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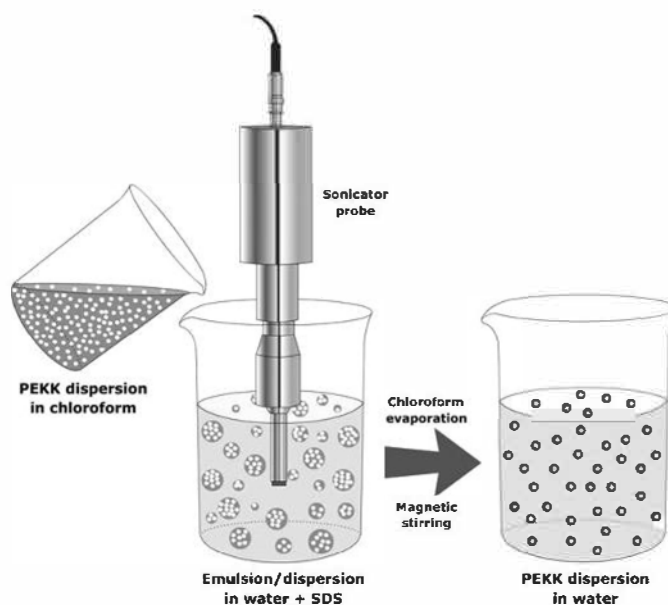
Original Preparation of PEKK Dispersion for Coating by Transfer from a Chloroform Stable Dispersion to an Aqueous Stable Dispersion, by Emulsion/Solvent Evaporation

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GRAPHICAL ABSTRACT



In this work, aqueous dispersions of PolyEtherKetoneKetone (PEKK) oligomers were obtained by an emulsion/dispersion solvent evaporation technique. The PEKK oligomers were synthesized by a Friedel–Crafts acylation with a number average degree of polymerization of 4. The synthesized PEKK oligomers had very good thermal stability and spontaneously formed a stable dispersion of swollen micrometric fibers in chloroform. After sonication of the chloroform dispersion in water in the presence of sodium dodecyl sulfate (SDS) and evaporation, we obtained aggregated particles with a mean diameter between 120 and 160 nm, decreasing linearly with the PEKK concentration. The most stable dispersions were obtained with 0.5% wt of surfactant and, at a fixed concentration of SDS, the stability decreased when the PEKK concentration was increased. The different dispersions of PEKK in water were very stable and, after water evaporation, formed homogeneous films for high-performance coating.

Keywords Chloroform dispersion, coating, emulsion/solvent evaporation, film formation, PEKK oligomers, sonication

INTRODUCTION

High-performance, temperature-resistant coatings are particularly sought after for aerospace, automotive, and special electrical applications.^[1] Coatings based on polymers for “high performance” fall into two groups: thermosets and thermoplastics.^[2,3] They differ in that thermosets undergo an irreversible chemical and physical change when cured and cannot be softened or remelted, whereas thermoplastics soften and eventually melt when heated and solidify on cooling. They can be remelted when sufficient heat is reapplied. Some thermosets, such as epoxy coatings, have found their way into many industrial applications^[4,5] but are still limited with regard to temperature compared with the higher-performing thermoplastic products.^[6–8] Among the thermoplastics, PEKK (PolyEtherKetoneKetone) thermostable polymers could be a good candidate for high-performance coating,^[9–15] with a T_g (glass transition temperature) of 165°C and a melting temperature (T_m) of 386°C. Also, PEKK has high stiffness, strength, and excellent chemical resistance. The term PEKK represents a variety of copolymers with different ratios of terephthalate (*T*) and isophthalate (*I*) moieties (Scheme 1). By varying the *T/I* ratio, it is possible to control the crystallization rate and mechanical properties of the polymer without substantially reducing its end-use temperature.^[9–11]

However, the major drawback of using PEKK, and polyaryletherketones in general, for coating is that they are insoluble in common organic solvents, and their high melting temperature limits their hot coating usefulness to very resistant supports. The ideal coating formulation would be a stable dispersion of PEKK in water, to avoid the use of toxic organic solvents, which, after evaporation of the water, would give a high-performance coating at room temperature that could be applied to any substrate.

