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Absorption of CO_2 in high acrylonitrile content copolymers: dependence on acrylonitrile content

Michael J. Bortner[a], Vinayak A. Bhanu[b], James E. McGrath[b], Donald G. Baird[a,*]

[a]Department of Chemical Engineering and Center for Composite Materials and Structures, Virginia Polytechnic Institute and State University, 128 Randolph Hall, 24061-0211 Blacksburg, VA, USA
[b]Department of Chemistry, Virginia Polytechnic Institute and State University, 128 Randolph Hall, 24061-0211 Blacksburg, VA, USA

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Abstract

In continuation of our goal to determine the ability of CO_2 to plasticize acrylonitrile (AN) copolymers and facilitate melt processing at temperatures below the onset of thermal degradation, a systematic study has been performed to determine the influence of AN content on CO_2 absorption and subsequent viscosity reduction. Our previous report focused on the absorption of CO_2 in a relatively thermally stable 65 mol% AN copolymer. In this study, the ability for CO_2 to absorb in AN copolymers containing 85–98 mol% acrylonitrile was determined, and subsequent viscosity and equivalent processing temperature reductions were evaluated. Eighty five and 90 mol% acrylonitrile/methyl acrylate (AN/MA) copolymers were found to absorb up to 5.6 and 3.0 wt% CO_2, corresponding to reductions of T_g of 37 and 27 °C, and subsequent viscosity reductions of 61 and 56%, respectively. CO_2 absorption in these copolymers was found to occur immediately, in contrast to the time dependent absorption observed in the 65 mol% copolymer. An Arrhenius scaling analysis was used to determine the equivalent reductions in processing temperature resulting from the viscosity reductions, and reductions of up to 25 and 9 °C were observed for the 85 and 90 mol% AN copolymers. Based on the specific conditions used for absorption, no significant CO_2 uptake was observed for AN copolymers containing greater than 90 mol% acrylonitrile. Higher temperatures than those used here may be required to absorb CO_2 into AN copolymers containing greater than 90 mol% AN.

Keywords: Carbon dioxide; Acrylonitrile; Plasticizer

1. Introduction

The need exists for a less expensive and environmentally benign process for producing AN copolymer fibers suitable for use as carbon fiber precursors and textiles [1]. Melt processing AN copolymers could potentially provide a less expensive and more environmentally friendly process as compared to solution spinning by increasing solids throughput on a per pound basis and eliminating the need for solvent use and recovery [2]. But because high AN content (greater than about 85 mol% AN) copolymers undergo a rapid crosslinking and cyclization reaction at a temperature of 220 °C, AN copolymer fiber precursors are conventionally produced using a solution spinning process. Toxic, organic solvents, including dimethyl formamide and dimethyl acetamide, are usually used in the ratio of 70–93 wt% solvent to process acrylonitrile/methyl acrylate (AN/MA) copolymers of high AN content (greater than about 85 mol% AN) into their desired fiber form [3]. Viscosities for these high AN content copolymers can become suitable for melt processing when temperatures of approximately 220 °C are approached [2]. However, at 220 °C the kinetics of the crosslinking reaction become rapid, rendering these high AN content copolymers intractable prior to extrusion into fiber form [4]. If the temperature is lowered to 200 °C, the kinetics of the crosslinking reaction are very slow, resulting in minimal crosslinking and cyclization during extrusion, but the pure AN/MA copolymer viscosities are generally too high for melt processing at these temperatures [2].

Numerous attempts have been made with varying degrees of success to melt process AN copolymers. Water and mixtures of acetonitrile, methanol, and water [5–8] have been investigated to plasticize AN copolymers, facilitating precursor extrusion into fiber form at

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* Corresponding author. Tel.: +1-540-231-5998; fax: +1-540-231-5022.
E-mail address: dbaird@vt.edu (D.G. Baird).

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temperatures below the onset of thermal degradation. Large plasticizer contents (25–45 wt%) were required and the acetonitrile had to be recovered because it degrades into cyanide at relatively low temperatures, resulting in a process that had little economic benefit over solution spinning when commercial production rates (~2×10^6 lb per year) were reached. Tailored AN/MA copolymers have also been investigated for melt processable PAN copolymer precursors, but 85 mol% AN was the maximum that could be utilized before the kinetics of degradation became significant and prevented melt processing [9]. Advantages and disadvantages of these acrylic melt processing studies were discussed in detail in a recent paper [10].

Carbon dioxide (CO_2) has been studied as a plasticizer to reduce the viscosity of a number of thermoplastic polymers, including polydimethylsiloxane, polystyrene, polypropylene, low-density polyethylene, poly(methyl methacrylate), and poly(vinylidene fluoride). Only a few studies have focused on the ability to absorb CO_2 into a polymer and measure the subsequent viscosity reduction [11–17]. The plasticizing ability of CO_2 in these polymers and the measurement techniques were presented in a recent paper [10]. In general, low levels of absorbed CO_2 (about 6 wt% or less) were observed to reduce the viscosity of the majority of the thermoplastics studied by up to 80%. Viscosity reductions and scaling predictions were reported for the thermoplastics containing absorbed CO_2, but the studies did not focus on the use of CO_2 to reduce the processing temperatures of acrylic copolymers or any other thermally unstable polymers.

We recently reported the use of carbon dioxide as a plasticizer to reduce the viscosity of a 65 mol% acrylic copolymer [10]. Low levels of absorbed CO_2 (6.7 wt%) were shown to reduce the glass transition temperature (T_g) up to 31 °C and viscosity up to 60% over the range of shear rates tested. The viscosity of the 65 mol% AN copolymer containing absorbed CO_2 at 180 °C was observed to be the same as the pure copolymer viscosity at 210 °C, suggesting that the plasticized copolymer could be processed at 30 °C below the processing temperature of the pure copolymer [10]. Plasticization of the 65 mol% AN copolymer with CO_2 provided a framework to establish a relationship between the T_g reduction, CO_2 absorption level, viscosity reduction, and equivalent processing temperature reduction obtainable for acrylic copolymers using CO_2 as a plasticizer.

