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An investigation of the microstructure of a cryogenically mechanically alloyed polycarbonate-poly(aryl ether ether ketone) system

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This work investigates processing-microstructure relationships of a model cryogenically mechanically alloyed polymer-polymer system consisting of polycarbonate (PC) and poly(aryl ether ether ketone) (PEEK). Powders mechanically alloyed for 10 hours were imaged via transmission electron microscopy (TEM) and were shown to have a two-phase microstructure physically mixed on a sub-micron level. These powders were processed into coupons using a laboratory scale ram-injection molder, and the resulting microstructure of the coupons was investigated as a function of mechanical alloying and injection molding parameters. Atomic force microscopy, TEM, and scanning transmission X-ray microscopy all revealed that the intimate blending achieved during the mechanical alloying process was not retained upon post-processing using this conventional polymer processing technique. © *2003 Kluwer Academic Publishers*

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1. Introduction

Mechanical alloying (MA) is a solid-state technique originally developed in the 1960's for metals processing. During MA, a ball mill is used to produce fine powders with two or more phases within each particle. The materials, generally in powder form, are placed in the ball mill's vial with metallic or ceramic balls, and the mill's motor vigorously shakes the vial. With each agitation, high energy impacts trap material between the balls, or a ball and the vial wall. The particles are repeatedly fractured, deformed, and fused together, generally creating a two-phase microstructure. Manipulation of processing parameters such as milling time, temperature, ratio of the total ball mass to powder mass (charge ratio), and ball mill design affect the resultant particle microstructure. Mechanical alloying is commonly used for producing metal alloys with refined microstructures; in addition, mechanical milling (MM) of individual materials may be used to refine particle size of metals. More recently, MA has also been used to process polymers [1–15], with the common aim of achieving intimate physical mixing in the powder state. Much of this research has been motivated by Shaw and coworkers' initial work in the field [1, 2, 16–19]; these researchers have claimed that mechanically alloying polymers could result in a virtually unlimited number of polymer blend combinations which are normally thermodynamically immiscible [17]. Other work in the field has, for the most part, been driven by such claims and the anticipation that microstructures exhibiting a high level of physical mixing in the powder phase will translate into improved polymer blend properties.

While the ultimate goal of many of these studies appears to be an improvement in properties due to this microstructural refinement, polymer blend thermodynamics does not predict that a refined microstructure

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formed by MA will remain stable when the powders are heated in a realistic post-MA processing step involving heat and/or shear. Because MA essentially traps in a very fine non-equilibrium microstructure, such systems exhibit behavior similar to that of a miscible polymer blend with a lower critical solution temperature [20]. Upon heating such a system, thermodynamics dictates that phase separation (demixing) will occur. Despite this fact, post-MA processing of these powders is rarely addressed in the literature. Only recent publications by Smith and coworkers [8, 10, 11] have considered this. Despite their considerations, the literature largely fails to address post-mechanical alloying processing using traditional polymer processing techniques, as well as the effects of microstructure on mechanical properties of mechanically alloyed polymer blends. In a previous study, we examined the mechanical properties of injection molded coupons produced from both mechanically alloyed and non-mechanically alloyed polymers [21, 22]. Data from quasi-static three point bend tests indicated no measurable improvement from the mechanical alloying process for this model system. The present work adds to the knowledge gained from prior findings by examining the microstructure of these injection molded coupons.

2. Materials and methods

2.1. Materials

Laserite^{TM} Polycarbonate Compound powder (LPC3000) ($M_w = 22,900$ g/mol, $M_n = 12,600$ g/mol) was obtained from 3D Systems of Austin, Texas. Victrex® PEEK 150PF powder ($M_w = 33,500$ g/mol, $M_n = 11,700$ g/mol) [23] was obtained from Victrex USA, Inc. of Greenville, South Carolina.

2.2. Mechanical alloying

Powders were mechanically alloyed in a 50/50 volume percent ratio using a cryogenic vibratory ball mill [24], with a continuous liquid nitrogen drip. A stainless steel vial and balls were used, and a motor speed of 425–450 rpm, corresponding to approximately 8 Hz, was employed. Individual materials were also mechanically milled for 10 hours. Sample designations and mechanical alloying conditions are summarized in Table I.

2.3. Injection molding

Powders were injection molded at temperatures between 350°C and 390°C using a DACA Instruments (Goleta, California) MicroInjector^{TM} miniature-ram injection molder. Four rectangular coupons (20 mm × 5 mm × 1.5 mm) were produced per injection, using approximately 4 g of material. Powders were pre-heated in the barrel for five minutes prior to injection.