Stable aqueous dispersions can be obtained by various methods such as emulsion polymerization, leading to latex formation, solvent diffusion, and emulsion/solvent evaporation.^[16–20] These last methods are widely used in

the pharmaceutical industry for the encapsulation of drugs and their delivery. Emulsion/solvent evaporation is an easy process for preparing stable aqueous dispersions, but it supposes that the polymer is soluble in a volatile and water-immiscible organic solvent like chloroform. Unfortunately, PEKK is insoluble in common organic solvents and, to overcome this problem, we decided to synthesize PEKK oligomers. We selected oligomers to improve the solubility in chloroform while maintaining the performance of PEKK as far as possible.

EXPERIMENTAL

Materials

Isophthaloyl chloride (IPC) (Aldrich), diphenylether (DPE) (Reagentplus), and aluminum trichloride (AlCl_3) (Aldrich) were used as purchased, as were 1,2-dichloroethane (DCE), nitrobenzene (NB), and sodium dodecyl sulfate (SDS) from Sigma Aldrich (St. Louis, MO, USA). Methanol (Sigma Aldrich) and chloroform (Sigma) were dried over molecular sieves.

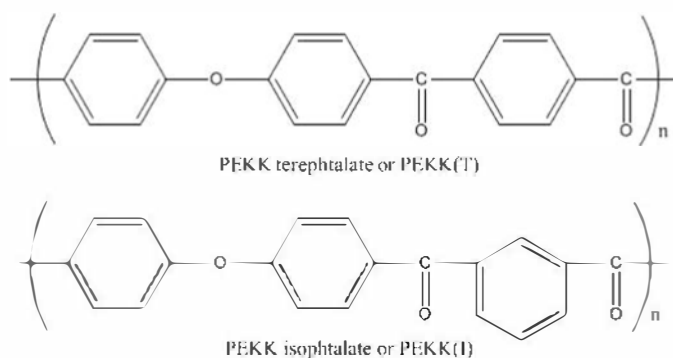
Synthesis of PEKK Oligomers

The PEKK oligomers were synthesized by Ohmori synthesis.^[21] In a 100 mL three-necked flask, under argon atmosphere, 0.84 g of DPE and 1.00 g of IPC were dissolved in 14 mL of a mix of DCE and NB (20/80, w/w). Then the solution was cooled in an ice bath and 1.71 g of AlCl_3 was added under magnetic stirring during 1 hour. Afterward, the reaction continued for 16 hours at room temperature. The solution was then poured into 50 mL of anhydrous methanol and the mixture was filtered under vacuum. Finally, the precipitate was washed with methanol using a Soxhlet procedure for 20 hours and then dried overnight at 100°C. The yield of the reaction was 60%.

Preparation of PEKK Dispersions by Emulsion/Dispersion/Evaporation

Emulsion/dispersion/solvent evaporation involves a two-step process: the emulsification of stable polymer dispersion, followed by solvent evaporation and polymer dispersal in water. During the water emulsification, the polymer dispersed in the volatile water-immiscible solvent is broken into microdroplets by the shear stress produced by either a homogenizer or a sonicator in the presence of a surfactant until the polymer forms stable microparticles in the water.^[22–25]

This method was used to prepare a stable aqueous dispersion of PEKK as a coating agent. We used SDS as the surfactant at different concentrations (0.3%, 0.5%, and 1% wt). The dispersions tested for PEKK in chloroform were 0.1%, 0.3%, and 0.5% wt. The PEKK dispersion in water at 0.5% wt in a 0.5% wt surfactant solution was



SCH. 1. Chemical structures of PEKK terephthalate and PEKK isophthalate.

prepared as follows. In a 5-mL flask, 0.1005 g of PEKK was directly dispersed in 2 mL of chloroform. This stable dispersion was poured into another flask containing 20 mL of the surfactant solution. The mixture was emulsified by ultrasound shearing (Vibra Cell, Bioblock Scientific 600 W and 20 kHz). The shearing lasted 5 minutes at power 4. A water bath was used to maintain the solution at room temperature. Then, magnetic stirring of the emulsion at 1200 rpm for 12 hours allowed total evaporation of the chloroform. Although the emulsion/evaporation method was performed on an organic solution, we were able to obtain an aqueous dispersion of PEKK from the chloroform dispersion.

