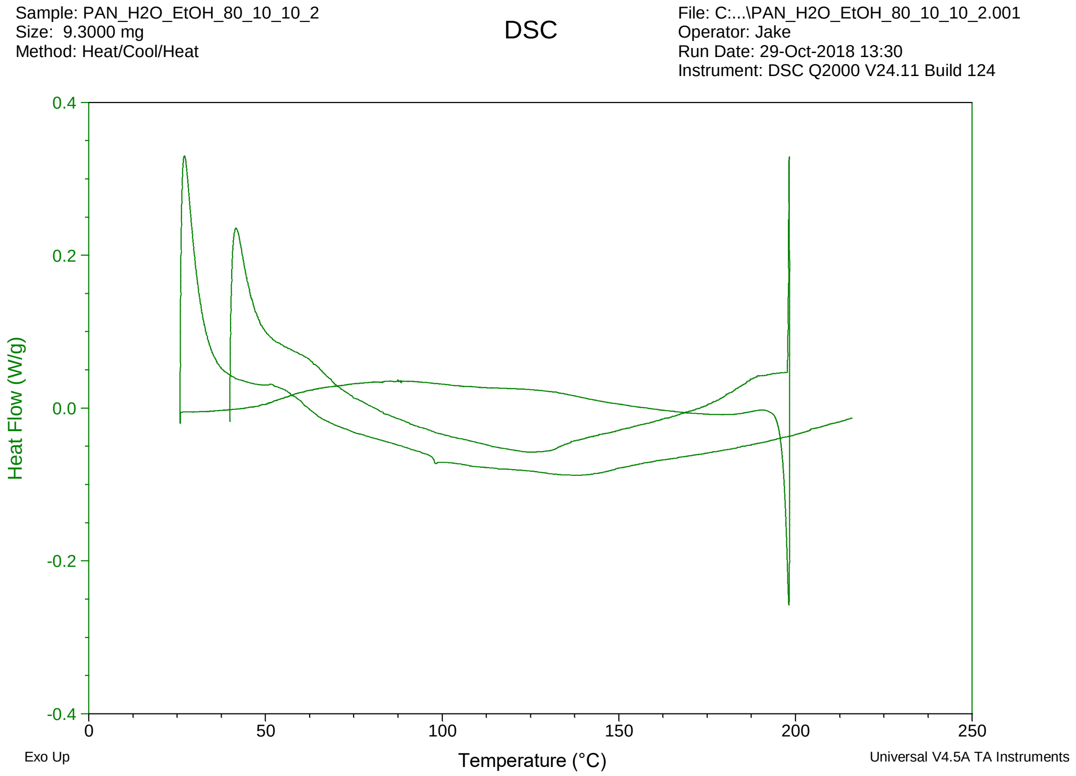
DSC Diagram for PAN/Acetonitrile with 70/30 wt% ratio



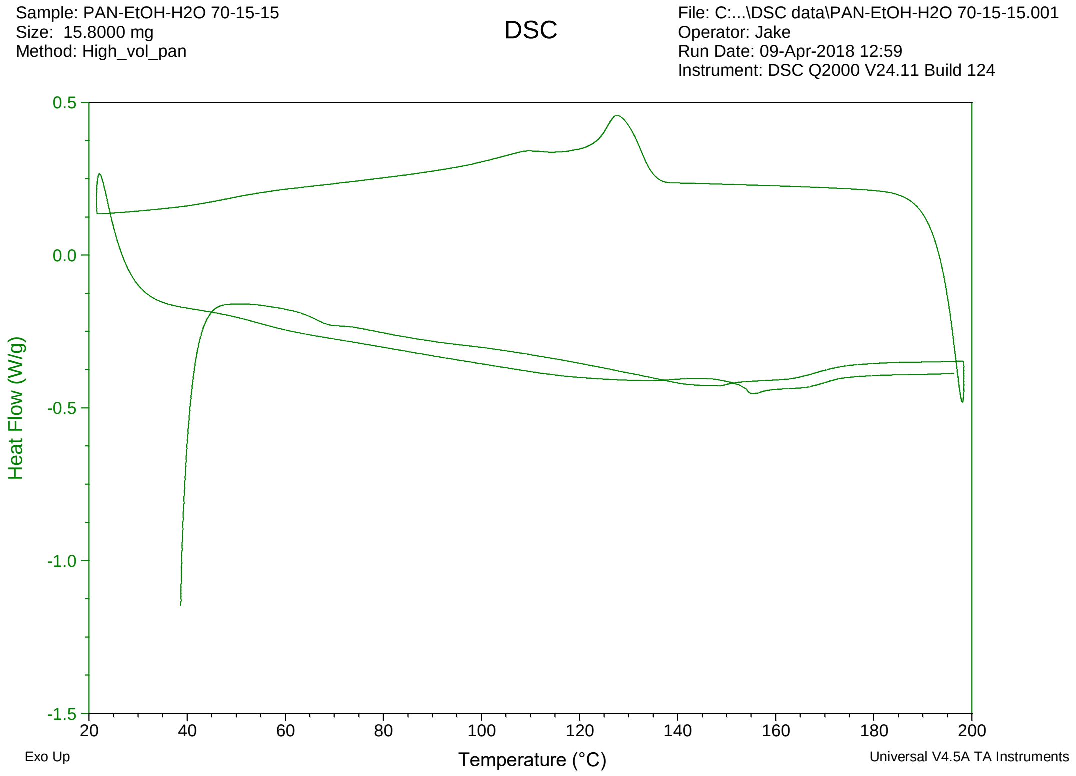
DSC Diagram for PAN/Ethanol with 80/20 wt% ratio



