Morphological and Structural Development of Poly(ether ether ketone) During Mechanical Pulverization

Mei Liang,[1] Canhui Lu,[1] Yigang Huang,[2] Changsheng Zhang[2]

[1]*State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu 610065, China*
[2]*The Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang 621900, China*

ABSTRACT: Micron size particles of poly(ether ether ketone) (PEEK) were prepared by self-made pan-type milling equipment operated at ambient temperature. The changes of particle morphology, crystalline properties, thermal behavior, and viscosity-average molecular mass during milling were studied by SEM, WAXD, DSC, TGA, and viscosimetry analyses, respectively. SEM analysis indicated that pan-milling firstly destroyed the original structure of PEEK through squeezing in-between mill pans, then to produce fine powder undergoing the processes of deforming and size reduction. The average particle size of PEEK was reduced to 100 μm only after 5 cycles of pan-milling and reached less than 50 μm after 50 cycles. DSC analysis showed that crystallinity of PEEK decreased with the pan-milling cycles, agreed with WAXD data. The crystallinity of PEEK decreased from 46.2 to 39.9% of 50 pan-milling cycles was offered. The glass transition temperature increased slightly along with pan-milling cycles. Mechanochemical effects caused by pan-milling were also studied. Viscometer test exhibited that molecular weight dropped quickly at earlier pan-milling stage then decreased slightly during later pan-milling. Pan-milling technique is an efficient, clean, and environmental friendly method for preparing fine PEEK powder. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3895–3902, 2007

Key words: morphology; poly(ether ketones); microstructure; degradation

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a semicrystalline thermoplastic with excellent thermal stability and processability, good mechanical properties at elevated temperatures, and fine solvent resistance.[1–3] It has a glass transition temperature of about 143°C and a high melting temperature in the range from 330 to 350°C. These properties make PEEK attractive as a high performance matrix for carbon fiber reinforced composites, and also for molded objects when particularly good thermooxidative stability is required.[4] Fine particulate of semicrystalline PEEK are desirable for both composite powder processing, and as high performance molding and sintering compounds by consolidating to produce void free components.

Brink et al.[5] have reported a process for preparing submicron diameter PEEK particles by rapidly hydrolyzing a soluble precursor polymer, poly(ether ether ketimine) to PEEK. The polymer rapidly nucleated and crystallized from the supersaturated PEEK solutions in the form of small particles. Facinelli et al.[6] describe a complementary ''rapid quenching'' method for generating small PEEK particles via supersaturated PEEK solutions. PEEK was dissolved at temperatures near its melting point in a mixture of terphenyls and quaterphenyls; then the solution was quenched to a temperature between PEEK's T_g and T_m (about 225°C) by adding a room temperature mixture of biphenyl ether and biphenyl. The rapid drop in temperature also creates a supersaturated PEEK solution and produces fine PEEK particles rapidly. This rapid quenching is desirable in that it eliminates the necessity for a separate synthesis process in preparing a soluble precursor and can get fine particles about 1 μm. But the two methods mentioned above were fussy operating, and produced a mass of solvent. It is an expensive and polluting method for preparing fine polymer powder.

In this article, a mechanical milling technique has been introduced to prepare fine polymer powder. Even though the mechanical milling, e.g., high-energy ball milling, technique has been extensively applied to metal and mineral systems, recent studies carried out in polymeric materials have shown that this technique is suitable to introduce structural changes affecting the physical properties of the poly-
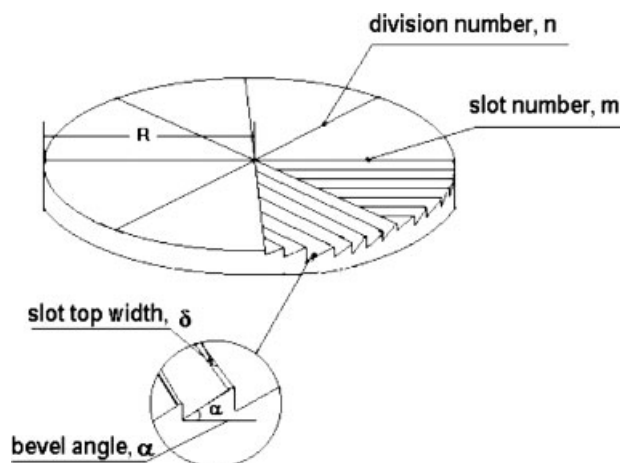
mer.[7–10] Mechanical milling has been also used for blending two polymers in solid state, overcoming the problems associated with the most common methods such as solution or melting. Pan and Shaw applied mechanical milling to polyamide, obtaining a material with high hardness and compressive strength.[7] Front et al. studied the influence of milling on the thermal behavior of poly(ethylene terephthalate) and bisphenol A polycarbonate, they also applied this technique to obtain PEEK powder with a grain size ranging between 100 and 200 μm.[8–10]

