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Effect of heat treatment on the thermal and mechanical properties of polyhydroxyamic acid presursor films

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Summary

Polyhydroxyamic acid (PHAA) with an inherent viscosity of 0.45 dL/g was prepared from 3, 3'-dihydroxybenzidine and pyromellitic dianhydride. The mechanical and thermal properties of PHAA films and powders before and after annealing were investigated on the basis of their potential use as fire-safe polymers. Cyclization of PHAA to the corresponding hydroxy-containing polyimide is an endothermic reaction. During annealing of PHAA, water was released at 180 °C and carbon dioxide at over 400 °C. The weight residue of PHAA at 900 °C was about 38 %. After annealing at 500 °C, this value increased to 75 %. After annealing at 450 °C, the ultimate stress and initial modulus of the PHAA precursor films increased from 133.8 MPa and 5.86 GPa to 306.2 MPa and 11.0 GPa, respectively.

Introduction

Aromatic polyimides (PIs) and polybenzoxazoles (PBOs) have been extensively investigated due to their excellent thermal stability and high mechanical properties, along with their good chemical resistance and electrical properties [1, 2]. Because of these outstanding properties, their use in fibers, films, coatings, and composites has been studied for many years. Generally, PIs and PBOs can be prepared from their precursor polymers, polyamic acids (PAAs) and polyhydroxyamides (PHAs) [3, 4]. It is well known that the conversion reaction of PAAs and PHAs into PIs and PBOs during heating is endothermic, and water can be released during the cyclization reaction [5-8]. These two characteristic properties contribute significantly to flame retardancy. In addition, PIs and PBOs produced during heating of PAAs and PHAs show high thermal stability. PAAs and PHAs are easy to process due to their good solubility in aprotic solvents such as N-methyl pyrrolidone, N, N-dimethyl acetamide, and N, N-dimethyl formamide. Their films and fibers have attracted considerable attention as fire resistant materials. Our group has studied the possibility of utilizing polyhydroxyamic acid (PHAA) synthesized from 3, 3'-dihydroxybenzidine and pyromellitic dianhydride as a fire-safe polymer. PHAA is also very stable in aprotic solvents. The cyclization pathway of PHAA has been recently investigated in our group. PHAA was converted to the related imide species at ca. 180 °C, and the imide structure was rearranged to the benzoxazole structure at over 400 °C (Scheme 1). During the first cyclization, water was given off, and during the second, carbon dioxide was released. Tullos et al. [9] reported similar results with hydroxy-containing imides. These hydroxy-containing polyimides show a high degree of water uptake [10], which further assists in flame retardancy.

In this continuation of our work, the thermal and mechanical properties of PHAA were evaluated to determine the possibility of its use as a fire-safe polymer. PHAA film was prepared, and its tensile and thermal properties were investigated before and after annealing. The rearrangement of PHAA is largely related not only to the polymer properties, but also to the release of flame-quenching material.

Experimental

Materials

3, 3'-Dihydroxybenzidine (DHB) was recrystallized from a water/DMAc cosolvent and dried at 60 °C *in vacuo*. Pyromellitic dianhydride (PMDA) was recrystallized from acetic anhydride and sublimed at around 200 °C under reduced pressure. N, N-Dimethyl acetamide (DMAc) was distilled over phosphorus pentoxide under reduced pressure. Other reagents were used as received. All monomers and solvents were kept in a desiccator before polymerization.

Polymerization

After DHB (0.3983 g, 1.84 mmol) was completely dissolved in 10 ml of purified DMAc under nitrogen, PMDA (0.4017 g, 1.84 mmol) was introduced into the solution with vigorous stirring. Stirring was maintained for 24 h at room temperature. The polymer concentration was adjusted to 8 % (w/v). The resulting viscous solution was poured into methanol and the precipitate was filtered, washed with excess methanol, and dried at 60 °C under vacuum. To obtain a polymer powder, the polymer mass was pulverized under liquid nitrogen and dried at 60 °C under vacuum until no weight change was observed.

