REDUCED COST FABRICATION OF LARGE COMPOSITE AEROSPACE STRUCTURES THROUGH NANOPARTICLE MODIFICATION OF THERMOPLASTICS

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ABSTRACT

To achieve superior mechanical properties and environmental durability in semi-crystalline engineering thermoplastic composites an intermediate degree of molecular ordering is required. While many thermoplastics achieve their potential crystallinities with autoclave processing, only a fraction of that which is desired is developed with lower cost manufacturing processes, viz. automated fiber placement and tape laying featuring polymer chilling from the melt in seconds. Implementation of such processes for the manufacture of large composite aerospace structures is therefore rooted in material selection and the minimization of cycle times. Polyetheretherketone (PEEK) has demonstrated utility in composite structures due to its processing behavior. The cost-driven replacement of PEEK with other materials depends whether desired laminate crystallinities may be attained avoiding costly annealing steps. Polyetherketoneketone (PEKK) represents an alternative but suffers from reduced crystallization rates. The use of nucleating agents presents a route towards enhancing the ordering phenomena in polymers. A study has been undertaken to evaluate the effectiveness of utilizing silicon-based nanoparticles in improving the crystallization kinetics of PEKK. Relevant findings including the impact of the addition of such nanoparticles on other properties will be discussed.

KEY WORDS: Advanced Composite Materials/Structures, Resins/Materials – Polyetherketoneketone (PEKK), Nanomaterials/Nanocomposites/Nanotechnology

1. INTRODUCTION

To achieve superior mechanical properties and environmental durability in engineering thermoplastic composites an intermediate degree of matrix resin crystallinity is generally required. Processing conditions ultimately control observed microstructures in this class of materials and while many resins achieve full crystallinity with autoclave processing, only a fraction of the final crystallinity is developed with lower cost manufacturing processes, viz. thermoplastic automated fiber placement and tape laying featuring resin chilling from the melt state in seconds. The realization of these low cost fabrication processes for the manufacture of large composite aerospace structures is therefore rooted in material selection and the minimization of processing cycle times.

Poly(ether-ether-ketone) (PEEK) has demonstrated significant utility in filament wound and tape-placed composite structures due to its rapid crystallization rate during processing. PEEK is unfortunately quite expensive in the current market. The successful insertion of reduced-cost semi-crystalline thermoplastics into processes with very short heating/cooling times is contingent on matching and ideally exceeding the crystallization rate of PEEK such that potential laminate crystallinities are attained and costly post-process annealing steps are deemed unnecessary. Poly(ether-ketone-ketone) (PEKK) is a lower-cost viable alternative to PEEK based upon physical property comparison but suffers from reduced crystallization rates due to the relative stiffness of the polymeric repeat unit. Circumventing this shortcoming would undoubtedly pave the way for adoptions in various aerospace structures.

The influence of the incorporation of silicon-based particles on the crystallization rates of certain polymers has been widely demonstrated in the literature. For instance, the crystallization rates of poly(ethylene 2,6-naphthalate) (1), high-density polyethylene (2), and polypropylene (3) have been shown to increase with the addition of small amounts of nanosilica particles. Heterogeneous nucleations in addition to decreases in crystallization activation energies have been shown to occur in various composite materials consisting of polymer matrices modified with montmorillonite, typically depending on the extents of intercalation and exfoliation (4-8). Polyhedral oligomeric silsesquioxanes (POSS), a class of materials asserting an emerging technological significance in the realm of composite materials, have also proven utility towards positively impacting the crystallization kinetics of polypropylene (9-10). The extent of this enhancement has been shown to depend strongly on the level of dispersion of the particles in the polymeric host as a function of the chemical nature of the organic periphery of the nanostructured molecules. In the case of polypropylene, to effectively enhance crystalline fractions and first-order transition rates it is apparent based on experimental observations that the interactions between POSS molecules should be stronger than those experienced between POSS and the polymer host such that nano-sized aggregates form, but not sufficient enough to induce gross phase separation into micro-sized domains. On the other hand, if POSS – polymer interactions are highly favorable, dispersion on a molecular level will be achieved thereby hindering any ordering phenomena. Nonetheless, in a generic sense, the appropriate sized nucleating agent for optimal crystallization enhancement should depend on the underlying physics of crystallization of the polymer in question as different species of macromolecules form nuclei homogeneously in a variety of ways.