However, for most existing pulverizing and milling equipment, the high-energy consumption and low efficiency of the preparation of polymer powder are unavoidable. For instance, IKA A10 ball mill, the sample mass milled is about 2 g every time, but the product-to-ball weight ratio is 1:30.[11] Another, cryogenic conditions are usually required to pulverize polymers.[12–15] Nevertheless, this method deserves particular consideration because of its convenience and simplicity of operation, and its potential to disperse polymeric particles with other materials in-situ.

In our previous work, a novel pulverizing equipment, pan-type mill, especially designed for pulverizing polymers, was developed. Figure 1 is a simple scheme of the pan-mill equipment and Figure 2 shows the structure of its key part, the milling pans. Theoretical analysis demonstrated that this equip-
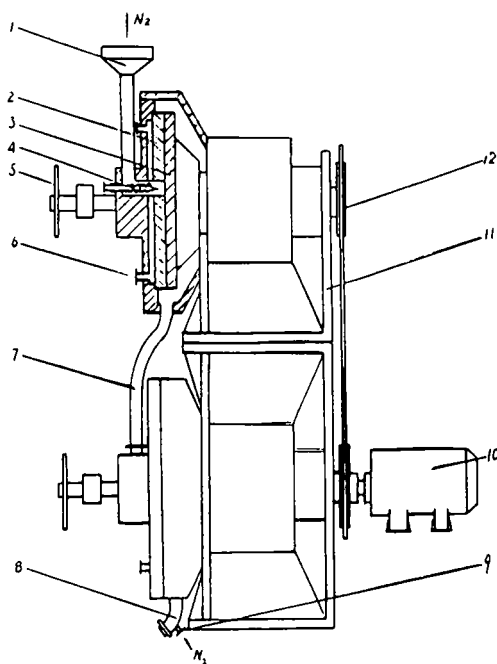
Figure 2 Schematic diagram of inlaid pan of pan-type milling equipment.

ment has excellent pulverizing and dispersing effects on polymeric materials owing to the ingenious design derived from the traditional Chinese stone-mill. Functioning like a pair of three-dimensional scissors, it can exert a strong squeezing force in normal direction and a shearing force in both the radial and tangential directions. Hopefully, this equipment can be used to pulverize brittle and ductile polymers. And we have successfully prepared many polymer powders by such a mechanical milling equipment, including ultrafine PA6 powder, HDPE/graphite composites, PP/carbon nanotube composite powder, ultrafine PP/iron composite powder, and etc.[16–19]

In the present study, we aimed to present the fine structure, morphology, and crystalline properties of PEEK micro powders prepared through pan-type mill. The changes of structure and morphology were characterized by FTIR, DSC, WAXD, and SEM methods. The approach proposed for preparing polymeric fine powder at ambient temperature is viable, highly efficient, environmentally friendly, and easy to be industrialized.

EXPERIMENTAL

Materials

PEEK powder (relative viscosity = 1.2, in 98% H_2SO_4) was supplied by Changchun Jida Special Engineering Plastics. (Changchun, China). Concentrated sulfuric acid (98%) was supplied by Chengdu Kelong Chemical Reagent Factory (Chengdu, China).

Preparation of PEEK fine powder

PEEK original powders were fed into pan-mill through the feed inlet in the middle of the milling pans at a specific rotating speed and pan spacing.

Figure 1 Schematic diagram of the pan-mill equipment. 1, inlet; 2, stationary pan; 3, moving pan; 4, feeding screw; 5, handle; 6, medium entrance; 7, flexible tube; 8, outlet; 9, entrance of insert gas; 10, motor; 11, stand; 12, drive system.