The ability for CO_2 to plasticize high AN content AN/MA copolymers, suitable for use in textile and carbon fiber precursors (containing 85 mol% or greater AN), has not been investigated. The goal of this paper is to establish a relationship between AN content and the ability of the copolymer to absorb CO_2, and the subsequent effect of CO_2 to plasticize and reduce the viscosity of the acrylonitrile copolymers (suitable for use as textile and carbon fiber precursors). Furthermore, the goal is to determine whether the processing temperature can be lowered enough to prevent the onset of thermal degradation. The role of AN content on the ability to absorb CO_2 was measured via differential scanning calorimetry (DSC), used to measure the T_g reduction, and thermogravimetric analyses (TGA), used to measure the wt% of absorbed CO_2. Viscosity effects resulting from CO_2 absorption were measured using a capillary rheometer modified to apply static pressures at the capillary exit. Equivalent processing temperature differences between the plasticized and pure copolymers were determined using an Arrhenius scaling analysis and related to the amount of absorbed CO_2 as a function of AN content.

2. Experimental

2.1. Materials

AN/MA copolymers containing 85, 90, 93, 95, and 98 mol% AN were utilized in this study. The 85/15 mol% AN/MA copolymer was produced via a heterogeneous free radical (emulsion) polymerization by Monomer Polymer, Inc. of Feastersville, PA, which was based on research by Bhanu and coworkers [9] and somewhat different than for solution and suspension polymerizations. The 85/15 AN/MA copolymer was produced in a 1 kg quantity, of which approximately 50 g were available for our measurements in this study. The kinetics of crosslinking was insignificant (crosslinking was minimal) at 200 °C, and the copolymer exhibited a stable steady shear viscosity at this temperature for at least 30 min, facilitating viscosity measurements without interfering effects of crosslinking. The 90/10 mol% AN/MA copolymer was an extrudable grade material produced by BP/Amoco named Amlon. Amlon was developed as a melt processable AN precursor containing less than 1 mol% of a stabilizer, but is no longer produced, and as a result only a small quantity (roughly 100 g) of the copolymer was obtained for our measurements. Possibly because of an unknown stabilizer, Amlon exhibited a stable steady shear viscosity at 220 °C for minimally 30 min, also facilitating viscosity measurements. The 93, 95, and 98 mol% AN copolymers were synthesized by a free radical homogeneous (solution) polymerization via the methods discussed in detail by Bhanu et al. [9]. Kinetics of crosslinking for these AN copolymers was found to be significant, with crosslinking occurring rapidly at 220 °C. All of the materials were in powder form except for the Amlon, which was in the form of 3.2 mm diameter pellets with 6.4 mm length. Proton NMR was used to confirm the copolymer ratios (in relation to the feed ratios) of the synthesized AN copolymers as detailed by Bhanu et al. [9].

Intrinsic viscosities and molecular weights (if available) for each sample are indicated in Table 1. Intrinsic viscosities were measured using a Cannon Ubbelhode viscometer. Absolute molecular weight measurements from gel permeation chromatography (GPC) were obtained at 60 °C with a Waters 2690 Separation Module equipped with a differential refractometer detector and an on-line differential

Table 1
Intrinsic viscosity and molecular weight data for the AN/MA copolymer samples

AN/MA molar ratio	Intrinsic viscosity (NMP/25 °C)	M_n (GPC, g/mol)	M_w (GPC, g/mol)
85/15	0.50	26,500	65,900
90/10	0.5	18,000	55,000
93/7	0.26	N/A	N/A
95/5	0.25	N/A	N/A
98/2	0.25	N/A	N/A

viscometric detector (Viscotek T60A) coupled in parallel. NMP containing 0.2 M P_2O_5 was used as a solvent. Sufficient samples were not available to obtain GPC data for the 93, 95, and 98 mol% AN copolymers.

2.2. Sample preparation

The samples that were in powder form were compression molded into pellets of similar size to the 90/10 AN/MA copolymer to ensure that the CO_2 absorption experiments would be performed on samples of equal dimension to the 90/10 copolymer pellets. Diffusion has been shown to be the limiting factor for CO_2 permeability into AN polymers, and as a result the powder samples (possessing a smaller diffusion length) were expected to absorb CO_2 more rapidly than the pellets for a given time scale [18]. It was found that the 85, 93, 95, and 98 mol% AN samples, which were all in powder form, could be molded into pellets at temperatures between 180 and 200 °C in 5 min or less. We believe that compression molding at these temperatures permitted preparation of sample pellets for thermal analyses without significant crosslinking (thermal degradation), as no color change was observed following molding. It was found that low levels of cyclization were clearly indicated by a deep yellow discoloration of the material (which was white in its initial powder form). A lack of color change suggested that minimal (and insignificant) levels of crosslinking occurred.

Larger quantities of pellets (15–20 g) were prepared for viscosity measurements of the 85/15 AN/MA copolymer by extrusion into fiber form using a capillary rheometer at 200 °C (residence time no greater than 15 min). The fibers were then chopped into pellets of similar size to the 90/10 AN/MA copolymer with a pelletizer. The thermal history imparted as a result of fiber extrusion and pelletization was not a problem because this material was shown to be thermally stable at 200 °C for at least 30 min [19].