Film Preparation

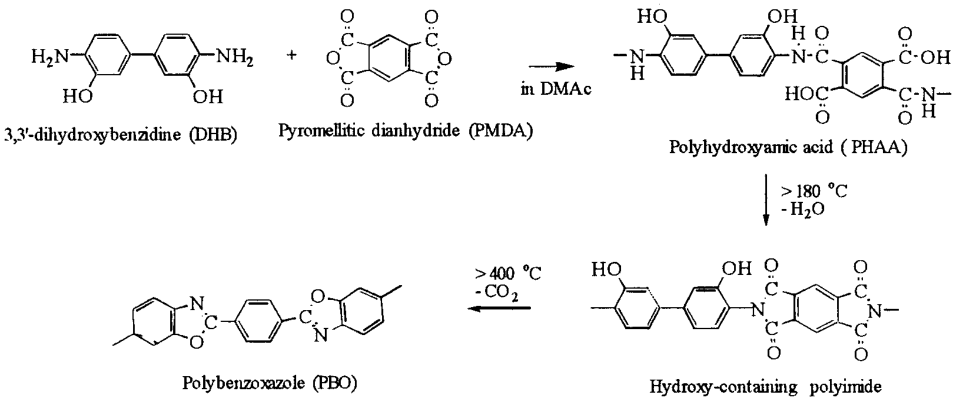
8 % PHAA solution was diluted to a 5 % solution in DMAc; this solution was then stirred vigorously to obtain a homogeneous solution. The film was prepared by pouring the solution onto a cover glass. After the film was dried *in vacuo* at 60 °C for 24 h, PHAA film was obtained as a free-standing form. In order to remove any DMAc which might be in the film, we cleaned the film in an ultrasonic cleaner for 30 min. The film was then dried again at 60 °C for 24 h under vacuum. The film thickness was 30-40 µm.

Measurements

The film was cut into strips of 2x20 mm. The sample films were tested with a Merlin Instron 5564 to determine their mechanical properties. The extension rate was 2 mm/min. The cyclization reaction and thermal stability were monitored by differential scanning calorimetry (DSC) and thermogravimetry (TGA) using a DuPont DSC 2910 and TGA 2950 under nitrogen at a heating rate of 10°C/min. The inherent viscosity of PHAA was determined at 0.5 g/dL in DMAc at 25 °C using an Ubbelohde viscometer. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) data was obtained using a CDS Analytical Pyroprobe 2000 with a CDS 1500 Valved Interface coupled to a Hewlett-Packard 5890 Series II Plus Gas Chromatograph 5972 Series Mass Selective Dector. The sample was heated in a quartz tube at 10 °C/ms to 450 °C and then held for 15 sec. The interface temperature and the GC inlet temperature were 150 °C. The initial temperature of the GC oven was 40 °C. The temperature was ramped at 10 °C /min to 250 °C and then held. The helum flow rate was 1 mL/min. The GC column was a capillary, HP5-MS (crosslinked 5 % PH Me Siloxane; 30 m x 0.25 mm).

Results and discussion

Polyhydroxyamic acid (PHAA) was prepared from 3, 3'-dihydroxybenzidine (DHB) and pyromellitic dianhydride (PMDA) as shown in Scheme 1. As for a general polycondensation reaction, monomer and solvent were carefully purified to obtain high molecular weight PHAA. DHB can be easily oxidized to turn its color to brown (DHB is originally white). Therefore, the PHAA solution colors varied from yellow to dark brown depending on monomer purity. In this study, a light yellow 8% PHAA solution in DMAc, with an inherent viscosity of 0.45 dL/g, was obtained and used for film casting.



Scheme 1. Polymerization and cyclization of PHAA.

Fig. 1 shows TGA thermograms of PHAA powder before annealing. The dried PHAA mass, which was obtained by precipitation, was pulverized and fully dried again before TGA and DSC measurement. In the case of PHAA, three weight loss steps occur during heating under nitrogen. According to our previous model compound study, hydrogen-containing amic acid was converted to the related imide species at ca. 180 °C, and the imide structure was rearranged to the benzoxazole structure at over 400 °C. During the first cyclization, water was given off, and during the second, carbon dioxide was released. Also, two moles of DMAc were complexed with one mole of hydroxy-containing pyromellitic diamic acid. The first weight loss of PHAA, which started at ca. 120 °C, was almost 34 %, which is due to the loss of DMAc and water during imidization. The theoretical weight losses of DMAc and water during cyclization are 28.6 and 5.9 %, respectively. The second weight loss, almost 18 %, was observed at approximately 400 °C, and was due to the loss of carbon dioxide during rearrangement of the hydroxy-containing polyimide (PI) to the corresponding PBO [9]. The third weight loss step is decomposition of the PBO. The decomposition of the PBO was observed to occur at about 600 °C. The weight residue of the PHAA at 900 °C was around 38 %. This low value is due to the loss of DMAc and water.