Milled particles were discharged from the brim of the pans. The discharged powders were collected for the next milling cycle. The operation was performed at ambient temperature and the heat of formation during milling was removed by cooling water, and the rotation speed was 40 rpm.

Measurement and characterization

The particle size (mean diameter) and particle size distribution of PEEK were measured by Masterizer 2000 Laser Particle Analyzer. The suspension medium was water (ρ = 0.998 g/mL, η = 0.938 cP) and the dispersant agent was p-octyl polyethylene glycol phenyl ether (OP). The more accurate data were obtained by breaking up the flocculates ultrasonically.[6]

The intrinsic viscosity number at 25°C, $\eta_{25°C}$, is given in deciliter per gram units and measured in an Ubbelhode viscometer at 25°C in concentrated sulfuric acid according to ISO 1628/1-1984 (E). The diameter, length, and constant of the apparatus are 0.80, 120, and 0.01094 mm^2 s^{-2}, respectively. The intrinsic viscosity (η) was taken as the following equations:[20]

$$\eta_{25°C} = 1/\left[c \times 2 \times (\eta_{sp} - \ln \eta_r)^{1/2} \right] \qquad (1)$$

where η_r is relative viscosity, η_{sp} is reduced viscosity, $\eta_{sp} = \eta_r - 1$, c is concentration of PEEK solution.

The molecular structure was detected by Nicolet 20SXB FTIR spectrometer, ranging from 400 to 4000 cm^{-1}, resolution is 2 cm^{-1}.

The morphology of PEEK fine powder was observed with Jed JSM-590LV scanning electronic microscope (Japan) at an accelerating voltage of 10 kV. The PEEK micropowder was dispersed with alcohol, and then gold coated prior to SEM observation.

Differential scanning calorimetry (DSC) was conducted on DSC 204 (NETZSCH, Germany). Samples of 5–8 mg, placed in an open aluminum crucibles, were thermally analyzed at the heating rate of 10°C/min, the temperature ranging from 50 to 380°C, and the gas atmosphere is nitrogen. All reported transitions are from a second heating scan, and the degree of crystalline is calculated as follows[21]:

$$Crystallinity = (\Delta H_f/\Delta H_f^o) \times 100\% \qquad (2)$$

where ΔH_f^o is the heat of fusion for 100% crystalline material, and for PEEK, is 130 J/mg. ΔH_f is the actuarial heat fusion for PEEK.[22]

Thermogravimetric analysis (TGA) was conducted on TGA 2950 TG analyzer under a nitrogen purge at a heating rate of 10°C/min. Samples of 5–8 mg were placed in an open aluminum (Al) crucibles, with the temperature ranging from 400 to 900°C.

Wide angle X-ray diffraction (WAXD) measurements were performed at room temperature in a Philips Analytical X'Pert X-diffractometer, using Cu-K a radiation (λ = 0.1540 nm), an accelerating voltage of 40 kV and the current of 40 mA. WAXD data were collected from 2θ = 10°–50° with a step interval of 0.02°.

RESULTS AND DISCUSSION

Intrinsic viscosity number of PEEK

At room temperature, PEEK has been described as insoluble in all common solvents except for some strong acids such as 98% sulfuric acid and hydrofluoric acid. At an elevated temperature approaching the melting point, it has been found that PEEK can be dissolved in high-boiling point esters and diphenyl sulphone.[23] In this study, 98% sulfuric acid was chosen as the solvent of PEEK. The variation of the intrinsic viscosity number η of PEEK during pan-milling is shown in Figure 3. The η value decreases dramatically at the beginning of pan-milling. The reduction of η during the pan-milling process results from mechanochemical degradation of PEEK caused by strong shear force exerted on PEEK molecular chain. After 30 milling cycles, it levels off and reaches a limit value. The slight decrease in η is mainly attributed to the scission and recombination of PEEK macromolecular radicals. The fitting equation is as follows:

