

## Melt and Solution Processing of the Poly(Hydroxy-Amide) Family of Polymers

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### Abstract

PMeOA and PMeOA/PHA copolymers were synthesized and characterized for their cyclization and degradation behavior using isothermal test in DSC and TGA. Dehydration rate of copolymers under isothermal condition became faster in the increasing order of 50/50 > 25/75 > 25/75/F10 and rate of weight loss of PMeOA part was faster in the increasing order of 25/75/F10 > PMeOA > 25/75 > 50/50. From the results of TGA, DSC and FT-IR spectra of PMeOA films cured at 300°, it was confirmed that degradation and demethylation occur simultaneously and that benzoxazole rings were formed. Fibers have been spun from the molten state of PMeOA using a Micro-Compounder. Fibers spun at 320°, with average diameter of 180µm, show an ultimate tensile strength, and elongation at break, and a Young's modulus of 60 MPa, 2.2% and 3.6 GPa, respectively. Films were also made by spin-coating or solvent casting to observe the effect of cyclization on tensile properties.. These films had an ultimate tensile strength and young's modulus of 120 MPa and 3 GPa, respectively.

## **Introduction**

Polybenzoxazoles (PBOs) have drawn attention because of their excellent thermo-oxidative stability, high mechanical properties, and good chemical resistance [1-3]. However, these polymers have some major disadvantages for the application in industrial fields. One of them is poor solubility causing the difficulty in using them as coating materials. Another is that thermal degradation of these polymers occurs before they are melted because they have very high glass transition temperature.

The poly (hydroxy-amide)s (PHAs), precursor polymer of PBO, can be one of the favorable solution to overcome such disadvantages of PBOs. They can be easily dissolved in aprotic solvents such as N-methyl pyrrolidone (NMP), N, N-dimethyl acetamide (DMAc), dimethylsulfoxide (DMSO) and N, N-dimethyl formamide (DMF). And glass transition temperature of PHAs can be lowered by introducing appropriate component into molecular backbone. In addition, generally, PHAs have better mechanical properties than PBOs [4] and release small molecules such as water or methanol during the cyclization to form into PBOs. Derivatives of the polymer may release phosphorus or fluorine compounds depending on the their structures. These small molecules assist in flame retardation [5].

The poly(hydroxy-amide) family has been studied as a fire-safe polymers for several years in our group. In PHAs, poly(hydroxy-amide), polymerized from 3,3'-dihydroxy benzidine and terephthaloyl/isophthaloyl chloride, shows the lowest heat release capacity. However, even though PHA has displayed excellent thermal properties, due to its limited processability, the members of the PHA family were investigated for ease of processing while maintaining their advantageous thermal properties. For example, poly(methoxy-amide) [PMeOA] and PMeOA/PHA copolymers has been

synthesized and characterized.

In this work, the thermal properties of PMeOA and its copolymers were investigated especially using isothermal characterization. Films of these polymers were evaluated for thermal/mechanical properties and for morphological aspects in terms of curing conditions. And PMeOA fiber was spun from molten state and evaluated for the mechanical properties.

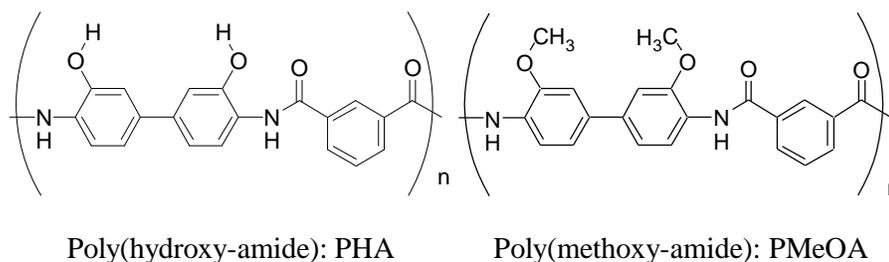
## **Experimentals**

### *Materials*

PMeOA, PMeOA/PHA copolymers and PMeOA/PHA/Flexible copolymer were synthesized in our research group. Table 1 denotes the sample code and the mol % composition of copolymers. Scheme 1 presents the chemical structure of PHA and PMeOA, respectively. Basically, PMeOA was synthesized by reaction between diamine and dichloride. 50/50 copolymer was synthesized with 1:1:2 mol ratio of 3,3'-dihydroxy benzidine, 3,3'-dimethoxy benzidine and isophthaloyl chloride. In the case of 25/75/F10 copolymer, 1:3 mol ratio of 3,3'-dihydroxy benzidine and 3,3'-dimethoxy benzidine was used as diamine, and 1:9 mol ratio of isophthalic chloride and glutaryl dichloride was employed as dichloride part.