The copolymer pellets were saturated with CO_2 in a sealed, constant volume, pressurized bomb for various amounts of time. A Parr Instruments model 4760 pressure vessel was used to saturate the samples. For the thermal analyses, approximately one gram of polymer was saturated for each test. For the viscosity measurements, approximately 20 g of polymer were saturated. The pressure vessel was initially charged with CO_2 at room temperature in the form of a high pressure gas at 5.86 MPa, and then heated to 120 °C, which increased the pressure to 10.3 MPa. It was necessary to use a saturation temperature above the T_g of the copolymers (ranging from 84 to 100 °C) to increase free volume and ensure dispersion of the CO_2 into the polymer. The soak temperature of 120 °C was chosen because it is above the T_g of the copolymers but below the temperature at which significant crosslinking begins to occur. Higher temperatures resulted in thermal degradation of the AN copolymers over the time scale used for the saturations. The sample was then held at 120 °C for various amounts of time, corresponding to the 'soak time' for the CO_2 absorption. Following the soak time, the pressurized bomb was cooled to room temperature via forced convection. Once cooled to room temperature, the pressure vessel was decompressed over the course of 12 min, corresponding to a decompression rate of 8200 Pa/s. The entire heating and cooling process will later be referred to as the 'cycle time' of saturation, which does not include the soak time at 120 °C.

Further high pressure saturations were performed in a similar manner. Following the batch pressurization and heating to 120 °C (corresponding to 10.3 MPa), a Trexel TR-1-5000L high pressure CO_2 pump was used to directly inject liquid CO_2 into the heated pressure vessel and raise the pressure to 17.2 MPa. This pressure was chosen as the upper limit so that reasonable pressures could be maintained in future extrusion studies. The absorption abilities of both the 85/15 and 90/10 AN/MA copolymer samples were tested at the 10.3 and 17.2 MPa soak pressures. Limited quantities of the three highest AN content samples (93/7, 95/5, and 98/2) were available, and the absorption behavior was only measured at one set of saturation conditions (10.3 MPa saturation pressure).

2.3. Differential scanning calorimetry

A Seiko model 220 differential scanning calorimeter (DSC) and a TA Instruments model 2920 modulated DSC were used to make the DSC measurements. Heating and cooling rates of 10 °C/min were used. A nitrogen purge was used during measurements in both DSC units. Aluminum pans with pierced lids were used to hold the 5–10 mg samples. The use of pierced lids allowed the escape of the absorbed CO_2. Glass transition temperatures were calculated using Universal Analysis software via the midpoint method.

Two heats were performed on each sample. The first heat allowed direct visualization of the T_g reduction resulting from absorbed CO_2. The second heat verified that no residual CO_2 was present, which was confirmed if the T_g of the pure material was obtained (as reported by Bortner [19]). Samples containing absorbed CO_2 were cooled to -20 °C to further prevent any degassing prior to running the thermal scan, as well as to establish a baseline for easy visualization of the T_g of the plasticized copolymers. The test comprised heating from -20 to 180 °C to ensure that all CO_2 had flashed out of the system, cooling back to −20 °C, and then performing the second heat.

In order to ensure that significant CO_2 was not lost between sample decompression and thermal analysis, a calculation was performed to determine the amount of time required to desorb a significant quantity of the absorbed gas (5%), which was found to be several hours due to the extremely low diffusivity of acrylonitrile at room temperature. DSC analysis was used to verify the calculation, which confirmed minimal gas loss within the first 2 h following decompression [19].

2.4. Methods

TGA and viscosity measurements (obtained with the pressurized capillary rheometer) of the AN copolymers containing absorbed CO_2 were performed in the same manner as described in a recent paper on the 65 mol% AN copolymer [10]. A capillary of diameter 0.027 in. and an *L/D* of 111 was used for the viscosity testing so that entry pressure corrections were not necessary. The actual pressure drop across the capillary (ΔP) was measured as the difference between the upstream force measured by the Instron load cell to push the polymer through the capillary (ΔP_{total}) and the applied static pressure (ΔP_{static}). Pressure drops were calculated as defined in Eq. (1):

$$\Delta P = \Delta P_{\text{total}} - \Delta P_{\text{friction}} - \Delta P_{\text{static}} \qquad (1)$$

where $\Delta P_{\text{friction}}$ is the correction to account for the friction imposed by the plunger seal. The measured entry pressures for the 65 mol% copolymer accounted for approximately 5% or less of the total measured pressure drop when tested with this capillary, and accordingly entry pressures corrections were not necessary [19]. This also facilitated viscosity testing of both pure and plasticized copolymers with the small amounts of materials available. Because entry pressure was not accounted for in the viscosity calculations, apparent viscosities are reported with which the shear stress was calculated with the pressure drops obtained from Eq. (1). The viscosities were otherwise calculated as in a recent paper [10].

2.5. Dynamic oscillatory shear viscosity measurements

Complex viscosity measurements were performed using a Rheometrics RMS 800 Mechanical Spectrometer. Samples in powder form were compression molded into circular disks of 25.0 mm diameter and 1.0 mm thickness using a press at room temperature. The 90 mol% AN copolymer, which was the only sample in pellet form, was compression molded into circular disks of the same dimensions at 210 °C. Frequency sweeps were made over the range of 0.1–100 rad/s using 25.0 mm parallel plates and 1% strain. Temperatures in the range of 190–230 °C were used for the 85/15 AN/MA copolymer, and 225–240 °C were used for the 90/10 AN/MA copolymer. Higher temperatures resulted in significant degradation before the measurements could be completed, which take approximately 7 min for the frequency range used. In order to minimize degradation during viscosity measurements, angular frequencies below 0.1 rad/s were not used because of the length of time required to obtain data. Strain sweeps were performed on both the 85 and 90 mol% AN copolymers to determine the linear viscoelastic range of response, and both samples were shown to be linear up to 10% strain [19]. Dynamic oscillatory shear viscosity measurements were only performed on pure copolymers that did not contain absorbed CO_2.

3. Results and discussion

In the following sections, the effect of AN content on the ability to absorb CO_2 using saturation methods described earlier is determined. Viscosity measurements on the 85/15 and 90/10 AN/MA copolymers, both pure and containing absorbed CO_2, are used to determine the ability to reduce the processing temperatures for these materials. The results are compared with the data obtained for the 65 mol% AN copolymer to establish the effects of AN content on the ability of AN copolymers to absorb CO_2 and exhibit a viscosity reduction.

