

Fine Poly(ether ether ketone) Powders

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ABSTRACT: The physical form of polymers is often important for carrying out subsequent processing operations. For example, fine powders are desirable for molding and sintering compounds because they consolidate to produce void free components. The objective of this work is to prepare fine polymeric particulates suitable for processing into fiber reinforced polymer matrix composites. Micron size particles of poly(ether ether ketone) (PEEK) were prepared by rapidly quenching solutions of these materials. PEEK pellets were dissolved at temperatures near the PEEK melting point in a mixture of terphenyls and quaterphenyls; then the solution was quenched to a temperature between the T_g and T_m ($\approx 225^\circ\text{C}$) by adding a room temperature eutectic mixture of diphenyl ether and biphenyl. A supersaturated, metastable solution of PEEK resulted, causing rapid nucleation. Fine PEEK particles rapidly crystallized from this solution. The average particle size was measured using transmission electron microscopy, atomic force microscopy, and by light scattering of aqueous suspensions which had been fractionated by centrifugation. The average particle diameter was about $0.6 \mu\text{m}$. Three dimensional photomicrographs obtained via atomic force microscopy showed some aggregates in the suspensions. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1571–1578, 1997

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INTRODUCTION

Poly(ether ether ketone) (PEEK) (Fig. 1) is a semicrystalline thermoplastic with excellent thermal stability and melt processability, good mechanical properties at elevated temperatures, and good solvent resistance.^{1–3} It has a glass transition temperature of $\approx 143^\circ\text{C}$ and a melting point of $\approx 334^\circ\text{C}$. 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. Fine particulates of these semi-crystalline poly(ether ketone)s are desirable for both composite powder processing, and as high performance molding and sintering compounds.

We previously reported a process for preparing submicron diameter PEEK particles by rapidly hydrolyzing a soluble precursor polymer, poly(ether ether ketimine), to PEEK.⁴ Supersaturated PEEK solutions formed, and the polymer rapidly nucleated and crystallized from the solutions in the form of small particles. This paper describes 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 be-

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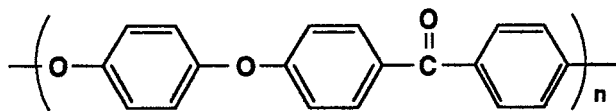


Figure 1 Poly(ether ether ketone) (PEEK).

tween PEEK's T_g and T_m ($\approx 225^\circ\text{C}$) by adding a room temperature mixture of diphenyl ether and biphenyl. The rapid drop in temperature also creates a supersaturated PEEK solution, and fine PEEK particles rapidly form. This provides a route to small, semicrystalline powders without any need to separately synthesize an amorphous precursor polymer.

EXPERIMENTAL

Materials and Apparatus

PEEK powder (Vitrex PEEK 450PF, melt viscosity 380–500 Pa s at 400°C and 1000 s^{-1} , average particle diameter $50\ \mu\text{m}$, all particles $< 104\ \mu\text{m}$ diameter) was purchased from Vitrex USA, West Chester, PA. Two heat transfer fluids were used to prepare and precipitate the PEEK powders; Therminol 75TM was purchased from Monsanto Chemicals, and Therminol VP-1TM, was generously donated by Monsanto. Therminol 75TM is a mixture of terphenyl and quaterphenyl isomers with 90% of the mixture boiling at $340^\circ\text{C}/50\text{ mmHg}$, and is a soft yellowish solid at room temperature (melting point $40\text{--}70^\circ\text{C}$). Therminol VP-1TM is a eutectic mixture of biphenyl and diphenyl ether (73.5 wt % diphenyl ether) with a boiling point of 257°C at 760 mmHg . It is a clear liquid at room temperature. Toluene (Ashland Chemicals, Reagent Grade) and THF (Fisher, Reagent Grade), used as extraction solvents to remove residual heat transfer fluids after particle formation, were used as received. The reaction vessel consisted of a 50 L roundbottom glass flask equipped with a heating mantle, a modified TurbomixerTM stirring assembly, thermocouple, and nitrogen inlet and outlet. The stirring assembly consisted of a 6" oval, variable pitch coiled spring, mounted perpendicular with respect to the shaft axis to the end of a 3/4" diameter shaft. A 6" marine propeller was mounted 7" above the coil. All materials used for the stirring assembly were 316 SS.

