Molecular Weight Effects on the Processing, Thermal, and Mechanical Properties of Oligomeric Bisphenol A Phthalonitrile Resins

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ABSTRACT

Oligomeric phthalonitrile (PN) resins are desirable materials for many high-temperature applications because they exhibit good structural performance over a large temperature range, have low thermal conductivity and water absorption, as well as excellent fire performance. However, integration of these materials into certain high temperature applications has been impeded because of their limited long term oxidative stability. This is due to the high stiffness of PN resins which makes them susceptible to microcracking at elevated operating temperatures. One strategy to prevent microcracking is to improve resin flexibility by increasing its molecular weight. Along these lines, a series of bisphenol A PN resins (BisA) were synthesized with varying molecular weights. The thermal and rheological properties of each resin were characterized in order to determine the optimum processing conditions for producing void free samples of the cured resins. These samples were then subjected to a series of measurements to probe molecular weight effects on the thermal and mechanical properties of the BisA resins. Long term oxidative studies were conducted by measuring the mass of these samples before and after heating at 300 °C for 1000 hours. Samples were also imaged to probe the presence of heating induced microcracking of BisA resins.

1. INTRODUCTION

Phthalonitrile (PN) resins are a class of high temperature thermoset resins with excellent thermal and mechanical performance.[1,2] However, the use of these materials in composite applications has been limited due to their poor processablilty.[3] For example, previous generations of PN resins were highly fluid and exhibited melting temperatures that were too high for facile implementation into traditional processing methods.[4] One strategy to improve processing while maintaining their desirable high temperature properties is to synthesize oligomeric resins which are capped with PN groups.[5-8] These resins can be processed at lower temperatures than their low

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molecular weight counterparts, making them intriguing candidates as matrix resins for the next generation of high-temperature composites.[9,10]

While oligomeric PNs exhibit improved processing, these materials are still highly crosslinked.[11,12] The crosslinking density enables their robust temperature performance, however, it yields brittle matrix which must be reinforced with a secondary phase to be useful for most applications. Because these materials are highly brittle, improving in their mechanical properties could be beneficial to overall composite performance. Additionally, it is possible that improved thermal performance would be observed due to reduced microcracking which has been observed in higher molecular weight polymers.[5] There have been many previous studies which have investigated how the composition of the resin can be modified to produce resins with enhanced thermal and mechanical stability, yet there has been very little investigation into how the molecular weight of oligomeric PNs effects material properties.[13,14] Furthermore, there has been lots of investigation into molecular weight effects on other matrix materials. For example, increases in the molecular weight of PEEK, a high temperature thermoplastic, has been shown to improve the mechanical performance of the polymer.[15] This study aims to assess how the molecular weight of a bisphenol A based PN oligomers with different spacer lengths (n = 1, 4, 10, 25) and characterizing their processing, thermal and mechanical properties.

2. EXPERIMENTATION

2.1 Materials and Methods

All starting materials were reagent grade and used without further purification. Differential scanning calorimetry (DSC) measurements were obtained using a TA Instruments DSC 2920 modulated thermal analyzer with a heating rate of 10 °C min^{-1} under flowing nitrogen (50 cm^3 min^{-1}). Char yield experiments were conducted using thermogravimetric analysis (TGA) on a TA Instruments TGA Q50. Samples were heated to 1000 °C at a constant rate (10 °C min^{-1}) under a nitrogen purge (100 cm^3 min^{-1}). All DSC and TGA thermograms were analyzed using Thermal Analysis software from TA instruments. Viscosity and mechanical characterizations were performed on a TA Instruments DHR-2 rheometer equipped with an environmental testing chamber for temperature control. Resin viscosities were measured for 1.0 g resin samples under flowing nitrogen using the parallel plate geometry equipped with a 25 mm top plate. Because of increased flow at elevated temperatures, a 40 mm cup was used to contain the resin in addition to serving as the bottom plate for rheological characterization. For mechanical characterization, the torsion fixture was used to measure the storage modulus of postcured samples (20 x 10 x 2 mm) via oscillatory testing from 30 - 450 °C.

