Mechanical Properties of a Cryogenically Mechanically Alloyed Polycarbonate–Poly(aryl ether ether ketone) System

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ABSTRACT: The processing–property relationship of a model cryogenically mechanically alloyed polymer–polymer system [polycarbonate (PC) and poly(aryl ether ether ketone) (PEEK)] was investigated. PC and PEEK powders were cryogenically mechanically alloyed for 10 h, and the resulting two-phase powder particles were processed into testable coupons with a miniature ram-injection molder. The bulk mechanical properties of the coupons made from the mechanically alloyed powders and nonmechanically alloyed powders were investigated as a function of mechanical alloying and injection-molding parameters. The injection-molded coupons were mechanically tested in the three-point-bending mode. The results demonstrated that no measurable improvement was achieved in the energy to break, strain at failure, or failure strength in the coupons made from the mechanically alloyed materials in comparison with those of the coupons made from the nonmechanically alloyed powders. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1196–1202, 2003

Key words: alloys; mechanical properties; polycarbonates; poly(ether ketones)

INTRODUCTION

A polymer blend can be defined as a "physical mixture of structurally different homo or copolymers".[1] The objective of blending two or more polymers is generally the creation of novel materials with improved or unique properties and/or improved processing. In addition, blends can be economical because they allow for quick modifications of performance with low capital investment in comparison with the development of new polymers, and they can lower the cost of using expensive resins by combining them with less expensive commodity resins. Conventional polymer blending techniques such as solution or melt blending often require solvents or compatibilizers to form blends because of the inherent immiscibility of most polymer combinations.

Mechanical alloying (MA) is a well-established technique for processing metals that is capable of producing alloys with fine microstructures. This technique uses a ball mill to process pellets or powders, generally creating fine powders consisting of two or more phases within each particle. Alternately, the mechanical milling (MM) of individual materials is sometimes used to refine the particle size. During the MA process, materials are placed in a ball-mill vial with two or more metallic or ceramic balls. The mill motor vigorously shakes the vial, and this results in high-energy impacts. With each agitation, these impacts trap the materials between the balls or between a ball and the vial wall. As MA occurs, the particles are repeatedly fractured, deformed, and fused together. This process of repeated fracturing and cold welding causes a refinement in the microstructure with the milling time. The result is generally a two-phase microstructure with phase domain sizes dependent on total milling energy.[2] Parameters that can be manipulated include the milling time, temperature, ratio of the total ball mass to the powder mass (charge ratio), and ball mill design.
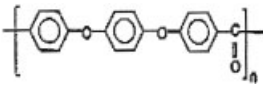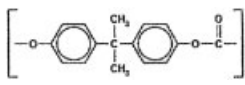
In addition to processing metals with this technique, some researchers[2–9] have also applied MA to combining polymers in anticipation of improved polymer blend properties due to intimately mixed phases. Although the initial polymers are not alloyed in the metallurgical sense of the word, the phases are brought into more intimate contact through repeated fracturing and cold welding. Shaw and coworkers[10] claimed that MA can produce solid-state blends of thermodynamically immiscible polymers without the use of solvents or compatibilizers, giving rise to an infinite number of polymer–polymer blend permutations and improved properties. Much of the work in the field of mechanically alloying polymers has been

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TABLE I
Selected Material Properties

	PEEK	Polycarbonate
Chemical structure		
T_g (°C)	145	144
T_m (°C)	346	No T_m (amorphous)

T_g and T_m values were measured with differential scanning calorimetry at 10°C/min

motivated by such claims. However, the existing body of work fails to address practical methods for post-MA processing. Some studies[2,3,8,9,11–16] have briefly examined physical and mechanical properties obtained from mechanically milled or mechanically alloyed polymers, but they have not systematically examined the mechanical properties of these mechanically alloyed polymers once processed above their glass-transition temperatures (T_g's), as is traditionally done in polymer processing. We used a model system to investigate the mechanical properties of coupons made from mechanically alloyed powders, comparing their properties to those exhibited by nonmechanically alloyed mixtures to determine if the MA process was warranted for this system. The question of microstructural retention after the subsequent processing of these mechanically alloyed materials is addressed elsewhere.[17]

