

Mechanical properties and thermo- gravimetric analysis of PBO thin films

G.M. Wu*, C.H. Hung

Advanced Materials Laboratory, Institute of Electro-Optical Engineering
Chang Gung University, Kweisan, Taoyuan 333, Taiwan R.O.C.

* Corresponding author: E-mail address: wu@mail.cgu.edu.tw

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Materials

ABSTRACT

Purpose: In the continued quest for high performance, high temperature, light weight materials, the research and development of poly(1,4-phenylene-cis-benzobisoxazole) or PBO polymer was a significant step. The thermal stability, stiffness, and tensile strength surpass those of many other engineering polymers. In this report, the superior mechanical properties of PBO thin film materials and the thermal characteristics of the isotropic thin films were investigated. Thermogravimetric analysis (TGA) and the Ozawa method were employed to analyze the thermal degradation kinetic parameters.

Design/methodology/approach: The quasi-isotropic thin films were processed from 14 wt-% PBO dope with the molecular weight about 130,000. Mini-tensile bar specimens of dog-bone-shape were prepared for MTS testing machine. The ASTM D1708 microtensile testing was carried out at room temperature. The TGA spectra were obtained by employing Thermal Analysis (TA) TA-2050 thermogravimetric analyzer under various heating rates in nitrogen. The Ozawa method has been used for the kinetic data analysis.

Findings: The results showed that PBO thin film exhibited outstanding specific tensile properties and thermal resistance. The onset of the decomposition temperature in nitrogen atmosphere was about 670°C. The temperature that corresponded to the maximum decomposition rate was around 750°C. The residual weight was still as high as 73% when heated up to 850°C. The reaction followed a first order mechanism. In addition, the activation energy (E_a) for PBO thin film material has been estimated to be 445 kJ/mol and the frequency factor ($\log A$) to be 25.2 min⁻¹.

Practical implications: The better understanding in PBO thin film processing and characteristics could help to advance the structure design and unique applications.

Originality/value: The outstanding specific mechanical properties and excellent thermal resistance should provide great potential applications for this new class of high performance rigid rod polymers.

Keywords: Engineering polymers; Mechanical properties; Thermogravimetric analysis; Activation energy; Thin films

1. Introduction

In the continued quest for high performance, high temperature, light weight materials, the research and development of poly(1,4-phenylene-cis-benzobisoxazole) or PBO polymer was a significant step [1-9]. The thermal stability, stiffness, and tensile strength of PBO surpass those of many other polymeric materials. With its excellent thermal stability, tensile stiffness, tensile

strength, radiation and environmental resistance, this material shall find a wide range of applications in the aerospace and electronics industry.

PBO belongs to the new class of high performance "rigid-rod" PBZ materials. It is formed by the polycondensation of terephthalic acid (TA) and 4,6-diaminobenzene-1,3-diol (DAR) in polyphosphoric acid (PPA). High levels of phosphorus pentoxide composition are necessary to drive the reaction and to

keep the polymers in the reaction solution. The synthesis route of PBO is shown in Figure 1. When the reaction is carried out at a sufficiently high monomer concentration, the solution becomes optically anisotropic while the molecules can achieve enough length to form a liquid crystalline phase [10].

Since PBO is so rigid and does not melt or soften upon heating before it decomposes, which starts at above 600°C, the polymer is dissolved in strong acids for processing. PBO dope, a solution of 14% PBO by weight in polyphosphoric acid, has become standard for that purpose. The dope is formed into a certain shape before the polymer is coagulated or precipitated in water or a suitable solution. The choice of coagulant and thus coagulation conditions can be designed to affect the polymer morphology. The coagulated article is then dried and further heat-treated to set the structure. For dense PBO without significant porosity, the density is about 1.58 g/cm³.

PBO is a polymer designed for considerably high-temperature applications. Studies have shown that the combustion gases of PBO fiber consisted of CO, CO₂, H₂O, and minor amounts of HCN and NO_x etc [1,2]. It is therefore interesting to investigate the thermal stability and degradation reaction mechanism of this rigid rod polymer. The dynamic weight changes in nitrogen atmosphere under various heating conditions are monitored by means of thermogravimetric analysis (TGA). The kinetic parameters such as activation energy (*E_a*), reaction order (*n*) and frequency factor (*A*) can thus be evaluated and compared with other polymeric materials.