$$\eta = 47.59 + 9.474 \times \exp(-c/19.28) \qquad (3)$$

when c = 0, η is 57.06. η is expected to be 47.59, when c is going to be an infinite value. The relative constant is 0.968, indicating the fitting is effective.
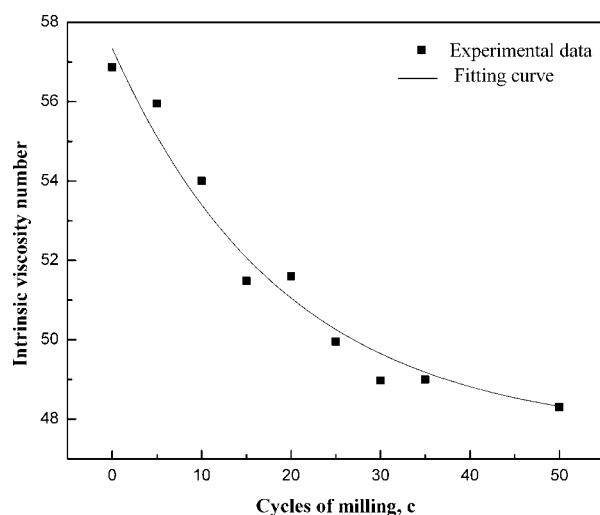
Figure 3 Effect of pan-milling cycles on the intrinsic viscosity number of PEEK (98% sulfuric acid, 25°C).
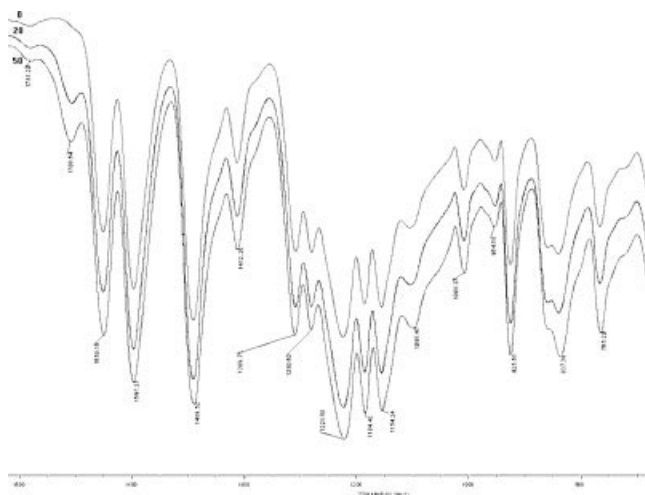
Figure 4 FTIR analysis of PEEK powder before and after pan-milling.

FTIR analysis of PEEK

As what were analyzed before, the PEEK original powder was pulverized and deformed. Mechanochemical degradation is often accompanied by the introduction of polar groups onto polymer chains. The FTIR analysis was conducted to confirm any new functional group generated during the degradation of PEEK. Figure 4 shows the infrared spectra ($1850–500$ cm^{-1}) of PEEK before and after milling. The transmittance at 1651 cm^{-1} characteristic C=O stretching vibration and, at 1597, 1489, 1412 cm^{-1} characteristic benzene ring bone vibration, and at 1222 cm^{-1} characteristic —O— asymmetric extending vibration, etc. In the carbonyl region, a decrease in transmittance around 1708 cm^{-1} was recorded. This weak peak fits the ester band of the O—C=O.[24,25] Since the transmittance corresponds to the aromatic ester structure, the decrease suggests a destruction of the ester bond. As seen in Figure 4, we can find that quantities and position of the other absorption bands are similar in three samples, which indicates that the pan-milling does not obviously influence on the other chemical structure of PEEK except of the ester structure.

Particle size reduction of PEEK during pan-milling

Figure 5 shows the effect of pan-milling cycles on average particle size [Fig. 5(a)] and particle size distribution [Fig. 5(b)] of PEEK powder. The result of Figure 5(a) indicated that the particle dimension decreased abruptly in the initial milling stage. When enough milling cycles were offered, the particles were pulverized and the size got down to finer. We can find a slight decrease of particle size after 20 cycles of pan-milling. This could be mainly attrib-

uted to the agglomeration of particles having finer size and the pulverization of the big particles. Namely, the pulverization and agglomeration occur simultaneously and reach an equilibrium state at a certain milling stage.

As showed in Figure 5(b), the particle size distribution of original PEEK powder was presented double peaks distribution, one peak is 500 µm and the other is 50 µm, this is because original PEEK powder is made of grains with much different size, and some of the bigger particle (200–2000 µm) is aggregated by many little primary grains (about 10–200 µm), the average particle size is 368 µm.