Despite the significant available body of literature on this subject matter, investigations concerning the enhancement of the crystalline behaviors of semi-crystalline engineering thermoplastics are currently few in number. In light of this and in conjunction with an emerging need for advanced yet cost-effective polymeric materials in many aerospace applications, a study has been undertaken to determine how the presence of selected nanoparticles, viz. various versions of POSS and nanosilica, dispersed in PEKK, affect the crystallization kinetics of this particular engineering thermoplastic.

2. Experimental

2.1 Materials Polyetherketoneketone (PEKK) was supplied in powder form from Cytec engineered materials. Three versions of polyhedral oligomeric silsesquioxanes (POSS) comprised of differing organic peripheries or cage structures were utilized in this study, all of which are commercially available and were supplied by Hybrid Plastics (i.e. phenyl8T8, phenyl12T12, and phenethyl8T8), with the exception of phenethyl8T8 (PhEt), which was synthesized in our laboratory. The chemical structures of the repeat unit of PEKK in addition to those of the POSS materials utilized in this work are depicted in Figure 1. Aerosil R150 fumed nanosilica devoid of surface treatment (hydrophilic) and Aerosil R202, treated with polydimethylsiloxane (hydrophobic) were purchased from Degussa with BET surface areas of 150 m^2/g translating into an average particle size of 14 nm.

2.2 Blending Methodology Melt processing and blending of PEKK with the selected nanoparticles was conducted on a DSM Micro 15 Compounder with a chamber free volume of 15 cm^3. Powders were pre-mixed in their appropriate ratios and charged to the compounder imposing a residence time of five minutes under an inert nitrogen atmosphere with the modular heating profile set at a flat 340°C. Blend extrudates were transferred to a DSM micro-injection molding machine for the fabrication of disks and tensile bars using a mold temperature of 170°C.

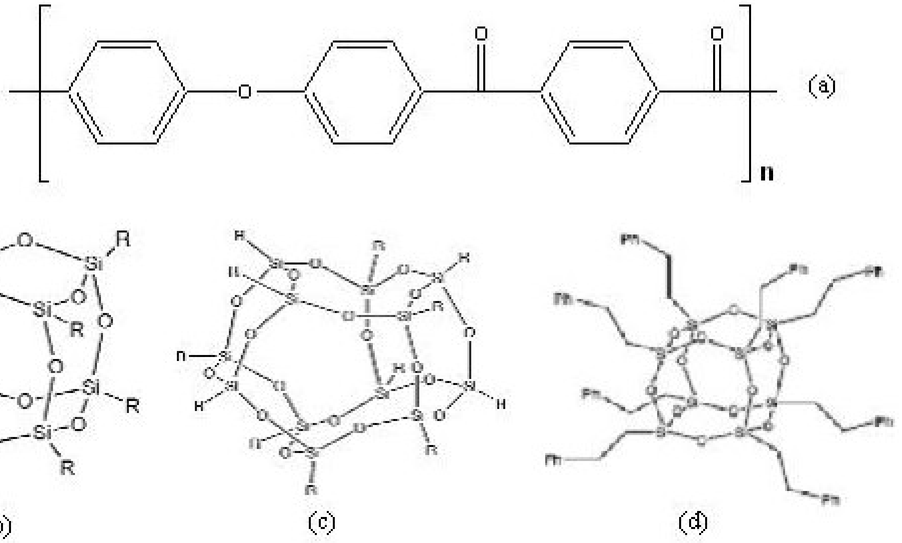

Figure 1. Chemical structures of (a) PEKK repeat unit, (b) phenyl8T8 POSS (R =phenyl), (c) phenyl12T12 POSS (R=phenyl), and (d) phenethyl8T8 POSS.

