Polymer Vol. 39 No. 23, pp. 5649–5654, 1998
0032-3861/98/$ – see front matter

PII: S0032-3861(97)10364-0

Effect of heat treatment on the thermal and mechanical properties of a precursor polymer: polyhydroxyamide

Jin-Hae Chang[a,*], Michael J. Chen[b] and Richard J. Farris[b]
[a]*Department of Polymer Science and Engineering, Kum-Oh University of Technology, Kumi 730-701, South Korea*
[b]*Department of Polymer Science and Engineering, University of Massachusetts at Amherst, Amherst, MA 01003, USA*
(Received 10 November 1997; accepted 28 November 1997)

The film type precursor polymer showed excellent thermal stability as determined using TGA under nitrogen. Endothermic enthalpy peaks were observed at 319–351°C for various annealing temperatures from DSC thermograms. It was unusual to observe such large heat capacities, from 221.1 to 131.7 J/g, which decrease with increasing annealing times and temperatures. The values of the tensile strength and initial tensile modulus of the precursor films were enhanced remarkably with increasing annealing temperature. The values of the tensile properties increased almost linearly with increasing annealing time at 250 and 350°C. But for films annealed at 450°C, the value of the tensile strength significantly increased from 137 to 332 MPa, but remained constant with increasing annealing time. Similar results were observed for the initial modulus. For determining the biaxial stress of the film in the precursor state, holographic interferometry was used to identify the resonant modes of vibration. The precursor polymer showed limited solubility in common solvents, but showed good solubility in DMAC and NMP with LiCl when heated above 80°C. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: precursor polymer; polyhydroxyamide (PHA); thermal stability)

INTRODUCTION

Heterocyclic polymers[1–5], particularly polybenzoxazoles (PBOs), polybenzthiazole (PBTs) and polyimides, have been extensively studied for their high temperature stability, excellent solvent resistance, light weight and outstanding flame resistance.

Wholly aromatic PBOs and PBTs are among the most thermally and thermo-oxidatively stable organic polymers known. But, fully heterocyclized polymers have shown some drawbacks in solubility and processing. This problem of processing is currently being exploited to obtain unusual combinations of physical properties in fibres and films[6].

Many researchers[7–10] have examined the possibility of heterocyclic precursor polymers that can be used as high performance, fire-retardant films, composites and fibres. Most materials of precursor type have properties similar to amorphous polymeric glasses before being cyclized, and the uncyclized forms have lower glass transition temperatures.

Precursor polymers[5–13] have the advantages that they are easier to process, do not require strong solvents and can adsorb large amounts of heat energy during the cyclization process. Thus, if these materials are used in the uncyclized form, they will have increased heat capacity, and when cyclized they will liberate water or a flame retardant, depending upon the design of the chemical groups undergoing the cyclization. Hence, the precursor will be converted to a high temperature heterocyclic polymer possibly containing a flame retardant, and will consume a considerable amount of energy in the process.

In this work, the materials were evaluated for physical and mechanical properties in both the uncyclized and fully cyclized forms to determine the advantages of utilizing the materials in their precursor form. We have investigated the thermal stabilities and tensile properties of the polyhydroxyamide (PHA) films as a precursor form at various annealing temperatures and times. To improve tensile properties, the optimum processing parameters, e.g. annealing conditions, were determined experimentally. In addition, we studied the correlation between the heat treatment and the measured tensile properties.

Holographic interferometry has been used to do nodal analysis on vibrating objects for a long time. Some applications[14] include the determination of resonant frequencies of objects with complicated geometries, the observation of resonance patterns on circular disks, and the observation of debonding and determination of Poisson's ratio in composite materials. Both in-plane and out-of-plane displacements can be measured using variations of holographic techniques. Holographic interferometry has also been used as a tool for stress measurement in polymer coatings[14–16]. An introduction to the holographic interferometry technique for the measurement of biaxial stresses in the precursor PHA membrane is presented in this paper.