TABLE I Mechanical alloying conditions and sample designations.

Sample designation	Material	Total polymer mass (g)	No. milling balls	Time (hr)
MA 10h	PC-PEEK	35.3	4	10
PC MM 10h	PC	33.9	4	10
PEEK MM 10h	PEEK	36.7	4	10

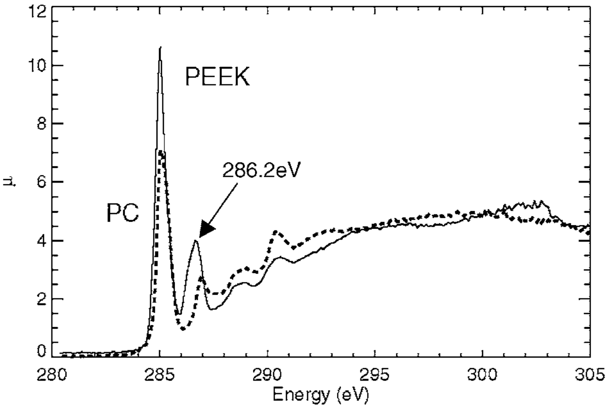

Figure 1 X-ray spectra of unmilled PC and PEEK.

2.4. Imaging techniques

Transmission electron microscopy (TEM) was performed on mechanically milled and alloyed powders. Powder particles were embedded in a commercial epoxy, cured at room temperature overnight, then microtomed. Resulting sections were collected onto 300 mesh gold grids. Injection molded coupons were also microtomed at room temperature and sections were collected from the center of the coupon onto identical grids. The sections were examined using a Philips 420T Transmission Electron Microscope at 100 kV.

A Digital Instruments Nanoscope IIIa^{TM} atomic force microscope was used in TappingMode^{TM} to image samples of injection molded coupons. An area from the center of each coupon was microtomed, and phase contrast images were collected.

Scanning Transmission X-ray Microscopy (STXM) data were collected at Brookhaven National Lab's X-1A beamline in Upton, New York. Beam energy calibration was performed with carbon dioxide gas prior to data collection. STXM images were obtained from the center of selected injection molded coupon samples. After initial X-ray spectra were obtained for individual PC and PEEK samples, a photon energy of 286.2 eV was chosen for data collection, as PEEK absorbs at this energy and PC does not, causing the PEEK phase to appear darker in the X-ray images (Fig. 1). In addition, principal component analysis was performed to determine the number of phases present in MA 10h powder samples.

3. Results and discussion

3.1. Transmission electron microscopy of powders

Except for the contrast between PC MM 10h particles and the embedding epoxy, PC MM 10h samples appeared featureless when imaged via TEM and are therefore not shown here. Fig. 2 shows representative micrographs of unmilled PEEK and PEEK MM 10h cross-sections. Both samples exhibited "chatter" perpendicular to the direction of microtoming, an artifact of the sample preparation process. Knife marks are visible in the image of the MM PEEK 10h sample, indicating the direction of microtoming.

Differences in electron densities of PC and PEEK provide contrast in the TEM micrographs of MA 10h powders, shown in Fig. 3. These particles exhibited

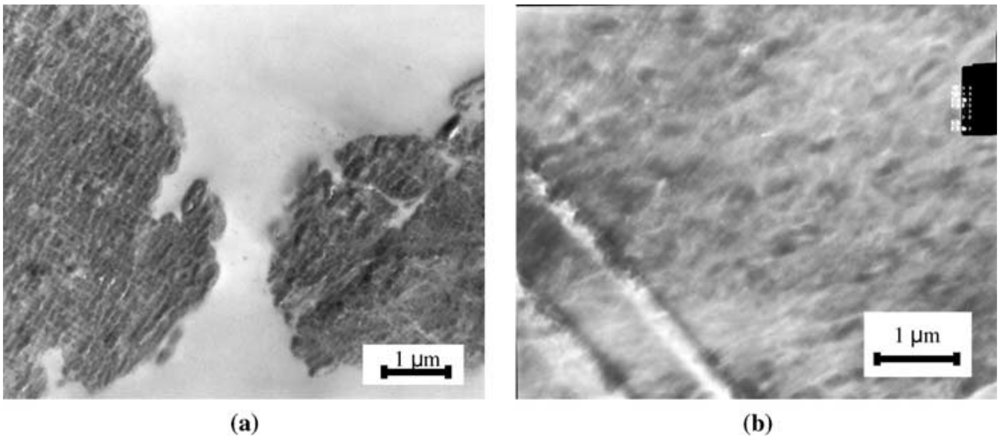

Figure 2 Transmission electron micrograph of unmilled (a) and MM PEEK 10h (b) particle cross-section.