DSC Diagram for PAN/Ethanol with 70/30 wt% ratio



DSC Diagram for PAN/Water/Ethanol with 80/10/10 wt% ratio



DSC Diagram for PAN/Water/Ethanol with 70/15/15 wt% ratio

Rheological Data of PAN with various plasticizers

PAN/Water (80/20) Time-dependent viscosity data

	T=170 C	T=180 C	T=180C	T=190C	T=190C
Time (min)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)
2	2969.17451	1253.842046	1291.271692	748.5418264	692.3973575
4	3243.263669	1366.130984	1309.986515	748.5418264	767.2566493
6	3563.034354	1422.275452	1253.842046	748.5418264	785.9714723
8	3608.715881	1328.701338	1309.986515	748.5418264	711.1121805
10	3654.397407	1253.842046	1384.845807	748.5418264	767.2566493
12	3471.671301	1253.842046	1422.275452	748.5418264	767.2566493
14	4019.849619	1085.408639	1422.275452	767.2566493	785.9714723
16	4430.983357	1216.4124	1478.419921	767.2566493	804.6862952
18	4568.027937	1384.845807	1553.279213	767.2566493	804.6862952
20	4659.39099	1160.267931	1515.849567	785.9714723	804.6862952
22	4659.39099	1291.271692	1515.849567	785.9714723	767.2566493
24	4750.754043	1272.556869	1422.275452	767.2566493	785.9714723
26	4476.664884	1291.271692	1515.849567	767.2566493	804.6862952
28	4568.027937	1141.553108	1497.134744	767.2566493	804.6862952
30	4476.664884	1160.267931	1459.705098	785.9714723	842.1159411
32	4568.027937	1197.697577	1459.705098	785.9714723	860.830764
34	4476.664884	1235.127223	1366.130984	785.9714723	860.830764
36	4476.664884	1197.697577	1384.845807	767.2566493	898.2604099
38	4385.301831	1160.267931	1459.705098	804.6862952	467.8194822
40	4430.983357	1160.267931	1422.275452	336.8157216	318.1008986
42	4385.301831	1160.267931	1459.705098	561.3935969	232.0127131
44	4385.301831	1160.267931	1478.419921	879.545587	306.8720048
46	4293.938778	1104.123462	1497.134744	1178.982754	516.4780218
48	4293.938778	1178.982754	1459.705098	1459.705098	729.8270034
50	4202.575725	1141.553108	1366.130984	1721.71262	1160.267931
52	4293.938778	1141.553108	1422.275452	2021.149787	1571.994036
54	4248.257251	1047.978993	1422.275452	2395.446246	1834.001557
56	4111.212672	1085.408639	1422.275452	2882.031642	2096.009078

58	4111.212672	1122.838285	1459.705098		2395.446246
60	4156.894198	1066.693816	1459.705098		2882.031642
62	4111.212672	1029.264171	1478.419921		
64	4065.531145	1029.264171	1515.849567		
66	4019.849619	991.8345247	1609.423682		
68	3882.80504	1066.693816	1646.853328		
70	3928.486566	991.8345247	1553.279213		
72	3974.168093	1029.264171	1759.142265		
74	3928.486566	1104.123462	804.6862952		
76	4111.212672	748.5418264	1010.549348		
78	4156.894198	467.8194822	1422.275452		
80	3745.76046	505.2491281	1871.431203		
82	3563.034354	804.6862952	2395.446246		
84	3288.945195	1609.423682			
86	3608.715881	2432.875891			
88	3791.441987				
90	3882.80504				
92	3380.308248				
94	2877.811457				
96	3425.989775				
98	3517.352828				
100	3380.308248				
102	3334.626722				
104	2055.543981				
106	1690.091769				
108	1187.594978				

