Fine polymeric powders from poly(arylene ether ketone)s*

A. E. Brink, S. Gutzeit, T. Lin, H. Marand, K. Lyon, T. Hua, R. Davis and J. S. Riffle†

Chemistry Department, Chemical Engineering Department, and NSF Science and Technology Center for High Performance Polymeric Adhesives and Composites, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212, USA

(Received 8 July 1992; revised 4 August 1992)

A relatively new method for graphite composite formation, aqueous dispersion prepregging, could potentially circumvent many of the environmental and processing problems of the current methods. However, aqueous dispersion prepregging requires that the high-performance polymer be in the form of a stable colloidal dispersion, preferably of small uniform particles. This research will examine the formation of submicrometre particles from the high-performance thermoplastic polymer, poly(ether ether ketone) (PEEK), for use in aqueous dispersion prepregging. The procedure will involve first the synthesis of the monomer 4,4′-difluoro(*N*-benzohydroxylidene aniline) and the polymerization of this monomer and hydroquinone to form the amorphous PEEK derivative poly(ether ether ketimine). 4,4′-Difluoro(*N*-benzohydroxylidene aniline) can also be copolymerized with 4,4′-difluorobenzophenone to form a semicrystalline, soluble PEEK derivative. The subsequent hydrolysis of these derivatives to semicrystalline PEEK results in the formation of submicrometre particles.

(Keywords: poly(ether ether ketone); 4,4′-difluoro(*N*-benzohydroxylidene aniline); ketimine; particle formation; graphite composites; aqueous dispersion prepregging)

INTRODUCTION

Current technology for the production of graphite composites typically involves either solution or melt prepregging. High-performance thermoplastic polymers are soluble only in dipolar aprotic solvents such as 1-methyl-2-pyrrolidinone (NMP), which makes large-scale solution prepregging impracticable. Melt prepregging of these types of materials is also impracticable, owing to both their high thermal transitions (causing degradation at melt temperatures) as well as their high viscosities. Aqueous dispersion prepregging[1,2], a relatively new method, could potentially circumvent many of the environmental and processing problems as mentioned above. However, aqueous dispersion prepregging requires that the high-performance polymer be in the form of a stable colloidal dispersion, preferably of small uniform particles. This paper will examine the formation of submicrometre particles from the high-performance thermoplastic polymer, poly(ether ether ketone) (PEEK), for use in aqueous dispersion prepregging. The procedure first involves synthesis of the monomer 4,4′-difluoro(*N*-benzohydroxylidene aniline) (*Figure 1*). This monomer and hydroquinone are then polymerized to form the amorphous PEEK derivative poly(ether ether ketimine) (*Figure 2*)[3]. 4,4′-Difluoro(*N*-benzohydroxylidene aniline) can also be copolymerized with 4,4′-difluorobenzophenone and hydroquinone to form a semicrystalline, but soluble, PEEK derivative (*Figure 3*). The subsequent hydrolysis of these derivatives to semicrystalline PEEK under controlled conditions results in the formation of submicrometre particles.

EXPERIMENTAL

Materials

Difluorobenzophenone was kindly supplied by ICI Americas Inc., and purified by recrystallization from ethanol. Hydroquinone was purchased from Aldrich (>99.9% purity) and used as received. Aniline was purchased from Aldrich, and purified by vacuum distillation from calcium hydride. Toluene was purchased from Aldrich, and purified by washing twice with sulphuric acid, followed by water, 5% sodium bicarbonate and then water. This was then dried over calcium sulphate, then phosphorus pentoxide, and distilled from sodium. The 1-methyl-2-pyrrolidinone (NMP) was purchased from Aldrich, and purified by vacuum distillation from phosphorus pentoxide. The 3 Å molecular sieves were purchased from Aldrich and regenerated by heating to 180°C under vacuum. Potassium carbonate was also purchased from Aldrich, and dried under vacuum at 180°C.