Although isothermal thermogravimetry study is obtainable, nonisothermal thermogravimetry has been more applicable for polymeric materials [11-13]. In a kinetic process [14,15], the rate of reaction (*r*) depends on both the temperature (*T*) and the composition (or conversion rate *α*):

$$r = \frac{dX}{dt} = k(T)f(\alpha) \quad (1)$$

where *r* is the derivative of the composition (*X*) over time (*t*). The temperature term *k*(*T*) is usually assumed to follow the Arrhenius type equation, or

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where *A* is the pre-exponential factor, *E_a* is the activation energy, and *R* is the gas constant. On the other hand, the conversion rate term *f*(*α*) can be assumed of reaction order *n*, or

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

If we substitute (1-*α*) by the residual weight *W* in the thermogravimetric curves, the rate of reaction (*r*) is thus expressed by

$$r = \frac{dW}{dt} = AW^n \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

When the non-isothermal heating rate is kept constant or $\beta = dT/dt$, the rate of reaction (*r*) can be also expressed by [16]

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right)(1 - \alpha)^n \quad (5)$$

In practice, several analytical methods have been proposed to evaluate the reaction kinetic parameters from the thermogravimetry analysis (TGA) data. The present study focused on the isotropic thin film of this high performance rigid-rod PBO polymer. The Ozawa method [17], an integral approach, has been used to elucidate the thermal stability and the nature and extent of the degradation of PBO in nitrogen atmosphere. In addition, the mechanical properties of the PBO thin films were evaluated by micro-tensile tests and the data would be compared with a list of engineering materials.

2. Experimental

2.1. Sample preparation

The isotropic thin film samples were molded from 14 wt-% PBO dope. The intrinsic viscosity of the polymer was around 30 dL/g, corresponding to a molecular weight of 130,000 based on light scattering technique [10]. The highly viscous polymer solution was pressed between a pair of Teflon coated plates at an elevated temperature above 90°C to reduce its original thickness. The quasi-isotropic thin film was then obtained from a slow vacuum evaporation process overnight to avoid defects. The samples were further washed in distilled water and dried at 100°C in an oven. The film thickness was about 0.05 mm. It does not contain significant preferential molecule orientation.

2.2. Mechanical characterization

More than ten dog-bone-shaped specimens were prepared for MTS testing machine using a die-cutter. The ASTM D1708 micro-tensile testing was carried out at room temperature with a gauge length of 22.25 mm. The width of the reduced section was 4.75 mm. The serrated grips with pneumatic control provided stable and adequate clamping. The cross-head speed was set at 1.3 mm/min.

2.3. Thermogravimetric measurement

The thermogravimetric curves were obtained by employing a Thermal Analysis (TA) TA-2050 thermogravimetric analyzer under various heating rates in nitrogen. About 7.0 mg thin film sample was used for each measurement. The nitrogen flow rate was kept at 100 ml/min to maintain a stable environment. The integral residual weights were recorded between 30°C and 900°C. However, the kinetic data analysis was performed based on the results between 600°C and 800°C, where the rigorous reaction actually took place. Three heating rates were used in this study, including 10 °C /min, 20 °C /min and 40 °C /min.

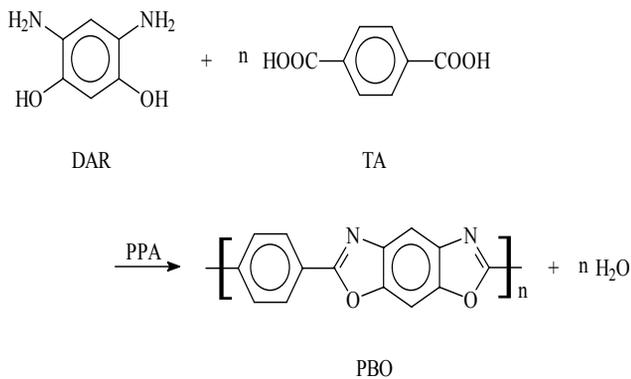


Fig. 1. The schematic illustration of the synthesis route of PBO from polycondensation of 4,6-diaminobenzene-1,3-diol (DAR) and terephthalic acid (TA) in polyphosphoric acid (PPA).

2.4. Kinetic data analysis

The Ozawa method has been widely used for kinetic data analysis [17,18]. This integral method compared heating rates with temperatures under the same conversion rates. By integration and some approximation, from various heating rates β , using the following equation:

$$-\log \beta_1 - 0.456 \frac{Ea}{RT_1} = -\log \beta_2 - 0.456 \frac{Ea}{RT_2} = \dots \quad (6)$$

By plotting $\log \beta_1$ versus $1/T$ into a straight line, the activation energy Ea and frequency factor $\log A$ could thus be obtained from the slope and the intercept, respectively.