PAN/Water (80/20) Steady-shear viscosity data

	shear rate (s-1)	shear stress(Pa)	Viscosity (Pa*s)
180 C	119.644418	291300.9006	2434.722033
	239.2888359	306844.4968	1282.318482
	478.5776719	394924.8752	825.2053918
	1196.44418	498548.8499	416.6921101
	2392.888359	560723.2346	234.3290411
	3988.147266	612535.222	153.5889177
	4785.776719	571085.6321	119.3297694
	7976.294531	591810.427	74.19616023
	11964.4418	633260.0169	52.92850495
	15952.58906	643622.4144	40.34595337
180 C	124.7477344	195448.724	1272.018082
	249.4954688	229126.5158	767.2928066
	498.9909375	267985.5063	488.6734158
	1247.477344	337931.6892	216.4747688
	2494.954688	374200.0803	118.7400856
	4158.257813	381971.8784	80.69648251
	4989.909375	402696.6733	81.68828297
	8316.515625	389743.6765	55.31459053
	12474.77344	415649.6701	41.60260925
	16633.03125	457099.26	32.77736212
190 C	98.66411719	125502.5411	1566.751693
	197.3282344	151408.5348	918.3594272
	394.6564688	192858.1246	537.0548564
	986.6411719	213582.9196	270.8920453
	1973.282344	234307.7145	149.982716
	3288.803906	265394.9069	91.85863301
	3946.564688	322388.093	80.70220179
	6577.607813	363837.6828	46.86381822
	9866.411719	410468.4714	33.31921595
	13155.21563	431193.2663	27.48141653

PAN/Water (70/30) Time-dependent viscosity data

	T=170 C	T=170 C	T=180 C	T=180C	T=190C
Time (min)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)
2	3288.945195	2101.225507	1151.049757	1242.412809	511.5083859
4	3334.626722	2466.677719	1096.231925	1370.321084	420.145333
6	3243.263669	2877.811457	1096.231925	1370.321084	456.6905542
8	3257.594978	3151.900616	1096.231925	1315.503252	474.9631647
10	3256.365663	3288.945195	1077.959314	1278.958031	456.6905542
12	3334.454822	3380.308248	730.779713	1169.322367	456.6905542
14	3151.58856	3517.352828	968.3236506	1096.231925	438.4179436
16	3257.403825	3106.21909	1004.868872	950.0510401	456.6905542
18	3151.900616	3288.945195	1004.868872	785.5975448	438.4179436
20	3608.715881	3334.626722	950.0510401	694.2344918	401.8727224
22	4065.531145	2923.492984	950.0510401	675.9618812	420.145333
24	4111.212672	3151.900616	895.2332083	657.6892706	420.145333
26	4293.938778	3106.21909	895.2332083	657.6892706	420.145333
28	4293.938778	3106.21909	858.6879871	639.41666	401.8727224
30	4293.938778	3106.21909	822.1427659	639.41666	347.0548906
32	4385.301831	2969.17451	803.8701553	639.41666	365.3275012
34	4385.301831	3060.537563	767.3249342	639.41666	365.3275012
36	4202.575725	3060.537563	730.779713	621.1440495	365.3275012
38	4111.212672	2969.17451	730.779713	657.6892706	347.0548906
40	4019.849619	3106.21909	694.2344918	675.9618812	347.0548906
42	4019.849619	3060.537563	675.9618812	657.6892706	347.0548906
44	3837.123513	3060.537563	639.41666	675.9618812	347.0548906
46	3837.123513	3106.21909	621.1440495	730.779713	328.78228
48	3745.76046	3060.537563	456.6905542	712.5071024	328.78228
50	3654.397407	3106.21909	529.7809965	730.779713	310.5096694
52	3563.034354	3106.21909	493.2357753	785.5975448	310.5096694
54	3563.034354	3106.21909	456.6905542	639.41666	283.1007536
56	3471.671301	3106.21909	456.6905542	730.779713	283.1007536
58	3471.671301	3106.21909	438.4179436	694.2344918	301.3733642
60	3380.308248	3060.537563	383.6001118	694.2344918	301.3733642
62	3380.308248	3060.537563	383.6001118	730.779713	283.1007536
64	3471.671301	3151.900616	365.3275012	657.6892706	292.2370589
66	3334.626722	3014.856037	328.78228	749.0523236	264.828143
68	3471.671301	3106.21909	310.5096694	675.9618812	301.3733642