3.1. Thermal analysis

DSC and TGA analyses were used to determine the reduction of T_g as a function of the amount of absorbed CO_2 for a given soak time and pressure for each sample. Thermal analysis data were then compared between samples to establish a relationship between the AN content and both the amount of absorbed CO_2 and T_g reduction. DSC and TGA data reported in a recent paper on the 65 mol% copolymer were also incorporated to cover the range of 65–98 mol% AN [10].

Thermal analysis data for the 85/15 and 90/10 AN/MA copolymers are shown in Figs. 1 and 2. The data in Fig. 1 represent the DSC scans of the 85/15 and 90/10 AN/MA copolymers saturated at 120 °C and both the 10.3 and 17.2 MPa soak pressures, and the TGA results in Fig. 2 provide the corresponding amount of absorbed CO_2 for each saturation. DSC data were collected for both heats and are shown in Fig. 1 for easy visualization of the T_g difference between the plasticized and pure copolymers (meaning pure in the sense that no residual CO_2 remains). The first heat of the polymer containing CO_2 is represented by the upper curve for each sample, and the second heat (following cool down) is represented by the lower curve. The DSC and TGA data for the 6 h, 10.3 MPa saturation at 120 °C indicate reductions of T_g up to 30 and 17 °C, corresponding to 4.3 and 2.0 wt% absorption, for the 85 and 90 mol% AN copolymers, respectively. Van Krevelen's relationships were used in a similar manner to that reported in a previous

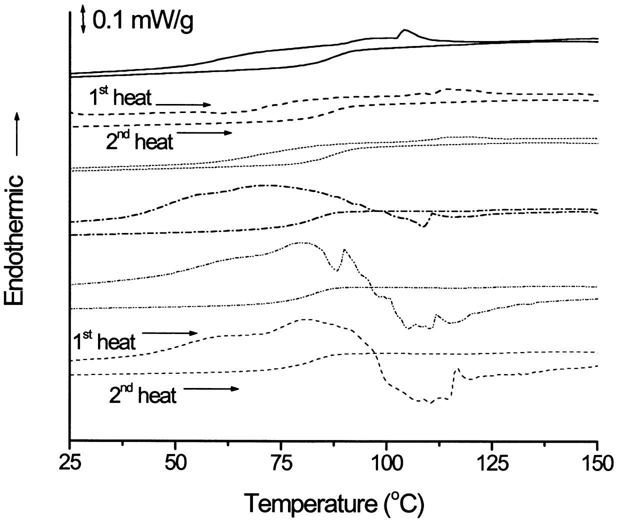

Fig. 1. DSC scans of 90/10 and 85/15 AN/MA copolymers containing between 1.8 and 5.6 wt% absorbed CO_2. Saturations were performed at 120 °C. From top to bottom: 90/10 samples: (—) 6 h, 17.2 MPa; (– –) 6 h, 10.3 MPa; (- - -) 0 h, 10.3 MPa; 85/15 samples: (– – –) 6 h, 17.2 MPa; (– - - –) 6 h, 10.3 MPa; (- - - - -) 0 h, 10.3 MPa.

paper [10] to predict the expected wt% of CO_2 absorption using these saturation conditions. For the 1500 psi saturation at 120 °C, 4.8 wt% CO_2 was expected to absorb in the copolymers, which is close to experimentally measured value for the 85 mol% copolymer, but about twice the value measured for the 90 mol% copolymer.

The thermal analysis data for the 10.3 MPa saturation suggest that the majority of CO_2 absorption occurs very quickly in the high AN content copolymers. DSC data for the 0 h saturation ('cycle time' of saturation) is shown for the 90 mol% copolymer in Fig. 1, which indicate the same reduction of T_g (17 °C in both cases) as for the sample with a 6 h. soak time under the same saturation conditions. The 0 h saturation of the 85 mol% copolymer resulted in a 30 °C reduction of T_g, also identical to that obtained for the 6 h saturation [19]. In a recent paper, absorption of CO_2 in the 65 mol% AN copolymer was found to be dependent on the length of the soak time at the saturation conditions. The results for the 85 and 90 mol% AN copolymers suggest, unlike the 65 mol% AN copolymer in our previous study, that the majority of the CO_2 absorption occurs almost immediately, with minimal additional absorption occurring over long saturation times. These results are confirmed for both the 85 and 90 mol% copolymer by the TGA data in Fig. 2, which show that the 85 mol% copolymer absorbed 4.3 wt% CO_2 for both the 0 and 6 h. soak time, and that only an extra 0.2 wt% CO_2 is absorbed in the 90 mol% copolymer after the 6 h soak time.

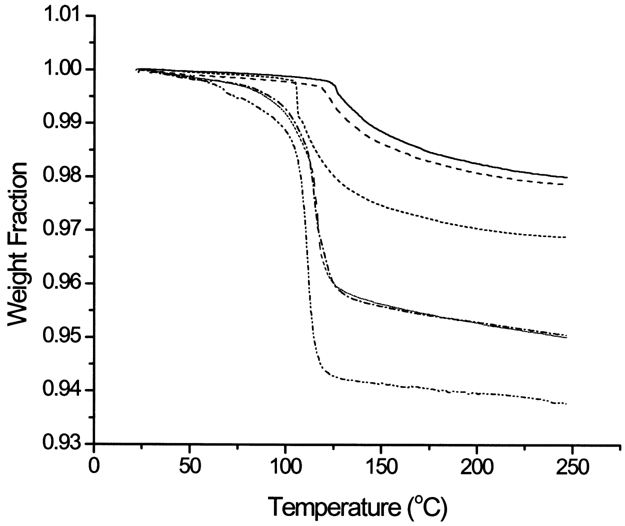

Fig. 2. TGA of 90/10 and 85/15 AN/MA copolymers containing 1.8–5.6 wt% absorbed CO_2. Saturations were performed at 120 °C. From top to bottom: 90/10 samples: (—) 0 h, 10.3 MPa; (– –) 6 h, 10.3 MPa; (- - -) 6 h, 17.2 MPa; 85/15 samples: (– – –) 0 h, 10.3 MPa; (— - —) 6 h, 10.3 MPa; (– - - –) 6 h, 17.2 MPa. 0 and 6 h saturations overlap for the 85/15 copolymer.