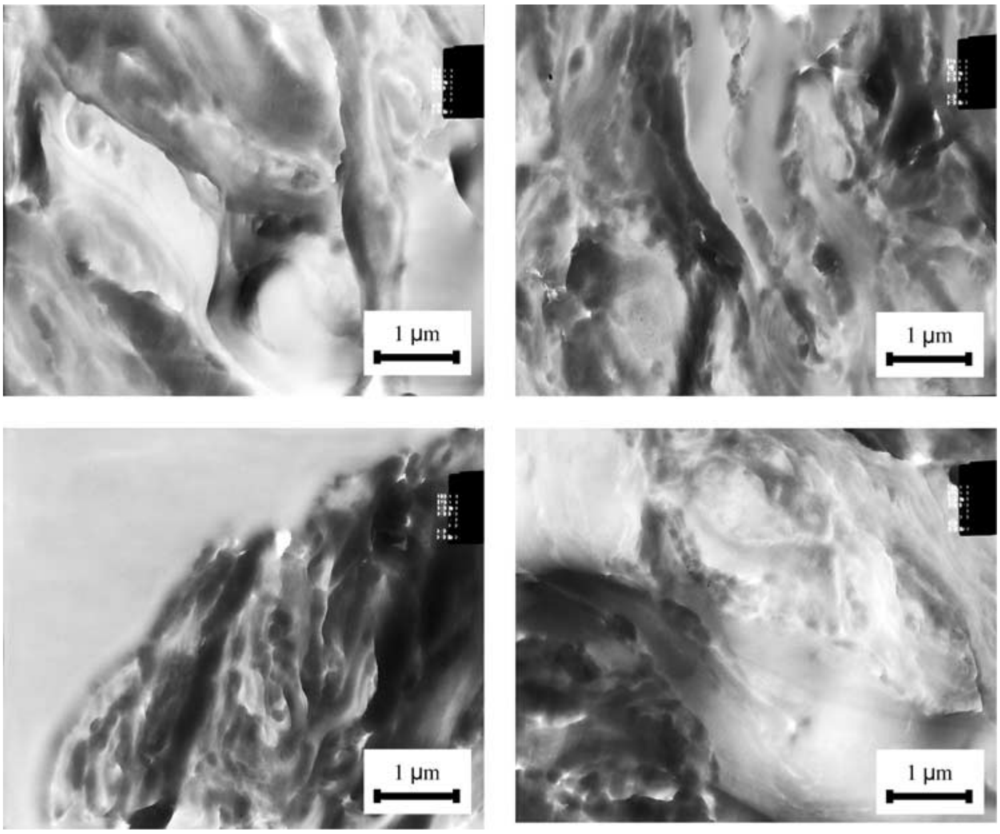

Figure 3 Transmission electron micrographs of MA 10h powder cross-sections.

a two-phase microstructure consisting of sub-micron sized phase domains. Both PC and PEEK phases are visible within each powder particle, along with a “swirled” appearance, which is a result of repeated fracturing and cold welding during the MA process. Darker areas visible in the cross-sectioned particles are PEEK-rich phases, whereas PC-rich areas appeared lighter because electrons are more easily transmitted through this amorphous polymer.

3.2. Transmission electron microscopy of coupons

In order to investigate the mechanical properties [21] and microstructure of parts made from these powders, the powders were injection molded into rectangular coupons. TEM was used in conjunction with atomic force microscopy to image the microstructure

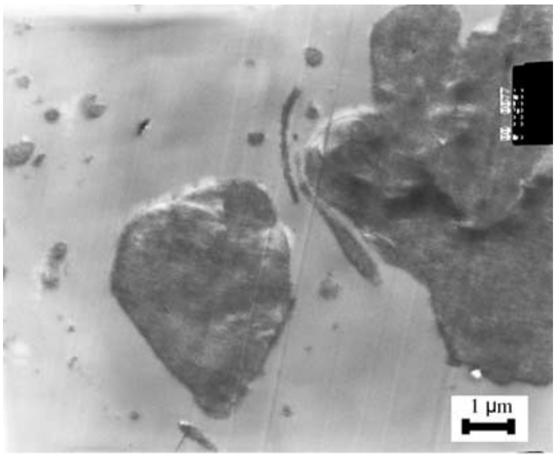

Figure 4 TEM micrograph showing the cross-section of a bar injection molded at 360°C. PEEK-rich phases appear darker, surrounded by a PC matrix.