2.3 Material Analyses Differential scanning calorimetry (DSC) experiments were carried out on a TA Instruments Q100 under a nitrogen blanket with scan rates of 10°C/minute. Thermogravimetric analyses (TGA) of materials were conducted on a TGA 2050 under a continuous nitrogen or air purge of 30 ml/minute scanning from room temperature to

600°C at a rate of 10°C/minute. Isothermal parallel plate viscometry was conducted on an Anton Paar MCR 500 rheometer in parallel plate configuration (gap width = 1.5 mm) at a temperature of 238°C with a frequency of 6.3 rad/sec and a strain of 0.5%.

3. Results and Discussion

3.1 Effects of Phenyl8T8 and Phenyl12T12 on the Crystallization Kinetics of PEKK

This study was initially structured around investigations specifically targeting phenyl8T8 POSS and phenyl12T12 POSS as candidate nucleating agents for two reasons: enhanced miscibility may be achieved due to the phenyl peripheries of the POSS molecules in light of the ketone and phenyl groups located in the backbone of PEKK, and even more importantly, these two versions of POSS represent solutions that are commercially attainable and relatively cost-effective in comparison with other versions of POSS.

The crystallization half-times of blends of PEKK containing either 1, 2, 5, or 10 weight percent phenyl8T8 or phenyl12T12 POSS were investigated by DSC, where crystallization exotherms were monitored isothermally as a function of time. The results of the phenyl8T8 blends are shown in Figure 2, at two annealing temperatures, where it may be discerned that these types of nanoparticles do not dramatically alter the rates of polymer crystallization in comparison to neat PEKK, and in fact, in the two weight percent-containing hybrids, the rate is retarded. The extrudates were rough indicating an apparent lack of dispersion. Optical microscopy confirmed these qualitative observations by revealing the existence of large POSS crystallites on the order of 20 – 30 μm embedded within the polymer matrix. PEKK – POSS interactions in these mixtures are clearly not sufficiently strong enough to promote the breakup and dispersion of these crystallites as the POSS – POSS interactions are clearly dominant in preserving the architecture of the POSS micro-crystallites.

The mechanical properties of PEKK / phenyl8T8 were examined during standard tensile experiments (ASTM D638). Although the elastic modulus of the blends in comparison with neat PEKK generally increased with increasing phenyl8T8 content (results not shown), the yield stress and strain, stress and strain at break, and most importantly, toughness, all decreased with increased loading levels of the POSS. These factors allude to poor miscibility and adhesion between POSS domains and the thermoplastic matrix therefore corroborating optical results.

Lastly, atomic force microscopy (AFM) was conducted on films containing phenyl8T8 to determine whether or not spherulitic structures are centered on POSS crystallites, a phenomenon characteristic of effective heterogeneous nucleation processes. No behavior of this type appears to have taken place in these mixtures although the instrument detected pronounced three-dimensional spherulitic structures.