The average particle size is 110 µm after 5 cycles of pan-milling, and the particle size distribution is narrower than unmilled sample. After 50 cycles of pan-milling, the particle size is decreased to 37 µm, and the particle size distribution is the narrowest in the three samples. The experimental results showed
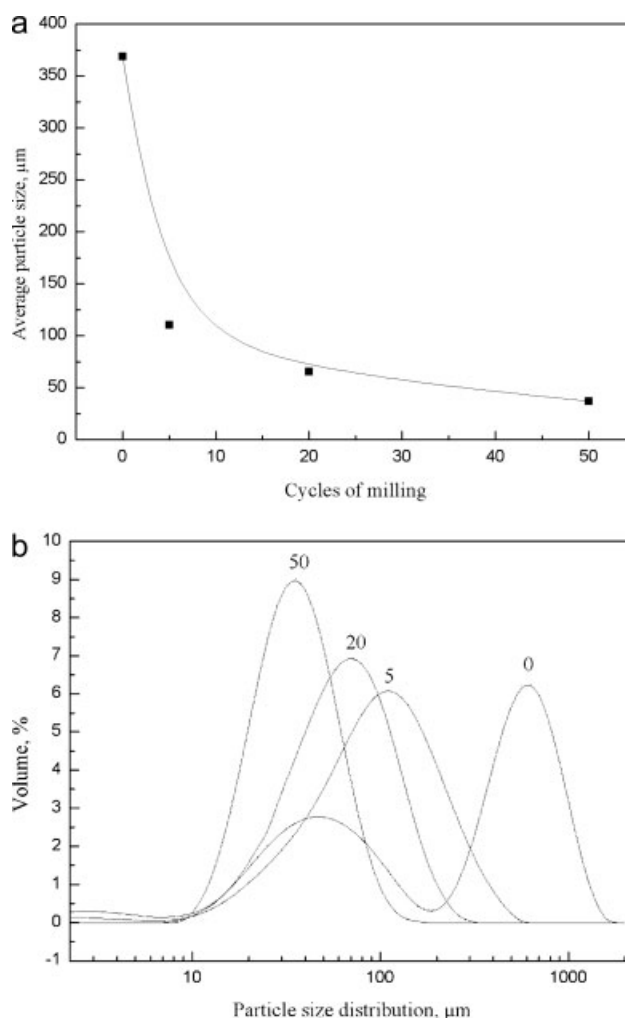
Figure 5 Effect of pan-milling on particle size and its distribution of PEEK powder (a) particle size (b) particle size distribution.
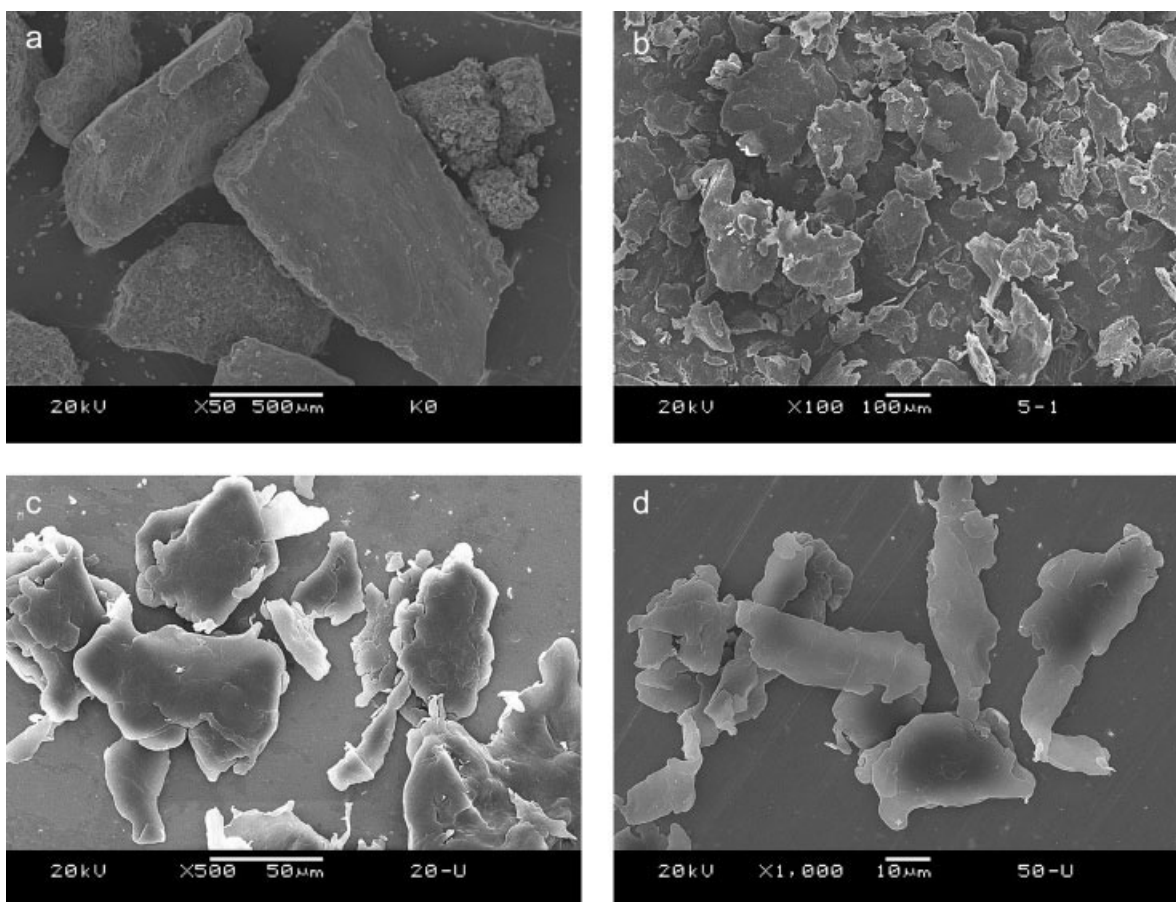
Figure 6 SEM photos of PEEK powder before and after pan-milling (a) unmilled PEEK (b) milled 5 cycles (c) milled 20 cycles (d) milled 50 cycles.