Particulate Formation

Therminol 75TM (15.5 kg) was charged to the flask and heated to 80°C to melt the solvent. PEEK

powder (2.15 kg) was added to the fluid, and the sides of the flask were rinsed with 2 kg Therminol VP-1TM. The mixture was stirred at 300 rpm and heated to 340°C for 4 h under a nitrogen atmosphere to dissolve the polymer; then the heating mantle was turned off, and the temperature was allowed to drop to 330°C . A clear, dark solution of PEEK in Therminol 75TM resulted. The stirring rate was increased to 1500 rpm, and 16 kg of Therminol VP-1TM was added at 25°C over 25 s to produce a PEEK solids content of $\approx 6\text{ wt } \%$. The temperature of the mixture fell to 225°C . The PEEK particles precipitated almost instantaneously after $\sim 12\text{ kg}$ of the Therminol VP-1TM had been added. It should be noted that stirring was inefficient after particle precipitation, but this did not cause severe aggregation of the particles. The mixture was allowed to cool to 100°C , then diluted with 16 L toluene. The resultant slurry was subdivided into two identical flasks to facilitate stirring. An additional 16 L of toluene was added to each of the flasks, and the slurries were stirred overnight at room temperature.

To remove the major portion of the heating fluids, the aggregates of PEEK powder were isolated by vacuum filtration in a Buchner funnel, resuspended in toluene (60 L total) and stirred under nitrogen at 100°C for $\approx 12\text{ h}$, filtered, resuspended in THF (60 L total) and refluxed for $\approx 12\text{ h}$, filtered again, and washed with hot deionized water twice, then suspended in deionized water. Note that, in the absence of a suitable suspension stabilizer, the small PEEK particles form a highly viscous suspension in water. Gas chromatography was used to monitor removal of this major portion of the heating fluid from the particles. Both residual Therminol VP-1TM and Therminol 75TM remained in the THF effluent after filtration.

To establish the approximate concentration of the suspension, 200 mL of the aqueous PEEK suspension was diluted with 200 mL of THF, filtered in a Büchner funnel, and washed with an additional 100 mL of THF. These particles were air dried for 2 days, then dried at 40°C in vacuo for $\approx 48\text{ h}$ to obtain 13.3 g of PEEK containing small amounts of water, THF, and residual heat transfer fluids. It should be noted that if the small PEEK particles are dried above $\approx 80^\circ\text{C}$, they irreversibly flocculate. Thus, it is important to maintain relatively low drying temperatures if the small particle form is to be preserved.

Purification of the PEEK Powder

Approximately 13.3 g of isolated PEEK particles (dried at 40°C) were refluxed in 290 mL THF for

Table I GC–Mass Spectrometry Analysis of PEEK Purification

Sample	Conc. (mg/mL)	Area (Diphenyl Ether) TIC ^a	Area (<i>o</i> -Terphenyl) TIC	mg T-VP1/ g PEEK	mg T-75/ g PEEK
Biphenyl–diphenyl ether std.	0.418	755,366			
Terphenyl–quaterphenyl std.	0.410		341,901		
Sample 1 1st extraction		1,948,535	1,567,665	23.7	42
Sample 2 2nd extraction		120,471	102,612	1.5	2.8
Sample 3 3rd extraction		1900	739	.02	.02

^a Total ion chromatogram.

24 h, then cooled to 20°C. A sample of the supernatant THF was removed for analysis by GC–MS (gas chromatography–mass spectroscopy) (Sample 1, Table I). The PEEK was placed in a 43 mm × 123 mm cellulose extraction thimble and soxhlet extracted for 24 h. The PEEK was refluxed again in 290 mL fresh THF for 24 h, cooled, and a second sample of the supernatant THF was withdrawn (Sample 2, Table I). The PEEK was again soxhlet extracted in THF for 24 h, then refluxed in fresh THF (290 mL) for 24 more h, and a third sample of the supernatant was removed for analysis (Sample 3, Table I). The sample was soxhlet extracted for 24 h a final time.

Characterization

Gas Chromatography/Mass Spectrometry

A Fisons GC 8060 coupled with a Fisons VG QUATTRO Mass Spectrometer was used to analyze the samples. The DB-5MS column, 15 m long, 0.25 mm i.d., with a 0.25 μm film, was purchased from J & W Scientific. A 2 min solvent delay was used, and the gas chromatograph column temperature was ramped from 50°C to 300°C at a heating rate of 10°C/min. Helium was used as the mobile phase, at a flow rate of 1 mL/min. The pressure at the column head was 5 psi. A 1 μL sample volume was used. Note that because no internal standard was used in this analysis, the error in delivering the 1 μL sample becomes the major error in this analysis. This error is estimated to be ±10%.