DSC and TGA data are also shown for the 17.2 MPa saturations for both the 85 and 90 mol% AN copolymers. Raising the saturation pressure to 17.2 MPa increased the reductions of T_g to 37 and 27 °C, corresponding to 5.6 and 3.0 wt% absorption (measured by TGA) for the 85/15 and 90/10 copolymers, respectively, at the 6 h, 120 °C saturation. The absorption level predicted by Van Krevelen's relationships was 12.6 wt% for these saturation conditions, which is between 2 and 4 times the experimentally observed absorption values for the 85 and 90 mol% copolymers. Only the 6 h saturations were performed, primarily because data from a recent paper suggest that no significant absorption would have been observed over longer soak times [19]. We also wanted to minimize any chance of thermal degradation occurring in the polymers, as well as maintain a basis for comparison to the 65 mol% copolymer, with which the 6 h saturation times were utilized. As previously discussed, shorter soak times could probably have been used to obtain comparable results, but consistency was maintained between our studies by utilizing the 6 h saturation. The TGA data in Fig. 2, in conjunction with the TGA data for the 65 mol% AN copolymer from a recent paper [10], indicate that the amount of absorbed CO_2 decreases as the AN content is increased for the saturation conditions utilized in this study. However, the data suggest that the corresponding reductions of T_g may pass through a maximum at an AN content between 65 and 90 mol% AN. Up to 37 °C reduction was obtained for the 85/15 copolymer, but only a 31 °C reduction was obtained for 65 mol% copolymer and only a 27 °C reduction was obtained for the 90 mol% AN copolymer.

Copolymers containing greater than 90 mol% AN were not observed to absorb CO_2 to any significant extent with the saturation methods used in this study. DSC scans following a 6 h, 10.3 MPa saturation at 120 °C are shown in Fig. 3 for the 93, 95, and 98 mol% AN copolymers. The data indicate that no reduction of T_g or absorption of CO_2 is observed using our saturation conditions for these copolymers (containing greater than 90 mol% AN). The conclusion

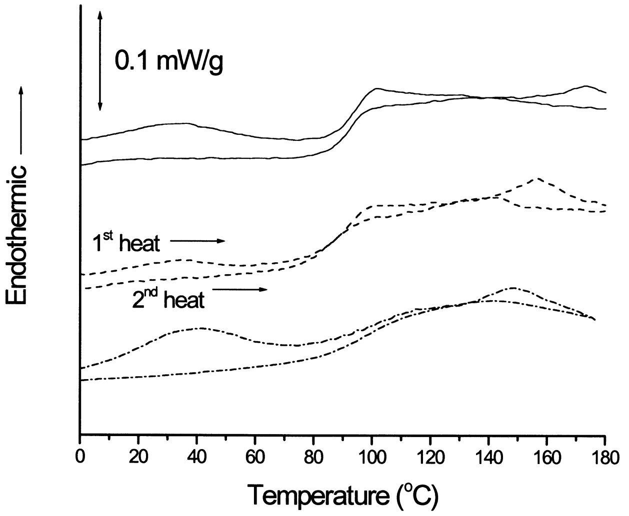

Fig. 3. DSC scans of (—) 93/7, (– –) 95/5, and (– - –) 98/2 AN/MA sample saturated at 120 °C, 10.3 MPa CO_2 for 6 h.

of no absorption was confirmed by weight measurements of the sample before and after saturation. No weight gain following saturation indicated that insignificant CO_2 was absorbed during the saturation experiment. We speculate that a critical copolymer ratio exists at approximately 10 mol% copolymer, at which the dipole–dipole interactions of the pendant nitrile groups generate strong intermolecular forces and significantly decrease the free volume of the copolymer. The existence of a critical copolymer ratio was also suggested by Rangarajan et al. [2]. We anticipate that higher saturation temperatures, obtained by direct injection of CO_2 into the copolymer melt, would generate enough free volume to facilitate CO_2 absorption, and will be addressed in future work.

3.2. Viscosity reduction

Viscosity reductions of the 85 and 90 mol% AN copolymers were measured for comparison to those observed in a previous paper for the 65 mol% AN copolymer to establish a relationship between potential viscosity reductions with our saturation methods and the AN content. Viscosity vs. shear rate data for the 85 mol% AN copolymer containing 5.6 wt% CO_2 are compared to the pure copolymer viscosity levels at 200 °C in Fig. 4. An average viscosity reduction of 61% is observed over the range of shear rates tested. The viscosity reduction is approximately equivalent to that obtained for the 65 mol% AN copolymer, with which a 60% viscosity reduction was obtained with 6.7 wt% absorbed CO_2. Only 5.6 wt% CO_2 was absorbed for the 85 mol% AN copolymer, but approximately the same viscosity reduction was observed.