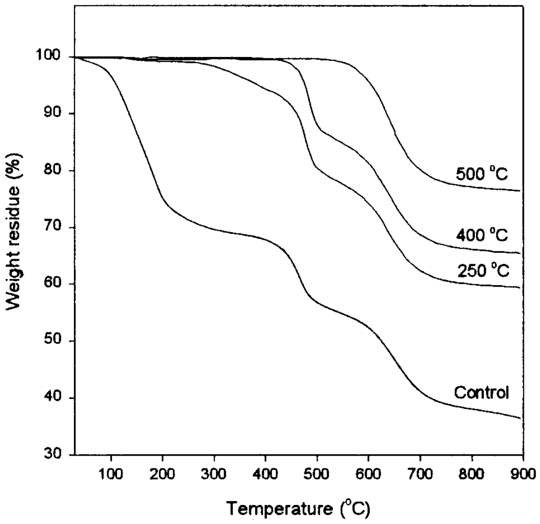


Figure 1. TGA thermograms of PHAA powder before and after annealing.

To identify the products given off during the cyclization and rearrangement reaction, a PHAA powder sample was cyclized at 450 °C at a heating rate of 10 °C /ms under a helium atmosphere using a commercially available resistively heated filament pyrolyzer. The sample was cyclized in a heated interface that was connected directly to the GC inlet. The releasing products during heating were swept directly onto the column where they were cold condensed. The GC oven was then ramped at 10 °C /min to 250 °C and the products were identified using a mass spectrometer. The GC chromatograms for the porducts given off during heating PHAA was shown along with the corresponding MS spectrum in Fig. 2. As can be seen in the chromatograms, PHAA has a much larger amount of DMAc. Water and carbon dioxide were also detected. Since the decomposition temperature of PBO is over 600 °C, this corbon dioxide should not be from the decomposition of PBO.

TGA thermograms of PHAA powder after annealing are also shown in Fig. 1. After annealing at 250 °C and 400 °C, the temperature at which the cyclization of PHAA to the corresponding polyimide was almost complete, the loss of DMAc and water almost ceased, because evaporation of DMAc and the imidization reaction have already occurred during annealing at these temperatures. Carbon dioxide was given off at over 400 °C. Over this temperature, the hydroxy-containing PI was rearranged to the corresponding PBO. In the case of PHAA powder annealed at 500 °C for 30 min, only the decomposition behavior was observed because the hydroxy-containing PI was almost completely rearranged to the corresponding PBO. The weight residues of PHAA powder at 900 °C after annealing at 250, 400, and 500 °C were ca. 59, 64, and 75%.

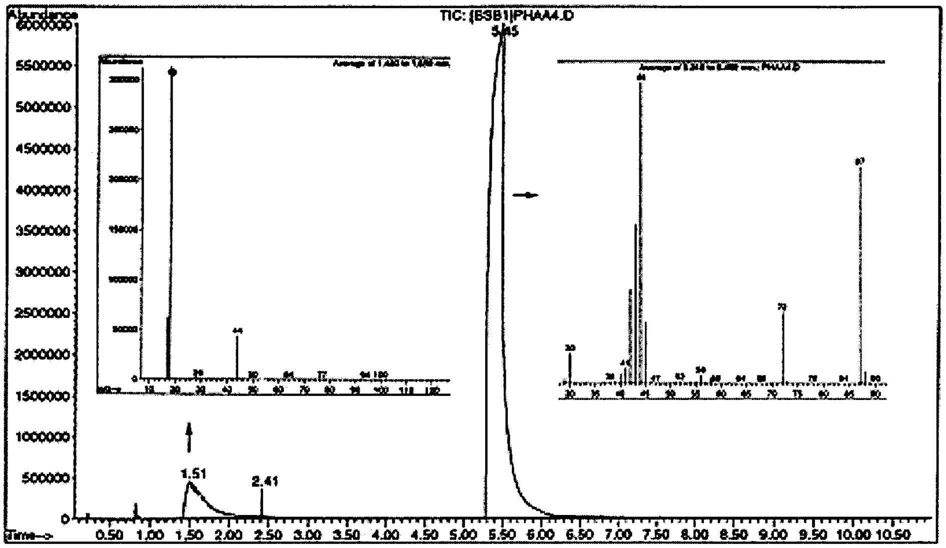


Figure 2. GC trace of products from the cyclization and rearrangement reactions of PHAA.