2.2 Synthesis of BisA Resins

Detailed synthetic procedure for BisA resins. Bisphenol A containing phthalonitrile resins of different molecular weight were synthesized according to a previously described procedure.[16] Briefly, bisphenol A (**2**), 4,4'-dichlorobenzophenone (**3**), and K_2CO_3 were dissolved in 4:1 DMSO/toluene mixture and refluxed in a nitrogen atmosphere at 180 °C for 12 hours. During reflux, water was collected using a Dean-Stark trap with an attached condenser. After reflux, toluene was removed by distillation and the reaction mixture was cooled to 50 °C. Once cool, 4-nitrophthalonitrile (**5**) was slowly added to the reaction. The reaction was then heated at 70 °C

for 4 hours followed by precipitation into a 5 % aqueous HCl solution. The resulting suspension was then filtered and washed with water until neutral.

n=1. Purchased from Chromak and used without further purification.

n=4. Bisphenol A (100 g, 0.438 mol) and 4,4'-dichlorobenzophenone (89.0 g, 0.354 mol) were dissolved in 4:1 DMSO/toluene mixture and refluxed in the presence of K_2CO_3 (63.3 g, 0.458 mol). After removal of the toluene and cooling to 50 °C, 4-nitrophthalonitrile (31.04 g, 0.179 mol) was added to the reaction mixture. After precipitation in to a 5 % aqueous HCl solution and filtering, n = 4 was isolated as a tan powder in 97% yield.

n=10. Bisphenol A (50.0 g, 0.219 mol) and 4,4'-dichlorobenzophenone (50.0 g, 0.199 mol) were dissolved in 4:1 DMSO/toluene mixture and refluxed in the presence of K_2CO_3 (36.3 g, 0.262 mol). After removal of the toluene and cooling to 50 °C, 4-nitrophthalonitrile (7.18 g, 0.041 mol) was added to the reaction mixture. After precipitation in to a 5 % aqueous HCl solution and filtering, n = 10 was isolated as a tan powder in 97% yield.

n=25. Bisphenol A (50.0 g, 0.219 mol) and 4,4'-dichlorobenzophenone (52.38 g, 0.208 mol) were dissolved in 4:1 DMSO/toluene mixture and refluxed in the presence of K_2CO_3 (36.3 g, 0.262 mol). After removal of the toluene and cooling to 50 °C, 4-nitrophthalonitrile (3.78 g, 0.021 mol) was added to the reaction mixture. After precipitation in to a 5 % aqueous HCl solution and filtering, n = 25 was isolated as a tan powder in 97% yield.

2.3 Preparation of BisA Samples for Mechanical Characterization

For n = 1, n =4, and n = 10 samples, 3.0 mol % of bis[4-(3-aminophenoxy)phenyl]sulfone (m-BAPS) was added to the powdered resin and thoroughly mixed with a mortar and pestle. The powdered resins were then poured into 13 mm x 50 mm molds and degassed in a vacuum oven heated to 200 °C. The samples were then cooled to room temperature and inspected for defects. These samples were then placed in an oven heated to 225 °C in air overnight to ensure gelation. The same procedure was used for the n = 25 resin, however, the powdered was poured into a square mold with a 50 mm x 50 mm cavity which was then degassed under vacuum at 300 °C. Smaller samples were then cut from the n = 25 square monolith for testing. The samples were then removed from their respective molds and then postcured in a tube furnace by slowly heating to 380 °C using a previously described procedure.[3]