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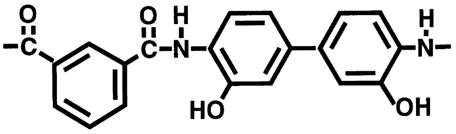
[*] To whom correspondence should be addressed

EXPERIMENTAL

Synthesis of the polymer

Polyhydroxyamide (PHA) was prepared by solution polymerization of 3,3′-dihydroxybenzidine and isophthaloyl dichloride[10]. The inherent viscosity of the polymer was measured in a solution of 0.2 g/dl in *N*-methyl-2-pyrolidone (NMP). Its inherent viscosity was 1.20. This material was supplied by Dr Kantor's group of the University of Massachusetts at Amherst. The chemical structure of PHA is as follows:



PHA

Film preparation

PHA was dissolved in NMP at 80°C with 0.1–0.5 wt% of LiCl. The polymer solution was coated on to a glass plate and dried in a vacuum oven at 60°C for one day. Then the films, while still on the glass plates, were cleaned in an ultrasonic cleaner five times for 30 min. These films with the solvent removed were dried again in a vacuum oven at 60°C for one day. The film thickness was 10–15 m.

Characterization

Differential scanning calorimetric (DSC) measurements under N_2 atmosphere were carried out on a DuPont 910 instrument. The scanning temperature was increased at 20°C/min. Thermal stability was examined under N_2 atmosphere using a DuPont 910 thermogravimetric analyser (TGA) at a heating rate of 20°C/min. Annealing was conducted in a high temperature vacuum oven preheated to a desired temperature.

The mechanical properties of the films were measured at room temperature on an Instron Mechanical Tester (Model 5564) with a crosshead speed of 5 mm/min. The reported values are the average of six measurements. The experimental uncertainty in tensile strength and modulus was ±1 MPa and ±0.05 GPa, respectively.

Equipment of holographic interferometry

A membrane is placed in a fixture rigidly mounted to a Wilcoxon Research piezoelectric shaker, driven by a Wavetek Model 190 frequency generator connected to a Wilcoxon Research PA7 power amplifier. The frequency is monitored using a B and K Precision 80 MHz frequency counter. An image of the stationary membrane is recorded on a thermoplastic holographic plate using a Newport Research Corporation HC3O1 holographic camera. The light source used for this reflection hologram is a 5 mW helium–neon laser. A schematic of the holographic setup is shown in *Figure 1*.

Sample preparation for biaxial stress measurement

Several methods can be applied to prepare a uniform film sample [14,15]. The method chosen is dependent upon the material. Therefore, the method described below is specific to the material system.

A rigid circular steel washer was adhered to the flat PHA film using Superglue, and pressure was applied to ensure uniform adherence. After the glue dried, the PHA film constrained by the washer was soaked in an ultrasonic cleaner with absolute ethyl alcohol and dried in a vacuum oven at 60°C for one day. Thus, a PHA membrane was prepared with a state of stress in tension.

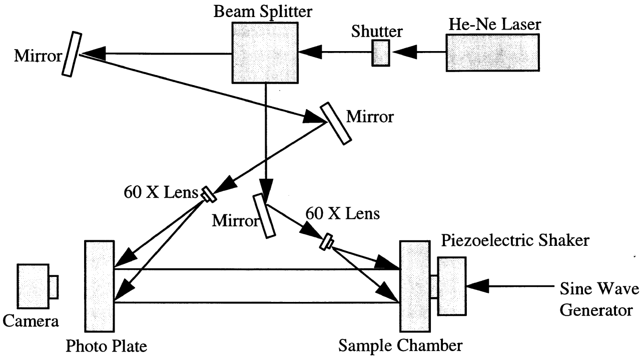


Figure 1 Schematic of the holographic interferometry

Table 1 Thermogravimetric analyses of the PHA films annealed for 30 min at several different temperatures

Ann. temp. °C	T_1^a °C	wt. red. ^{b} °C	T_2^c °C	wt_{900}^{Rd} %
25 (r.t.)	255	11(10)^e	577	45
250	258	11	576	45
350	305	5	577	60
400	322	4	577	70
450	—	0	578	75
500	—	0	577	75

[a] First weight reduction onset temperature.
[b] Weight reduction between 250 and 400°C in TGA thermogram.
[c] Second weight reduction onset temperature.
[d] Weight percent of residue at 900°C.
[e] Values in parentheses represent calculated value.