Characterization of PEKK Oligomers

Proton Nuclear Magnetic Resonance (^1H NMR)

The ^1H NMR spectra were recorded on a Brüker Avance 400 spectrometer operating at 400 MHz. The PEKK oligomers were dissolved in a $\text{CDCl}_3/\text{CF}_3\text{COOD}$ mixture (50/50 v/v). All chemical shifts are reported relative to tetramethylsilane.

Thermal Stability, Thermogravimetric Analysis (TGA)

The measurements of thermal stability were carried out using a Thermal Analysis Q50 spectrometer at a heating rate of $20^\circ\text{C min}^{-1}$ under a nitrogen atmosphere from room temperature to 950°C . The analysis was performed on samples with an average mass of 10 mg.

Differential Scanning Calorimetry (DSC) Analysis

The different thermal transitions of the PEKK oligomers were determined using a DSC7 calorimeter (Perkin-Elmer, Waltham, MA, USA). The measurements were made under nitrogen atmosphere at a heating rate of $20^\circ\text{C min}^{-1}$ from 50 to 250°C . The samples had an average mass of 10 mg.

Characterization of PEKK Dispersions and Films

Particle Size Analysis

Dynamic light scattering (DLS) was performed using a Malvern Instruments Nano ZS with a He-Ne laser (633 nm) at a scattering angle of 173° and at $25 \pm 1^\circ\text{C}$. The hydrodynamic mean diameter of the nanoparticles was determined using the software provided by Malvern Instruments. The Contin model was applied to obtain size data. All the autocorrelation function fits were checked and found to be in accordance with the experimental data. The accuracy on the mean hydrodynamic diameter was ± 10 nm.

Evaluation of Stability Using Analytical Centrifugation

The separation analyzer (LUMiFuge, L.U.M. Berlin, Germany) allows the separation behavior of suspensions to be determined under the influence of various centrifugal forces (5–1000 g). This apparatus is based on a low-speed

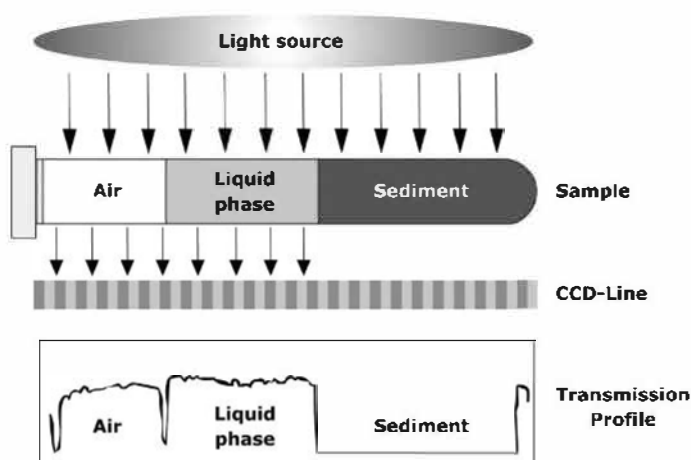


FIG. 1. Measuring principle of the separation analyzer (LUMiFuge).

centrifuge, which is combined with an optoelectronic measuring system that records the light transmission over the entire sample cuvette (Figure 1). The cuvettes containing the suspension are positioned in the horizontal plane on the rotor of the centrifuge. During centrifugation, a light source positioned above the rotor emits radiation (near-infrared) onto the sample. The light transmitted is detected by a CCD line sensor below the rotor plane and is analyzed by a microcontroller, which generates a light-transmission profile of the sample area for every measurement step.

This technique is very appropriate for the study and optimization of very stable aqueous dispersions. The centrifugal force accelerates the destabilization of the dispersion and rapidly determines its shelf life.^[26] Moreover, the possibility of studying eight samples at the same time enables different formulations to be compared immediately.^[27,28]

The data acquisition rate for the chloroform dispersion was 255 profiles recorded every 23 seconds at 3000 rpm and corresponded to 3 months of ageing. The aqueous dispersions are naturally stable for over 6 months, so we chose to simulate 3 years of ageing. The data acquisition corresponded to 255 profiles recorded every 194 seconds at 4000 rpm. The temperature was 20°C .

RESULTS AND DISCUSSION

Characterization of the PEKK Oligomers

^1H NMR

The number average degree of polymerization (DP_n) was estimated at 4 by end-group analysis.