EXPERIMENTAL

Materials

A semicrystalline polymer, poly(aryl ether ether ketone) (PEEK), and an amorphous polymer, polycarbonate (PC), were chosen as a model system for this study. Victrex PEEK 150PF powder was obtained from Victrex USA, Inc. (Greenville, SC). The intrinsic viscosity reported by the supplier was approximately 1.5 Pa s, corresponding to weight-average (M_w) and number-average (M_n) molecular weights of 33,500 and 11,700 g/mol, respectively.[18] The chemical structures and thermal properties for both materials are given in

Table I. A commercial grade of PC, Laserite polycarbonate compound powder (LPC3000), was obtained from 3D Systems (Austin, TX). Gel permeation chromatography (GPC) analysis indicated that the as-received material had an M_w value of 22,915 g/mol and an M_n value of 12,605 g/mol.

MA processing

A vibratory ball mill, designed and built at Virginia Tech,[19] was used with a stainless steel vial and balls to form blends at cryogenic temperatures. Liquid nitrogen was continuously dripped over the vial into the mill unit, and a thermocouple was used to ensure that the vial was kept cold throughout the milling process, so that the polymers remained below their T_g's. This mill, which provided linear vibratory motion on a single axis, was designed as an alternative to a commercially available mill because of its cryogenic capabilities and comparatively larger vial volume milled per batch. A schematic of the ball mill is shown in Figure 1.

Binary blends of PEEK–PC were produced from resins in powder form in a 50/50 (v/v) ratio. Powders were cryogenically processed in the ball mill for 1 h with two stainless steel milling balls (MA 1h) and for 10 h with four milling balls (MA 10h). The MA 1h samples represent minimal MA conditions for this system. Individual components were also mechanically milled for 10 h with four balls to evaluate the effects of MM on individual polymer molecular weight distributions. The ball-mill motor speed was
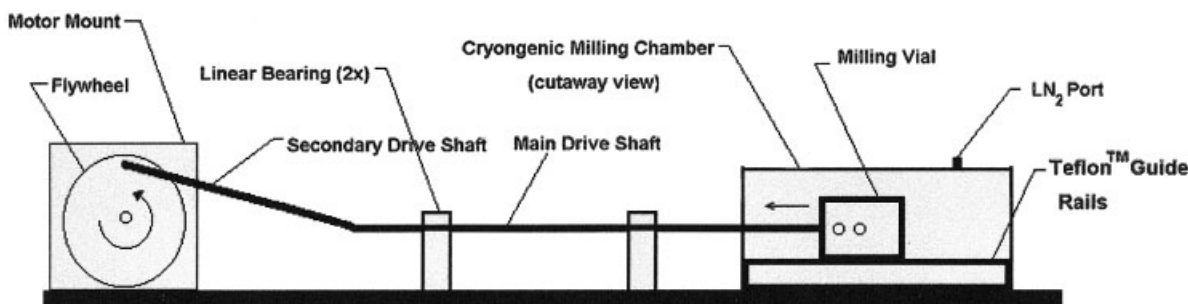

Figure 1 Schematic of the ball mill.[19]

TABLE II
Mechanical Alloying Conditions and
Sample Designations

Sample designation	Material	Total polymer mass (g)	Milling balls	Time (h)
Mixed	PC–PEEK	35.3	—	0
MA 1h	PC–PEEK	35.3	2	1
MA 10h	PC–PEEK	35.3	4	10
PC MM 10h	PC	33.9	4	10
PEEK MM 10h	PEEK	36.7	4	10

set between 425 and 450 rpm (corresponding to ca. 8 Hz) for all samples. Nonmechanically alloyed (i.e., mixed PC–PEEK) samples were also prepared by the hand mixing of PC and PEEK powder with a spatula. Table II summarizes the MA conditions employed and the corresponding sample designations.

Post-MA processing

To examine the effects of post-MA processing on the mechanical properties of the materials used in this study, we used a Daca Instruments (Goleta, CA) MicroInjector miniature ram injection molder to make coupons suitable for mechanical testing. Injections consisting of four rectangular coupons (20 mm × 5 mm × 1.5 mm) were made with approximately 4 g of powder per shot from 50/50 (v/v) mixed PC–PEEK and mechanically alloyed powders. Before molding the coupons, the barrel was preheated, the polymers were packed in the barrel, and they were then allowed to equilibrate to the molding temperature for 5 min before being injected into the room-temperature mold.