**Table 1. Sample code and composition of PMeOA and copolymers.**

Sample code	PHA/PMeOA (mol %)	Flexible group
PMeOA	100/0	0
50/50	50/50	0
25/75	25/75	0
25/75/F10	25/75	10



**Scheme 1. Chemical structure of PHA and PMeOA.**

### ***Isothermal characterization***

All specimens were dried at 160°C *in vacuo* for 1 day in order to remove the residual solvents. Isothermal characterization was conducted in DSC and TGA instrument at selected temperature between 250 - 350°C. The selected temperatures varied according to each sample.

### ***Film and fiber preparation***

Films of PMeOA and copolymers were prepared in two ways. Films with the

thickness of 70-100  $\mu\text{m}$  were made by casting the polymer solution of DMSO and used for the X-ray diffraction, thermal analysis and mechanical test. Films with the thickness under 10  $\mu\text{m}$  were made by spin-coating method and used for IR spectroscopy. In both cases, the films were dried at 60 $^{\circ}\text{C}$  *in vacuo* for 1 days. Solvent cast thick film and spin-coated thin film contain about 20% and 10% DMSO, respectively. Fiber of PMeOA was spun from the molten state at 320-330 $^{\circ}\text{C}$  using a Micro-Compounder with twin mixing screws (DACA Co.).

Solvent cast thick film and spin-coated thin film were cured at 300 $^{\circ}\text{C}$  for different times under nitrogen atmosphere after pre-baking at 250 $^{\circ}\text{C}$  for 1 hour. After curing, each film was examined by X-ray diffractometer (Rigaku RU-200, Rotating Anode type, CuK $\alpha$  radiation) and FT-IR spectrometer (Perkin Elmer Spectrum 2000) to identify their micro and chemical structural changes during curing, respectively.

## **Results and Discussion**

### ***Isothermal characterization***

Even though PBO has a excellent thermal stability, it has a limitation in application due to its poor solubility and too high glass transition temperature. PBO films can be prepared by casting a PHAs solution and thermal curing of the resulting PHAs films. In our previous work, poly (hydroxy amid) was synthesized and prepared into films by casting a solution in DMAc. The dehydration of PHA occurs between 250 $^{\circ}\text{C}$  -350 $^{\circ}\text{C}$  under heating rate of 10 $^{\circ}\text{C}/\text{min}$ . This cyclization precedes thermal degradation in terms of heating temperature.

TGA data of pure PMeOA shows three steps in weight loss (Figure 1). First weight

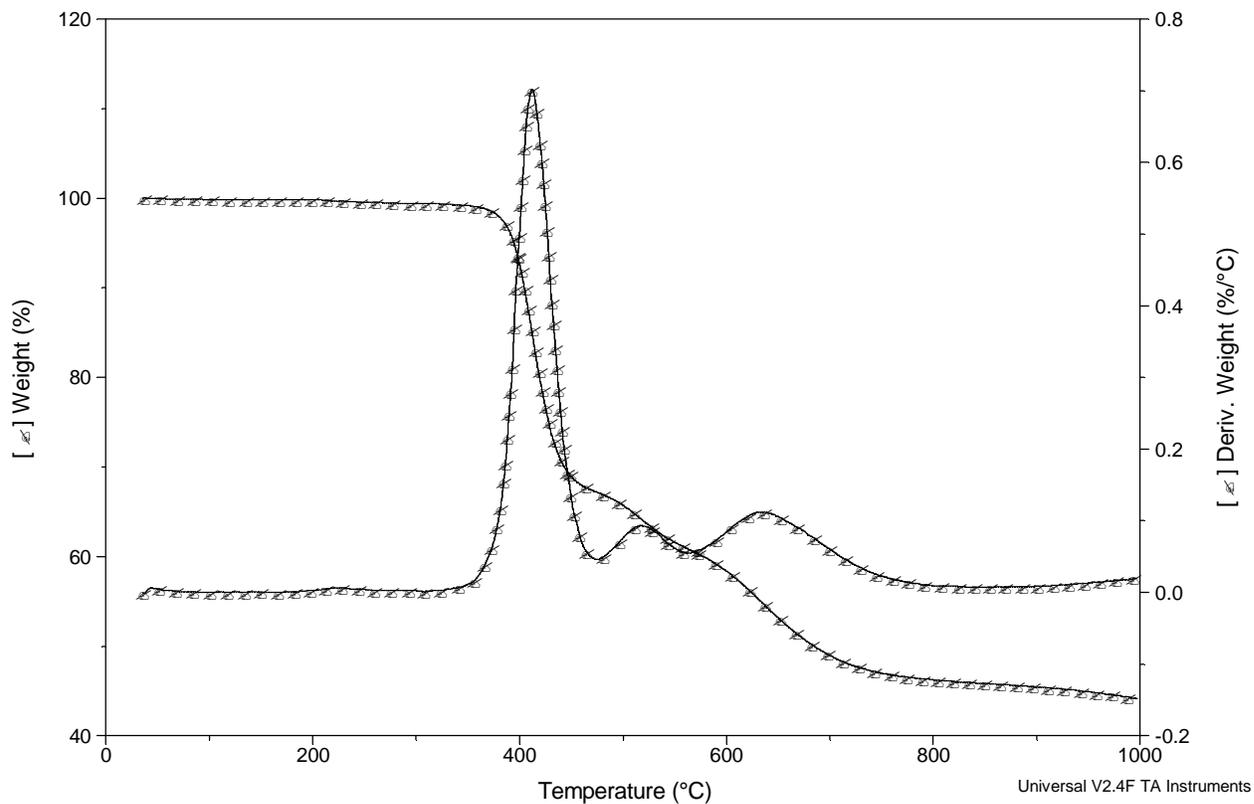
loss step was started from 350°C and showed its maximum at 400°C. Second and third step was observed between 500°C and 700°C. Weight loss in second and third steps was about 20% by weight and that of first step was about 30% by weight. The first step showed very neat single weight loss process. The theoretical value of weight loss calculated from demethylation of PMeOA is about 17% by weight, meaning the first weight loss step during 10°C/min heating in TGA was composed of demethylation and degradation. To identify the optimal curing temperature and time for PMeOA, weight loss behavior under isothermal condition was monitored by TGA (Figure 2). No weight loss was observed at 250°C curing isothermally. The rate and amount of weight loss increased with curing temperatures. As the curing temperature of 300°C shows about 18% weight loss after 15 hours, the temperature of 300°C was selected as curing temperature for PMeOA film.