Samples of each of the heating fluid mixtures were analyzed by GC–MS to identify peaks from the heating fluids. Biphenyl–diphenyl ether eutectic fluid (20.9 mg) was diluted to 50.0 mL with THF and 20.5 mg of the terphenyl–quaterphenyl fluid was diluted to 50.0 mL with THF. One μL

aliquots of each standard were injected into the GC–mass spectrometer.

Thermal Analysis

Differential scanning calorimetry was conducted on a Perkin–Elmer Series 7 thermal analyzer under a nitrogen purge at a heating rate of 10°C/min. All reported transitions are from a second heating scan. Thermogravimetric analysis was conducted on a Perkin–Elmer Series 7 thermal analyzer under an air purge at a heating rate of 10°C/min.

Rheological Measurements

A Bohlin VOR Rheometer with the fluids head and high temperature cell heating oven was used for rheology measurements. The torque bar had a calibrated torsional resistance of 1.52 g/cm. The 25 mm diameter parallel plate fixture was used. Dynamic viscosity measurements were taken at 380 ± 1°C with an oscillatory frequency of 0.1 Hz. Nitrogen gas was used as the heating medium. The as-received PEEK 450PF from Victrex was dried at 120°C for 2 h in a convection oven prior to sample preparation. The precipitated PEEK particles were dried under vacuum for 48 h at 160°C prior to sample preparation. Each sample was then pressed at room temperature into a 25 mm diameter, 1.4 mm thick disk using a matched cylindrical mold and a laboratory press.

Particle Size Analysis

The particle size (median diameter) and particle size distribution were measured by a centrifugal particle size analyzer (model SA-CP3) by Shimadzu. This instrument measures the turbidity of the sedimenting suspension and utilizes Stokes law to correlate the sedimentation rate to particle

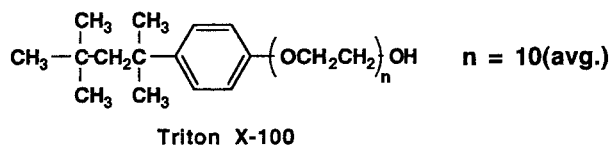


Figure 2 Triton X-100 stabilizer.

size. The range of size analysis was 0.3–100 μm . The solvent density and viscosity as well as the density of the particle are required in the calculations.⁵ The suspension medium was water ($\rho = 0.998 \text{ g/mL}$, $\eta = 0.938 \text{ cP}$). Density of the particles was approximated by that of bulk poly(ether ether ketone) (1.3 g/mL). A dilute aqueous suspension was prepared for this analysis by adsorbing Triton X-100 stabilizer (Fig. 2) onto the particles, then by breaking up the flocculates ultrasonically.

The particle size was also examined by scanning transmission electron microscopy (STEM). The samples were placed on a Formvar Support Film Grid (200 mesh) obtained from Electron Microscopy Services as a dilute aqueous suspension stabilized by Triton X-100 surfactant ($\approx 0.5\% \text{ v/v}$), dried in air overnight, and then examined directly using a Philips 420T scanning transmission electron microscope (STEM) operating at 100 kV in the STEM mode.

The atomic force microscope (AFM) used was a Nanoscope IIIa Dimension 3000 Scanning Probe Microscope (Digital Instruments). AFM images were recorded in the tapping mode in air. Samples were prepared by placing a drop of a dilute aqueous suspension (prepared using a Triton X-100 stabilizer) on a glass substrate. After drying at room temperature, the samples were directly imaged. The cantilever used for the measurements had a spring constant between 20–100 N/m.

RESULTS AND DISCUSSION

The physical form required of thermoplastic polymers is often coupled with subsequent processing operations to be used. Fine particles are desirable for molding and sintering compounds because smaller particles coalesce more efficiently under analogous temperature/time cycles to produce void free components.^{6,7} The driving force for this behavior is reduction in the large amount of high energy surface area of small particles during consolidation. We are particularly interested in possibilities for preparing carbon fiber reinforced com-

posites by applying semicrystalline polymer powders to fiber tow, or fabric preforms, from stabilized aqueous suspensions.⁸ Carbon fibers are typically 6–8 μm in diameter. Carbon fiber reinforced structural composites are prepared with high fiber volume fractions ($\approx 60 \text{ vol } \%$) to take full advantage of the high stiffness and strength of these fibers. The space, at the closest point, between the fibers is calculated to be $\approx 2 \mu\text{m}$ by assuming an idealized hexagonal packing arrangement of fibers, 60 vol % fiber, and 8 μm diameter fibers. Thus we anticipate that small particles may afford better bundle penetration, and result in more homogeneous particle distributions throughout the bundle, than larger particles.