Molding temperatures between 350 and 390°C were chosen because they represent the range of processing for this blend system: at 350°C [ca. the melting temperature (T_m) of the unmilled PEEK semicrystalline component], the polymer was too viscous to fully fill the mold. At 390°C, the PC began to thermally degrade if it remained in the barrel more than a few minutes. Although the MA 10h blend flowed easily even at the lower end of this processing temperature range because of the decreased crystallinity of the PEEK phase, mixed PC–PEEK and MA 1h blends necessitated higher molding temperatures (for further discussion, see the Results and Discussion section). Therefore, all sample sets were processed using the same molding conditions to ensure identical thermal molding histories.

Thermogravimetric analysis (TGA)

A PerkinElmer TGA-7 thermogravimetric analyzer (Wellesley, MA) was used to determine the degradation temperatures (T_d's) of the individual components and mechanically alloyed powders. The samples were heated at a rate of 10°C/min in a nitrogen environment. The temperature corresponding to the peak in the first derivative of the weight percentage with time is reported as T_d, which indicates the temperature corresponding to the highest rate of degradation. Three replicates of each test were performed. Additional tests were conducted in air to simulate the preheating step during the injection-molding process.

GPC

GPC was performed on four replicates of unmilled and PC MM 10h powders at Viscotek Corp. (Houston, TX) with a Viscotek model 300 triple detector system. The powders were dissolved in methylene chloride, and data were collected at a flow rate of 1.0 mL/min. The results were analyzed with Viscotek's TriSEC software. PEEK is not soluble in common solvents at room temperature; therefore, GPC data were not obtained for this material.

Melt rheology

Because GPC molecular weight data were not obtained for PEEK, preliminary viscosity data were collected at 375°C in a nitrogen environment with a TA Instruments AR1000 advanced rheometer (New Castle, DE) on unmilled PEEK and PEEK MM 10h samples with a frequency sweep of 0.1–100 rad/s. A plate gap of 1000 μm was used with 5% strain, and seven points per decade were recorded. Zero-shear viscosities (η) were extrapolated from plots of log viscosity versus log frequency; η values were used to estimate the M_w values of unmilled PEEK and PEEK MM 10h samples as follows:

$$\eta = kM_w^a \tag{1}$$

where k and a are material constants.

Quasistatic three-point-bending testing

A TA.XT2i Texture Analyzer (Texture Technologies Corp., Scarsdale, NY, and Stable Micro Systems, Godalming, United Kingdom) with a three-point-bending fixture was used to test injection-molded coupons of mixed and mechanically alloyed systems. Six replicate tests were performed on each sample type at 0.1 mm/s with a span width of 5.14 mm.

If samples did not fracture by the time at which 40% strain was reached, the test was stopped because at this point the specimen slid down into the three-point-bending fixture; this rendered results past a 40% strain inaccurate. The failure strength and strain-at-failure were obtained by the identification of the point at which either (1) the sample fractured or (2) the test was stopped. In addition, the energy absorbed per
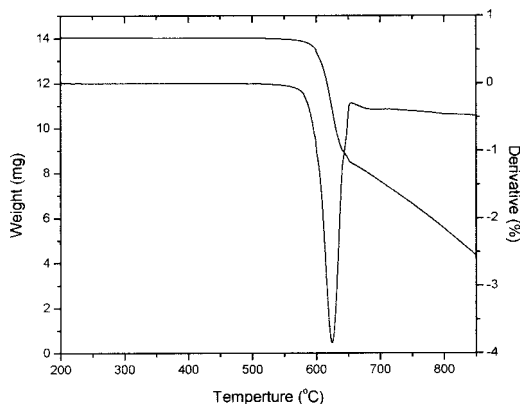
Figure 2 Typical TGA raw data and derivative plot for unmilled PC.