DSC isothermal scanning of PMeOA above 280°C showed the irregular exotherms. And DSC heating scan of these cured sample reveals that the exothermic peaks in DSC isothermal test originated from thermal degradation. Thermal degradation of PHAs is exothermic reaction and cyclization with releasing small molecules such as dehydration/demethylation is exothermic reaction. When PMeOA was cured at 250°C for 15 hours or cured above 280°C for less than 1 hour, DSC heating scan showed a relative big endotherms ( $\Delta H = 25 \text{ j/g}$ ) due to melting of crystals, meaning that crystallization occurred before degradation at isothermal condition.

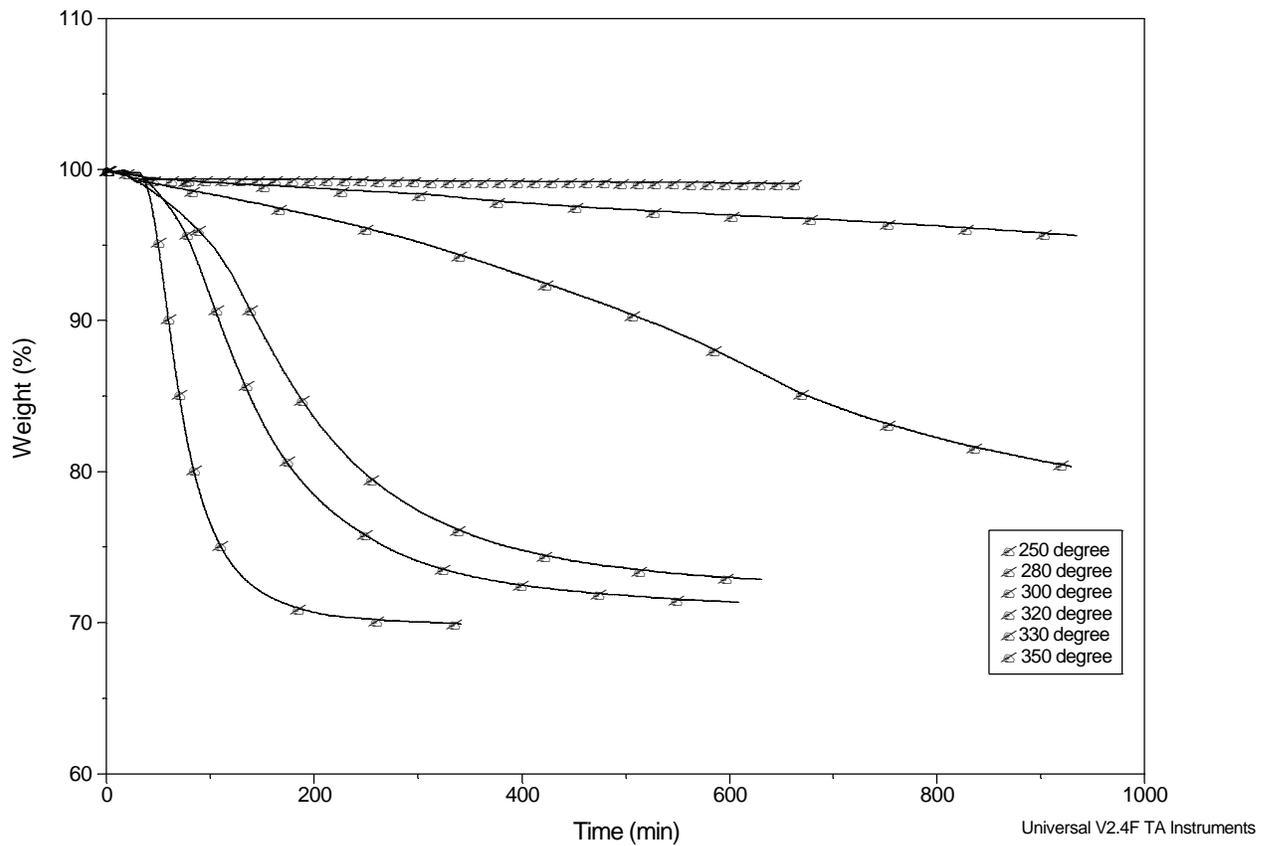
Sample: PMEOA powder  
Size: 14.1340 mg  
Method: yoo1