70	3471.671301	3380.308248	310.5096694	675.9618812	283.1007536
72	3471.671301	3106.21909	273.9644483	712.5071024	283.1007536
74	3425.989775	3014.856037	273.9644483	639.41666	292.2370589
76	3334.626722	3471.671301	310.5096694	675.9618812	273.9644483
78	3471.671301	3654.397407	319.6459747	675.9618812	237.4192271
80	3471.671301	3060.537563	292.2370589	694.2344918	246.5555324
82	3517.352828	3106.21909	292.2370589	675.9618812	273.9644483
84	3517.352828	3563.034354	328.78228	675.9618812	292.2370589
86	3608.715881	3654.397407	319.6459747	657.6892706	310.5096694
88	3928.486566	3471.671301	310.5096694	639.41666	319.6459747
90	4065.531145	3106.21909	292.2370589	639.41666	347.0548906
92		3471.671301	292.2370589	657.6892706	365.3275012
94		3425.989775	292.2370589	621.1440495	383.6001118
96		2877.811457	301.3733642	602.8714389	401.8727224
98		3106.21909	283.1007536	602.8714389	465.8268595
100		3334.626722	292.2370589	566.3262177	538.9173018
102		3334.626722	310.5096694	548.0536071	621.1440495
104		3014.856037	319.6459747	511.5083859	803.8701553
106		3197.582143	301.3733642	383.6001118	1096.231925
108		3060.537563	310.5096694	273.9644483	1589.592411
110			356.1911959	228.2829218	1872.817875
112			347.0548906	164.3287847	2375.314666
114			301.3733642	155.1924794	3106.21909
116				155.1924794	4019.849619
118				164.3287847	
120				164.3287847	

PAN/Water (70/30) Steady-shear viscosity data

	shear rate (s-1)	shear stress(Pa)	Viscosity (Pa*s)
180 C	119.644418	73690.55379	615.9130116
	239.2888359	92342.86923	385.9054639
	478.5776719	144154.8566	301.2151737
	1196.44418	213582.9196	178.5147383
	2392.888359	265394.9069	110.9098575
	3988.147266	327569.2917	82.1357061
	4785.776719	337931.6892	70.61167058
	7976.294531	353475.2853	44.3157263
	11964.4418	369018.8815	30.84296684
180 C	98.66411719	86125.43075	872.9154348
	197.3282344	102705.2667	520.4793274
	394.6564688	123430.0616	312.7531699
	986.6411719	187676.9259	190.2180157
	1973.282344	218764.1183	110.8630597
	3288.803906	244670.112	74.39486176
	3946.564688	265394.9069	67.24706876
	6577.607813	312025.6955	47.4375646
	9866.411719	343112.8879	34.77585344
190 C	96.96301172	92342.86923	952.3514956
	193.9260234	108922.7052	561.6714211
	387.8520469	129647.5001	334.2705064
	969.6301172	166952.131	172.1812555
	1939.260234	192858.1246	99.44932672
	3232.100391	239488.9132	74.0969909
	3878.520469	239488.9132	61.74749242
	6464.200781	275757.3044	42.65914901
	9696.301172	291300.9006	30.04247655

PAN/Acetonitrile (80/20) Time-dependent viscosity data

	T=160 C	T=160 C	T=180C	T=180C
Time (min)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)
2	3608.715881	4522.34641	2329.63314	2283.951613
4	3837.123513	4659.39099	2420.996192	2923.492984
6	3974.168093	4476.664884	2740.766878	3014.856037
8	3928.486566	4385.301831	2877.811457	2832.129931
10	3928.486566	4248.257251	2603.722298	3014.856037
12	3791.441987	4019.849619	2420.996192	2923.492984
14	3791.441987	4339.620304	2329.63314	2512.359245
16	3517.352828	3928.486566	2283.951613	2695.085351
18	3517.352828	3791.441987	2375.314666	2832.129931
20	3517.352828	3837.123513	2466.677719	2695.085351
22	3563.034354	3882.80504	2512.359245	2466.677719
24	3563.034354	3974.168093	2420.996192	2877.811457
26	3425.989775	3882.80504	2466.677719	3014.856037
28	3380.308248	3882.80504	2466.677719	2969.17451
30	3151.900616	4065.531145	2238.270087	3060.537563
32	3060.537563	4156.894198	2238.270087	2649.403825
34	3060.537563	4248.257251	2192.58856	2786.448404
36	3288.945195	4202.575725	2009.862454	2558.040772
38	3288.945195	4339.620304	1964.180928	2283.951613
40	3288.945195	4293.938778	2009.862454	2192.58856
42	3334.626722	4385.301831	1964.180928	2055.543981
44	3425.989775	4476.664884	1872.817875	2146.907034
46	3471.671301	4430.983357	1872.817875	2146.907034
48	3563.034354	4430.983357	1735.773295	2009.862454
50	3563.034354	4476.664884	1690.091769	2055.543981
52	3700.078934	4476.664884	1735.773295	1918.499401
54	3745.76046	4385.301831	1827.136348	1964.180928
56	3745.76046	4476.664884	2009.862454	2146.907034
58	3837.123513	4476.664884	2192.58856	2238.270087
60	3791.441987	4476.664884	2420.996192	2420.996192
62	3791.441987	4568.027937	2512.359245	2558.040772
64	3837.123513	4568.027937	2695.085351	2786.448404
66	3882.80504	4705.072516	2877.811457	3014.856037
68	3928.486566	4705.072516	3014.856037	3334.626722
70	3928.486566	4705.072516	3106.21909	3745.76046
72	3974.168093	4705.072516	3243.263669	3928.486566
74	3882.80504	4613.709463	3471.671301	4385.301831
76	3928.486566	4659.39099	3608.715881	5116.206254