RESULTS AND DISCUSSION

TGA

Representative raw data (weight vs temperature) and first derivative plots obtained from TGA data are shown in Figures 2 and 3 for unmilled PC and unmilled PEEK samples, respectively. Typical weight-loss/temperature data for mixed PC–PEEK samples are shown in Figure 4 along with the derivative curve. The derivative plot for the mixed PC–PEEK sample exhibits two separate peaks, one corresponding to the degradation of PC ($T_d \cong 486°C$) and one corresponding to the degradation of PEEK ($T_d \cong 580°C$). Measured T_d's for unmilled, mechanically milled, mixed PC–PEEK, MA 1h, and MA 10h samples are shown in Table III.

No differences in T_d's of the unmilled and mechanically milled materials were observed for either material for milling times up to 10 h. Likewise, no significant changes in the peak shape or onset were observed for PC MM 10h or PEEK MM 10h samples. The T_d
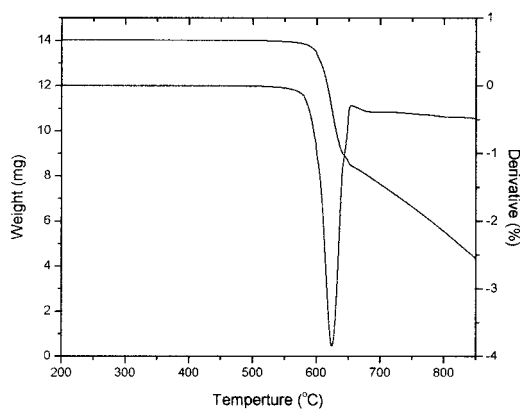

Figure 3 Typical TGA raw data and derivative plot for unmilled PEEK.
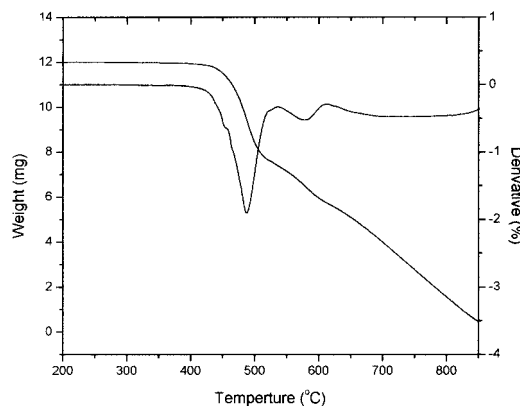

Figure 4 TGA raw data and derivative plot for mixed PC–PEEK.

values measured for PEEK phase degradation in the mixed PC–PEEK, MA 1h, and MA 10h samples were not significantly different. However, the T_d value of PC was lower for the MA 1h sample ($T_d \cong 476°C$) than that for the mixed 1h sample ($T_d \cong 486°C$). The T_d's of each component in both of these systems were significantly lower than those measured in tests of the unmilled PC and unmilled PEEK, however, indicating that the presence of PEEK accelerated T_d of PC and vice versa. These TGA results indicate that no measurable mechanical degradation occurred as a result of the MM or MA process itself. However, some thermooxidative degradation did occur during heating in the mold, as evidenced by a simulation of molding conditions: MA 10h powders were heated to each injection-molding temperature, followed by a 5-min hold during which the weight loss was recorded. The weight-loss results reveal that degradation increased with the molding temperature during the preheating step in the mold barrel. Under the 390°C molding condition, nearly 6% of the weight was lost during the heating step. In addition, the presence of a shear force during molding may have caused chain scission and resulted in even more degradation. Specific degradation mechanisms for PC were reviewed by Robertson,[20] and subsequent molecular weight and property changes resulting from thermal degradation in this temperature range have been reported.

TABLE III
T_d's Measured by TGA*

Sample	T_d (°C)
Unmilled PC	517.9 ± 2.5
PC MM 10h	518.3 ± 4.6
Unmilled PEEK	623.7 ± 1.6
PEEK MM 10h	624.5 ± 0.78
Mixed PC–PEEK	$485.6 \pm 2.1, 580.4 \pm 2.1$
MA 1h	$475.9 \pm 3.0, 577.4 \pm 2.2$
MA 10h	$494.1 \pm 3.0, 575 \pm 5.0$

* Mean values and standard deviations are reported.

