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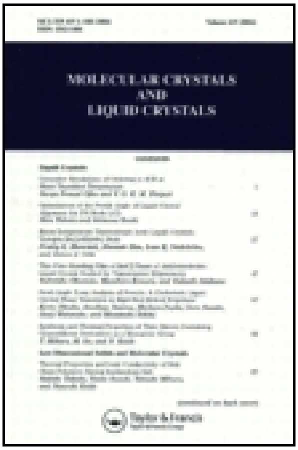

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MELT PROCESSING OF POLY(P-OXYBENZOATE)

T. Karis, R. Siemens, W. Volksen, and J. Economy, IBM Almaden Research Center, San Jose, California, U.S.A.

Abstract Examination of the thermal transitions, decomposition rate, and softening temperature of poly(p-oxybenzoate) indicates a process window of several minutes near 440^{0}C where the powder can be compression molded. The nature of the thermal transitions and molding time, pressure, and temperature aimed at achieving the optimum flow properties are discussed.

INTRODUCTION

More demanding applications for polymer materials require that high modulus and strength be maintained at elevated temperatures. The easily synthesized, low cost polymer poly(p-oxybenzoate), also referred to as poly(p-hydroxybenzoic acid), and poly-PHBA, or Ekonol[1,2], which retains its high modulus up to at least 325 °C, satisfies these requirements provided it can be readily fabricated.

Traditionally, the homopolymer has been fabricated into coatings via plasma spraying or into relatively simple parts by high energy rate forging (HERF). These are novel processes and provide limited flexibility for preparing structural components. Samples can also be compression sintered at 400 °C, but the shapes have relatively low elongation at break indicating inadequate fusion of the powder particles.

An alternative approach to achieving improved processability is synthesis of the copolyesters of PHBA with other monomers[3,4] such as polyethylene terephthalate (PET) biphenylene terephthalate (BPT), hydroxynapthoic acid (HNA), etc. These act

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to lower the melting point[4] as low as 230 °C (PET/PHBA 60/40). In the case of the copolyester PHBA-BPT, it can be injection molded at 400 °C, since the flow properties are modified such that the viscosity decreases dramatically with shear rate[5]. Although the copolyesters of PHBA afford easier processing, the material is inevitably oriented, resulting in a large directional component to the mechanical properties[4,6–12] .

The present study was undertaken with the intent of taking advantage of a recent report[13] of a high temperature transition in the poly-PHBA at 440 °C, where flow appeared to occur. In addition, samples with M_n values in excess of 12,000 were used to minimize potential problems of brittleness associated with lower M_n material.

THERMAL TRANSITIONS

Three temperature transitions were identified by Differential Scanning Calorimetry (DSC) with a heating rate of 160 °C/min, of which two are reversible (see Figure 1). We observed the earlier reported transition near 350 °C[14]. This is accompanied by an increase in the specific volume, and a decrease in the modulus during small amplitude oscillation measured by a Dynamic Mechanical Thermal Analyzer (DMTA). The new transition near 440 °C is accompanied by a gradual increase in the specific volume, and a dramatic softening, Figure 2. This softening is shown by the penetration of a Thermo Mechanical Analyzer (TMA) indenter into a pressed sample as the 440 °C transition is approached, Figure 3.

However, when the poly-PHBA softens it also begins to decompose with time at temperatures above 440 °C, Figure 4. The material can be molded rapidly above the softening temperature in several minutes since the amount of decomposion is small.

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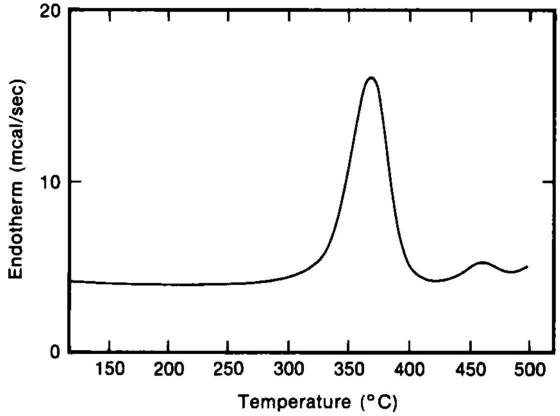

FIGURE 1. Differential scanning calorimetry of poly-PHBA showing the two reversible thermal transitions. Heating rate 160 °C/min.