Methods for obtaining fine particulates from semicrystalline polymers such as PEEK by precipitation, or coagulation, are limited because the materials are essentially insoluble under mild conditions. Numerous solvents have been identified for PEEK,⁹ but temperatures near its melting point are required for dissolution. Grinding operations require extensive time to achieve particles even as small as about 20 μm diameter, and are impractical for smaller particles. We previously reported a method for forming submicron diameter PEEK particles by synthesizing a soluble, ketimine containing, precursor to PEEK; then by rapidly hydrolyzing the ketimine to the corresponding ketone under acidic conditions (Fig. 3). Conversion to the ketone could be quantitatively achieved within seconds under certain conditions,⁴ thus producing a supersaturated solution of PEEK in the *N*-methylpyrrolidone solvent. The rate of particle nucleation in the supersaturated solutions was fast; many particles formed; and submicron particles resulted. From a practical standpoint, we were interested in developing a method for creating supersaturated PEEK solutions without the need for first preparing a soluble polymer in a separate synthetic procedure.

The process reported in this paper (Fig. 4) is to dissolve PEEK in a high boiling solvent at approximately the PEEK melting point. Therminol 75TM, a mixture of terphenyl and quaterphenyl isomers, has a boiling point well above the PEEK melting point and is a solvent for PEEK near the polymer melting point where it cannot crystallize.⁹ The all aromatic structure of the solvent is important to maintain good thermooxidative stability at the elevated temperatures required. The temperature of this mixture can then be rapidly quenched to yield the required supersaturated

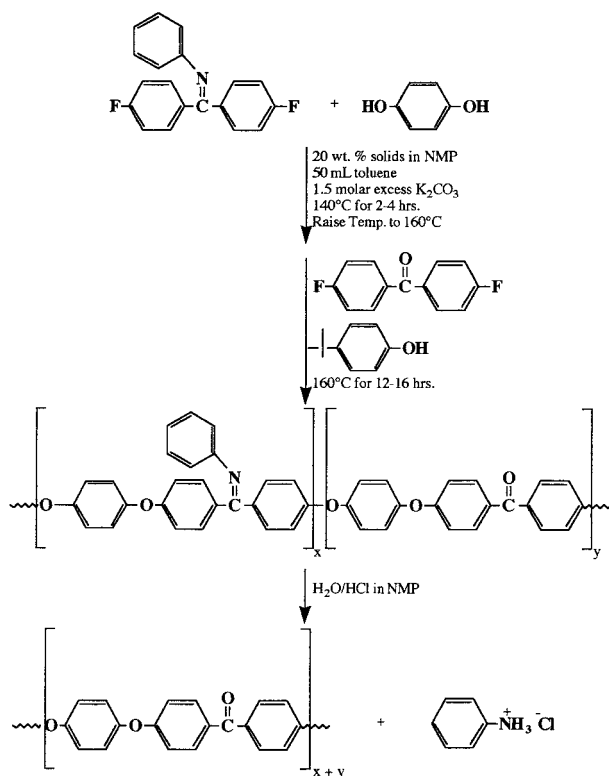


Figure 3 Preparation of the PEEK-ketimine precursor, then hydrolysis to PEEK.

PEEK solution by pouring a colder solvent into the solution. Therminol VP-1TM was chosen as the quenching solvent because it is a liquid at room temperature (unlike Therminol 75TM), and yields a miscible mixture of PEEK and the two fluids. A dark, clear PEEK solution results for an instant after quenching, then the PEEK particles rapidly precipitate. Upon particle formation, the mixture

becomes quite viscous. The volume of suspension in the experiment detailed herein was ≈ 35 L. Stirring was visibly inefficient after the particles formed, yet approximately 0.5–1 μm diameter particles resulted (Figs. 5 and 6). While we assume it is important to rapidly mix the cold solvent into the hot PEEK solution, the small particle size suggests that the stirring rate was probably not very important during the particle precipitation step (once the supersaturated solution was formed).