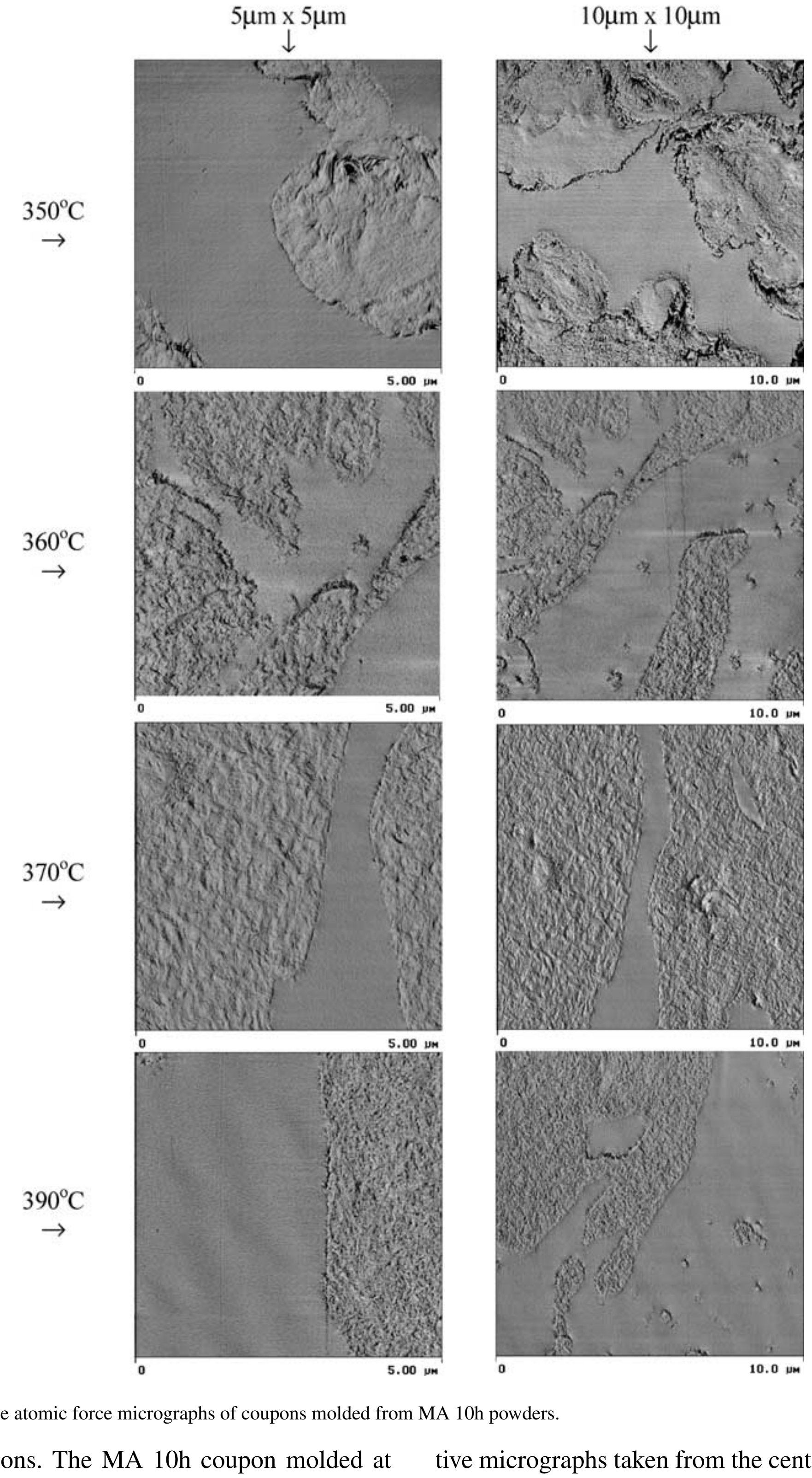

Figure 5 Phase image atomic force micrographs of coupons molded from MA 10h powders.

of molded coupons. The MA 10h coupon molded at 360°C was imaged using TEM (micrograph shown in Fig. 4), revealing (darker) PEEK-rich phases of varying size and shape within a (lighter) PC continuous matrix. In addition, knife marks are faintly visible (indicating the microtoming direction); these demonstrate that no microstructural directionality results from TEM sample preparation of coupons.