78	4065.531145	4613.709463	3700.078934	5938.473731
80	4065.531145	4522.34641	3882.80504	6121.199837
82	4065.531145	4568.027937	4019.849619	5207.569307
84	4202.575725	4613.709463	4202.575725	5024.843201
86	4339.620304	4659.39099	4476.664884	5390.295413
88	4156.894198	4750.754043	4568.027937	5664.384572
90	4339.620304	4750.754043	4796.435569	6121.199837
92	4111.212672	4705.072516	5024.843201	6669.378154
94	4293.938778	4705.072516	5298.93236	
96	4339.620304	4796.435569	5390.295413	
98	4248.257251	4659.39099	5573.021519	
100	4248.257251	4659.39099	5755.747625	
102	4248.257251	4659.39099	5938.473731	
104	4385.301831	4750.754043	6303.925943	
106	4339.620304	5024.843201	6486.652049	
108	4430.983357	4842.117096	6943.467313	
110	4293.938778	4705.072516	7217.556472	
112	4476.664884	4750.754043	7674.371737	
114		4613.709463		
116		4705.072516		
118		5024.843201		
120		5207.569307		
122		5116.206254		

PAN/Acetonitrile (80/20) Time-dependent viscosity data （continue）

	T=170 C	T=175 C	T=190C
Time (min)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)
2	2192.58856	3380.308248	2466.677719
4	1598.728716	3288.945195	2329.63314
6	1530.206426	3334.626722	3060.537563
8	1507.365663	3334.626722	3563.034354
10	1507.365663	2832.129931	4476.664884
12	1507.365663	2740.766878	5207.569307
14	1575.887953	2649.403825	4659.39099
16	1621.569479	2283.951613	3563.034354
18	1598.728716	2238.270087	3197.582143
20	1621.569479	1827.136348	3060.537563
22	1598.728716	1553.047189	3106.21909
24	1575.887953	1507.365663	2969.17451
26	1507.365663	1553.047189	3014.856037
28	1553.047189	1507.365663	3014.856037
30	1553.047189	1507.365663	3106.21909
32	1553.047189	1598.728716	3197.582143
34	1553.047189	1598.728716	3380.308248
36	1507.365663	1644.410242	3608.715881
38	1553.047189	1735.773295	3974.168093
40	1553.047189	1735.773295	4339.620304
42	1530.206426	1781.454822	4750.754043
44	1553.047189	1781.454822	5481.658466
46	456.6905542	1781.454822	6578.015101
48	347.0548906	1827.136348	
50	438.4179436	1918.499401	
52	529.7809965	1918.499401	
54	694.2344918	1964.180928	
56	1023.141482	2032.703217	
58	1461.684137	2101.225507	
60	1872.817875	2124.06627	
62	2375.314666	2192.58856	
64	2512.359245	2238.270087	
66	2558.040772	2283.951613	
68	2558.040772	2420.996192	
70	2558.040772	2443.836956	
72	2603.722298	2512.359245	
74	2649.403825	2558.040772	
76	2695.085351	2763.607641	

78	2695.085351	2558.040772
80	2695.085351	2695.085351
82	2649.403825	2832.129931
84	2695.085351	2992.015273
86	2695.085351	3060.537563
88	2649.403825	3837.123513
90	2649.403825	3151.900616
92	2649.403825	3608.715881
94	2603.722298	4842.117096
96	2558.040772	4476.664884
98	2512.359245	5298.93236
100	2466.677719	5938.473731
102	2420.996192	6395.288996
104	1278.958031	5481.658466
106	1233.276504	5527.339993
108	1187.594978	6121.199837
110	1096.231925	6578.015101
112	1096.231925	7583.008684
114	1096.231925	
116	1050.550398	
118	1050.550398	
120	1004.868872	