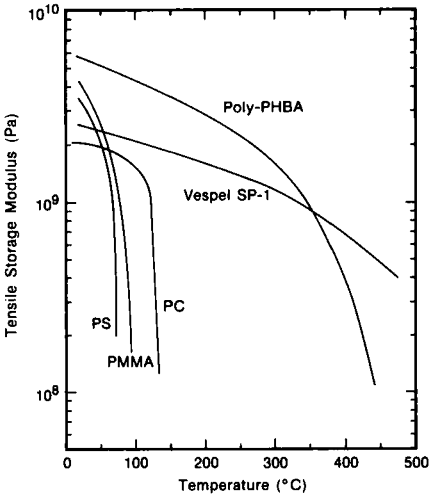

FIGURE 2. Tensile storage modulus as a function of temperature showing the softening temperature of compression molded poly-PHBA, three common thermoplastics, and a polyimide (PS-polystyrene, PMMA- Plexiglas, PC-Lexan, Vespel SP-1-unfilled polyimide, frequency 10Hz, heating rate 10 °C/min).

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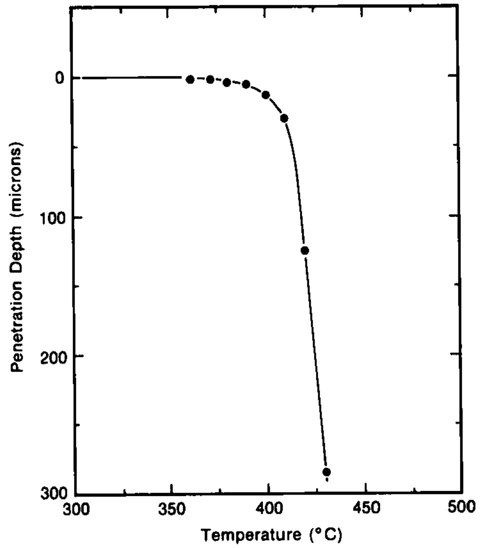

FIGURE 3. Thermomechanical analysis showing the penetration of the indenter into a molded poly-PHBA sample approaching the 440 °C transition (indenter pressure ≈1.4MPa).

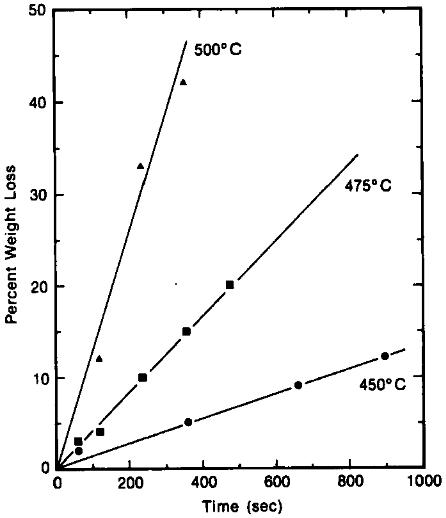

FIGURE 4. The fractional weight loss of poly-PHBA due to thermal decomposition as a function of time.

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MOLDING

Since the poly-PHBA softens near 440 °C and the thermal stability is adequate for at least a few minutes, this allows for the possibility of rapid melt processing by powder molding[15]. Thus, samples 25 mm in diameter and approximately 1 mm thick were molded in a cylindrical compression mold over a range of temperatures from 250 °C to 450 °C at pressures of 13.8 or 55.2 MPa. Prior to molding the powder was stored in a vacuum oven at 60 °C, minimizing water adsorption.