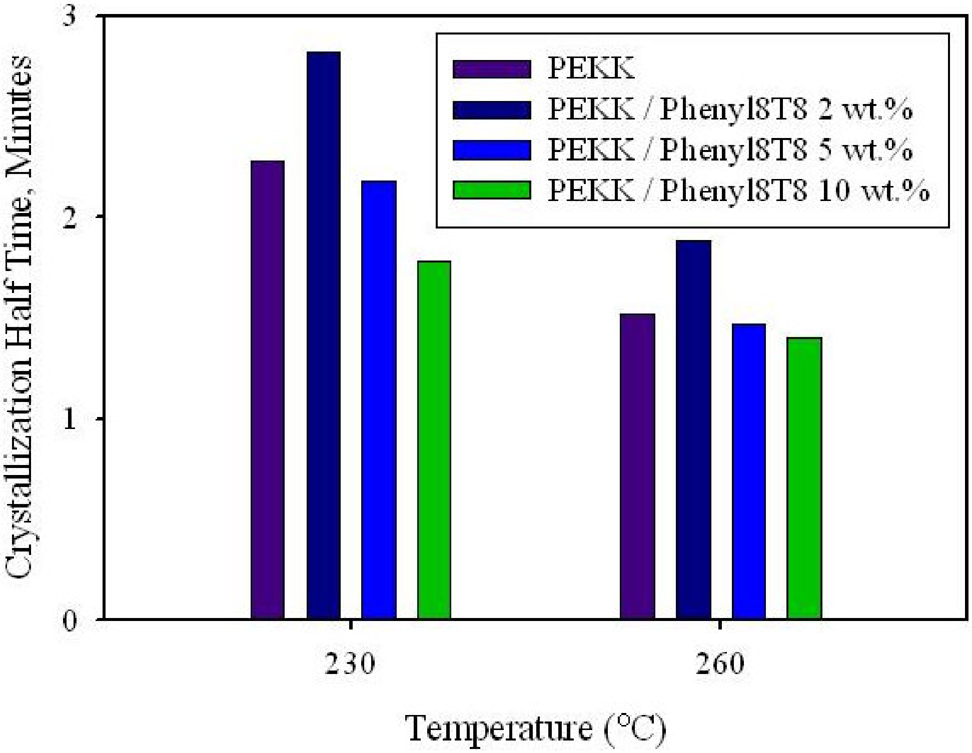

Figure 2. Crystallization half-times of PEKK and phenyl8T8 POSS containing hybrids.

3.2 Revised Strategy: Concentration on Nanoparticle Dispersion In light of the aforementioned results, a literature search was conducted to assist in discerning the physics of the homogeneous nucleation and subsequent crystallization of neat PEKK. Ezquerra et al. elucidated through dynamic real time wide- and small-angle x-ray scattering techniques that amorphous PEKK, when annealed above its glass transition temperature, forms a long range ordered structure on the order of 12 nm during the induction period prior to crystallization (11). In essence, this finding characterizes the nature (length scale) of the seed formed during the homogeneous nucleation process. With this knowledge in hand, it would likely be advantageous to pursue nucleating agents that are on the size order of nanometers rather than microns such that the favored thermodynamic avenue towards crystallization may be most efficiently pursued. Along this vein, a search was initiated for nanoparticles that may be more miscible with PEKK to heighten the possibility of truly enhancing the crystallization kinetics of this fairly rigid thermoplastic. It is fair to say that the formation of the precursors (seeds) in homogeneous nucleation consumes a considerable time, especially in the case of a more rigid chemical species, dependant of course on the extent of supercooling, and the strategic selection of nucleating agents would circumvent the necessity for PEKK to form the initial long-range structures required to act as crystallization templates. Fundamentally, this represents the technology behind heterogeneous nucleation.

In pursuit of achieving a nanoscale dispersion of particles in PEKK while attempting to remain within the framework of utilizing POSS molecules as nucleating agents, a novel version of POSS was synthesized at AFRL with the hopes of exhibiting increased solubility over its phenyl8T8 and phenyl12T12 counterparts. To disrupt crystalline packing observed in the commercially available materials, a 1-napthyl corner-capped version of phenyl8T8 was synthesized and isolated, namely 1-napthylphenyl7T8 POSS. The goal was successfully achieved in that the novel POSS exhibited no melting point as observed by DSC, however, blending studies in PEKK revealed very similar observations as those witnessed in the previously studied systems with 20 – 30 μm sized particles and no detectable impact on the crystallization kinetics of the thermoplastic.