PAN/Acetonitrile (80/20) Steady-shear viscosity data

	shear rate (s-1)	shear stress(Pa)	Viscosity (Pa*s)
160 C	130.4180859	451918.0613	3465.148702
	260.8361719	462280.4587	1772.30196
	521.6723438	488186.4524	935.8104915
	1304.180859	602172.8245	461.7249365
	2608.361719	685072.0042	262.6445555
	4347.269531	747246.389	171.8886726
180 C	110.0048203	255032.5094	2318.375765
	220.0096406	296482.0993	1347.586853
	440.0192813	332750.4904	756.2179763
	1100.048203	363837.6828	330.7470362
	2200.096406	410468.4714	186.5684023
	3666.827344	519273.6448	141.6138793
	4400.192813	539998.4397	122.7215403
	7333.654688	602172.8245	82.11087789
	11000.48203	664347.2093	60.39255438
	14667.30938	685072.0042	46.70740807
190 C	100.9322578	384562.4777	3810.104778
	201.8645156	415649.6701	2059.052671
	403.7290313	488186.4524	1209.193332
	1009.322578	643622.4144	637.677615
	2018.645156	799058.3763	395.8389486
	3364.408594	850870.3637	252.9033974
	4037.290313	861232.7611	213.3195026

PAN/Water/EtOH (70/15/15) Time-dependent viscosity data

	T=170 C	T=170 C	T=180C	T=180C	T=190C
Time (min)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)	Viscosity (Pa*s)
2	785.5975448	383.6001118	931.7784295	1598.728716	822.1427659
4	968.3236506	365.3275012	1077.959314	1370.321084	767.3249342
6	1096.231925	447.5542489	1077.959314	1553.047189	712.5071024
8	1224.140199	447.5542489	1151.049757	1690.091769	694.2344918
10	1224.140199	493.2357753	1224.140199	1690.091769	639.41666
12	1224.140199	484.09947	1242.412809	1735.773295	657.6892706
14	1260.68542	465.8268595	1278.958031	1735.773295	694.2344918
16	1260.68542	538.9173018	1297.230641	1735.773295	621.1440495
18	1242.412809	584.5988283	1333.775862	1735.773295	694.2344918
20	1205.867588	730.779713	1333.775862	1735.773295	730.779713
22	1205.867588	968.3236506	1388.593694	1735.773295	767.3249342
24	1242.412809	1242.412809	1388.593694	1735.773295	712.5071024
26	1278.958031	1151.049757	1443.411526	1735.773295	767.3249342
28	1260.68542	1132.777146	1461.684137	1553.047189	803.8701553
30	1278.958031	1041.414093	1498.229358	1553.047189	822.1427659
32	1278.958031	1096.231925	1498.229358	1507.365663	822.1427659
34	1260.68542	1151.049757	1516.501968	1598.728716	840.4153765
36	1278.958031	1205.867588	1461.684137	1644.410242	840.4153765
38	1260.68542	1205.867588	1370.321084	1644.410242	785.5975448
40	1260.68542	1205.867588	1479.956747	1644.410242	767.3249342
42	1278.958031	1224.140199	1534.774579	1644.410242	749.0523236
44	1297.230641	1224.140199	1571.3198	1690.091769	858.6879871
46	1297.230641	1242.412809	1626.137632	1690.091769	840.4153765
48	1315.503252	1187.594978	1644.410242	1690.091769	822.1427659
50	1333.775862	1205.867588	1690.091769	1735.773295	803.8701553
52	1333.775862	1242.412809	1735.773295	1735.773295	840.4153765
54	1333.775862	1224.140199	1735.773295	1690.091769	876.9605977
56	1352.048473	1205.867588	1735.773295	1690.091769	913.5058189
58	1370.321084	1278.958031	1735.773295	1735.773295	986.5962612
60	1370.321084	876.9605977	1735.773295	1735.773295	1169.322367
62	1388.593694	1077.959314	1735.773295	1735.773295	1260.68542
64	1406.866305	1169.322367	1735.773295	1735.773295	1370.321084
66	1406.866305	1297.230641	1735.773295	1735.773295	1571.3198