RESULTS AND DISCUSSION

Thermal stabilities

The thermal stabilities of the polymers were evaluated by thermogravimetric analysis (TGA) in N_2. A comparison of the annealed polymers by isothermal annealing for 30 min at each annealing temperature is shown in *Table 1*. The annealed PHA films showed heterocyclization (T_1) at 255–322°C. This phenomenon is associated with the cyclization of PHA to form PBO. At the higher annealing temperatures (450 and 500°C), the samples exhibited no T_1s, which can be attributed to complete heterocyclization. Weight reductions in the temperature range of 200–400°C, as indicated by the concurrent loss of H_2O, decreased gradually with increasing annealing temperature from 11 to 0%. The result of weight reduction is in good agreement with the calculated value, as given in parentheses in *Table 1*. Every polymer shows an initial decomposition temperature (T_2) at 576–578°C. Weight residues at 900°C were in the range of 45–75% depending on the degree of the cyclizations. The higher wt% of residues is thought to be the result of char formation in combustion. These observations suggest that all of the annealed PHA films are fairly thermally stable. A typical TGA trace for the PHA films at different annealing temperatures is shown in *Figure 2*. *Table 2* showed TGA results with various annealing conditions. This table compares the thermal stabilities of PHA films before and after annealing. With increasing annealing temperature and time, the cyclization onset temperature, T_1, and weight

Table 2 Thermogravimetric analyses of the PHA films at different annealing temperatures

Ann. temp. °C	Ann. time hr	T_1^a °C	wt. red.^{b} %	T_2^c °C	$\mathrm{wt}_{900}^{\mathrm{R}d}$ %
25		255	11(10)^e	577	45
250	0.5	258	11	576	45
	3	261	11	575	49
	6	282	7	575	57
	9	285	3	575	74
350	0.5	305	5	577	60
	3	305	5	578	67
	6	309	2	579	75
	9	317	2	577	74
450	0.5	—	0	578	75
	1	—	0	577	75

[a] First weight reduction onset temperature.
[b] Weight reduction between 250 and 400°C in TGA thermogram.
[c] Second weight reduction onset temperature.
[d] Weight percent of residue at 900°C.
[e] Values in parentheses represent calculated value.

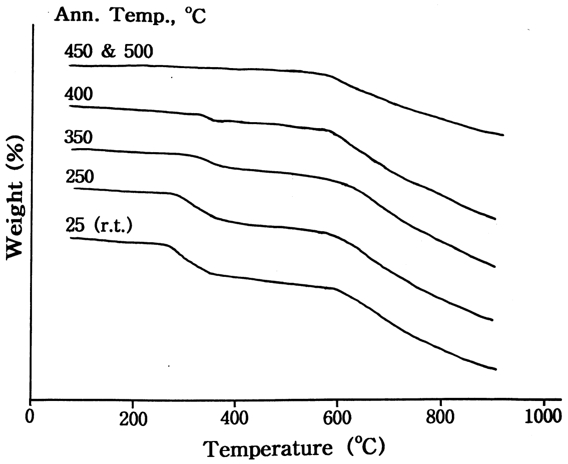


Figure 2 TGA thermograms of the PHA before and after annealing. The annealing time was 30 min

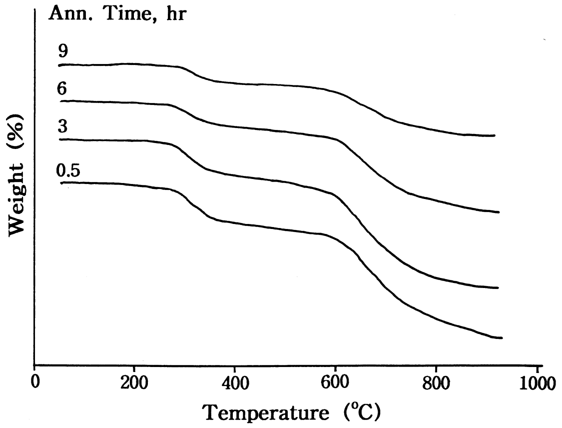


Figure 3 TGA thermograms of the PHA before and after annealing. The annealing temperature was 250°C

residue % at 900°C increased from 255 to 317°C, and from 45 to 74%, respectively. On the other hand, T_2 was constant regardless of the annealing conditions. *Figure 3* shows how the TGA thermogram of the PHA films changes with annealing time at 250°C.