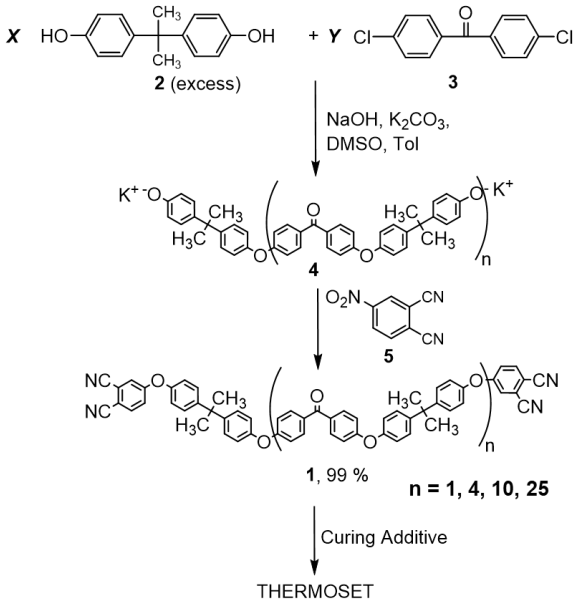
2.4 Long-Term Oxidative Stability

From the samples described in Section 2.3, smaller samples were cut (~ 150 mg) for thermo-oxidative studies. These samples were placed into separate ovens heated to 300 °C and 329 °C, respectively, and heated under air for a period of 13 days. The mass of these samples was monitored at several points during this study. Prior to the aging study all samples were heated at 150 °C, in order to remove any adsorbed volatile species which may affect the initial weight of each sample. To examine the surface of these samples prior to heating as well as investigate thermally induced cracking, optical microscope images were taken of each sample before and after heating.

3. RESULTS AND DISCUSSION

3.1 Synthesis

Previous studies have used a one-pot synthesis (Scheme 1) to form a variety of oligomeric PN resins by reacting 4,4'-dichlorobenzophenone (**3**) with different dihydroxybenzenes in the presence of base (e.g. NaOH, K_2CO_3).[16] Mechanistic studies indicate that an oligomeric dipotassium salt intermediate (**4**) is formed in the first step of this reaction via a stepwise nucleophilic displacement reaction between **3** and the deprotonated dihydroxybenzene species. The introduction of 4-nitrophthalonitrile (**5**) to the reaction mixture resulted in the addition of phthalonitrile groups to the oligomeric salt via displacement of the nitro group. After precipitation into a dilute acid solution to neutralize excess base, the oligomeric PN resin can be isolated 97% high yield.



Scheme 1. Synthetic pathway of BisA PN resins.

Due to the abundance of dihydroxybenzene starting materials, this synthetic pathway clearly allows for the production of PN resins of different compositions, however, the molecular weight of resins can also be modified simply by changing the molar ratio of the starting materials. In this study, molecular weight effects on oligomeric PN resins were investigated by synthesizing a series of PN derivatives with different spacer lengths (n =1, 4, 10, 25). For this particular study, bisphenol A (BisA) was selected as a phenolic building block because it is inexpensive compared to other dihydroxybenzene derivatives (e.g. resorcinol, 4,4'-Biphenol). In addition, previous studies have shown that the n = 1 BisA PN oligomer exhibited low water absorption and high char yields compared to traditional high temperature resin families (e.g. cyanate ester, polyimide, phenolic).[3,17] Due to these robust properties, any enhancements to material properties that arise from changes in molecular weight will help optimize an already useful resin system. Throughout the study, the various BisA resins will be referenced by the spacer length. For example, n = 4 will refer to the BisA resin which contains 4 subunits.

3.2 Curing Behavior of BisA Resins

In order to determine molecular weight effects on the processing parameters of BisA resins, a series of thermal and rheological characterizations were conducted (Figure 1). For these measurements, 3.0 mol % of bis[4-(3-aminophenoxy)phenyl]sulfone (m-BAPS) was added to the powdered resin in order to initiate curing. According to differential scanning calorimetry (DSC, Figure 1a) measurements, the melting temperature of BisA exhibited a strong molecular weight dependence, where the melting point increased with increasing spacer length. For instance, the n = 1 derivative exhibited a melting peak near 80 °C whereas the n = 25 did not melt until it was heated above 145 °C. The thermograms of each resin also contained exothermic peaks attributable to crosslinking of the PN groups. While these transitions occurred over roughly the same temperature range regardless of molecular weight, the strength of the transition was gradually muted due to the smaller relative concentration of PN moieties for high molecular weight resins.