Viscosity vs. shear rate data for the 90 mol% AN copolymer containing 2.0 and 3.0 wt% CO_2 are compared to the pure copolymer viscosity levels at 220 °C in Fig. 5. The viscosity vs. shear rate curves begin to merge at rates above approximately $400\ s^{-1}$ for both CO_2 absorption levels, corresponding to pressure drops in excess of 70 MPa. Below this pressure, the average viscosity reduction is approximately 31 and 56% for the copolymer containing 2.0 and 3.0 wt% absorbed CO_2, respectively. At pressures in excess of 70 MPa, the range of the viscosity reduction is only 10–15% and 20–30% for the copolymer containing 2.0 and 3.0 wt% absorbed CO_2, respectively. As the total pressure drop is increased above 70 MPa, the difference in viscosity between the pure and plasticized copolymer continually decreases within the range evaluated. These trends suggest that pressures above 70 MPa may be causing

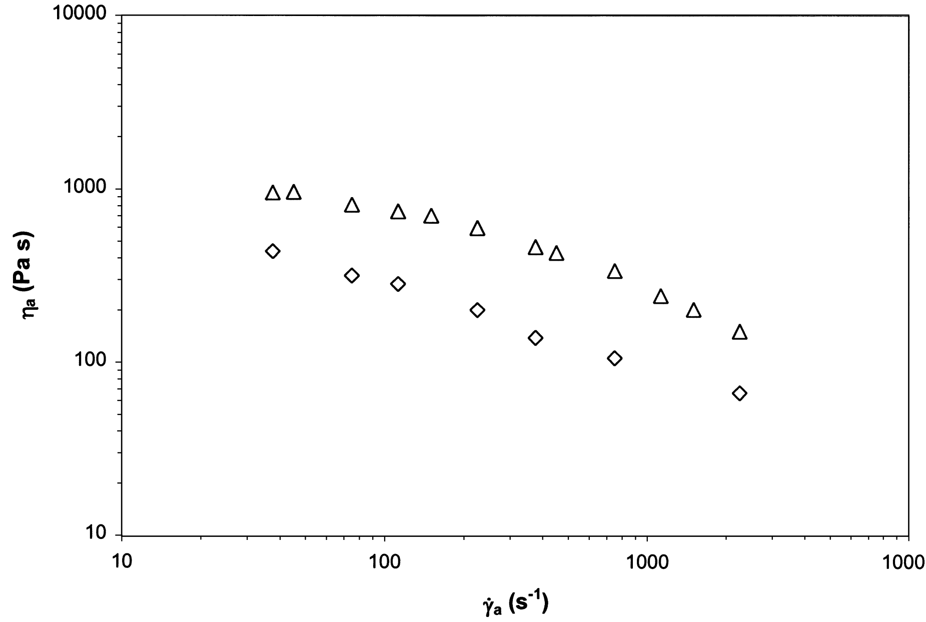

Fig. 4. Apparent viscosity vs. shear rate for the 85/15 AN/MA copolymer. (△) pure and (◇) plasticized copolymer containing 5.6 wt% absorbed CO_2. Test temperature 200 °C. $D = 0.69$ mm. $L/D = 111$.

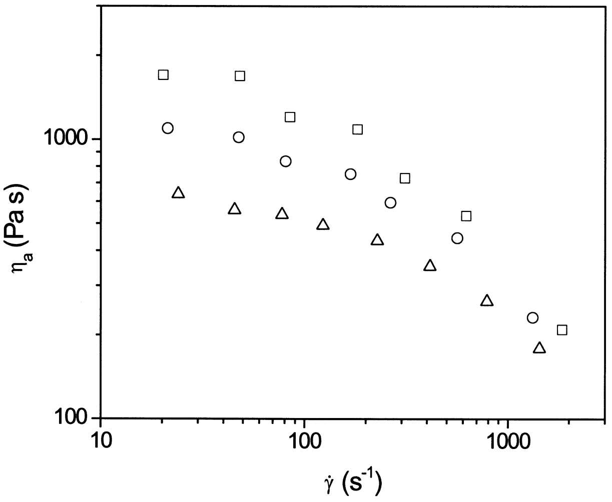

Fig. 5. Apparent viscosity vs. shear rate for the 90/10 AN/MA copolymer. Data are shown for the (□) pure copolymer and plasticized copolymer containing (○) 2.0 and (△) 3.0 wt% absorbed CO_2. Test temperature 220 °C. $D = 0.69$ mm. $L/D = 111$.

the viscosity to increase as a result of pressure effects on viscosity for the polymer/CO_2 solution and thereby compensating for the reduction in viscosity due to the plasticizing effect.

It is interesting that a similar viscosity reduction was obtained for the 65, 85, and 90 mol% AN copolymers at the 17.2 MPa saturation pressure, even though different amounts of absorbed CO_2 were present in each sample. The viscosity reduction for all three copolymers was found to be approximately 60%. However, the amount of absorbed CO_2 decreased from 6.7 wt% for the 65 mol% AN copolymer to 3.0 wt% for the 90 mol% AN copolymer. Similarly, almost identical viscosity reductions of approximately 30% were obtained over the range of shear rates (under 70 MPa) for the 65 and 90 mol% copolymers at the 6 h, 10.3 MPa soak, which corresponds to 4.7 and 2.0 wt% absorbed CO_2, respectively. These results suggest that as the AN content is increased, a smaller amount of absorbed CO_2 is required to plasticize the polymer and obtain a comparable reduction in viscosity.

3.3. Equivalent processing temperature reductions

In order to determine the ability for small amounts of absorbed CO_2 to reduce the processing temperature, an Arrhenius scaling analysis was used for each absorption level to determine the temperature, where the pure copolymer viscosity was equal to that of the plasticized copolymer viscosity. The difference between these two temperatures corresponded to an equivalent processing temperature reduction. This analysis was used because attempts to measure viscosities from the capillary rheometer at elevated temperatures (to obtain an equivalent processing temperature reduction similar to a recent paper [10]) resulted in significant degradation over the rather long (30–45 min) measurement time. Dynamic oscillatory data collected for the Arrhenius analysis required approximately 7 min, in which no significant degradation was observed over the range of temperatures used for these copolymers.