Synthesis of 4,4′-difluoro(N-*benzohydroxylidene aniline*)

First, 120 g (0.55 mol) of 4,4′-difluorobenzophenone (used as received from ICI) and 80 ml (0.88 mol) of aniline

* Presented at 'Advances in Polymeric Matrix Composites', 5–10 April 1992, San Francisco, CA, USA

† To whom correspondence should be addressed

0032-3861/93/040825-05

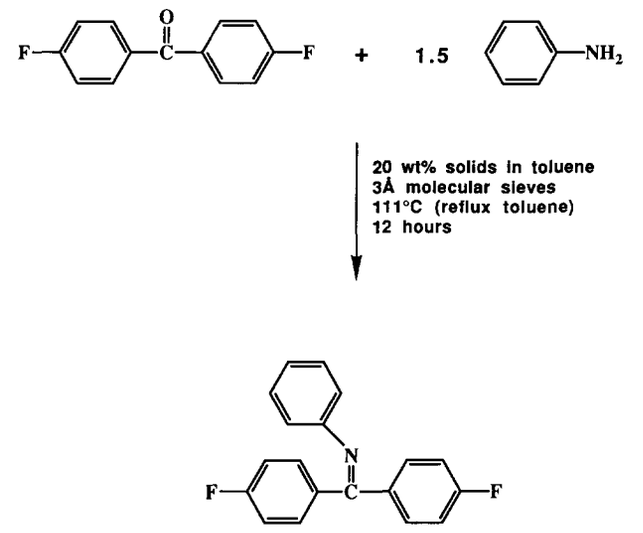
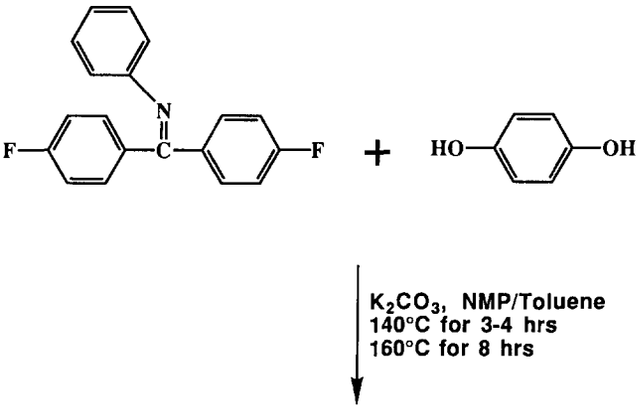


Figure 1 Synthesis of 4,4′-difluoro(*N*-benzohydroxylidene aniline)



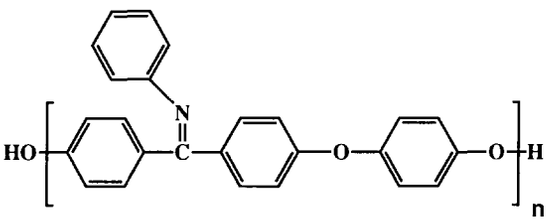


Figure 2 Synthesis of poly(ether ether ketimine)

were added to a two-necked round-bottomed flask equipped with a nitrogen inlet, Dean–Stark trap and a condenser. Then 500 ml of toluene were added along with about 300 g of 3 Å molecular sieves. This reaction mixture was heated to toluene reflux until 100% conversion to the ketimine had occurred as determined by ^{1}H n.m.r. The solvent and excess aniline were then removed by rotary evaporation. The resulting product was recrystallized twice from toluene to provide a pure yellow crystalline material with a melting point of 114–115°C in about 50% yield.

Synthesis of poly(ether ether ketimine)

The following is a procedure for the synthesis of a poly(ether ether ketimine) via nucleophilic aromatic substitution in a polar aprotic solvent. The molecular weight was controlled to 20 000 g mol^{-1} by offsetting the stoichiometry according to the Carothers equation to provide a hydroquinone-terminated polymer.

First, 0.0987 mol (28.936 g) of 4,4′-difluoro(*N*-benzohydroxylidene aniline), 0.100 mol (11.064 g) of hydroquinone and 0.15 mol (20 g) of potassium carbonate were dissolved in 200 ml of NMP in a 500 ml three-necked flask equipped with a condenser, Dean–Stark trap, overhead stirrer and nitrogen inlet. Then 60 ml of toluene were added as an azeotroping agent. The reaction mixture was heated to 140°C for 3 h and then at 170°C overnight. The solution was then diluted with 200 ml of tetrahydrofuran, and neutralized with 10 ml of glacial acetic acid. This was then precipitated into methanol/water (80:20), Soxhlet extracted with methanol and dried under vacuum.