A different approach to attaining a high level of dispersion of POSS in polymers is to utilize an additive that exhibits a melting point below that at which the melt processing occurs. Phenethyl8T8 POSS characterized by phenyl groups connected to the $8\bullet SiO_{1.5}$ cage structure through ethyl linkages demonstrates such a first order transition at 73°C conveniently as the melt processing of PEKK occurs at 340°C. At such an elevated temperature relative to the melting point of phenethyl8T8 POSS, the thermal stability of this POSS should be of concern. To investigate the volatility of phenethyl8T8 POSS, a TGA experiment was conducted with a temperature sweep to 600°C and compared with the weight change profile of phenyl8T8 as demonstrated in Figure 3. As shown in the plot, phenethyl8T8 exhibits significantly worse thermal stability than phenyl8T8 due to the weaker electronic nature of the organic periphery; however, noticeable weight loss does not commence until 350°C. Mimicking processing conditions, an isothermal experiment conducted at 340°C would likely yield very little decomposition of phenethyl8T8 POSS after five minutes under a nitrogen atmosphere and is even less of a concern since the thermoplastic should exert a protective buffer on the POSS molecules during short time intervals.

Qualitatively, the extrudates appear smooth subsequent to mixing with only the 5 and 10 weight percent blends appearing slightly opaque indicating a favorable degree of miscibility between this pair of materials. To investigate the crystallization behavior of PEKK in the blends, DSC experiments were conducted where the blends were heated to 340°C to erase thermal history and cooled to 70°C to obtain dynamic crystallization exotherms. The results of this analysis are depicted in Figure 4 where it is apparent that the presence of phenethyl8T8 POSS positively influences not only the rates of crystallization of PEKK but in addition the overall heats of reorganization in some fashion, which may be interpreted as the integrations of the cooling exotherms (not shown). Although PEKK ordering in the blends seems to be accelerated by the presence of the nanoparticles in all cases, it is evident that the effect is much more pronounced in the 2 weight percent blend. It is conceivable that concentrations less than 2 weight percent POSS are not adequate to form nano-phase-separated domains within the thermoplastic matrix (experiments conducted but results not shown) while at concentrations above a critical proportion, the POSS molecules may hinder PEKK organization through a plasticization effect.

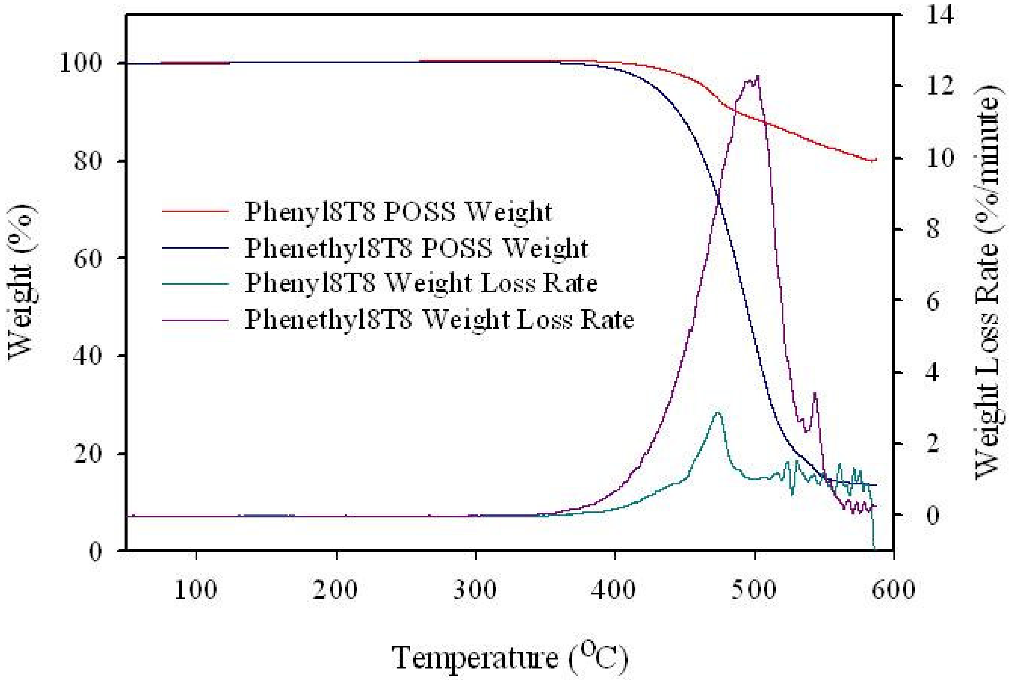

Figure 3. Weight loss change profiles via TGA and derivatives of phenethyl8T8 and phenyl8T8 POSS under a nitrogen purge, scan rate 10°C / minute.