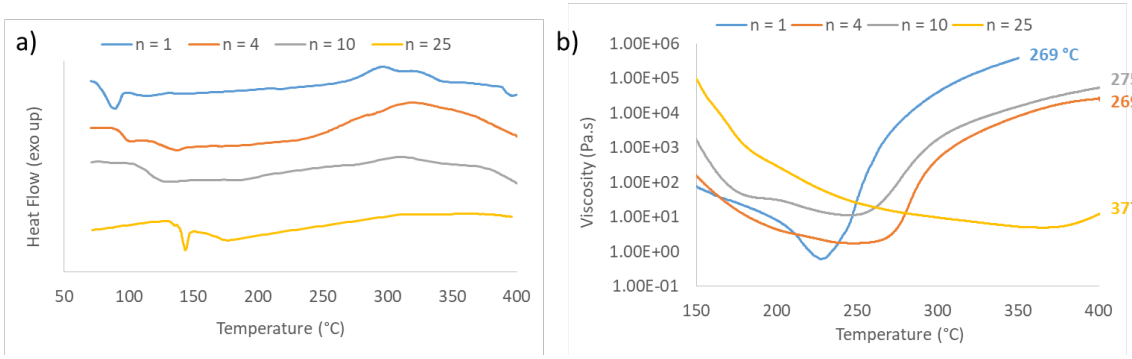


Figure 1. Differential scanning calorimetry (a) and rheological characterization of BisA resins with different molecular weights. The heating rates for DSC and rheological measurements were 10 °C/min and 3 °C/min, respectively. The gel point was also collected as part of rheological characterization and was defined by the crossover point of the loss and storage moduli (not shown).

Comparison of the DSC results to rheological characterization (Figure 1b) showed a similar molecular weight dependence on the curing behavior of BisA resins. For example, at 225 °C (above the melting point for each resin) there is a direct correlation between resin viscosity and increasing chain length of the oligomer. This trend also applies to the gel point of each oligomeric resin. For n = 1, the gel point occurs at 269 °C whereas the gel point for n = 25 is over 100 °C higher (377 °C). This difference can be attributed to the decreased chain mobility of the large oligomers which comprise the n = 25 sample. Though large differences in viscosity are observable below the cure temperature, samples which contain intermediate spacer lengths (n = 4, n = 10) exhibit very similar gel points. This suggests that the increased viscosity which arises from molecular weight differences does not substantially impede the curing reaction for those samples.

3.3 Preparation and Characterization of BisA Samples

Using the curing information described in Section 3.2, rectangular test samples were made from each BisA resin. For all but the n = 25 derivative, samples were made in a stainless steel

mold with rectangular cavities, which allowed the production of form factors suitable for mechanical testing. These particular molds were suitable because the low viscosity of these resins allowed for facile degassing when heated under vacuum at 200 °C. When the n = 25 sample is degassed under vacuum air remains trapped by the highly viscous resin, therefore, a larger mold was used so that bubbles formed during degassing could be manually broken up. Testable samples were then cut from the larger n = 25 sample.

3.3.1 Thermal Properties

The molecular weight dependence on the thermal properties of postcured BisA resins was investigated using both DSC and thermogravimetric analysis (TGA). Specifically, DSC characterizations were done to ensure that the heating procedure used for postcuring resulted in fully crosslinked samples. In addition, DSC allows for observation of potential glass transitions (T_g) that may be introduced as a result of increased molecular weight. According to DSC thermograms, no exothermic transitions are observed regardless of molecular weight, which indicated that none of the samples required additional heat treatment. Further examination of the DSC thermograms suggests that n = 1 does not experience a T_g over the temperature range tested. However, small features near 350 °C that may be indicative of a T_g are observed in both n = 4 and n = 5 samples, however, further characterization are needed in order to confirm the presence of these transitions. A clear transition was noted near 160 °C for the n = 25 sample, which confirms that a glass transition can be observed in sufficiently long oligomeric resins.