The DP_n can be controlled by the solvents used.^[21] The introduction of NB has two effects. First, the dissolution of AlCl_3 is improved and second, HCl , produced during the synthesis, is trapped by NB which limits the advancement of the reaction. Therefore, we chose to use a mix of DCE and NB to obtain oligomers of the desired size.

TGA

The thermal stability was determined by TGA to ensure that the PEKK oligomers were thermostable, i.e., that the degradation temperature was above 350°C. Figure 2 shows that there was one sharp decrease beginning at 400°C, with only 1% weight loss at this temperature. The thermostable property of PEKK was maintained even though the oligomers were small.

DSC

The second scan of PEKK, obtained after cooling at 20°C min⁻¹, is illustrated in Figure 3. Three transitions can be detected. The first one, at 70°C, is a second-degree transition, corresponding to the glass transition. The second one, at 154°C, is exothermic and is associated with cold crystallization. The last transition, at 214°C, is endothermic and corresponds to melting. This is a typical thermogram of a semi-crystalline polymer.

Behavior of PEKK Oligomers in Chloroform

A solubility study showed that the PEKK oligomers were insoluble in common solvents. However, it was possible to obtain a stable dispersion in chlorinated solvents, notably in chloroform.

To study the stability of this spontaneous dispersion, a LUMifuge analysis was carried out. The different profiles were recorded during the centrifugation and a creaming phenomenon was observed. This result allows us to state that the density of the PEKK oligomers was less than 1.49. From these profiles, the graph in Figure 4 was extracted. It corresponds to the position of the creaming front as a function of time.

The curve obtained decreases sharply for 8 minutes, and then reaches a plateau, which shows that the dispersion was completely destabilized at that time. The slope calculated from the first part of the curve corresponds to the creaming

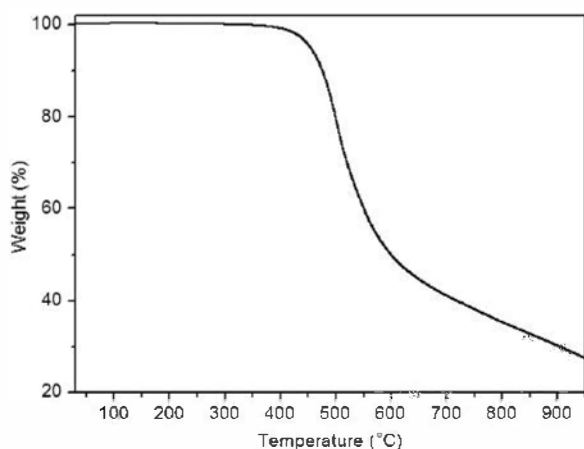


FIG. 2. PEKK oligomers TGA thermogram (heating rate 20°C min⁻¹).

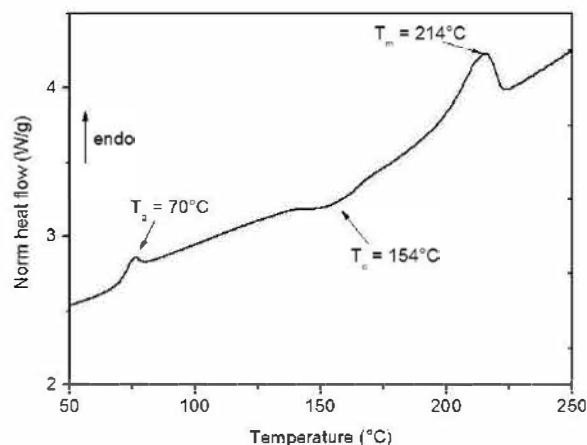


FIG. 3. PEKK oligomers DSC thermogram (heating rate 20°C min⁻¹).

velocity. Considering that Stokes' law applies, the creaming velocity at 1 g can be extracted from the following formula:

$$v_{\text{cream}}(\times 1g) = \frac{v_{\text{cream}}(\text{exp})}{\text{RCF}}$$

where v_{cream} is the creaming velocity at normal gravity, $v_{\text{cream}}(\text{exp})$ is the experimental creaming velocity, and RCF is the relative centrifugal force.