Synthesis of poly((ether ether ketimine)-co-(ether ether ketone))

The following is a procedure for the synthesis of a poly((ether ether ketimine)-*co*-(ether ether ketone)) via nucleophilic aromatic substitution in a polar aprotic solvent. The molecular weight was controlled to 20 000 g mol^{-1} by offsetting the stoichiometry according to the Carothers equation by adding the monofunctional end-capping agent t-butylphenol.

First, 0.0455 mol (13.346 g) of 4,4′-difluoro(*N*-benzohydroxylidene aniline), 0.0897 mol (9.877 g) of hydroquinone and 0.103 mol (14.23 g) of potassium carbonate were dissolved in 200 ml NMP in a four-necked 500 ml flask equipped with an overhead stirrer, Dean–Stark trap, condenser and nitrogen inlet. Then 60 ml of toluene were added as an azeotroping agent. The reaction mixture was heated to 140°C for 3 h to dehydrate the system, and then to 170°C. Once the reaction temperature equilibrated at 170°C, 0.455 mol (9.928 g) of 4,4′-difluorobenzophenone and 0.0026 mol (0.394 g) of

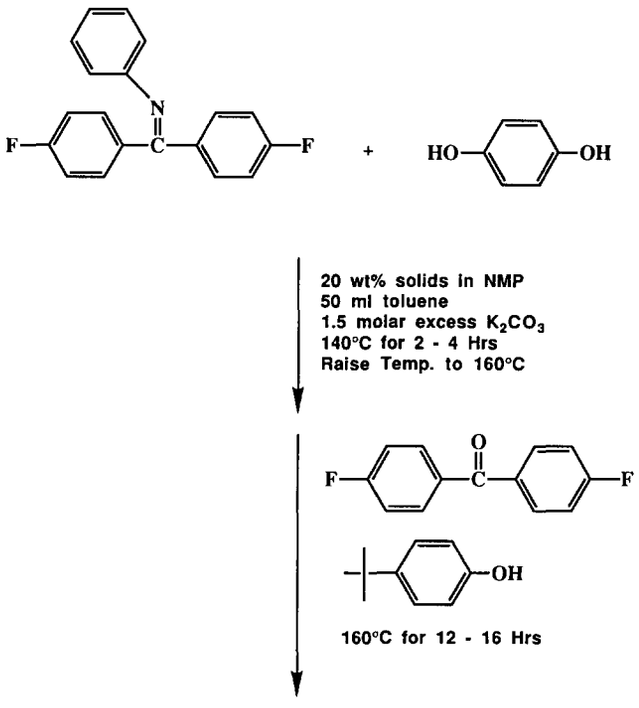


Figure 3 Synthesis of poly((ether ether ketimine)-*co*-(ether ether ketone))

t-butylphenol were added. The reaction was allowed to stir overnight at 170°C. The solution was then diluted with 200 ml of tetrahydrofuran, and neutralized with 10 ml of glacial acetic acid. This was then precipitated into methanol/water (80:20), Soxhlet extracted with methanol and dried under vacuum.

Hydrolysis of poly(ether ether ketimine) to poly(ether ether ketone)

The following is a procedure for the conversion of the imine functionality to the ketone via acid hydrolysis. These reactions were done at various temperatures to determine the optimum temperature to obtain the smallest particle size. The composition of the resulting poly(ether ether ketone) was determined by g.c.–pyrolysis–mass spectral analysis, and also thermogravimetric–mass spectral analysis. In all cases the composition was determined to be 100% PEEK, as there was no imine detected.