### TGA

File: C:\...\POWDER\pmeoa\_poweder  
Operator: yoo  
Run Date: 20-Aug-01 22:39



**Figure 1. Weight change of pure PMEOA during heating scan at 10 °C/min..**



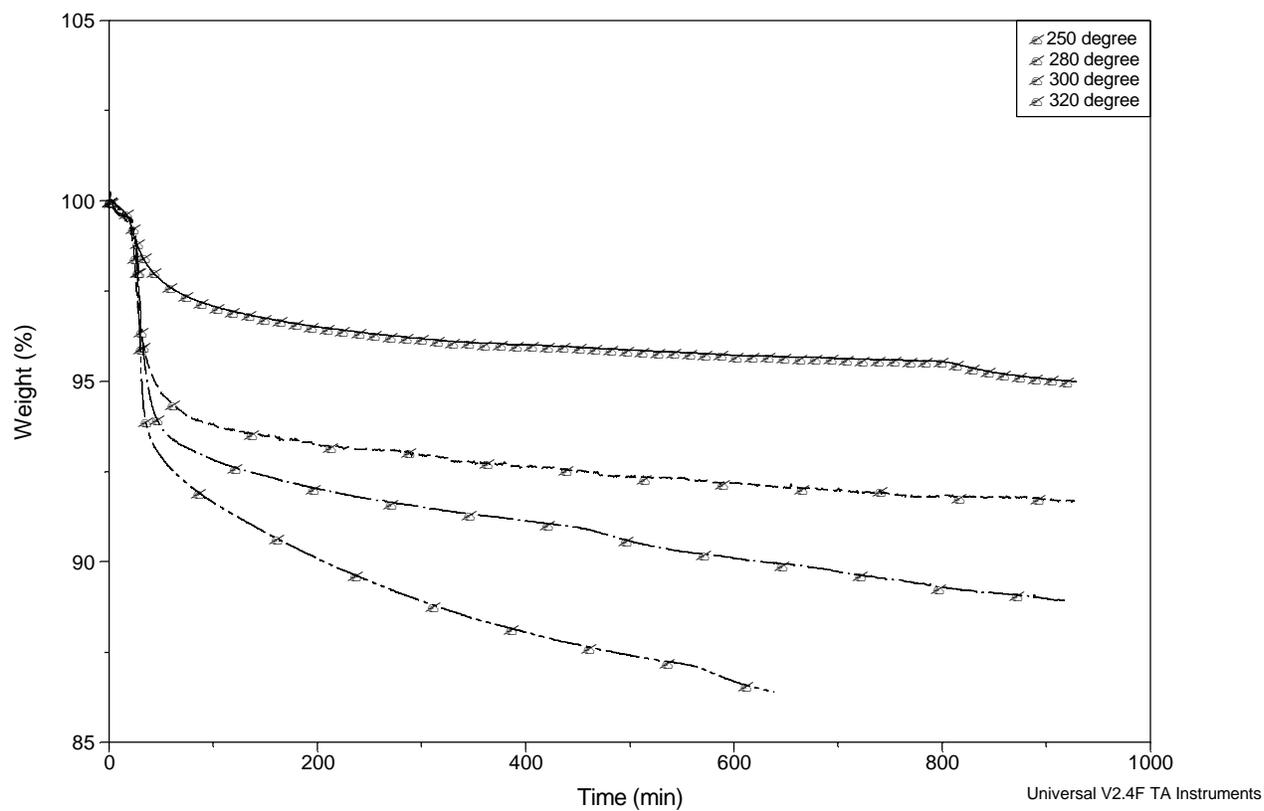
**Figure 2. Weight change of pure PMeOA powder at different isothermal condition.**

Figure 3 is the weight change of 50/50 copolymer during isothermal curing at different temperatures. Isothermal TGA test for copolymers always shows two steps weight loss procedure. First step was accomplished within 50 min at any curing temperature and might correspond to the dehydration of PHA parts in copolymers. The calculated value of weight loss from dehydration of PHA component in 50/50 copolymer is about 5% by weight, that agrees with the first step weight loss in Figure 3. Second step of weight loss in this figure might come from demethylation and degradation of PMeOA part. The rate and amount of weight loss in second step still depends on the curing temperature like pure PMeOA.