3. Results and discussion

3.1. Mechanical properties

The tensile mechanical testing results of PBO thin film materials are shown in Table 1. The mechanical properties of various engineering materials, including metals, glasses and polymers, are also listed for the purpose of comparison [19]. This isotropic thin film material exhibited excellent stiffness and strength when compared with other engineering polymeric materials such as epoxy and polyether ether ketone (PEEK). The tensile modulus (E) of PBO thin film has been 5.5 GPa, the tensile strength (σ) was 110 MPa, the specific modulus (E/ρ) was 3.5 $\text{GPa} \cdot \text{cm}^3 \cdot \text{g}^{-1}$, and the specific strength (σ/ρ) was 70 $\text{MPa} \cdot \text{cm}^3 \cdot \text{g}^{-1}$. Though the tensile modulus and strength were lower than metals and glasses, the specific mechanical properties have been in the fairly competitive ranges. This has been benefited from the lower density of polymers than those of conventional engineering materials. Nevertheless, the highly oriented PBO fiber can have even much higher values for modulus and strength [3,4].

3.2. Thermal stability

Figure 2 displays the isothermal spectra of PBO thin films at the different designated temperatures. The polymer showed little weight loss at under 500°C. The polymer thin film started to show some weight degradation at above 600°C. The highest applicable temperature was thus about 500-600°C, depending on duration. The degree of degradation also intensified with both temperature and time.

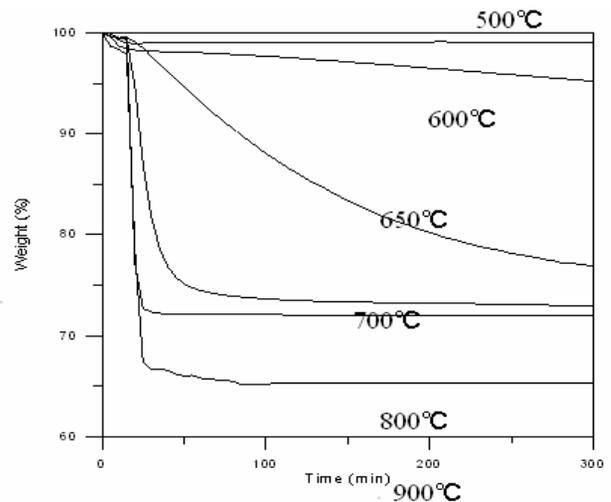


Fig. 2. The isothermal degradation behavior of PBO thin film at different temperatures (500-900°C).

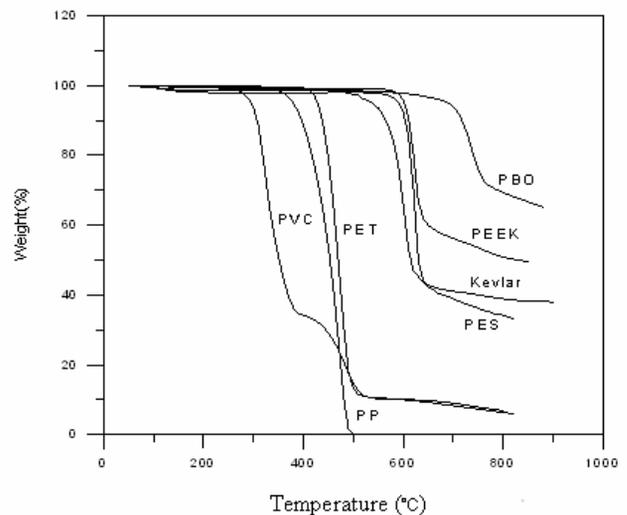


Fig. 3. The non-isothermal degradation behavior of PBO thin film and the various polymeric materials.

Figure 3 shows the non-isothermal degradation behavior of PBO thin film material together with several other polymers. It has been clearly evidenced that the PBO thin film material displayed excellent thermal stability. This thin film material had much higher thermal resistance than both regular heat resistance

polymers like polyvinyl chloride (PVC) and high temperature engineering thermoplastic such as polyether ether ketone (PEEK) and polyether sulphone (PES). In addition, the thermogravimetric (TGA) curves of PBO thin film at the various heating rates are also given in Figure 4. When the heating rate was chosen at 40 °C/min, the residual weight along testing temperature can be used to depict the thermal properties. The initial decomposition temperature or the onset weight loss of PBO was about 670°C. The temperature that corresponds to the maximum weight loss

rate was around 750°C. The decomposition process slowed down after reaching 790°C. The residual weight has been still as high as 73% when heated up to 850°C. The reaction appeared to be a one-stage reaction in nitrogen atmosphere. In addition, the theoretical carbon content of PBO is about 71% based on its chemical structure. The char yield was therefore very high. This characteristic along with the rigid rod aromatic backbone main chain structure provided excellent fire retardation characteristics for this polymeric thin film materials.