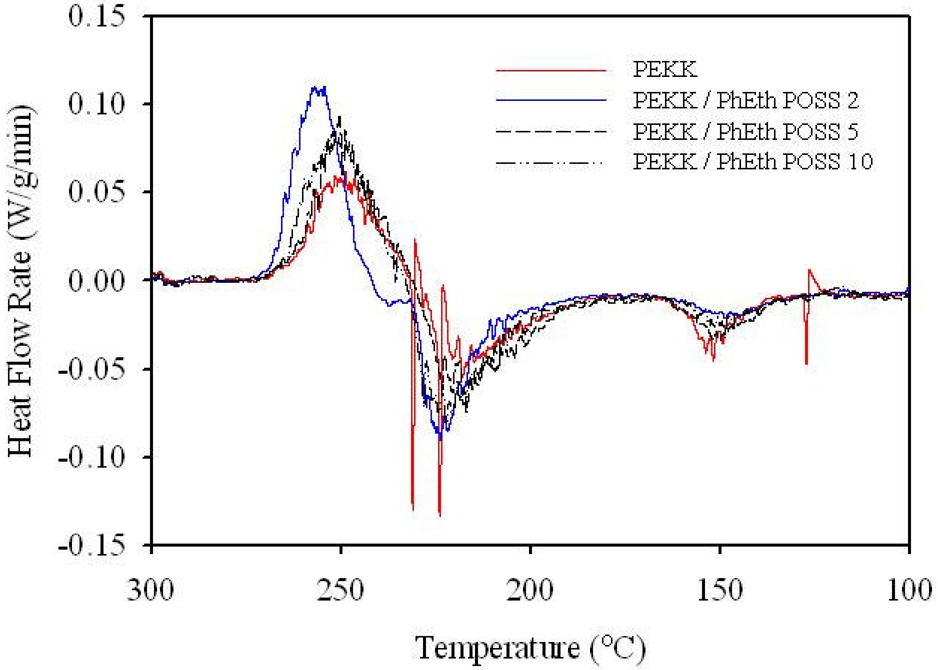

Figure 4. DSC First derivative of cooling curves of PEKK / phenethyl8T8 POSS blends, scan rate 10°C / minute.

Second heating curves executed immediately following the cooling scans are shown in Figure 5. It is noteworthy to point out that the heats of cold crystallization are significantly reduced in the blends compared to neat PEKK proving the existence of a catalytic effect of POSS that is likely acting as a nucleating agent for the macromolecules. Table 1 summarizes the relevant statistics from DSC analysis. The glass transition temperatures of PEKK in the mixtures decrease modestly with increasing POSS content likely due to plasticization effects and higher degrees of free volume in the amorphous phases. Interestingly, the overall heats of fusion of PEKK in the blends are generally larger than neat PEKK, suggesting that greater fractions of crystallinity are achieved in the hybrid materials.