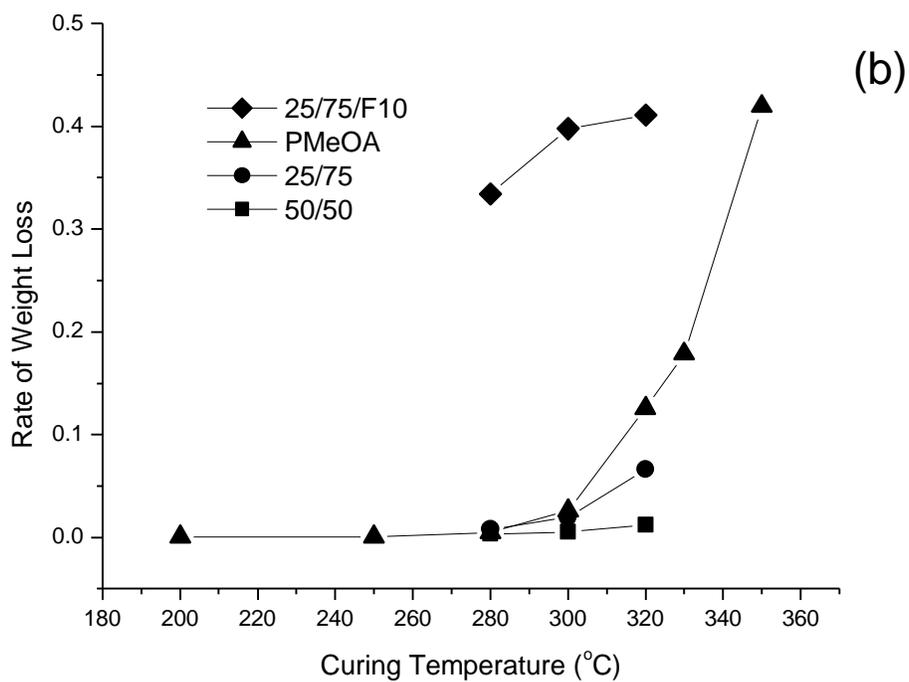
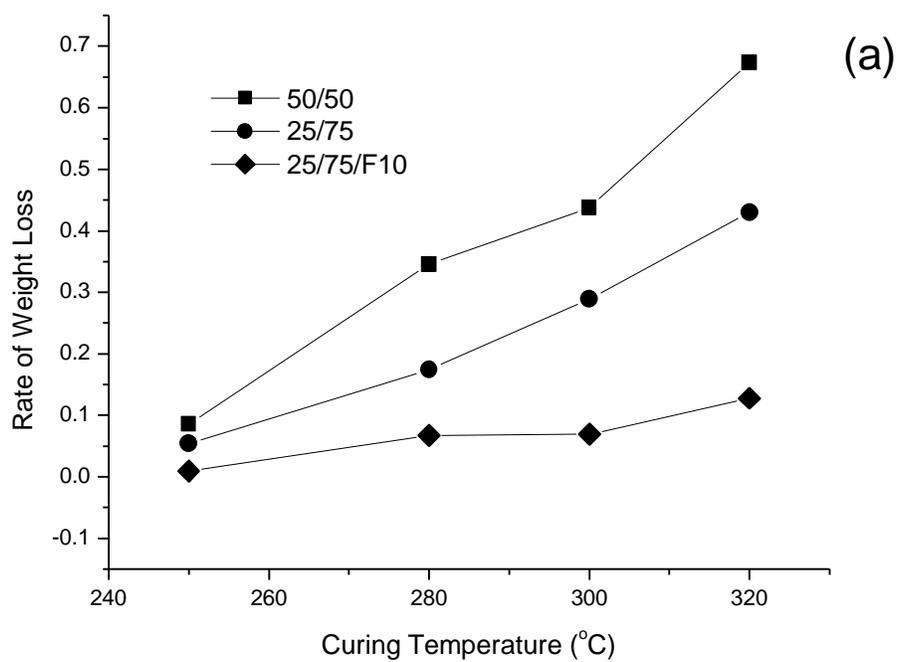
The dependency of weight loss rate on curing temperature in thermogravimetric analysis was presented in Figure 4. Figure 4 (a) and (b) are the plots of inclination of PHA and PMeOA parts in TGA curve, respectively. Rate of dehydration of copolymers became faster in the increasing order of 50/50 > 25/75 > 25/75/F10 at any curing temperature. Higher contents of PHA part, faster rate of dehydration. Flexible group might disturb the dehydration in copolymers. Rate of weight loss of PMeOA part became faster in the increasing order of 25/75/F10 > PMeOA > 25/75 > 50/50. Flexible group might contribute greatly to the rate of demethylation and degradation of PMeOA part in copolymers. The rate of weight loss of 25/75/F10 was four times of that of pure PMeOA at 320° .