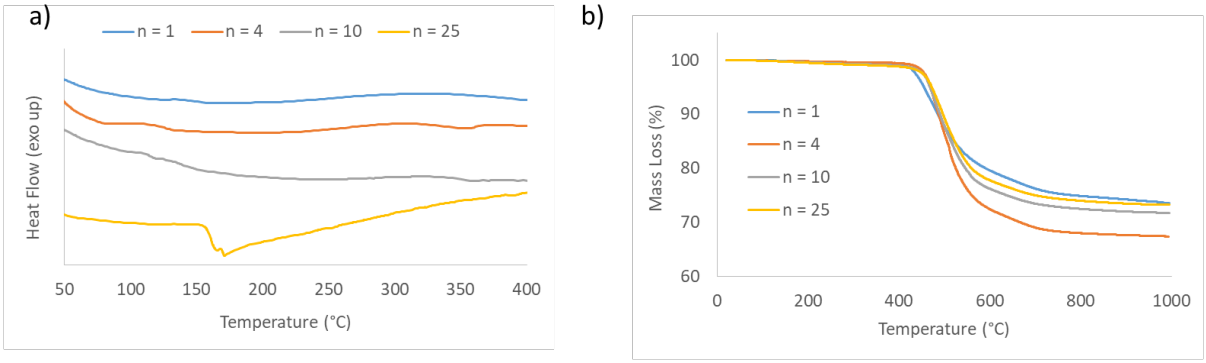


Figure 2. Differential scanning calorimetry (a) and thermogravimetric analysis (b) characterizations of postcured BisA samples with different molecular weights. A heating rate of 10 °C/min was used for both measurements.

According to the TGA scans for each sample, there is very little molecular weight dependence on the char yield for BisA samples. With the exception of n = 4, each sample exhibits a char yield between 78-79 %. The char yield for n = 4 is only slightly lower (70 %) which indicates that oligomeric BisA resins exhibit high char yields compared to most resin systems irrespective of the molecular weight of the resin. This is a somewhat surprising result given the lower concentration of PN groups contained in higher molecular weight resins, and that the char yield of a resin typically can be improved by increasing its crosslinking density. One potential explanation for this observation is that the resin may form highly reactive species due to thermal decomposition of the methyl groups in the polymer backbone.[18] Therefore, additional crosslinking may occur as it chars which may lead to higher mass retention upon heating.

3.3.2 Mechanical Properties

Dynamic mechanical measurements were used to measure the storage modulus and tan δ of each resin as a function of temperature (Figure 3). For these measurements, 20 mm x 13 mm square pieces were cut from the samples previously described in Section 3.3. Examination of the storage modulus for the n = 25 resin shows a sharp decrease occurring at 160 °C which is indicative of a T_g. This result is in good agreement with DSC measurements which also show a transition at this temperature. The trends in storage modulus for the other resins indicate that increased molecular weight has very little effect for these samples. For instance, a narrow range of initial storage moduli (1400 – 1700 MPa) are detected, which gradually decreased to a minimum near 400 MPa at 425 °C. While the storage modulus profiles for these resins are largely featureless, inspection of the n = 1 sample shows a decrease in storage modulus beginning at 380 °C, which may be indicative of a T_g. However, the modulus decrease is not as sharp as the one observed for the n = 25 sample.