68	1425.138915	1406.866305	1735.773295	1690.091769	1781.454822
70	1443.411526	1461.684137	1735.773295	1735.773295	1964.180928
72	1461.684137	1461.684137	1735.773295	1781.454822	2329.63314
74	1498.229358	1498.229358	1735.773295	1827.136348	2877.811457
76	1516.501968	1461.684137	1735.773295	1872.817875	3654.397407
78	1553.047189	1443.411526	1352.048473	1964.180928	
80	1461.684137	1598.728716	1187.594978	2101.225507	
82	1461.684137	1644.410242	1278.958031	2238.270087	
84	1507.365663	1461.684137	1352.048473	2420.996192	
86	1598.728716	1735.773295	1370.321084	2466.677719	
88	1598.728716	1553.047189	1406.866305	2649.403825	
90	1598.728716	1735.773295	1461.684137	2649.403825	
92	1690.091769	1827.136348	1571.3198	2786.448404	
94	1690.091769	1872.817875	1735.773295	2969.17451	
96	1781.454822	1964.180928	1918.499401	3288.945195	
98	1872.817875	1964.180928	1964.180928	3745.76046	
100	1964.180928	1964.180928	2101.225507	4339.620304	
102	1964.180928	2009.862454	2146.907034	4750.754043	
104	1964.180928	2146.907034	2238.270087	5207.569307	
106			2329.63314		
108			2420.996192		
110			2558.040772		
112			2740.766878		
114			2969.17451		
116			3197.582143		
118			3517.352828		
120			3745.76046		
122			4019.849619		
124			4339.620304		

PAN/Acetonitrile (80/20) Steady-shear viscosity data

	shear rate (s-1)	shear stress(Pa)	Viscosity (Pa*s)
	90.725625	113067.6642	1246.259413
	181.45125	164879.6515	908.6718966
	302.41875	213582.9196	706.2489332
	362.9025	189749.4054	522.866074
	604.8375	265394.9069	438.7871236
170 C	1209.675	280938.5031	232.2429604
	1814.5125	291300.9006	160.5394841
	3629.025	400106.0739	110.251672
	6048.375	457099.26	75.57389547
	9072.5625	498548.8499	54.95127202
	18145.125	560723.2346	30.90214229
	101.499293	125502.5411	1236.486851
	202.9985859	179387.0079	883.6859977
	338.3309766	193894.3644	573.0907833
	405.9971719	198039.3234	487.7849825
	676.6619531	249851.3107	369.2409623
180 C	1353.323906	286119.7018	211.4199716
	2029.985859	306844.4968	151.1559774
	4059.971719	358656.4841	88.33965085
	6766.619531	394924.8752	58.3636886
	10149.9293	410468.4714	40.44052519
	20299.85859	462280.4587	22.77259502
	110.5718555	169024.6105	1528.640446
	221.1437109	193894.3644	876.7799164
	368.5728516	223945.317	607.6012275
	442.2874219	213582.9196	482.9052535
	737.1457031	234307.7145	317.8580754
180 C	1474.291406	260213.7082	176.5008648
	2211.437109	286119.7018	129.3817946
	3685.728516	306844.4968	83.25206142
	7371.457031	348294.0866	47.24901538
	11057.18555	379381.279	34.31083592
	22114.37109	462280.4587	20.9040744
	128.7169805	189749.4054	1474.159856
190 C	257.4339609	213582.9196	829.6610082
	429.0566016	270576.1056	630.6303286

	514.8679219	275757.3044	535.5884347
	858.1132031	301663.298	351.5425435
	1716.226406	343112.8879	199.9228579
	2574.339609	358656.4841	139.3198018
	4290.566016	369018.8815	86.00703968
	8581.132031	389743.6765	45.41867845
	12871.69805	415649.6701	32.29175114
	25743.39609	441555.6638	17.15219166
	110.5718555	166952.131	1509.897164
	221.1437109	203220.5221	918.9523014
	368.5728516	270576.1056	734.1183825
	442.2874219	280938.5031	635.1944215
	737.1457031	296482.0993	402.2028454
190 C	1474.291406	332750.4904	225.7019806
	2211.437109	363837.6828	164.5254488
	3685.728516	405287.2727	109.9612386
	7371.457031	431193.2663	58.49498471
	11057.18555	451918.0613	40.8709847
	22114.37109	519273.6448	23.48127571