### ***Characterization of cured films***

Solvent cast PMeOA films were cured at 300° for different time under nitrogen atmosphere, being based on TGA isothermal analysis. From the results of TGA and DSC heating scans of cured PMeOA films, it is assumed that degradation and



**Figure 3. Weight change of 50/50 copolymer at different isothermal condition.**



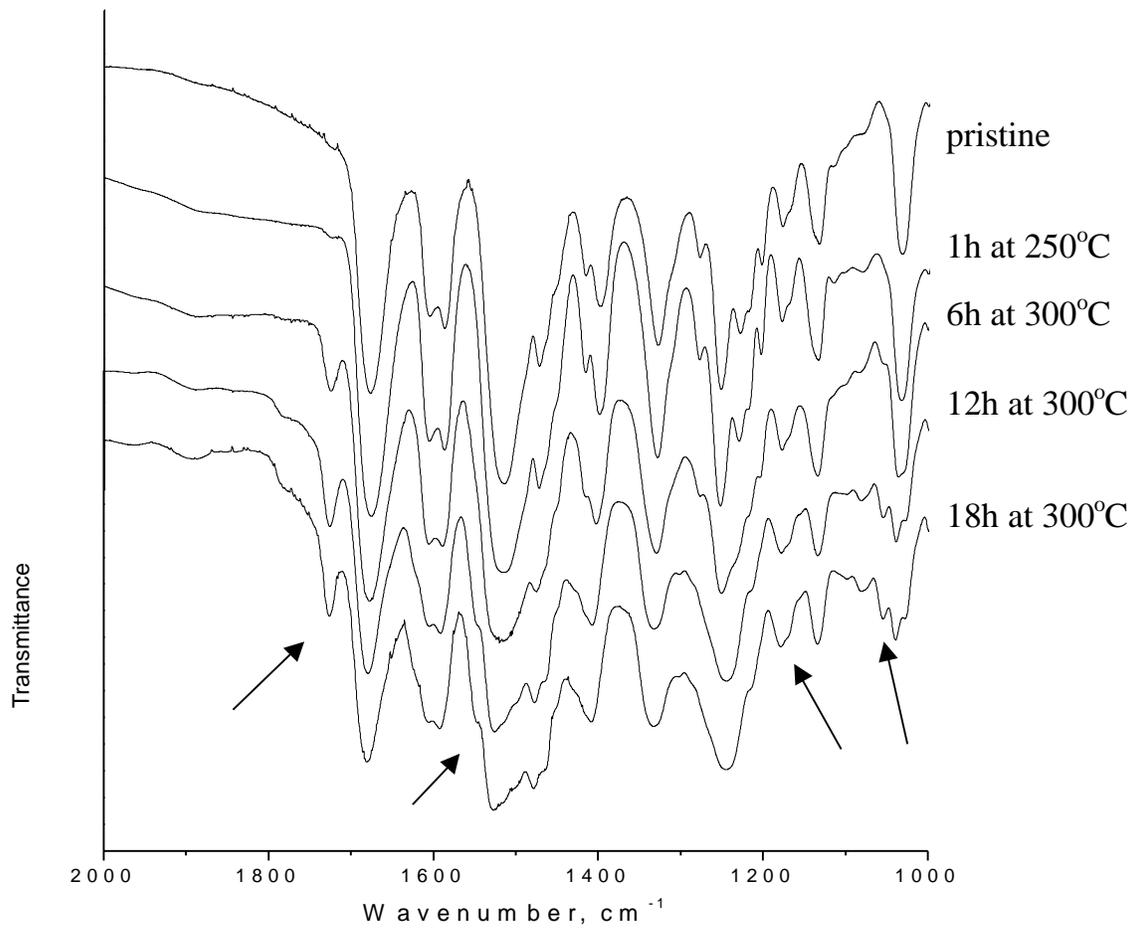
**Figure 4. Plots of rate of weight loss as a function of curing temperature; (a) PHA part (b) PMeOA part in copolymers**

demethylation occur at the same time at 300°. Actually, the PMeOA films were too brittle to be measured for mechanical properties after curing.