Table 3 Properties of the PHA films at different annealing temperatures (30 min)

Ann. temp. °C	T^a °C	ΔH^b J/g
25 (r.t)	319	221.1
250	320	216.3
350	319	131.7
400	351	8.4
450	n.o.	n.o.

[a] Minimum point in endothermic curve.
[b] Endothermic enthalpy.

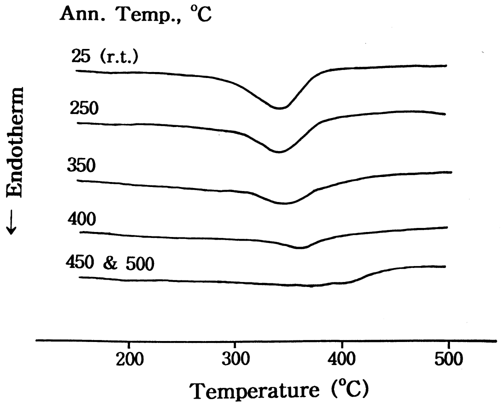


Figure 4 DSC thermograms of the PHA before and after annealing. The annealing time was 30 min

Table 4 Tensile properties of annealed PHA films

Ann. temp. °C	Ann. time h	Ult. str. MPa	Ini. modu. GPa	E.B.^{a} %
25 (r.t)	0	137	5.94	9
250	3	143	6.27	4
	6	171	7.33	4
	9	189	8.28	4
350	3	280	9.16	4
	6	300	10.58	4
	9	320	11.03	4
450	0.5	332	11.71	4
	1	331	11.75	4
	3	334	11.70	4

[a] Elongation percent at break.

In order to determine the flame retardancy, the samples were subjected to heat at each isothermal temperature (see *Table 3*). Endothermic enthalpy peaks were observed at 319–351°C for various annealing temperatures. Unlike other polymers, it is unusual to observe such large heat capacities, from 221.1 to 131.7 J/g, with increasing annealing conditions. As mentioned earlier, we did not observe the endothermic peak for the film annealed at 450°C. *Figure 4* shows the DSC scans of annealed PHA films. Broader endotherms were observed on DSC thermograms. The corresponding DSC results also confirm the solvent removal and the endothermic character of cyclization reaction to produce the imide ring. The advantage of these large endothermic cyclizations is that the reaction acts as a heat sink to further slow down combustion [9].

Tensile properties

As shown in *Table 4*, the values of the ultimate strength and initial modulus of the films were enhanced remarkably with increased annealing conditions. At constant annealing

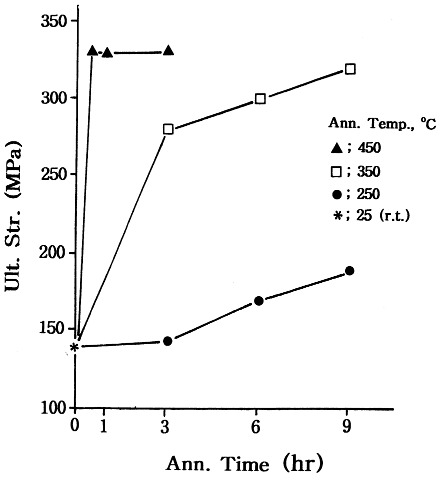


Figure 5 Ultimate tensile strength of the PHA film *versus* annealing time

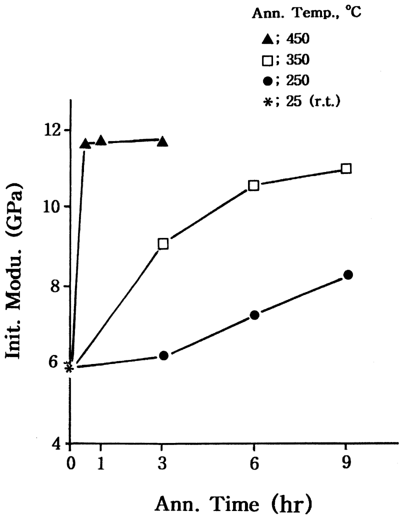


Figure 6 Initial tensile modulus of the PHA film *versus* annealing time

temperatures, the values of the tensile properties increased linearly with increasing annealing time. The strength of the precursor film annealed at 250°C was higher than that of the unannealed sample. With increasing annealing time from 3 to 9 h, the value of ultimate strength and initial modulus increased linearly from 143 to 189 MPa, and 6.27 to 8.28 GPa, respectively. For the case of the 350°C annealing, the ultimate strength and initial modulus increased from 280 to 320 MPa, and 9.16 to 11.03 GPa, respectively, with increasing annealing time.