Table 1.

The mechanical properties of various engineering materials [19].

Material	Tensile Modulus (E) (GPa)	Tensile Strength (σ) (MPa)	Density (ρ) (g/cm ³)	Specific Modulus (E/ ρ)	Specific Strength (σ/ρ)
Steel	210.0	340-2100	7.8	26.9	44-269
Aluminum alloys	70.0	140-620	2.7	25.9	52-230
Glass	70.0	700-2100	2.5	28.0	280-840
Epoxy (BASF)	4.1	69	1.3	3.2	53
PEEK (ICI)	3.6	92	1.3	2.8	71
PBO thin film	5.5	110	1.58	3.5	70

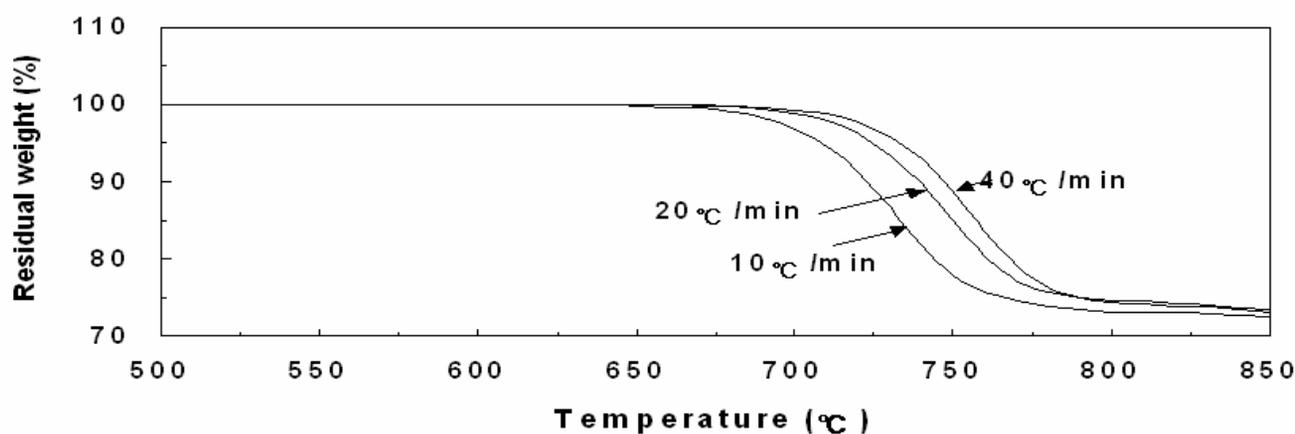


Fig. 4. The thermogravimetric scans of PBO thin film from 500°C to 850°C at three different heating rates.

Table 2.

Activation energy and frequency factor of PBO thin film by the Ozawa method.

Conversion rate α (%)	Activation energy E_a (kJ/mol)	Frequency factor Log A (min ⁻¹)	Coefficient of Determination R^2
5	408.2	23.8	0.9608
10	439.9	25.2	0.9542
15	448.7	25.4	0.9383
20	447.4	25.1	0.9353

3.3. Analysis of kinetic parameters

The analysis of reaction kinetic parameters was performed on the TGA scan results that were obtained between 600°C and 800°C using the Ozawa method. In Figure 4, it was evident that for a higher heating rate the onset of the decomposition process could be delayed to a somewhat higher temperature. However, the shape of the curve remained approximately the same. We could almost superimpose these curves by shifting them in the horizontal direction. This was in accordance with the general aspects of polymeric materials.

The plot of $\log(\text{heating rate})$ versus $1000/T$ is provided in Figure 5. Four different conversion rates ranging from 5% to 20%, with intervals of 5%, were used for the data analysis. Three different heating rates were used in this analysis, including 10°C/min, 20°C/min and 40°C/min. The slopes of these four straight lines have been about the same, indicating similar level in activation energy data.