Python code for RTD calculation (Chapter 5)

```
import pandas as pd
from math import sin
from math import cos

def RTD (en, gz, errors, div):

    ######## variables ########
    ## constant value ##
    sa = (1-en)/(2*en)
    a1 = 0.1; # coef step size y3
    a2 = 0.2; # coef step size y4
    a3 = 10.0; # coef step size gx
    theta = 17.74*3.14159/180
    h = 1.0/div # interval size
    num = div//2
    asize = div*2+1 # max possible size of result arrays

    ## variable arrays
    px = [0]*asize
    pz = [0]*asize
    q = [0]*asize # integral of pz
    f = [0]*asize # position
    fc = [0]*asize # complement position
    rtd = [0]*asize # residual time
    t = [0]*asize # reversed time list
    Ft = [0]*asize
    T = [0]*asize
    Y = [0]*asize

    ######## initiation ########
    def dpx(y):
        return gx*(y-y3)*(gx**2*(y-y3)**2+gz**2*(y-
y4)**2)**sa
    def dpz(y):
        return gz*(y-y4)*(gx**2*(y-y3)**2+gz**2*(y-
y4)**2)**sa

    count = 0 # number of iterations to determine gz
    y3, y4 = 0, 0
    gx = 1.0
```

```
    ############# get y3, y4, gx ################
    while True:
        count += 1
        # integrate to solve for z component of velocity
        while True:
            y = 0.0
            for i in range(1,num+1):
                pz[i] = pz[i-
1]+(h/3.0)*(dpz(y)+4.0*dpz(y+h)+dpz(y+2.0*h))
                y += 2.0*h
            if abs(pz[num] - cos(theta)) <= errors:
                break
            y4 += a1*(pz[num]-cos(theta))
        # integrate to solve for x component of velocity
        while True:
            y = 0.0
            for i in range(1,num+1):
                px[i] = px[i-
1]+(h/3.0)*(dpx(y)+4.0*dpx(y+h)+dpx(y+2.0*h))
                y += 2.0*h
            if abs(px[num] - sin(theta)) <= errors:
                break
            y3 += a2*(px[num]-sin(theta))
        sum = 0.0
        for i in range(1,num+1):
            sum += h*((px[i]+px[i-1])/2.0)*2.0
        if abs(sum) <= errors:
            break
        gx += a3*sum
    print(count)
    ############## get Q, Q*, t_b ##############
    for i in range(1,num+1):
        q[i] = q[i-1]+h*(pz[i]+pz[i-1])
    cum = q[num] # q*
    tau = 1.0/(cum*sin(theta)) # t_b
    print(cum,tau)
    ############## get position f, conplemental position
fc ##############
    p = 1.0
    mm = 1
    yc = h*2
    f[0] = 1.0
    ind = -1 # from back, last element in the integral of
```

```
px that larger than 0
    for i in range(1,num):
        if px[num-i]<=0:
            break
        y = 1-h*p*2 # choose y position in upper channel
        ind = i
        nn = num-i
        f[i] = y
        summ = 0.0
        for j in range(nn,num):
            summ += h*((px[j]+px[j+1])/2.0)*2.0
        conv = 1000.0
        while True:
            sumn = 0.0
            for j in range(1,mm+1):
                sumn += h*((px[j]+px[j-1])/2.0)*2.0
            if summ+sumn<=0:
                break
            else:
                mm += 1
            if conv-(summ+sumn)<=0:
                break
            else:
                yc += 2*h
            conv = summ+sumn
        fc[i] = yc
        p += 1
    for i in range(1,ind+1):
        f[i+ind] = fc[ind-i]
        fc[i+ind] = f[ind-i]
    ############## get residual time rtd, V_L, Q_L
##############
    quan = div//2.0
    mp = 0
    ind2 = num-ind
    for i in range(1,ind2+1):
        nn = num-i
        mm = round(fc[i]*quan)
        r = abs(px[nn]/px[mm])
        # CALCULATE FRACTION OF TIME A PARTICLE SPENDS IN
UPPER PART OF CHANNEL
        tf = 1/(1+r)
        # CALCULATE DOWN CHANNEL VELOCITY TN UPPER PART
```

```
OF CHANNEL
        vl = -px[nn]*cos(theta)+pz[nn]*sin(theta)
        # CALCULATE DOWN CHANNEL VELOCITY IN LOWER PART
OF CHANNEL
        vlc = -px[mm]*cos(theta)+pz[mm]*sin(theta)
        # CALCULATE THE AVERAGE DOWN CHANNEL VELOCITY
        vl_bar = vl*tf+vlc*(1-tf)
        # CALCULATE THE AVERAGE RESIDENCE TIME
        t[i] = 1/(vl_bar*tau)
        # CALCULATE RESIDENCE TIME DISTRIBUTION, F(T)DT
        dq = q[nn+1]-q[nn]
        dqc = q[mm]-q[mp]
        rtd[i] = (dq+dqc)/cum
        if f[i]>0:
            mp = mm
        else:
            break

    for i in range(1,ind+1):
        Ft[i] = Ft[i-1]+rtd[ind+1-i]
        T[i] = t[ind+1-i]
        Y[i] = f[ind+1-i]
    ############# return result #############
    T,Ft,Y = T[:ind+1],Ft[:ind+1],Y[:ind+1]
    # print(T)
    # print(Ft)
    return cum,tau,Ft,T
```