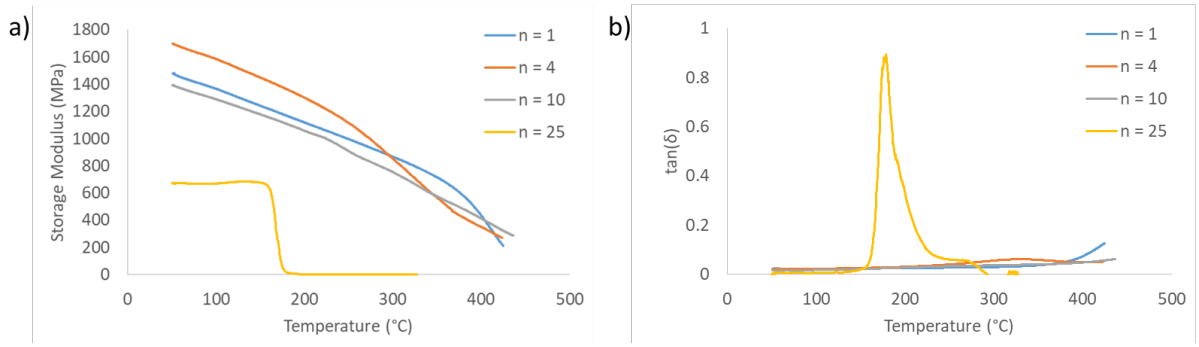


Figure 3. Storage modulus as a function of temperature (heating rate = 3 °C/min) for BisA samples with different molecular weights.

Like the storage modulus data, the tan δ for the n = 25 derivative shows a sharp peak near 180 °C that is clear evidence of a T_g. The tan δ for the other resins are relatively featureless when compared to their n = 25 counterpart, which indicates that there is little flexibility in these samples. For the n = 4 sample there is a slight peak in tan δ near 320 °C, whereas the n = 1 resin begins to increase near 400 °C. Given that these transitions are not intense when compared to the n = 25 sample, it is difficult to conclude that these resins exhibit a T_g over the temperature range of this experiment. However, the storage modulus and the tan δ for the n = 1 sample suggest that it may undergo a T_g just above the range tested.

3.4 Oxidative Aging of BisA Samples

In order to determine if molecular weight has any effect on the long-term oxidative stability of BisA resins. Samples (~150 mg) were heat treated under air at 300 °C and 329 °C for 13 days. These temperatures were selected because they are representative of extreme prolonged operating temperatures for most high temperature applications. Specifically, 329 °C was used because most organic molecules decompose at this temperature. Optical microscope images were also obtained before and after heating in order to examine surface cracking of the materials. Inspection of these images before heating indicates that the n = 1, 4, and 10 samples have almost no surface defects which could lead to poor long term oxidative stability. However, the n = 25 derivate contain several voids that are roughly 20 μm in diameter and can be attributed to the

limited processability of this resin as a result of its high viscosity. Given that these samples already contain some amount of porosity, it is possible that they would exhibit lower oxidative stability compared to the other samples.

Inspection of the results for samples heated at 300 °C indicates that all samples retain more than 95% of their initial mass over the first 216 hours of heating. Over this time interval, there appears to be no correlation with the molecular weight of the sample given that the mass retention for each resin fluctuates within each data point collected. After heating for 288 hours, all samples retained less than 95% of their initial mass and the n = 4 and n = 25 resins lost significantly more mass than the other resins. However, all samples retained over 85% of their initial mass. The trends in this data can be interpreted based on the degree of cracking observed in the optical microscope images obtained after heat treatment at 300 °C. For n = 1 and n = 10, samples which retained the most mass, there are only small circular voids and no cracking is noted. Significant cracking is detected in the n = 25 and n = 4 samples which likely contributed to the higher mass loss for these samples.