Analysis of the PEEK particles after formation showed that residual levels of the heat transfer fluids had become trapped in the particles. The fluids were removed by repeated extractions in THF, and GC-mass spectrometry was used to monitor the THF effluents. Diphenyl ether and *o*-terphenyl in the Therminol VP-1TM (T-VP1) and Therminol 75TM (T-75), respectively, were the components in the heat transfer fluids present in the greatest amounts. Therefore, the decrease in heat transfer fluids in the THF extraction solvent was quantified by analysis of these two components. The peak areas of the remaining components in the heat transfer fluids decreased in a manner approximately proportional to the diphenyl ether and the *o*-terphenyl peak areas. The mass of Therminol VP-1TM and Therminol 75TM extracted from the PEEK were calculated for each reflux sequence using the relationships between the standards concentrations and the total ion chromatogram areas (Table I). This analysis showed that almost all of the residual fluids could be removed in the first extraction.

The size of the PEEK particles prepared using the quenching method was analyzed using trans-

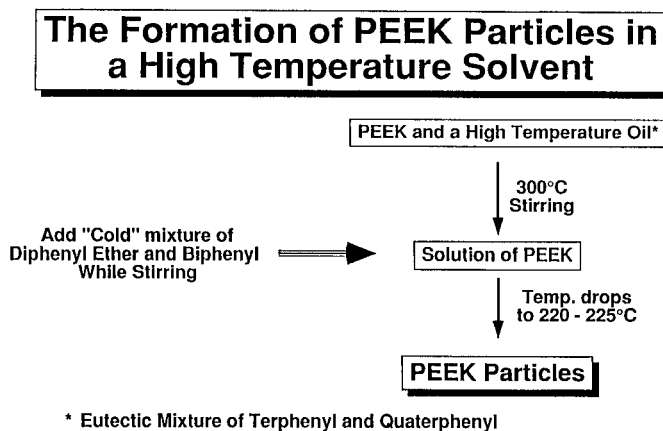


Figure 4 Preparation of PEEK particles by rapidly quenching PEEK/Therminol solutions.

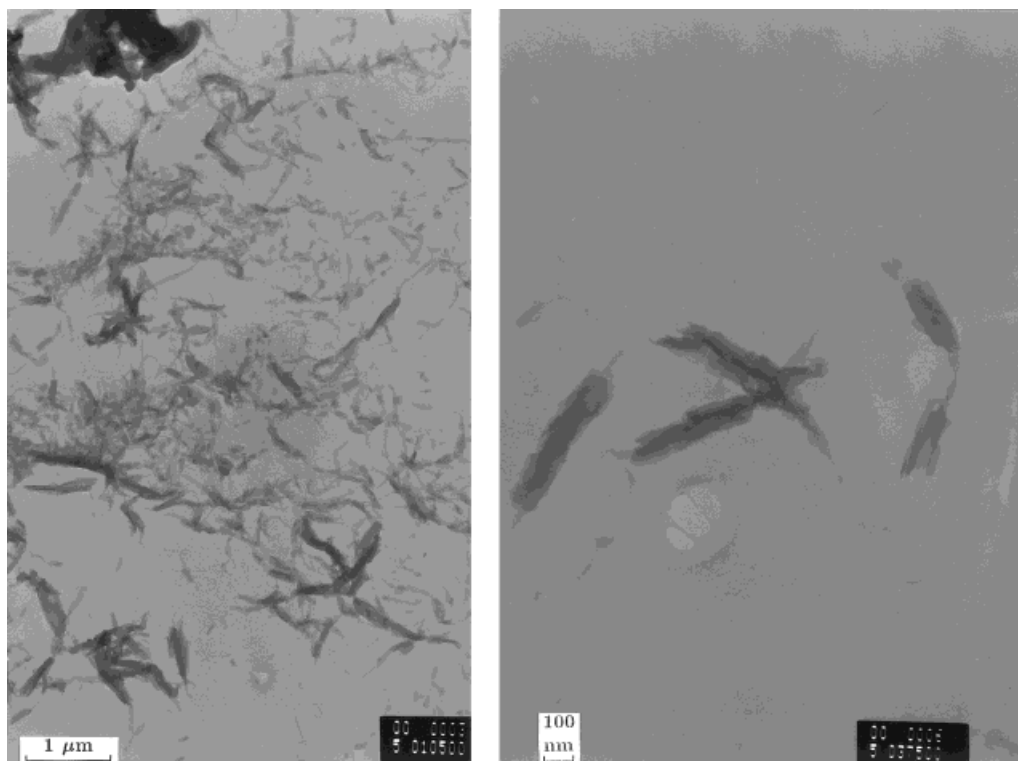


Figure 5 Scanning transmission electron photomicrographs of particles prepared by rapidly quenching PEEK/Therminol solutions.