TABLE IV
Molecular Weight Values Measured by GPC for
Unmilled and PC MM 10h Samples*

| Sample	M_w (g/mol)	M_n (g/mol)	Polydispersity
Unmilled PC	22,915 ± 17	12,605 ± 72	1.82
PC MM 10h	22,640 ± 50	12,270 ± 130	1.85

* Mean values and standard deviations are reported.

GPC

M_n's and M_w's, as well as polydispersity values, of PC powders cryogenically mechanically milled at various times and charge ratios were determined from GPC data. The results from five replicate tests are summarized in Table IV.

Statistical T tests performed at a 95% confidence level on M_w and M_n values obtained for unmilled PC and PC MM 10h samples indicated that small yet statistically significant differences existed in the values measured for these two sample sets, suggesting that some chain degradation might have occurred during cryogenic MM of PC. Further tests may elucidate these results.

Melt rheology

Viscosity data are shown in Figure 5 for unmilled PEEK and PEEK MM 10h samples along with the η values obtained from a linear fit of low-frequency viscosity data. The η values calculated for unmilled PEEK and PEEK MM 10h samples are given in Table V. Using $a = 3.4$ (a reasonable value for most polymers above the critical molecular weight for entanglement) for the power constant in eq. (1) and assuming that the k values are equivalent for both PEEK samples, we obtained an estimate for M_w's of the unmilled PEEK and PEEK MM 10h samples, using the M_w value for
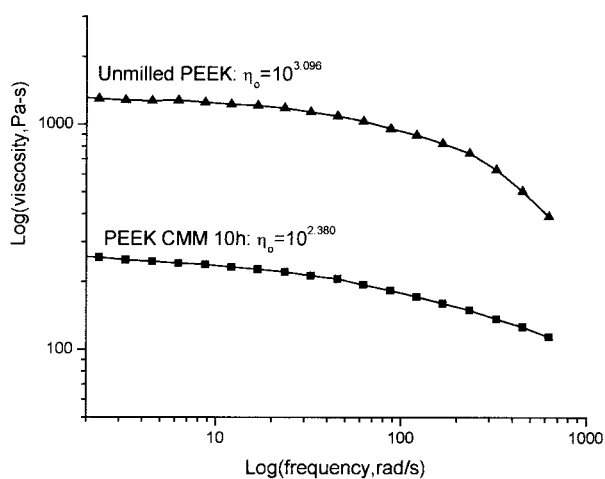
Figure 5 Melt rheology data obtained for unmilled PEEK and MM 10h PEEK.

TABLE V
Melt Rheology Data for Unmilled
and PEEK MM 10h Samples

|	η (Pa s)	Approximate M_w (g/mol)
Unmilled PEEK	1247.4	33,500
PEEK MM 10h	239.9	20,628

unmilled PEEK (33,500 g/mol) provided by the supplier.

These data suggest that a significant decrease in the molecular weight may have occurred as a result of cryogenically mechanically milling PEEK powder for 10 h. In addition, the shapes of the curves of log viscosity versus log frequency indicate that the molecular weight distribution of the PEEK MM 10h sample may have possessed a larger polydispersity index than the unmilled PEEK sample.

Quasistatic three-point-bending testing

Energy-to-failure values were calculated by the integration of the area under the stress–strain curves to fracture or 40% strain, whichever occurred first. Energy-to-failure, strain-at-failure, and failure strength values obtained from TA.XT2*i* data for the sample sets at each injection-molding temperature are shown in Figure 6(a–c). The coupons that did not break during this test actually had higher energy-to-failure, strength, and strain-at-failure values than are reported because the test was stopped at 40% strain. For sample sets for which the test was stopped before fracture for the majority of the coupons tested, this is indicated by an arrow next to the plotted point. Because the load distribution in the three-point-bending test resulted in a point stress concentration in the sample, any flaw resulting from molding could greatly influence the probability of failure. The scatter exhibited by the data is, therefore, higher than what might be the case for a tensile test, which distributes the load over the entire cross section of a sample.