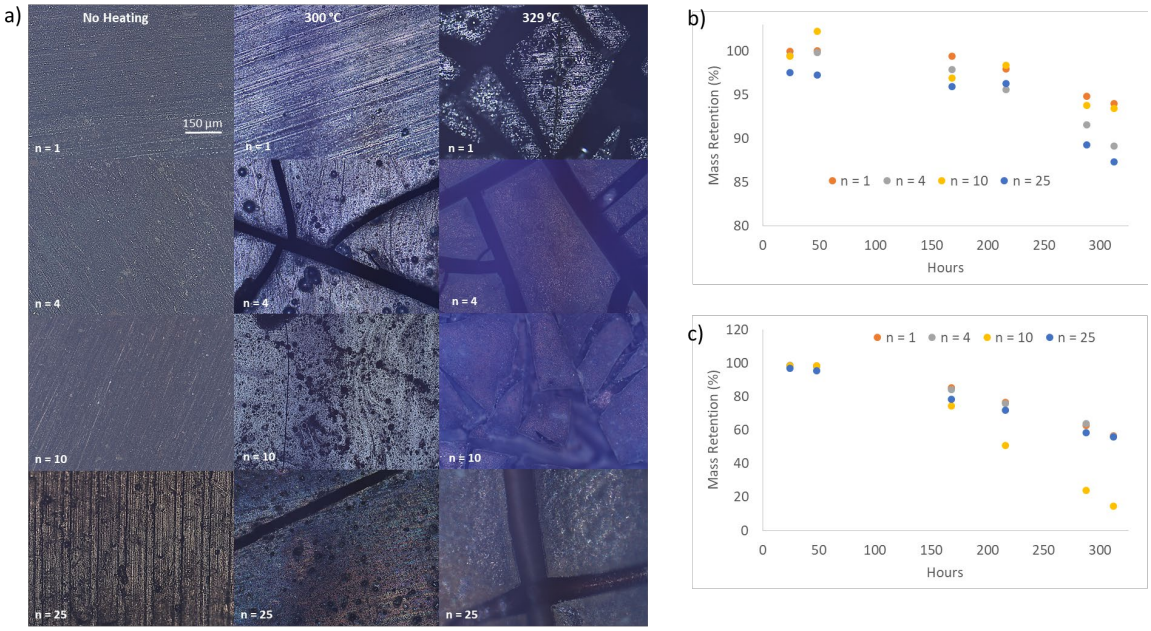


Figure 4. Optical microscope images (a) of BisA samples with differing molecular weights heated at 300 °C (b) and 329 °C (c) for 13 days.

When heated at 329 °C, no significant mass loss was observed over the first 48 hours of heating as all samples retained more than 95% of their initial mass. Further heating resulted in more rapid mass loss when compared to the samples heated at 300 °C. With the exception of n = 10, the rate of mass loss was relatively similar such that these samples all retained approximately 56% of their initial mass at the conclusion of the study. The n = 10 sample lost substantially more mass than the other samples given that it retained less than 15% of its initial mass. Like, the samples heated at 300 °C these results can be interpreted based on the cracking density detected in the optical microscope images after heating. All images show cracking, however, the image for the n = 10 sample heated at 329 °C shows much more compared to the other samples.

The results of this study do not appear to suggest any molecular weight dependence on the long term oxidative stability of these samples, which is not what was predicted based on the increased flexibility observed in higher molecular weight BisA resins. This may be due, in part, to the sensitivity of this experiment to sample preparation. Since there is a definite correlation between the oxidative stability and cracking density, samples which contain defects to begin with are more likely to crack. Another explanation may be that thermal degradation of samples is largely independent of molecular weight. However, further investigation into the mechanism of thermal degradation is needed in order to precisely determine any potential molecular weight effects.

4. CONCLUSIONS

A one-pot synthesis was used to produce BisA PN resins of different molecular weights. The processing parameters of these resins were characterized using DSC and rheometer. According to these measurements, higher molecular weight resins were more viscus and gelled at higher gel temperatures compared to their low molecular weight counterparts. While this limited their prcessability, quality resin samples could still be produced from these resins. Thermal, mechanical and oxidative testing was done on postured samples made from each resin. According to characterization using DSC of these samples, the n = 25 sample exhibits a T_g at 160 °C which was subsequently confirmed by dynamic mechanical measurements. Surprisingly, all samples exhibited similarly high char yields as measured by TGA, which indicates that the molecular weight of these samples does not affect pyrolysis of these samples. Long term oxidative aging measurements at 300 °C and 329 °C showed that the mass retention of resins was correlated to cracking density of each sample. Based on these measurements, the long term oxidative stability was primarily determined by sample preparation and the molecular weight of the sample had little effect.

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