that the particle size and distribution was getting smaller and narrower respectively with the pan-milling cycles, because of the strong squeezing, shearing, and pulverizing action generated by pan-mill reactor. Finally, the PEEK micropowder was formed and the big fraction of particle size is less than 50 μm.

Morphology analysis

Figure 6 illustrates morphology of PEEK powder before and after pan-milling. It can be found from Figure 6(a) that original PEEK powder is made of particles of more than 1000 μm. As shown in Figure 6(b–d), the PEEK particles were deformed and pulverized, and squeezed to irregular flake-like shape. It is concluded from Figure 6 that the PEEK are pulverized down to microsize particle when enough mill cycle was offered.

X-ray diffraction patterns

X-ray diffraction patterns obtained before and after pan-milling were showed in Figure 7. The profile of

PEEK before milling, known as orthorhombic structure,[26–28] changes into a somewhat different one at the initial milling stage (5 milling cycles), which indicates the difference of crystal structure. It can be
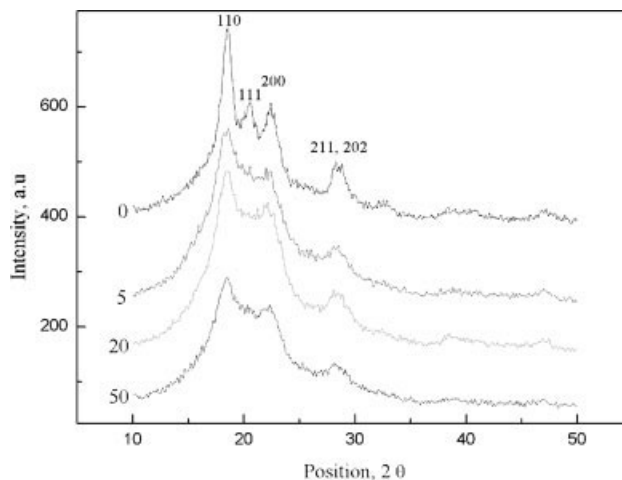
**Figure 7** WAXD patterns of PEEK powders before and after pan-milling.
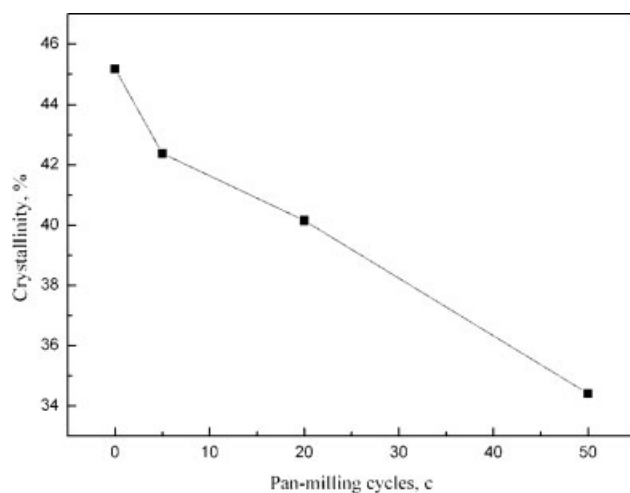
Figure 8 Crystallinity changes of PEEK before and after pan-milling.