Because the weight residue is related to char formation in combustion, a higher value is more favorable for fire safety. The weight residue was somewhat different after annealing at 250 and 400 °C, because annealing at 400 °C may give more perfect imidization than annealing at 250 °C, and carbon dioxide starts to be released at around 400 °C. After annealing at a high temperature, the yellow color of the PHAA powder changed to dark brown.

Fig. 3 shows DSC thermograms of PHAA powder before and after annealing at various temperatures. PHAA showed an endothermic reaction during heating, which is due to the imidization reaction. The initial stage of the endothermic reaction might be mainly due to evaporation of DMAc. It appeared that the two reactions accounted for the endothermic behavior of the PHAA. It is likely that, in this case, loss of DMAc occurs first, followed by imidization, although it has not been possible to separate these steps. After annealing at 100 °C for 30 min, the DMAc was almost evaporated and the endothermic reaction was mainly due to imidization of PHAA. The enthalpy of the endothermic reaction of PHAA was 232 J/g. After annealing at 100 °C, this value decreased to 160.1 J/g. This value seems to be close to the one obtained by imidization of PHAA, rather than by evaporation of DMAc. After annealing at 150 °C, the enthalpy of the endothermic reaction was reduced to 38.6 J/g. This endothermic peak completely disappeared after annealing at 250 °C, which means that the imidization of PHAA was almost complete. The imidization temperature increased after annealing at 150 °C because imidization occurred to some extent during annealing. As the imidization process continues, the polymer's glass transition temperature increases, affecting molecular mobility [11]. There was no enthalpy change at 400-450 °C, where carbon dioxide was released.

Fig. 4 shows the tensile properties of PHAA films. The ultimate stress, initial modulus, and elongation at break of the PHAA films were 134 MPa, 5.86 GPa, and 12.0 %. According to our previous results [5], these values are equal to those of polyhydroxyamide film, 137 MPa, 5.94 GPa, and 9.0 %. After annealing at 250 and 450 °C, the ultimate strength and initial modulus increased to 209 MPa, 10.3 GPa and

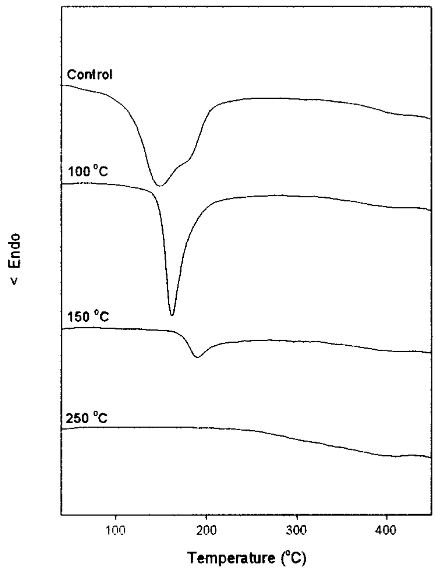


Figure 3. DSC thermograms of PHAA powder before and after annealing at various temperature.

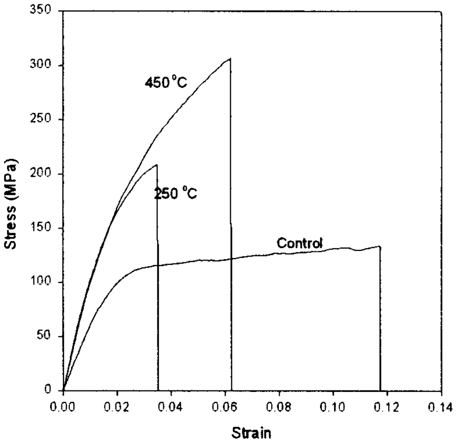


Figure 4. Stress-strain curves of PHAA films before and after annealing at various temperature.

306 MPa, 11.0 GPa, respectively. However, the elongation at break decreased, to 3.5 and 6.2 %, respectively. This increase in the tensile properties of PHAA film after annealing is due to imidization of PHAA and rearrangement of the hydroxy-containing PI to the corresponding PBO.

In the future, we will prepare high viscosity PHAA solution and try to spin PHAA fiber by a dry-jet wet spinning method.

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