First, 2 g of the purified, dried polymer were dissolved in 38 ml of NMP. Then 1.6 ml of water were added to the solution. Once this solution was homogeneous, 3 ml of an HCl/NMP solution (3 ml of 12.1 N aqueous HCl in 27 ml NMP) were syringed into the polymer solution. The polymer typically precipitated immediately. The precipitate was then filtered and washed with water to remove the solvent and acid. The washed 'particles' were then suspended in water using an aqueous solution of a LaRC TPI poly(amic acid) and ammonium hydroxide (800 ml water, 26.5 g poly(amic acid) and 7.2 ml of ammonium hydroxide) as a steric stabilizer. Once the particles were suspended, they were sonicated for 3 min at 75 W to break up any aggregates. The particle size was then measured by a centrifugal particle size analyser (Shimadzu model SA-CP3). This instrument uses centrifugation to determine the average particle size and requires the input of the solvent density and viscosity as well as the density of the particle[4]. The solvent used was water ($\rho = 0.998$ g ml^{-1}, $\eta = 0.938$ cP). The density of the particle was approximated by that of bulk poly(ether ether ketone) (1.3 g ml^{-1}). This procedure was also carried out using 3 ml of a more concentrated HCl/NMP solution (taken from a solution of 6 ml of 12.1 N aqueous HCl in 24 ml NMP) to study the effect of an increased acid concentration on particle size.

RESULTS AND DISCUSSION

The homopolymerization of 4,4'-difluoro(*N*-benzohydroxylidene aniline) and hydroquinone to form poly(ether ether ketimine) (PEEKt) is well established[3,5,6]. These monomers form an amorphous polymer with a T_g of 164°C. The copolymerization of 4,4'-difluoro(*N*-benzohydroxylidene aniline) and 4,4'-difluorobenzophenone (50:50 mol%) with hydroquinone was also attempted using the same procedure as for the homopolymer. However, this procedure failed as the forming polymer precipitated out of solution. This was believed to be caused by the extremely short lamellar thickness of PEEK (only two repeat units) required for crystallization[7–9], resulting in the oligomer crystallizing out of solution. This was avoided by introducing only the ketimine monomer and hydroquinone into the reaction vessel at first, and not adding the ketone monomer until a temperature of 160°C had been reached (*Figure 3*). This alteration in procedure resulted in the polymer remaining in solution until polymerization was complete, and high molecular weight was achieved. The molecular weight was controlled to 20 000 g mol^{-1} by using a monofunctional end-capping agent, t-butylphenol, and gel permeation chromatography with a viscosity detector showed an $M_n = 20\,200$ with $M_w = 26\,600$ g mol^{-1}. The 50:50 copolymer was semicrystalline with a $T_g = 162$°C and a $T_m = 228$°C. This alteration in synthetic method also allowed for the preparation of a 70:30 mole ratio ketone/ketimine copolymer (*Table 1*).

Table 1 D.s.c. data for copolymers as a function of amount of ketone

Ketone (%)	T_g (°C)	T_m (°C)
100 (PEEK)	144	335
70	154	302
50	162	228
0 (PEEKt)	164	None

Table 2 Copolymer cloud points as a function of solvent composition (23°C)

Ketone (%)	Polymer (wt%)	NMP (wt%)	Water (wt%)
0	2.9	90.0	7.1
15	2.9	90.0	7.1
30	2.9	89.9	7.2

Once the homopolymer and copolymers were characterized, it was of interest to determine the mechanism of phase separation (crystallization or insolubility) of these materials as they were hydrolysed to PEEK. This was done by examining the solubility of the ketimine polymer as a function of composition. Controlled hydrolysis of the ketimine homopolymer produced a series of amorphous copolymers with 0, 15 and 30 mol% ketone, as determined by ^{1}H n.m.r. Their relative solubility was determined by examining cloud points at room temperature in NMP/water solvent compositions as a function of water content[10]. As shown in *Table 2*, all three have identical cloud points, and therefore identical solubility in NMP/water. From this it was concluded that the polymer must be crystallizing out of solution rather than precipitating as an amorphous polymer and then crystallizing. This is important in that it shows that the polymer is not undergoing a liquid–liquid phase separation, which has both binodal and spinodal phase separation regions, but crystallization from solution, which occurs exclusively by nucleation and growth.