seen from Figure 7 that there was a progressive change in width and height of peaks with increasing pan-milling cycles. This could be regarded as a change toward lower crystallinity or a gradual decrease in crystalline order. The degree of crystallinity of PEEK can be calculated by the following equation[29]:

$$W_{c,x} = \frac{I_{110} + 1.351\,I_{111} + 1.80\,I_{200} + 4.10\,I_{211}}{I_{110} + 1.35\,I_{111} + 1.80\,I_{200} + 4.10\,I_{211} + 0.91\,I_a}$$

$$(4)$$

where I is the integral intensity of different crystal face, I_a is the integral intensity of amorphous part, and the calculated results are showed in Figure 8. The data indicate that the crystallinity of PEEK decreases with the pan-milling cycles. The material suffered from strong shear deformation and the crys-
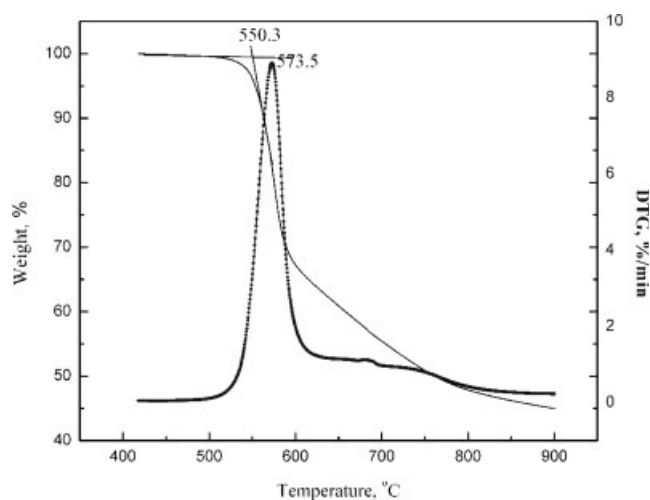
Figure 9 Thermogram curves for decomposition reaction of PEEK.

TABLE I
TGA Analysis Data of PEEK Powder

Sample	T_{os} (°C)	T_1 (°C)	T_2 (°C)
Before milling	550.3	573.5	–
Milled 20 cycles	544.7	564.1	743.5
Milled 50 cycles	544.7	569.7	648.5

talline lattice was destroyed afterward. Once the shear action is strong enough, some crystalline lattice breaks up and transfers into amorphous structure.

TGA analysis

Figure 9 is a continuous trace of change in sample weight as a function of temperature where PEEK was heated from 400 to 900°C and a high decomposition temperature (loss 5 wt % in T_d = 553.5°C) was observed. The TGA data of unmilled and milled samples are listed in Table I. After 20 cycles of pan-milling, the initial decomposition temperature of PEEK powder decreases slightly, illustrating that pan-milling results in faster degradation and lower onset temperature (T_{os}). Pan-milled PEEK undergoes two steps of decomposition and the heat resistance drops with pan-milling cycles. The mechanism and kinetic parameters associated with the thermal degradation of PEEK have been studied in the past.[30–35] According to Hay and Kemmish,[33] degradation in PEEK is initiated by random homolytic scission of either the ether or the carbonyl bonds in the polymer chains; however, there is conflicting evidence about which bond is more stable. From the results of FTIR, we can see that the ether bond is more stable than carbonyl bonds, or the thermal stability will conversed. A similar observation has also been reported earlier.[36]

DSC analysis

The DSC data of PEEK powder before and after pan-milling are listed in Table II and the melting curves are illustrated as Figure 10. The melting peak temperature increases and the crystallinity decreases with the pan-milling cycles, respectively. The drop of crystallinity shows that the pan-milling destroys some crystalline structure, which is in accordance with WAXD analysis very well. The cause of the rise