The Arrhenius scaling equation, which is shown in Eq. (2), is often used to describe the dependence of viscosity at temperatures above the upper limit of the WLF equation (which is $T_g + 100$ °C):

$$\ln\left(\frac{\eta_T}{\eta_{T_o}}\right) = \left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \qquad (2)$$

where E_a is the activation energy for the viscous flow, T_o is an arbitrary reference temperature, and R is the ideal gas constant. The viscosity measurements were obtained at 116 and 133 °C above the T_g of the 85 and 90 mol% copolymers, respectively, which are both above the usable temperature range of the WLF equation. To determine activation energies of flow, a plot of the viscosities obtained at an angular frequency of 0.1 rad/s was used to generate a plot of η vs. $1/T$ for each copolymer, and the slope of the plot was used to calculate the activation energy of viscous flow. A shear rate of 0.1 s^{-1} was used to maintain consistency between previous experiments [10] and to minimize the experimental variables in this study. Dynamic oscillatory shear viscosity measurements obtained for both the 85 and 90 mol% AN copolymers at temperatures in the range 190–230 and 225–240 °C, respectively, are illustrated in Figs. 6 and 7. The data used to calculate the activation energy for the 85 and 90 mol% copolymers are shown in Fig. 8. Activation energies of 8.69×10^3 K and 2.29×10^4 K were determined for the 85 and 90 mol% copolymers, respectively. The activation energy of flow for the 85 mol% copolymer is comparable to that reported for other thermoplastics, including polypropylene, polyethylene, and polyphenylenesulfide [20]. However, the activation energy for the 90 mol% copolymer is approximately three times higher than that reported for most thermoplastics [20].

Once the activation energies were calculated, the equivalent processing temperature reductions were determined using Eq. (2). Calculations were performed to determine the equivalent processing temperature reductions for three absorption levels: the 85/15 copolymer containing 5.6 wt% absorbed CO_2, and the 90/10 copolymer containing 2.0 and 3.0 wt% absorbed CO_2. For each absorption level, the average viscosity reduction obtained over the range of shear rates (from pressurized capillary rheometry) was used to define the ratio (η_T/η_{T_o}) in Eq. (2). T_o was then chosen as the temperature at which the viscosity reductions were measured (with the pressurized capillary rheometer), which was 200 and 220 °C for the 85 and 90 mol% copolymers, respectively. The temperature T was then calculated from Eq. (2), and the difference between T and T_o corresponded to the equivalent reduction in processing temperature. A temperature difference of 25 °C was calculated for the 85 mol% copolymer containing 5.6 wt% absorbed CO_2. For

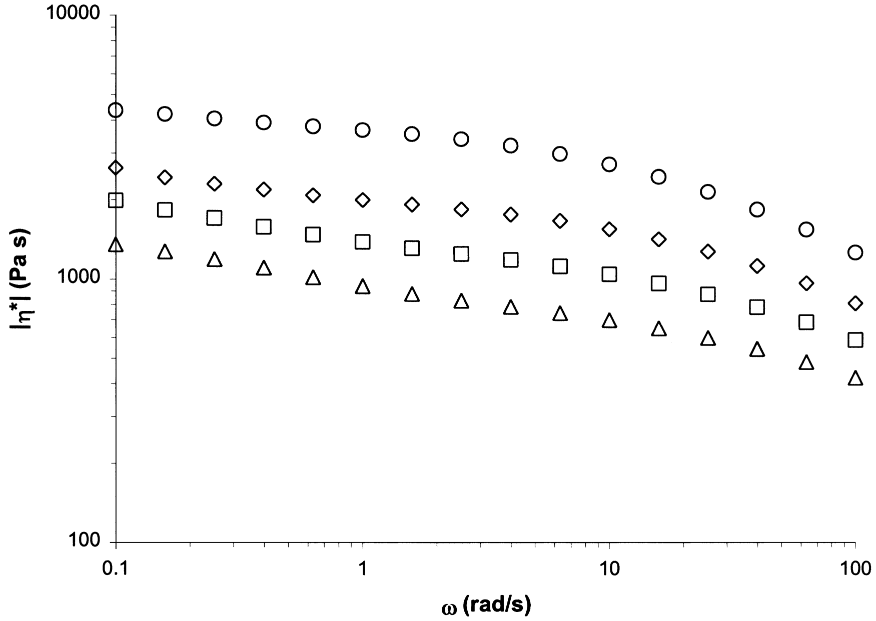

Fig. 6. Temperature dependence of the complex viscosity (magnitude) for the 85/15 AN/MA copolymer at (○) 190 °C; (◇) 200 °C; (□) 210 °C; (△) 220 °C.

the 90 mol% copolymer, temperature differences of only 4 and 9 °C were calculated for the 2.0 and 3.0 wt% absorptions, respectively. The potential processing temperature reduction obtained for the 85 mol% copolymer was similar to that obtained for the 65 mol% copolymer, which we expected because both materials had similar viscosity reductions. However, the processing temperature reductions for the 90 mol% copolymer were much lower than expected, primarily because of the exceptionally high value for the activation energy of flow. The complex viscosity data in Fig. 7 indicate approximately a six fold drop in viscosity over a 15 °C rise in test temperature for the 90 mol% copolymer, which directly correlates to the calculated high value for the activation energy. For comparison, the complex viscosity data for the 85 mol% AN copolymer in Fig. 6 indicate that the viscosity only changes by approximately a factor of 3 over a 40 °C temperature range and the range of angular frequencies measured.