The mold is preheated to the desired temperature, 0.8 g of the powder is placed in the bottom of the mold, and then immediately pressed after turning off the heaters. The residence time at the maximum temperature is about one minute. If the sample is held at 450 °C for five minutes, significant discoloration is observed. The mold is then allowed to cool below 100 °C under pressure before removing the sample.

MECHANICAL PROPERTIES

The tensile storage modulus at room temperature for the samples measured by DMTA in the single cantilever mode is approximately 4-8 GPa. This is consistent with the modulus calculated from the ultrasonic velocity, 5.7 GPa (density 1398 kg/m^3 and assumed Poissons ratio 0.3).

A three point bending apparatus with a vertical air slide was constructed to measure the relative ultimate strength. This consists of a rectangular bar that is vertically mounted and held from twisting by a frictionless guide. Weights were placed on top of the slide and a 6.25 mm diameter ball bearing was mounted on the bottom of the slide to contact the center of the sample.

Specimens approximately 3 mm wide were cut from the center of the 25 mm diameter molded disks with a miniature band saw and polished with number 600 paper to remove any nicks. The air slide was then lowered onto the sample and the weight was increased in 10 g increments until the sample fractured. The load at fracture L_f is adjusted for small variations in sample width w and thickness t to get the normalized fracture load = L_f/wt^3. The maximum normalized fracture load from a number of samples made at each set of conditions is shown in Figure 5.

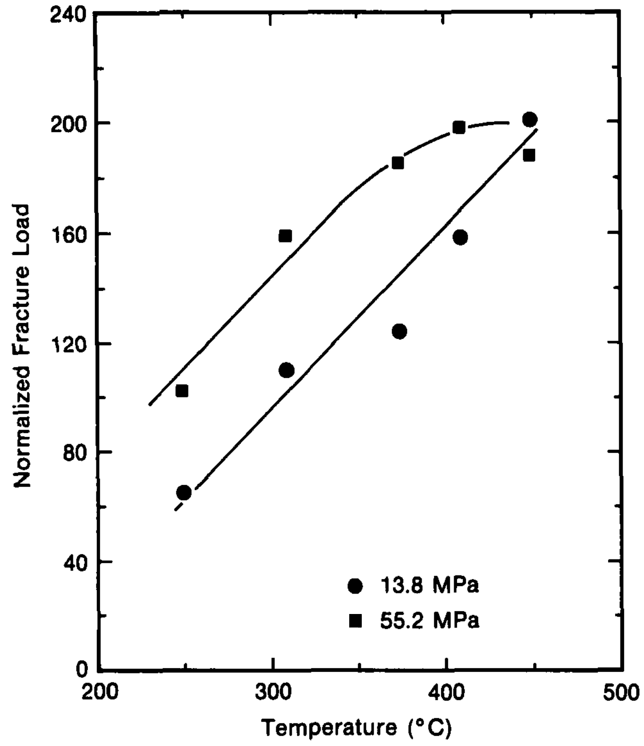

FIGURE 5. The maximum normalized fracture load as a function of mold temperature and pressure for poly-PHBA.

DISCUSSION

The tensile modulus of the compression molded poly-PBHA (Figure 2) is above that of other high performance polymers such as XYDAR, Vespel, and molded poly(p – phenylene)[15].

The main problem with this material is the ultimate strength and elongation at break. The ultimate strength increases with in-

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creased molding pressure and temperature up to 450°C. This is due to increasing fusion and flow at the particle interfaces. Increased particle fusion with temperature is shown at a fracture surface in Figure 6, where the outline of the original powder particles is clearly visible in Figure 6a after molding at 250 °C. The sample shown in Figure 6b was molded at 450 °C and shows significant fusion. X-ray diffraction parallel and perpendicular to the flow direction of compression from a sample molded at 450 °C and 41.4 MPa indicates a small amount of molecular orientation in the sample, Figure 7.