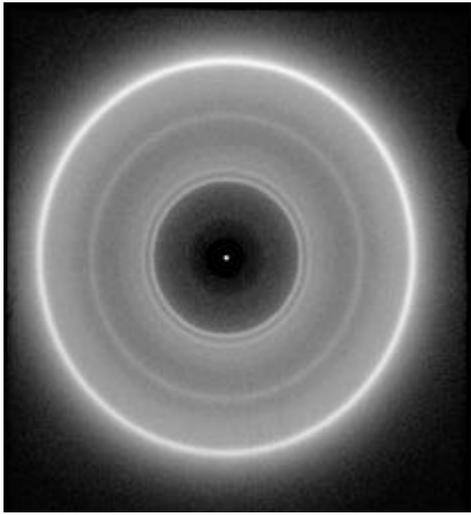
Figure 5 is the FT-IR spectra of cured PMeOA films. New bands at 1720, 1545, 1180 and 1060  $\text{cm}^{-1}$  appeared and grow with curing time. Bands at 1545 and 1060  $\text{cm}^{-1}$  were assigned to the evidence of benzoxazole ring [6, 7]. The origin of other bands and the path of demethylation of PMeOA are still in process of investigation.

During the PMeOA film was pre-baked at 250°, the crystallization phenomenon was observed. The crystallization occurred only when the film was attached on the substrate (glass) and crystals grow inward from the edge to the center due to the in-plane orientation at the edge. Figure 6 shows wide angle X-ray diffraction photographs of PMeOA film before and after curing. Transmittance (in-plane) X-ray diffraction mode, Figure (a), provides the information about intra molecular ordering and reflection (out of plane) X-ray diffraction mode, Figure (b), gives the information about inter molecular ordering. As the reflection mode shows some orientation, crystalline region might have in-plan orientation. In Figure (c), PMeOA film cured at 300° for 18 hours shows totally new diffraction pattern than PMeOA crystals. Although we presume this might be the diffraction of poly benzoxazole crystals, more details are under investigation.

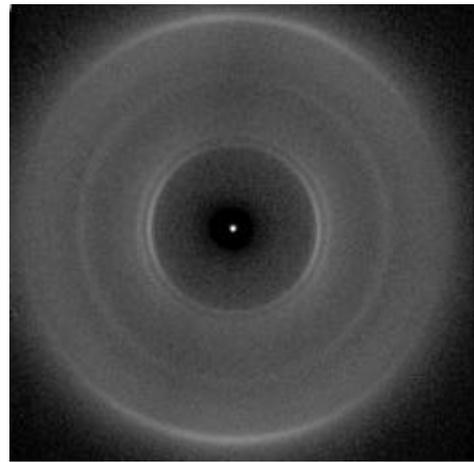
Figure 7 is the WAXD patterns of palletized powder sample of each copolymers. Amorphous hallow is shown around 24° of two theta in all specimens. Another broad band appears between 10 -17°. This band moves to higher angle as PHA ratio increase. We supposed that this periodicity arises from the repeat distance along the polymer chain. Thus, the repeat distance calculated from the center of peaks varied from 7.3 Å to 5.3 Å. This distance corresponds to the mean length of the chemical repeat unit projected along the axis of the fully extended polymer chain.



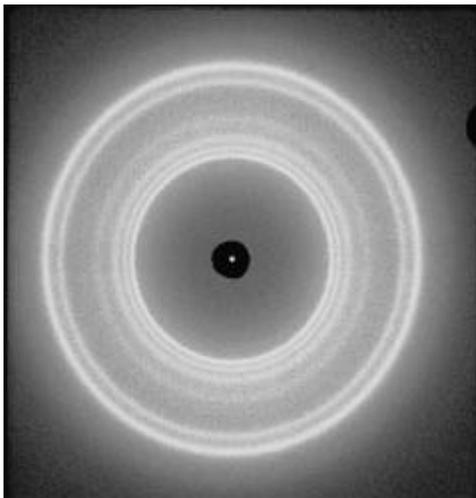
**Figure 5. FT-IR spectra of PMeOA after curing.**



(a)



(b)



(c)

*Figure 6. WAXD photographs of PMeOA film cast from DMSO: (a) in-plane and (b) out of plane diffractions of pre-baked PMeOA film; (c) in-plane diffraction of cured PMeOA film at 300°C for 18 hours.*