The mechanical data for mixed PC–PEEK and MA 1h samples exhibit similar trends: an increase in the energy-to-failure, strain-at-failure, and failure strain values occurred as the injection-molding temperature increased from 350 to 360°C. These data support the observation made during molding that it was easier to fill the mold at 360°C than 350°C because of improved flow (lower viscosity). For both mixed PC–PEEK and MA 1h sample sets, average energy-to-break values were equivalent for molding temperatures of 360°C and higher according to statistical T tests performed at a 95% confidence level. The data for the MA 10h samples, however, follow a different trend: namely, there was a significant decrease in the mechanical properties of the MA 10h samples at the 370°C molding temperature. This sharp decrease in the measured

(a)

(b)

(c)
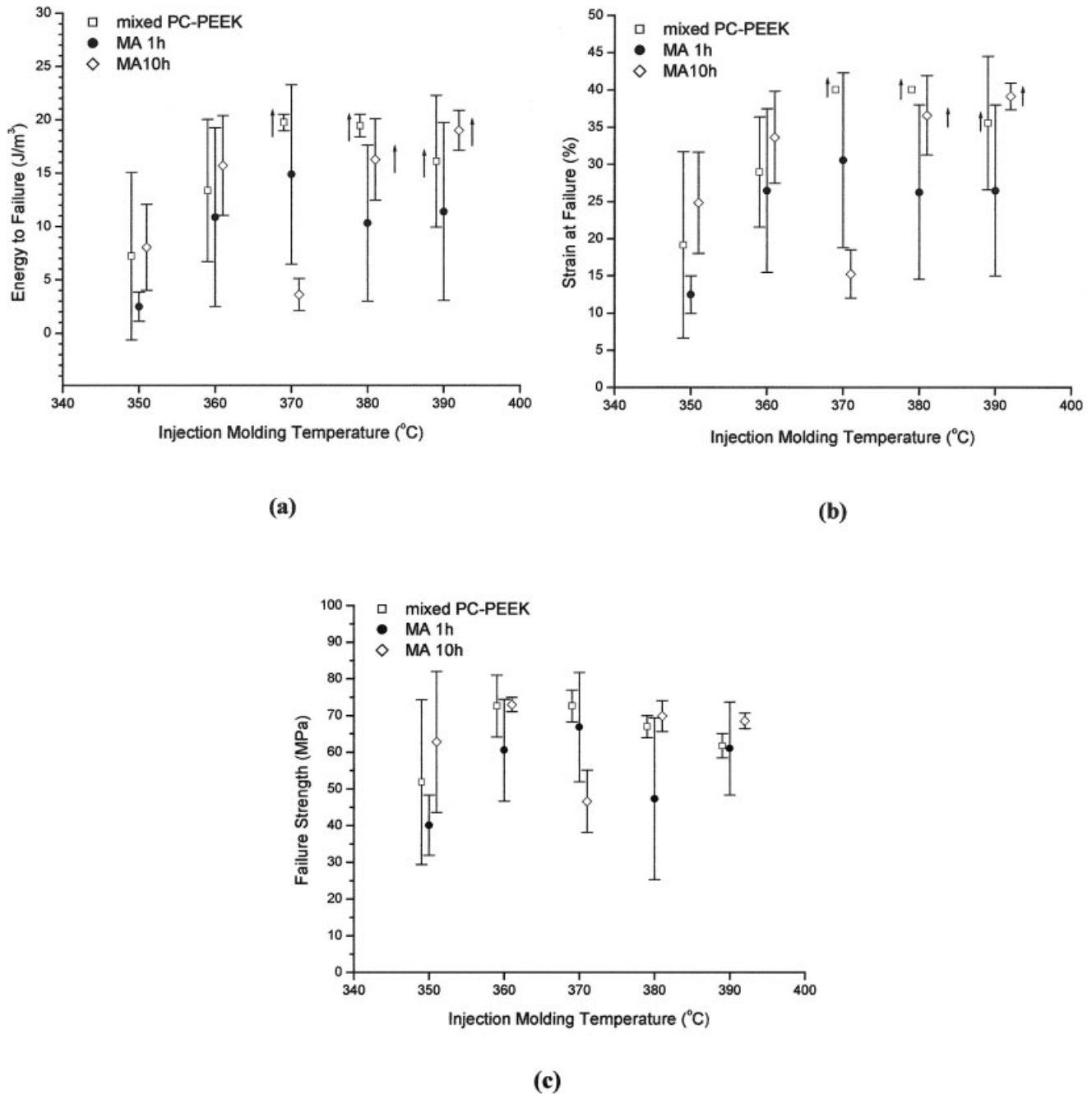
Figure 6 Property changes with the injection-molding temperature for mixed PC–PEEK, MA 1h, and MA 10h samples: (a) energy-to-failure, (b) strain-at-failure, and (c) failure strength. The arrows indicate samples for which the actual values were higher than the measured values because the test was stopped before fracture. Data points for mixed PC–PEEK and MA 10h samples have been slightly shifted horizontally around each injection-molding temperature for clarity. Mean values and standard deviations are reported.