TABLE II
DSC Analysis Data of PEEK Powder for the First Temperature Programming

| Sample	ΔH_f (J/mg)	T_{peak} (°C)	Crystallinity (%)
Before milling	60.05	339.0	46.2
Milled 05 cycles	57.33	343.9	44.1
Milled 20 cycles	56.35	344.7	43.3
Milled 50 cycles	51.88	344.8	39.9
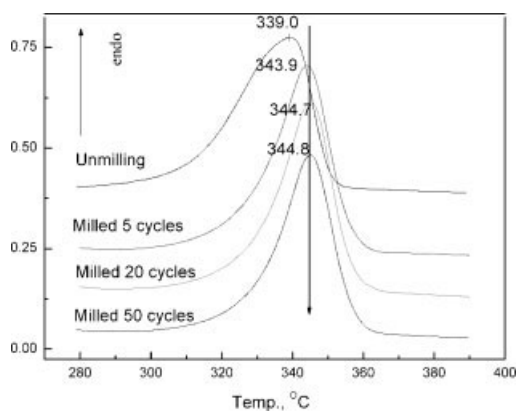
Figure 10 Effect of pan-milling on melting curves of PEEK.

of melting point probably is that the pan-milling mainly destroys the imperfect fraction of crystalline region.

As seen from Figure 11, glass transition temperature increases with the cycles of pan-milling. A previous study reported that aromatic ethers are dissociated from main molecular chains and subsequently recombined to esters by UV radiation.[37–39] Crosslinking reactions are caused in parallel to chain scission for the mechanochemical treatment of aromatic polymers.[38,40,41] The main chain scissions occur as consequences of primary mechanochemical degradation and secondary radical formation.[42] If free radicals migrate, they can recombine with other radicals and then produce crosslinking.[38,40,42] According to these studies, our chemical analysis results indicate that pan-milling causes both chain scission and crosslinking.

The effect of crosslinking could definitely be seen in the results of thermal properties after pan-milling. The T_g of pan-milling sample was shifted to higher
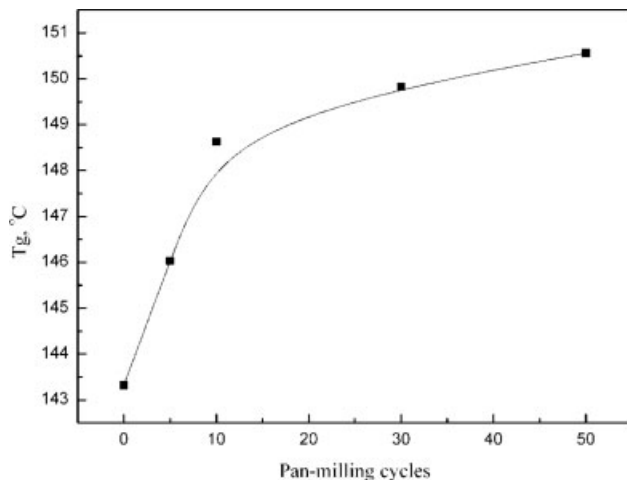
temperature. ΔH_c and ΔH_m decreased after pan-milling. Similar aromatic polymer results regarding the change of thermal parameters caused by ion or UV irradiation have been reported.[40,43–45] Based on the thermal parameters of previous studies and our tests, mechanochemical treatment clearly causes crosslinking. The increase of T_g suggests that the crosslinking degree similarly increases with the pan-milling cycles.

CONCLUSIONS

PEEK can be effectively pulverized to a micro size powder by the specially designed pan-mill equipment at ambient temperature. The primary particle size of the PEEK was reduced to below 50 μm after 50 cycles of milling, without additional milling media. The particle size distribution of PEEK powder prepared through pan milling is in accordance with Gaussian distribution. DSC and WAXD results illustrate that the degree of crystallinity of PEEK is decreased through pan-milling treatment. The thermal stability and molecular chain activity are also influenced by the pan-milling. Occurrence of mechanochemical degradation and recombination is also confirmed by molecular weight change and FTIR analysis.

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Figure 11 Effect of pan-milling on glass transition temperature of PEEK powder.

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