A similar thermal analysis was conducted on blends consisting of PEKK and Aerosils R150 and R202 at nanoparticle concentrations of 2, 5, and 10 weight percent. Figure 6 depicts the first derivatives of cooling thermograms for the PEKK / Aerosil R150 blends. The presence of the nanosilica in PEKK exerts a more significant impact on the crystallization kinetics of the thermoplastic over phenethyl8T8 POSS, with the hybrid containing 2 weight percent Aerosil R150 outperforming the other mixtures. In contrast to the POSS additive, 10 weight percent nanosilica appears to impede the thermoplastic from organizing and packing by DSC which may allude to an exceptional level of dispersion. As in the case of the phenethyl8T8 POSS blends, the cold crystallization exotherms are reduced with increasing nanosilica content up to 10 weight percent (results not shown) where reorganization during cooling is hindered. Based on the tabulated results of this DSC analysis shown in Table 2, it appears that 2 weight percent Aerosil R150 is optimal in both influencing the crystallization rate as well as the overall ultimate crystalline fraction, demonstrating a 15% rise in crystallinity over neat PEKK. In addition, the glass transition temperatures of the amorphous phases in these materials seem to be less influenced than those of the POSS blends. PEKK / Aerosil R202 blends exhibit similar behavior to those analyzed here. The results are not shown here for the sake of brevity.

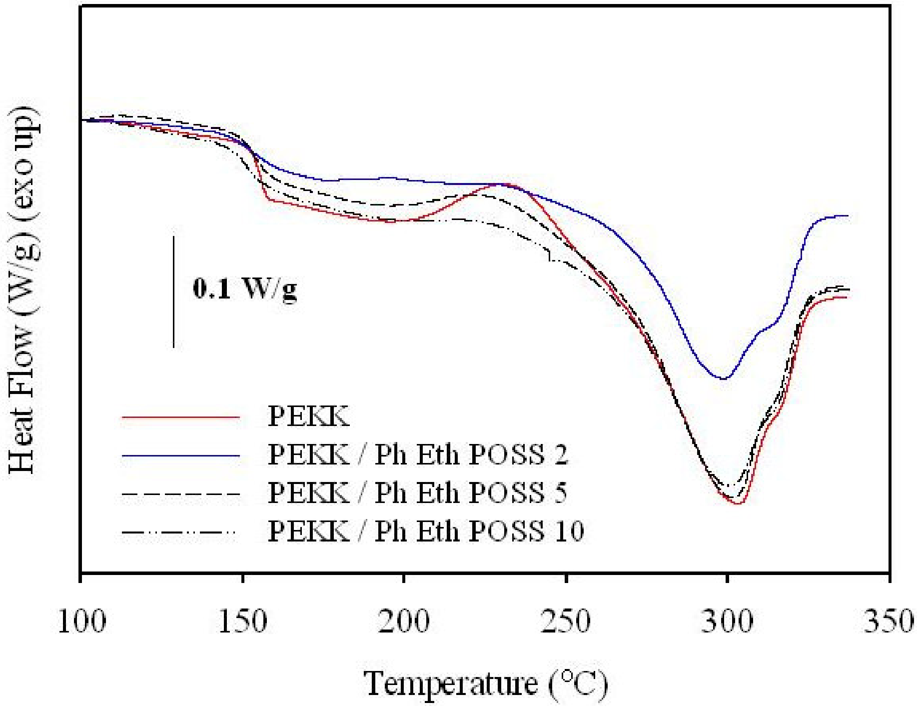

Figure 5. Second heating DSC curves of PEKK / phenethyl8T8 POSS blends demonstrating reduced heats of cold crystallization.

	Tg (°C)	$\Delta H_{cryst,\ hot}$ (J/g)	$\Delta H_{cryst,\ cold}$ (J/g)	ΔH_{fusion} (J/g)	Crystallization Peak Temp. (°C)	Crystallization Max. Rate Temp. (°C)
PEKK	156.7	29.97	9.03	40.68	231.1	259.4
PEKK / PhEt 2	152.4	39.79	0.60	40.20	241.8	263.6
PEKK / PhEt 5	152.9	39.47	5.41	43.94	230.4	258.1
PEKK / PhEt 10	151.6	42.1	3.77	46.13	232.2	260.9

Table 1. DSC statistics for PEKK and PEKK / phenethyl8T8 POSS blends.