mission electron microscopy, atomic force microscopy, and particle size analysis with a light scattering detector. In the absence of a suspension stabilizer, these particles form aggregates in water. Aqueous suspensions were prepared by adsorbing Triton X-100TM, a steric suspension stabilizer, onto the PEEK particles, then ultrasonification was used to break up the PEEK aggregates in the presence of the stabilizer. The particle size analyzer separates fractions of the particles by centrifuging fractions from the suspension, then by measuring the average particle size remaining in suspension by light scattering. Using this method, a median particle diameter of $\approx 0.6 \mu\text{m}$ was obtained. A drop of the suspension was placed on a substrate, and the water was evaporated. The resultant samples were analyzed by both scanning transmission electron microscopy and atomic force microscopy (Figs. 5 and 6). The transmission electron photomicrographs show small elongated structures on the order of $1 \mu\text{m}$ long and $0.1 \mu\text{m}$ wide together with a minor amount of somewhat larger particles. A three dimensional atomic force micrograph of one of the particle structures suggests that these are aggregates of smaller particles. It is suspected that

small particles precipitated from the solution, then aggregated. The oblong nature of the particles is presumed to be a result of the shear force imposed by stirring.

Thermal analysis of the particles prepared by rapid quenching demonstrates that the percentage of crystallinity, as well as the transitions, are similar to the PEEK powder which was originally used for preparing the particles (Table II). The samples described in Table II are the PEEK as received from Victrex (prior to particle preparation), the PEEK particles which contained residual amounts of the heat transfer fluids (prior to the extractions described in Table I), and the purified particles. The level of crystallinity in the PEEK particles was calculated based on an enthalpy of fusion representing 100% crystallinity of 130 J/g .¹⁰ Calculations from the gas chromatography-mass spectrometry analyses showed that the second entry in Table II had approximately 6.5 wt % of residual heat transfer fluids which were later removed by the extractions. These impurities reduced the glass transition temperature by $\sim 3\text{--}4^\circ\text{C}$, and resulted in slightly reduced crystallinity. Thus, the heat transfer fluids which had become "trapped" in the material upon precipitation were probably at least