At constant annealing times, as shown in *Table 4*, the ultimate strength and initial modulus increased with annealing temperature. For samples annealed for 3 h at different annealing temperatures, the value of the ultimate strength drastically increased from 137 to 280 MPa. The initial modulus also increased from 5.94 to 9.16 GPa. For the sample annealed for 3 h at 350°C, the ultimate strength was more than twice that of the unannealed sample. The effect of heat treatments on the tensile properties is shown in *Figures 5* and *6*. For samples annealed for 30 min at 450°C, the tensile strength significantly increases from 137 to 332 MPa, and then remains constant with increasing annealing time. Similar results were observed for the initial modulus. This is because the high annealing temperature may induce heterocyclization. Therefore, heterocyclization causes the tensile properties to increase. It can be suggested that the hydroxyamide main chain was changed to the more rigid fully-cyclized structure.

Table 5 Residual biaxial stress for PHA membrane tested in vacuum

Number	m, n	Z_{mn}	Freq. (s^{-1})	Stress (MPa)
1	0, 1	2.405	1385	7.31
2	1, 1	3.831	2102	6.85
3	2, 1	5.136	2846	6.97
4	3, 1	6.380	3612	7.28
5	4, 1	7.586	4390	7.61

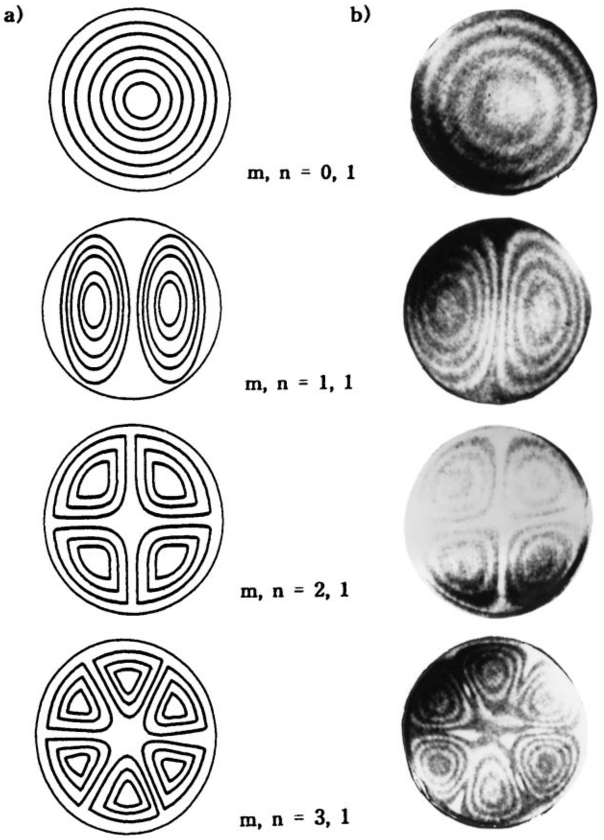


Figure 7 (a) Schematic representations of the holographic patterns. (b) Corresponding mode shapes of a PHA membrane observed using holographic interferometry

The elongation percent at break, however, was 9 and 4% for the unannealed and annealed samples, respectively, without regard to the annealing time.

Biaxial stress of a membrane

A summary of the stress values, their corresponding mode number and their resonant frequency of vibration is given in *Table 5*. The mode number is simply an integer which indicates the sequence of the observed modes of vibration of the membrane. Generally, for a given sample, the many modes of vibration can be seen with each mode occurring at a unique resonant frequency. However, all of them give the same value of stress when calculated using equation (1). This leads to good redundancy in stress measurements.