When a polymer crystallizes from solution, phase separation occurs by both nucleation and growth. To minimize the diameter of the resulting polymer particle, nucleation must be maximized and growth minimized. One way to do this is to extend the system rapidly as far into the phase separation region as possible (termed 'undercooling' when temperature is the dynamic variable). Unlike most cases, for this system the temperature will be kept constant, and the composition will be changing. Analogous to those cases where temperature is the variable, the ketimine functionalities must be converted to ketones as rapidly as possible. The parameters affecting this conversion, and therefore the particle size, have been determined to be a complex function of variables including the initial copolymer composition, ketimine concentration in solution,

Table 3 Particle size as a function of hydrolysis temperature and initial copolymer composition

Temp. (°C)	Initial imine (mol%)	HCl/repeat unit	Particle diameter (μm)
85	100	0.65	9.0
25	50	0.65	1.3
65	50	0.65	1.5
85	50	0.65	0.2
25	50	1.30	0.4
65	50	1.30	0.3

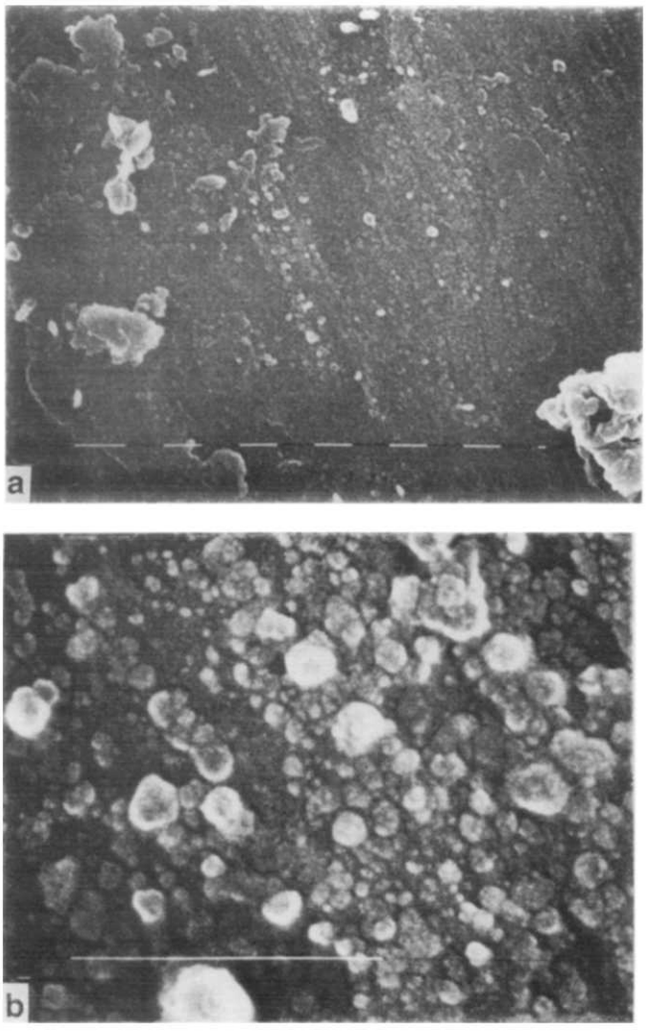


Figure 4 Scanning electron micrographs of PEEK particles formed at 65°C with a HCl/repeat unit ratio of 1.30: (a) magnification = 12 500, (b) magnification = 100 000; both display a 0.5 μm marker

acid concentration, water concentration and hydrolysis temperature. Some of the results obtained by varying these parameters are shown in *Table 3*. The median particle size reported is that obtained by centrifugal particle size analysis as mentioned in the 'Experimental' section. The particles were also viewed by scanning electron microscopy (SEM). *Figure 4* shows two typical photographs taken of particles formed at 65°C with a HCl/repeat unit ratio of 1.30. The first (a) was taken at a magnification of 12 500 times, the second (b) was taken at a magnification of 100 000 times. Both photographs have a scale bar of 0.5 μm. As seen in these photographs, there are several large aggregates of the order of 2–3 μm in diameter. However, the large majority of the particles are significantly smaller in size. Photograph (b) indicates that the actual average particle size is significantly lower than 0.3 μm (approximately 0.05 μm or 50 nm) as measured by the centrifugal particle size analyser. The limits of detection for the particle size analyser are currently being investigated.