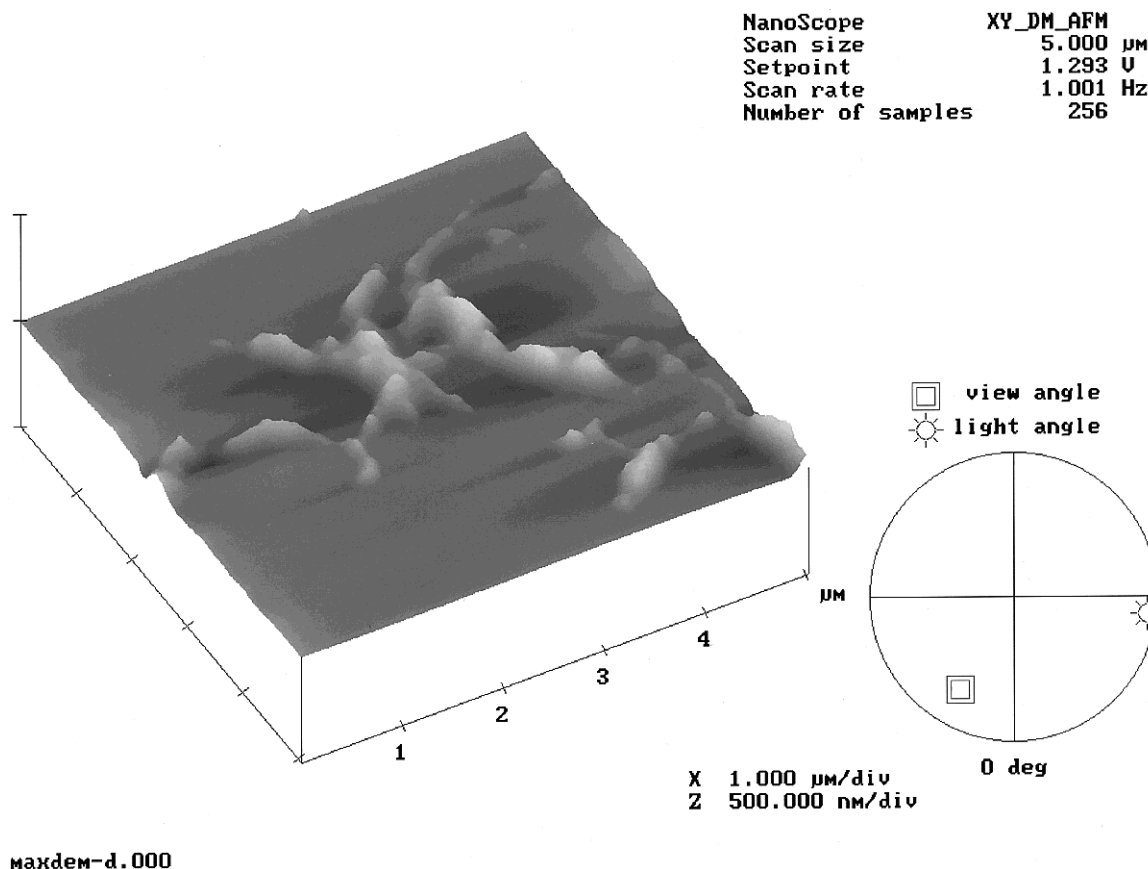


Figure 6 Atomic force micrograph of a PEEK particle aggregate.

partially mixed on a very small scale, rather than simply physically occluded in larger domains. The thermal properties of the purified PEEK particles were quite similar to the original material.

The complex melt viscosities of the as received material relative to the precipitated fine particles (purified as previously described) were compared at 380°C and 0.1 Hz. The as-received material had an initial complex viscosity under these conditions of approximately 2650 Pa s which increased gradually to 3450 Pa s over a 1 h period at 380°C. The viscosity of the fine precipitated particles had a significantly lower initial melt viscosity (≈ 1000

Pa s) which increased to 2650 Pa s over a 1 h period, then remained constant at that level for an additional hour. One plausible explanation for the low initial viscosity of the fine particles could be that very low levels of residual heat transfer fluids had been retained within the material, which volatilized during the first hour of heating at 380°C under the nitrogen purge used. Thermogravimetric analysis of this recovered material was conducted isothermally at 380°C under a nitrogen atmosphere. Consistent with the viscosity data, 0.47 wt % of the mass was lost within the first hour under these conditions, then approxi-

Table II Thermal Properties of the PEEK Before and After Particle Formation

Sample	T_g (°C)	T_m (°C)	ΔH_f (J/g)	Crystallinity ^a (%)
Victrix PEEK 450PF™	150-151	340	43	33
PEEK particles before extraction	146-147	341	39	30
Purified PEEK particles	149-150	339	41	32

^a Based on $\Delta H_f = 130$ J/g for 100% crystalline PEEK.

mately 0.1 additional wt % volatilized during the second hour. The fact that the viscosity remained constant after reaching the same level as the original material before precipitation was encouraging, since this suggests that the molecular weight and distribution of the precipitated material may be similar to the original PEEK. Although it is not within the scope of this paper, a detailed analysis of the rheology of the PEEK particles is warranted.

CONCLUSIONS

Fine, semicrystalline poly(ether ether ketone) particles can be prepared by forming highly supersaturated solutions of these materials. These supersaturated solutions can be formed by rapidly quenching the solutions with a cold solvent, or by chemically transforming a soluble material to the semicrystalline polymer isothermally. Rapid quenching is desirable in that it eliminates the necessity for a separate synthesis process in preparing a soluble precursor. The aromatic heat transfer fluids used for a solvent in this process appear to be good solvents for several commercial semicrystalline poly(arylene ether)s and poly(arylene sulfide)s. Notably, a similar process was successfully demonstrated on about a 1 L scale with poly(phenylene sulfide) (Phillips Petroleum) and with the poly(ether ketone) prepared from a mixture of terephthaloyl and isophthaloyl chlorides and diphenyl ether (DuPont's PEK material). Future work will focus on developing aque-

ous suspensions of these materials for composite fabrication.

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