The strain at break follows a similar trend with molding temperature and pressure as does the ultimate strength. The brittleness of the poly-PHBA as molded in this study is attributed to two factors (1) the heterogeneity of the microstructure caused by incomplete flow of the initial powder and (2) frozen-in stress while cooling through the 350 °C transition under pressure. If samples are removed from the mold above 350 °C, they warp. The initial particles which are about 40 μm in diameter have deformed and fused together at the interfaces, but the microstructure of the fracture surface has a domain size on the order of 40 μm, Figure 6. Apparently the fracture propagates along the fused interface around the original powder particles.

CONCLUSIONS AND FURTHER WORK

There is a thermal transition of poly-PHBA near 440 °C which is accompanied by pressure induced flow. This was shown by TMA, SEM's of the fracture surface, and x-ray diffraction, and expains HERF and plasma spraying of poly-PHBA. The potential for processing near 440 °C was demonstrated, and preliminary conditions for compression molding were defined. Conditions for optimization are under study. In addition, the availability of techniques to form films or fibers with the residence time at 450 °C less than one minute should permit formation of a much broader spectrum of products than heretofore possible.

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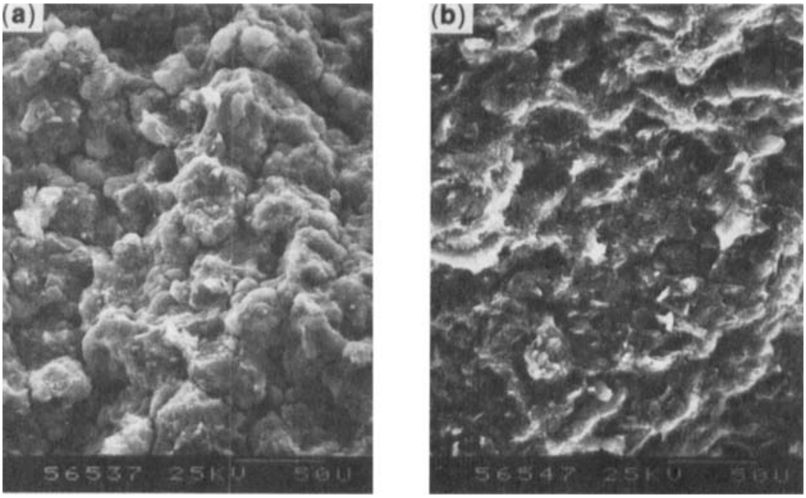

FIGURE 6. SEM micrographs of poly-PHBA molded under 13.8MPa at (a) 250 °C and (b) 450 °C showing increased fusion at the higher temperature

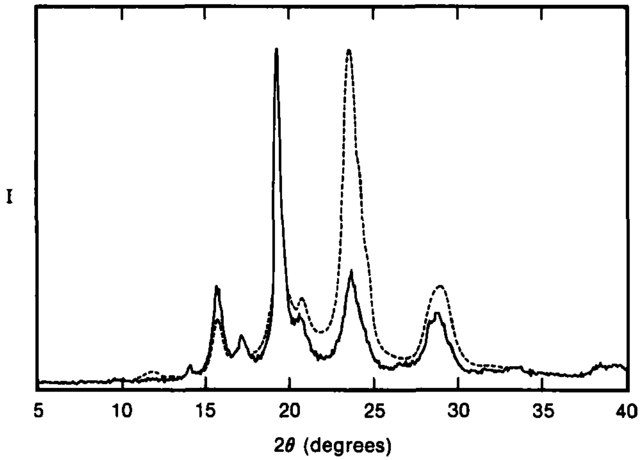

FIGURE 7. X-ray diffraction by reflection parallel ———— and perpendicular - - - - - - to the direction of compression, poly-PHBA molded at 450 °C and 41.4MPa, Cu-α 1.5406Å.

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