From Figure 5, the activation energy E_a and frequency factor $\log A$ could be evaluated from the slope and the intercept by using Equation (6). Table 2 summarizes the activation energy and frequency factor analysis results of PBO isotropic thin film at the various conversion rates. The kinetic analysis has shown similar data under the four different conversion rates, in accordance with the prediction model. The coefficients of determination R^2 have been in the acceptable range, with slightly higher coefficients for the lower conversion rate analyses. The activation energy (E_a) for the thermal decomposition of PBO thin film has been in the range of 408.2-448.7 kJ/mol. The frequency factor ($\log A$) has been in the range of 23.8-25.4 min^{-1} . Therefore, the activation energy (E_a) was estimated to be about 445 kJ/mol and the frequency factor ($\log A$) to be around 25.2 min^{-1} . The thermal degradation kinetic parameters for several polymeric materials are listed in Table 3 for comparison [20]. It has been suggested that PBO thin film had the highest activation energy among many polymers, which self-explained its high degree of thermal stability and resistance to heat. Most of the polymers showed the major thermal degradation reaction order of one.

Table 3. Thermal degradation kinetic parameters for the polymeric materials.

Polymer	Activation energy (kJ/mol)	Reaction order	Log A (min^{-1})
ABS copolymer	190	1	16.2
Polypropylene	328	1	23.9
Polystyrene	218	1	16.1
Polyurethane	122	1	13.1
Polyvinylchloride	142	1	14.7
PBO thin film	445	1	25.2

4. Conclusions

The quasi-isotropic thin films have been successfully prepared from 14 wt-% PBO dope using a press and a slow vacuum evaporation process. The samples were also coagulated and

washed in distilled water to set the structure. The PBO thin film material exhibited outstanding specific tensile properties, outperforming many engineering polymeric materials such as epoxy and polyether ether ketone (PEEK). The tensile modulus (E) of PBO thin film has been 5.5 GPa, the tensile strength (σ) was 110 MPa, the specific modulus (E/ρ) was 3.5 $\text{GPa}\cdot\text{cm}^3\cdot\text{g}^{-1}$, and the specific strength (σ/ρ) was 70 $\text{MPa}\cdot\text{cm}^3\cdot\text{g}^{-1}$. Though the tensile modulus and strength were lower than metals and glasses, the specific mechanical properties have been in the fairly competitive ranges. From the isothermal TGA spectra at different elevated temperatures, the polymer thin film showed little weight loss until above 600°C. The highest applicable temperature was thus estimated at 500-600°C, depending on the duration of use. The degree of degradation also intensified with both temperature and time. From the non-isothermal degradation curves, the onset weight loss of PBO was about 670°C. The temperature that corresponded to the maximum weight loss rate was around 750°C. The decomposition process slowed down after reaching 790°C. The residual weight has been as high as 73% when heated up to 850°C. The high char yield along with the rigid rod aromatic backbone structure warranted excellent fire retardation characteristics for this polymeric thin film material. The major thermal degradation reaction appeared to be a one-stage reaction in nitrogen atmosphere. In addition, the thermogravimetric kinetic analysis has been carried out using the Ozawa method. The activation energy (E_a) for the thermal decomposition of PBO thin film has been in the range of 408.2-448.7 kJ/mol. The frequency factor ($\log A$) has been in the range of 23.8-25.4 min^{-1} . The activation energy (E_a) was thus estimated to be about 445 kJ/mol and the frequency factor ($\log A$) to be around 25.2 min^{-1} . It has been concluded that the PBO thin film had the highest activation energy among many polymers, which self-explained its high degree of thermal stability and resistance to heat. Therefore, the outstanding specific mechanical properties and excellent thermal resistance should provide great potential applications for this new high performance rigid rod polymers.

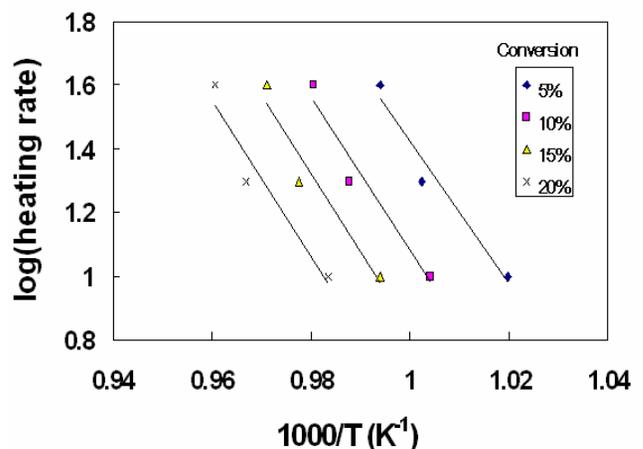


Fig.5. The plot of $\log(\text{heating rate})$ versus $1000/T$ for the kinetic data analysis using the Ozawa method. Four different conversion rates ranging from 5% to 20% were used.

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