The smallest particle sizes were obtained when the 50:50 ketone/imine copolymer (initially 50 mol% imine) was used as the starting material. This can be explained by considering the process occurring during hydrolysis. When the hydrolysing polymer reaches some critical composition, crystallization by nucleation and growth can occur, which results in insoluble polymer particles[11]. This is apparently around 50% ketone. If one starts at 100% ketimine, the polymer is converted towards the ketone and, at any given time, there will be a composition distribution. Within this distribution, some of the copolymer will crystallize out of solution, while some will still be soluble. With further conversion, more mass of polymer will be able to crystallize. However, at this point in the process, there will already be some nuclei present on which polymer can grow. This results in relatively large particles. If one begins the process with a polymer containing only 50% ketimine, a larger concentration of the polymer reaches the critical composition before nucleation can occur. This results in a larger number of nuclei formed, and therefore a smaller particle size. Likewise, a higher temperature or increased acid concentration results in a faster hydrolysis rate. This also converts a larger portion of the polymer past the critical composition, resulting in smaller particles. Careful control of the experimental parameters allows the formation of submicrometre PEEK particles. The particles, with the use of a steric stabilizer, form stable aqueous suspensions.

CONCLUSIONS

The copolymer of 50% 4,4′-difluoro(*N*-benzohydroxylidene aniline) and 50% 4,4′-difluorobenzophenone with hydroquinone, although semicrystalline, is a soluble PEEK derivative. Methods have been established to hydrolyse the ketimine polymers to insoluble, semicrystalline PEEK. This very rapid process causes the polymer to crystallize out of solution, forming small particles. The size of the particles formed is dependent on the temperature, acid concentration, water concentration, solvent concentration and copolymer composition. The careful control of these five parameters can produce submicrometre PEEK particles. Future work will involve the stabilization and characterization of these particles, as well as utilizing them for aqueous dispersion prepregging.

ACKNOWLEDGEMENTS

The authors wish to thank ICI Americas Inc. for the generous contribution of 4,4′-difluorobenzophenone. This research was supported by the NSF Science and Technology Center at VPI&SU under contract number DMR-8809714.

REFERENCES

1 Towell, T. W., Hirt, D. E. and Johnston, N. J. *Int. SAMPE Tech. Conf.* 1990, **22**, 1156

2 Hirt, D. E., Marchello, J. M. and Baucom, R. M. *Int. SAMPE Tech. Conf.* 1990, **22**, 360
3 Mohanty, D. K., Lowery, R. C., Lyle, G. D. and McGrath, J. E. *Int. SAMPE Conf.* 1987, **32**, 408
4 Provder, T. (Ed.) 'Particle Size Distribution: Assessment and Characterization', ACS Symp. Ser. No. 332, American Chemical Society, Washington, DC, 1987
5 Lyon, K. R., Mohanty, D. K., Lyle, G. D., Glass, T., Marand, H., Prasad, A. and McGrath, J. E. *Int. SAMPE Conf.* 1990, **36**, 417
6 Roovers, J., Cooney, J. D. and Toporowski, P. M. *Macromolecules* 1990, **23**, 1611
7 Jonas, A. and Legras, R. *Polymer* 1991, **32**, 1102
8 Attwood, T. E., Dawson, P. C., Freeman, J. L., Hoy, L. R., Rose, J. B. and Staniland, P. A. *Polymer* 1981, **22**, 1096
9 Abraham, R. J. and Haworth, I. S. *Polymer* 1991, **32**, 121
10 Lin, T., Stickney, K. W., Rogers, M. E., Riffle, J. S., McGrath, J. E. and Marand, H. *Polym. Prepr.* 1992, **33**(1), 445
11 Everett, D. H. 'Basic Principles of Colloid Science', Royal Society of Chemistry, London, 1992