3.4. Summary of AN content effects

The relationship between the AN content and CO_2 absorption, T_g reduction, viscosity reduction, and equivalent processing temperature reduction are summarized in

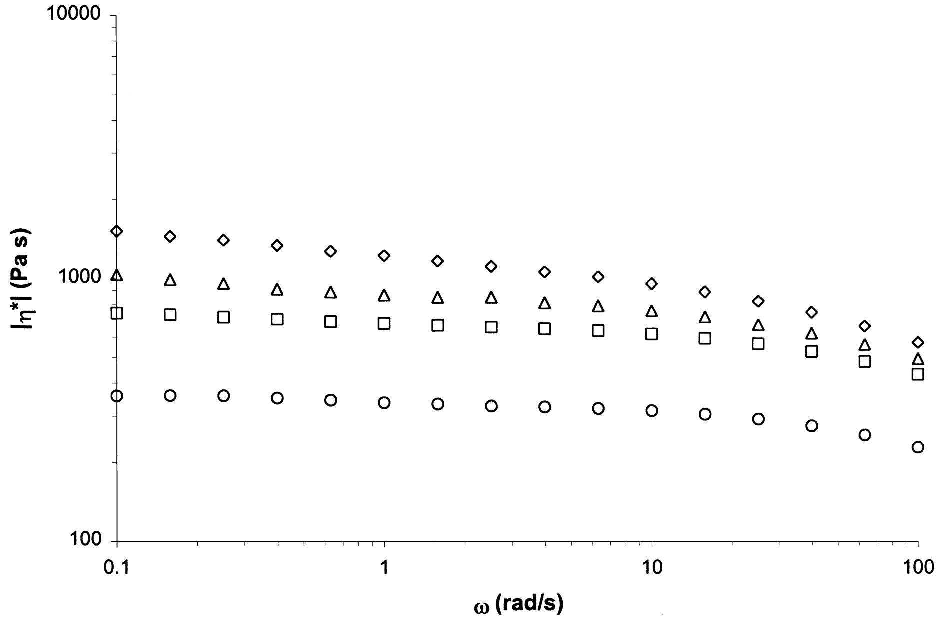

Fig. 7. Temperature dependence of the complex viscosity (magnitude) for the 90/10 AN/MA copolymer at (◇) 225 °C; (△) 230 °C; (□) 235 °C; (○) 240 °C.

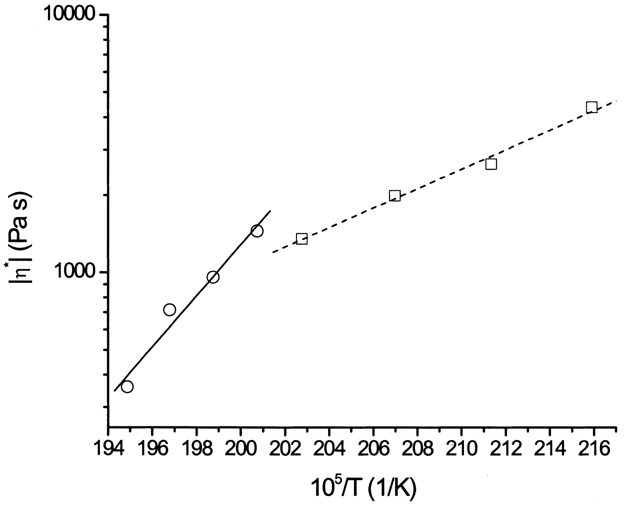

Fig. 8. Arrhenius plot to calculate activation energy of flow calculation for the 85/15 and 90/10 AN/MA copolymers. Open symbols are experimental data, lines are linear fits of the data. (□), (—) 85/15 copolymer; (○), (– –) 90/10 copolymer.

Table 2. The data suggest that the amount of absorbed CO_2 decreases as AN content is increased, at least in copolymers containing greater than 65 mol% AN. We speculate that less free volume exists because of significantly higher sequencing and crystallinity of the AN comonomer [21], resulting in a reduced ability to absorb CO_2. However, the actual reductions in T_g measured by DSC are not proportional to the levels of absorbed CO_2 measured by TGA, considering that the greatest reduction of T_g was observed for the 85 mol% AN copolymer. This suggests that the T_g reduction may pass through a maximum as a function of AN content between 65 and 90 mol% AN. Even more interesting is that regardless of CO_2 content and reduction of T_g, the 65, 85, and 90 mol% AN copolymers all exhibit approximately 60% viscosity reductions following the 6 h, 17.2 MPa saturation, which corresponds to 6.7, 5.6, and 3.0 wt% absorbed CO_2, respectively. Equivalent processing temperature reductions resulting from CO_2 absorption generally decrease as AN content increases, especially between the 85 and 90 mol% copolymers, where the equivalent temperature reduction drops from 25 to 9 °C, which is a result of the high activation energy of flow for the 90 mol% AN copolymer.

Table 2
Summary of CO_2 absorption experiments on copolymers with AN contents in the range 65–90 mol%

AN content (mol%)	CO_2 absorption (wt%)	T_g reduction (°C)	Viscosity reduction (%)	Potential process T reduction (°C)
65	6.7	31	60	30
85	5.6	37	61	26
90	3.0	27	56	9

4. Conclusions

This study has shown that AN copolymers containing up to 90 mol% acrylonitrile are plasticized by low levels (2.0–5.6 wt%) of absorbed CO_2, resulting in a reduction of T_g, viscosity, and (potentially) processing temperature. As AN content is increased, the data suggest that the amount of absorbed CO_2 and equivalent processing temperature reduction decreases. Viscosity reductions over the measured range of shear rates (and below a total pressure drop of 70 MPa) do not appear to depend on AN content up to 90 mol% AN, but rather on the conditions of saturation. The data suggest that reductions of T_g appear to pass through a maximum, possibly around 85 mol% AN, but sufficient data is not available to confirm this hypothesis. Also, the data suggest that the absorption of CO_2 in high AN content copolymers (85 mol% and greater) occurs immediately, and as a result no soak time is required to absorb CO_2 into the copolymers. These findings will be significant for further studies regarding melt processing of these copolymers.

AN copolymers containing greater than 90 mol% AN do not absorb CO_2 to any significant extent with our methods of saturation. However, we anticipate that these copolymers (containing greater than 90 mol% AN) can absorb CO_2 and exhibit reductions of T_g and of viscosity if the saturation temperature is increased to temperatures, where the free volume of these polymers is significantly increased. This saturation method would have to be performed on a short time scale, and could possibly be performed by direct injection of CO_2 into the copolymer melt in an extruder. Future studies will address the feasibility of direct melt plasticization of AN copolymers containing greater than 90 mol% acrylonitrile.

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