3.3. Atomic force microscopy of coupons

Phase image AFM was used to additionally characterize the microstructure of MA 10h coupons' cross-sections molded at various temperatures. Representative micrographs taken from the center of each coupon are shown in Fig. 5. Images taken from coupons molded at designated temperatures are shown in rows, with columns representing 5 and 10 square micron scans. Two phases were readily distinguishable in these images: the amorphous PC appears featureless in the phase image AFM mode, while the semi-crystalline PEEK appeared "rough." In general, these micrographs show agglomerations of PEEK within a PC matrix, indicating that the PC flowed around the semi-crystalline PEEK phase during molding. Micrographs shown in Fig. 5 demonstrate that the sub-micron phase domains present previously in the MA 10h powder underwent a great

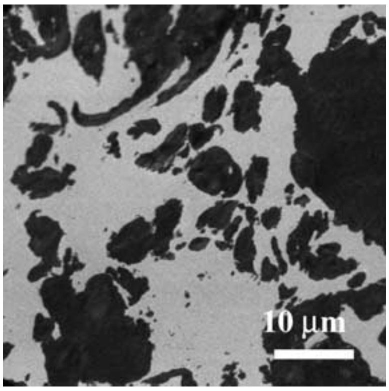

Figure 6 STXM image of MA 10h bar molded at 380°C, taken at 286.2 eV.

deal of demixing upon post-MA injection molding using these conditions. In the coupons molded from MA 10h powders, PC and PEEK phases were sized on the order of microns (or even tens of microns) rather than the sub-micron phase domains present in the MA 10h powders. These micrographs also reveal some differences in the microstructure of the MA 10h coupons injection molded at various temperatures. At 350°C, the crystalline portion of the PEEK phase was not completely melted prior to molding, hindering flow of the blend through the die. In contrast, the PEEK phase was molten at 370°C and therefore flowed more easily during molding. Coupons molded at 370°C appeared to consist of a PC matrix containing isolated islands of the PEEK phase with some PC areas trapped inside. At 390°C, both phases were highly mobile (due to a low viscosity), and the image of the coupon revealed PEEK phases in a PC matrix.

3.4. Scanning transmission X-ray microscopy of powders and coupons

Principal component analysis revealed the presence of two different phases within the MA 10h powder particles, complementing TEM images showing an intimately mixed two-phase material. Principal component analysis was also corroborated with FTIR data (not shown), which indicated that a third phase was not formed upon mechanical alloying PC and PEEK.

Scanning transmission X-ray microscopy was used to obtain X-ray images of a molded coupon (MA 10h molded at 380°C). Individual spectra of PC and PEEK revealed that at 286.2 eV, PEEK absorbed X-ray energy and thus appeared dark, while PC did not absorb X-ray energy and thus appeared light. A representative image collected at this energy is shown in Fig. 6. These results corroborate results obtained via AFM and TEM: injection molded coupon microstructure consisted of a continuous PC matrix with PEEK phases of varying size and shape.

4. Summary and conclusions

Results from this study indicate that the mechanical alloying conditions employed in this work resulted in powders that were physically mixed on a sub-micron level. Three complementary imaging techniques were employed to characterize the microstructure of subsequently injection molded coupons; all offered evidence that the microstructure present in the MA 10h powder prior to injection molding underwent substantial demixing upon post-MA processing in this manner.

This study has demonstrated that even with the minimal post-MA processing conditions employed in this work, the mechanically alloyed microstructure was not retained upon post-processing above the polymers' glass transition temperatures. Therefore, any anticipated physical property benefit derived from the intimate phase mixing achieved during mechanical alloying is likely to be lost upon post-MA processing. In fact, other work has shown [21] that cryogenically mechanically alloying this system for 10 hours does not measurably improve mechanical properties such as toughness, strain at failure, and failure strength of injection molded coupons compared to non-mechanically alloyed PC-PEEK samples. An improvement in properties of this or other mechanically alloyed systems may be feasible, however, by the creation of a chemical bond between polymer components during mechanical alloying [11, 12, 25], which is likely to hinder the thermodynamically driven demixing process. While the results presented here are specific to this system, an understanding of the thermodynamics of polymer mixing leads to the conclusion that traditional polymer processing techniques are not compatible with retaining sub-micron microstructure afforded by the mechanical alloying process.

Acknowledgments

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