The free vibration of a circular membrane under uniform biaxial tension is described by equation (1),

$$\sigma = \rho(\omega_{mn} R / Z_{mn})^2 \qquad (1)$$

where: σ = biaxial stress (N/m^2), ρ = density (kg/m^3),

Table 6 Solubility of PHA films before and after annealing

Ann. temp. (°C)	25	250		350		450	
Ann. time (hr)		6	9	6	9	0.5	1
Solvent							
Cl-SA[a]	+ + +	+ + +	+ + +	+ +	+	+	+
MSA[b]	+ + +	+ + +	+ + +	+ +	+	+	+
H_2SO_4	+ + +	+ + +	+ +	+	+	+	+
DMAC[c]	+	+	+	—	—	—	—
NMP[d]	+	+	+	—	—	—	—
DMSO[e]	—	—	—	—	—	—	—

[a] Chlorosulfonic acid.
[b] Methanesulfonic acid.
[c] *NN′*-Dimethyl acetamide.
[d] *N*-Methy1-2-pyrrolidinone.
[e] Dimethyl sulfoxide.
+ + + : excellent, + + : good, + : soluble with LiCl after heating above 80°C, —: not soluble.

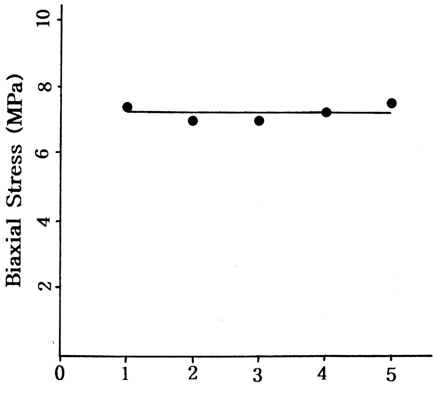


Figure 8 Calculated biaxial stress for a PHA membrane

ω_{mn} = angular frequency (rad/s), R = radius of membrane (m), Z_{mn} = nth zero of the mth order Bessel function.

The radius of the membrane is 2.050 cm and the film density is 1.368 g/cm^3. The number of the zero and order of the Bessel function is determined directly from the observed vibration pattern at a given frequency. The indices m and n represent the number of radial and tangential nodal lines, respectively. As seen in *Table 5*, the biaxial stress is fairly constant, 6.85–7.61 MPa, with increasing frequency from 1385 to 4390 s^{-1}. For this sample, we were able to observe vibration patterns from five modes of vibration in vacuum. A few examples of typical patterns are shown in *Figure 7*. For the same membrane sample, higher resonant modes can be excited at specific resonant frequencies, but all of them give the same value of stress when substituted into equation (1). This leads to good redundancy in stress measurements. A plot of biaxial stress for a PHA membrane is shown in *Figure 8*.

Polymer solubilities

The solubility of PHA films annealed at 350 and 450°C showed marked differences from those annealed at 25 and 250°C, as shown in *Table 6*. Polymers annealed at 25 and 250°C were soluble in DMAC and NMP with 0.1–0.5 wt% of LiCl at 80–100°C, whereas the polymers at 350 and 450°C were soluble only in strong acids, e.g. chlorosulfonic acid (Cl-SA), methanesulfonic acid (MSA) and sulfuric acid. However, sufficient concentration could not be achieved to observe anisotropic phase separation. To determine the decomposition effects in a strong acid, the polymers annealed at 350°C for 9 h were dissolved in Cl-SA and H_2SO_4 for one day and then precipitated in ethanol. The DSC and TGA thermograms of the dried samples did not change with solvent treatment (not shown here).

CONCLUSIONS

The PHA precursor polymer shows a large thermal endothermic peak in DSC that decreases with increasing heat treatment times and temperatures. Annealing increases the thermal stabilities and mechanical properties of the precursor polymer. Therefore, we concluded that the PHA precursor has high potential for flame retardancy. Residual biaxial stress was determined using holographic interferometry. Regardless of the vibration modes, the biaxial stresses were constant. Precursor films become insoluble upon annealing. It is believed that annealing causes cyclization which, in turn, reduces solubility.

ACKNOWLEDGEMENTS

This research was supported in part by the YonAm Foundation in KOREA and by the Federal Aviation Administration (FAA) in USA. One of the authors (Jin-Hae Chang) thanks the YonAm Foundation in KOREA for financial support (1996–1997).

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