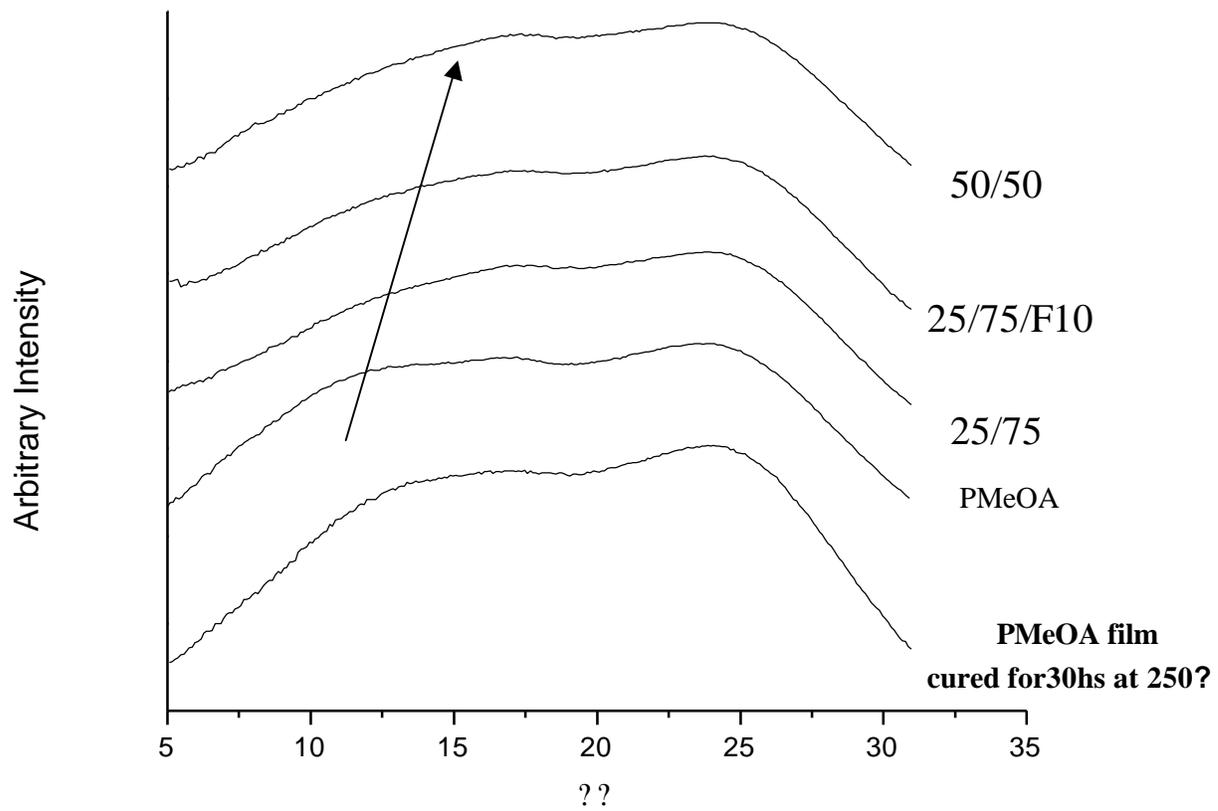


Figure 7. WAXD patterns of the palletized powder samples of PMeOA and copolymers.

The methoxy group in PMeOA might make the polymer chain extended than hydroxy group in PHA part. So, higher contents of PHA part, shorter the projected chain length.

Films cast from solution and cured at 250° for 30 hours had an ultimate tensile strength and young's modulus of 120 MPa and 3 GPa, respectively. Films cured above 300° were too brittle to be measured for its mechanical properties. Fibers spun at 320°, with average diameter of 180um, show an ultimate tensile strength, and elongation at break, and a Young's modulus of 60 MPa, 2.2% and 3.6 Gpa, respectively, even though they are somewhat brittle.

### **Summary**

PMeOA and PMeOA/PHA copolymers were synthesized and characterized for their cyclization and degradation behavior using isothermal test in DSC and TGA. In the case of pure PMeOA, crystallization are always followed by thermal degradation at the isothermal temperature above 280°. Dehydration rate of copolymers became faster in the increasing order of 50/50 > 25/75 > 25/75/F10 and rate of weight loss of PMeOA part became faster in the increasing order of 25/75/F10 > PMeOA > 25/75 > 50/50. Flexible group might contribute greatly to the rate of demethylation and degradation of PMeOA part in copolymers.

From the results of TGA and DSC heating scans of cured PMeOA films, it was concluded that degradation and demethylation occur at the same time under isothermal temperature of 300°. Benzoxazole ring formation at 300° was confirmed by FT-IR spectrum.

By the way, for the crystalline region of PMeOA film, as the reflection X-ray diffraction mode showed orientations, crystalline region might have in-plan orientation.

PMeOA film cured at 300°C for 18 hours showed totally different crystal structure.

### **Acknowledgement**

This work was financially supported by the members of Cluster F of the Center for Research on Polymers (CUMIRP) at the University of Massachusetts/Amherst; Boeing - Commercial Airplane Group, bp, Federal Aviation Administration, Foster-Miller, Inc., General Electric Co., Schneller, Inc., Solutia, Inc., and the United States Army.

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