mechanical properties was attributable to residual stresses in the coupons trapped during the molding process of this highly nonequilibrium structure. A complete explanation for this behavior is given elsewhere.[17] For molding temperatures of 360°C and higher, statistical T tests of the populations revealed that the measured properties of the two mechanically alloyed systems (MA 1h and MA 10h) were not improved over those of the mixed PC–PEEK system. The

MA 10h samples exhibited more ductile behavior (higher energy-to-failure and strain-at-failure values) at the 350°C molding temperature than the mixed PC–PEEK or MA 1h samples. This behavior was attributable to the fact that mechanically alloying this system for 10 h resulted in a completely amorphous blend (evidenced by wide-angle X-ray data; see Fig. 7), lowering the viscosity and thereby improving the mold-filling capability at the lower end of the process-
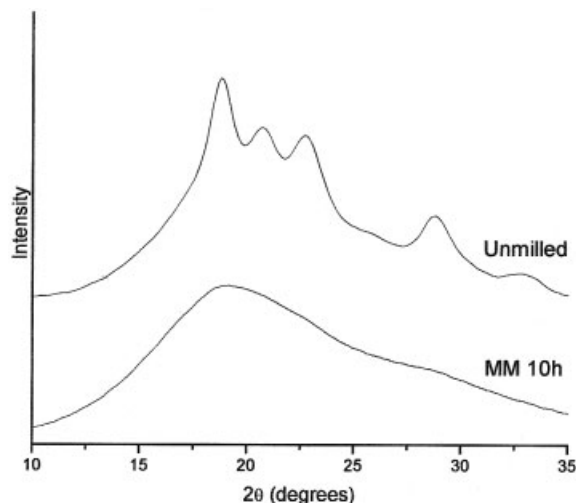
Figure 7 Wide-angle X-ray spectra of semicrystalline, unmilled PEEK and amorphous PEEK MM 10h.

ing temperature window at which the PEEK component was semicrystalline in the mixed PC–PEEK and MA 1h systems. Differential scanning calorimetry data (not shown) agreed with the wide-angle X-ray data.

These data demonstrate that the time and expense expended to cryogenically mechanically alloy this system did not result in a significant improvement in properties over those of samples that were hand-mixed before injection molding. Processing these materials in the ball mill (regardless of the time or the number of balls used) did not positively influence the properties of the subsequently injection-molded coupons. The lack of improvement (or, at some molding temperatures, the decline) in the measured properties with MA could be due to a number of factors. These include changes in the molecular weight distribution, thermal degradation, molding residual stresses, viscosity, and nonequilibrium microstructure. Residual stresses from the molding process can be blamed for the decreased properties of MA 10h coupons at one molding temperature (370°C). However, the presence of residual stresses in molded coupons cannot account for the lack of mechanical property improvement for the mechanically alloyed samples with respect to non-mechanically alloyed (mixed PC–PEEK) materials. Another possible explanation for the decrease in the measured properties of the mechanically alloyed samples is the measured decrease in the molecular weight of the starting materials. This is not conclusive, however, because the molecular weight of a polymer only influences its properties to a significant degree if the polymer is below its critical molecular weight for entanglement. Even after individually mechanically milling the materials for 10 h, we found that the mo-

lecular weight averages of both materials were above their respective critical molecular weights for entanglement.

One would expect a measurable improvement in the mechanical properties of coupons made from mechanically alloyed powders if the intimate mixing of the two phases achieved by the MA process were retained after subsequent processing. These results, however, indicate that the efforts to mechanically alloy this system did not result in superior mechanical properties compared to those of a hand-mixed system and, therefore, raise questions regarding the microstructure of the injection-molded coupons. This issue is examined in another work.[17,21]

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