In our case, the experimental velocity was -1095.41 µm/min with an RCF of 1206. The real creaming velocity was -0.91 µm/min. The creaming phenomenon was confirmed by the negative sign of the velocity. This result shows that the dispersion was stable enough to be used in the emulsion/evaporation process.

PEKK Water Dispersions

Particle Size

The first parameter to be considered was the particle size as it is well known that, the smaller the particles are, the more stable the dispersion will be. DLS was performed on all the dispersions. The influence of the surfactant concentration and the PEKK concentration on the mean diameter of particles can be seen in Figure 5.

The mean diameters of the particles were between 120 and 140 nm and decreased quite linearly with PEKK concentration. This suggests an important reorganization of the oligomers after chloroform evaporation and precipitation in water. The effect could be explained by the fact that we started from a dispersion (not a solution) in chloroform, and then there was a disaggregation of the dispersed fibrous particles after sonication. During the evaporation step, the oligomers inside the droplets of chloroform did not precipitate but reorganized and aggregated more or less rapidly as the solvent evaporated. At similar size, the droplets with higher oligomer concentrations contained less

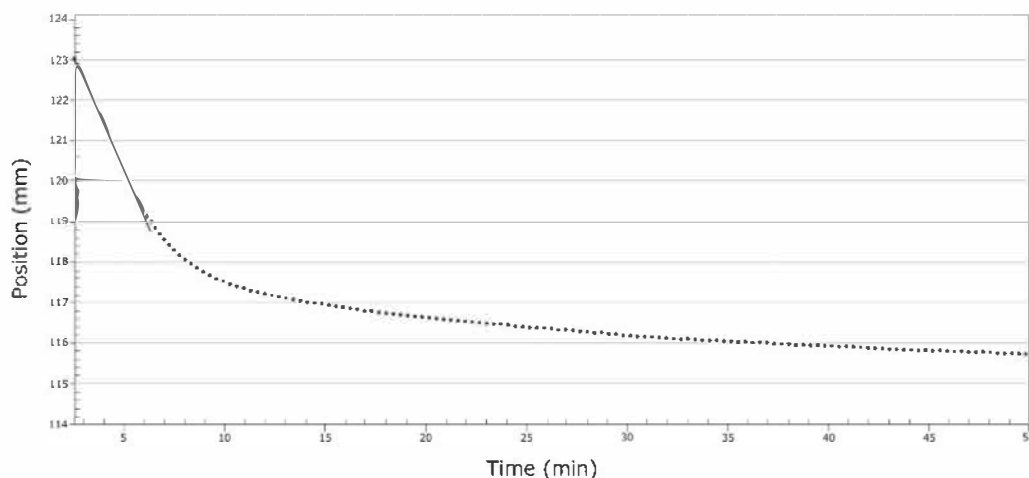


FIG. 4. Position of the creaming front versus time.

chloroform and evaporated faster, leading to large, coarse aggregates easily disaggregated by the ultrasound to small particles. The diffusivity of the solvent in the droplets was strongly dependent on the concentration of polymer in the dispersed phase, as described in the literature.^[29] At low PEKK concentration, evaporation was slower, leading to more compact, resistant particles, even after sonication, which finally formed larger particles. This behavior was also reflected by the decrease in polydispersity index as we increased the PEKK concentration in the chloroform (Figure 6). We also observed that the diameter of the particles was smaller in the dispersion at 0.5% wt in SDS, in accordance with a decrease in the interfacial tension.

Stability Analysis

The LUMifuge analysis allowed a clarification velocity to be determined, corresponding to the slope of the first linear part of the curves, calculated by the “SEPView” software. The steeper the slope was, the more unstable

the dispersion was. The same analysis was carried out in a previous work.^[30] The clarification velocity was calculated for the different dispersions and compared to highlight the effect of different parameters.

As shown in Figure 7, the dispersions at 0.3% of SDS were less stable than the 0.5% ones except for the dispersions at 0.1% of PEKK. At a low particle concentration, the surfactant concentration had no influence. On the other hand, the higher the PEKK concentration was, the higher was the clarification velocity and so the lower the stability. This result is related to the fact that it would be necessary to considerably increase the surfactant concentration to stabilize an increased interfacial area due to a decrease in the particle sizes. Although the shelf life cannot be determined directly from the clarification velocity, the real stability period extrapolated from the data was estimated to be around 10 months for the 0.5% PEKK, 0.5% SDS dispersion and 8 months for the 0.5% PEKK, 0.3% SDS dispersion.

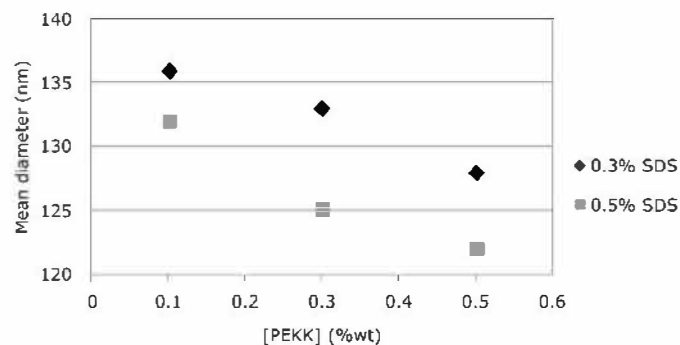


FIG. 5. Influence of the SDS and PEKK concentration on the particle diameter.

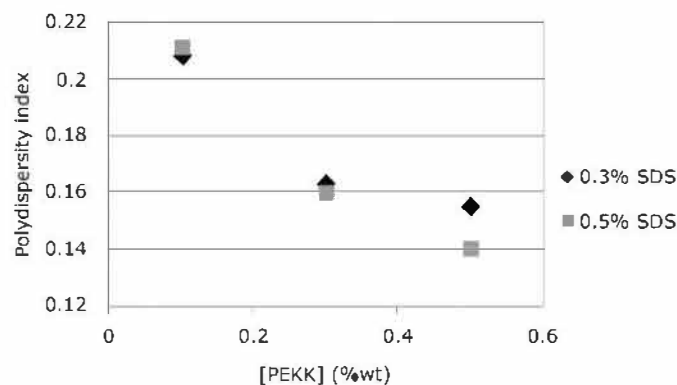


FIG. 6. Polydispersity index of PEKK dispersions.

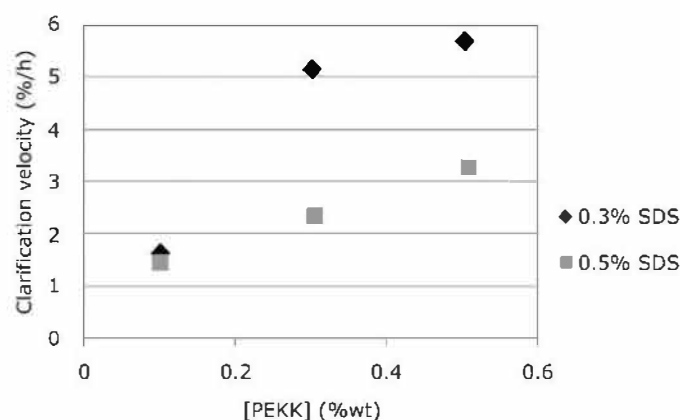


FIG. 7. Influence of the SDS and PEKK concentration on the clarification velocity.

CONCLUSIONS

The PEKK oligomers synthesized had very good thermal stability, like thermostable thermoplastic polymers (PEEK or PEI). They could form a spontaneous, stable dispersion in a chlorinated solvent such as chloroform. The analyses performed on this organic dispersion indicate that the PEKK oligomers formed swollen micrometric fibrous particles stabilized by steric repulsion. The size decrease observed after emulsion/evaporation resulted from the mechanical effect of the ultrasound both on the initial fibers and on the reaggregated particles, according to the evaporation rate of the chloroform. This hypothesis is in accordance with the DLS results. The final size of the aggregates in water was controlled both by the mechanical effect of the ultrasound and by the chloroform evaporation. The study on the surfactant concentration showed that the more stable dispersions were those with 0.5% wt. On the other hand, the results obtained by the LUMifuge analysis showed that, for a fixed concentration of SDS, the stability of the dispersions decreased with increasing PEKK concentration. This behavior was related to an increased interfacial area due to a decrease in particle size. Regardless of the different formulations, the different dispersions were all stable for 8–10 months and, after water evaporation, formed a homogeneous film that was ideal for coating applications.

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