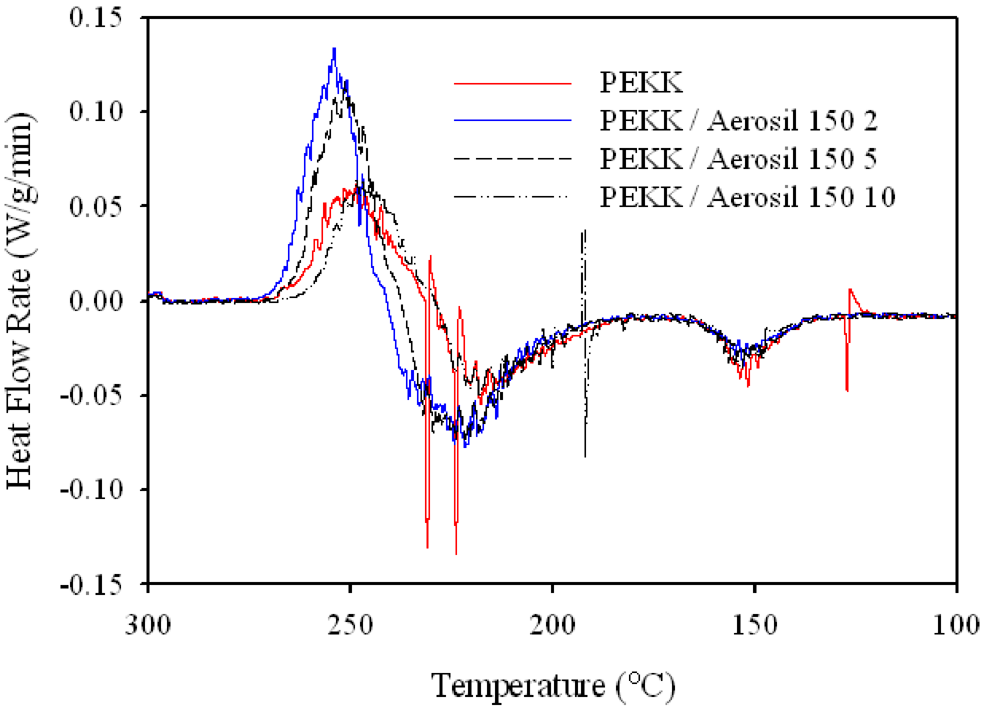

Figure 6. First derivative rate cooling curves of PEKK / Aerosil R150 blends, scan rate 10°C / minute.

	Tg (°C)	$\Delta H_{\text{cryst, hot}}$ (J/g)	$\Delta H_{\text{cryst, cold}}$ (J/g)	ΔH_{fusion} (J/g)	Crystallization Peak Temp. (°C)	Crystallization Max. Rate Temp. (°C)
PEKK	156.7	29.97	9.03	40.68	231.1	259.4
PEKK / Aerosil R150 2	155.1	42.31	0.82	46.67	240.9	261.9
PEKK / Aerosil R150 5	155.2	39.12	2.15	42.76	237.4	259.3
PEKK / Aerosil R150 10	155.1	27.69	6.05	35.31	229.1	255.2

Table 2. DSC statistics for PEKK and PEKK / Aerosil R150 blends.

3.3 Influence of PEKK Molecular Weight on Crystallization Behavior The PEKK grade was switched mid-study to a higher molecular weight (MW) version characterized by a melt index reduction from 150 to 120 g / 10 minutes. Since polymer crystallization rates generally correlate with MW^{-3}, there is concern that the higher MW version will respond differently to the nanoparticles utilized in this study. To investigate this matter, DSC experiments were again conducted on blends consisting of the higher MW PEKK. Although this version of PEKK was more sluggish in terms of ordering in comparison with its lower MW counterpart, concerns were alleviated as witnessed in Figure 7, where the rates of crystallization of the PhEt8T8 POSS containing blends are plotted against temperature. PEKK exhibited an exceptional response in terms of crystallization when compounded with two weight percent PhEt8T8 POSS. In addition, the achieved fraction of crystallinity in this blend surpassed that of the neat PEKK control as observed through thermal cycling.

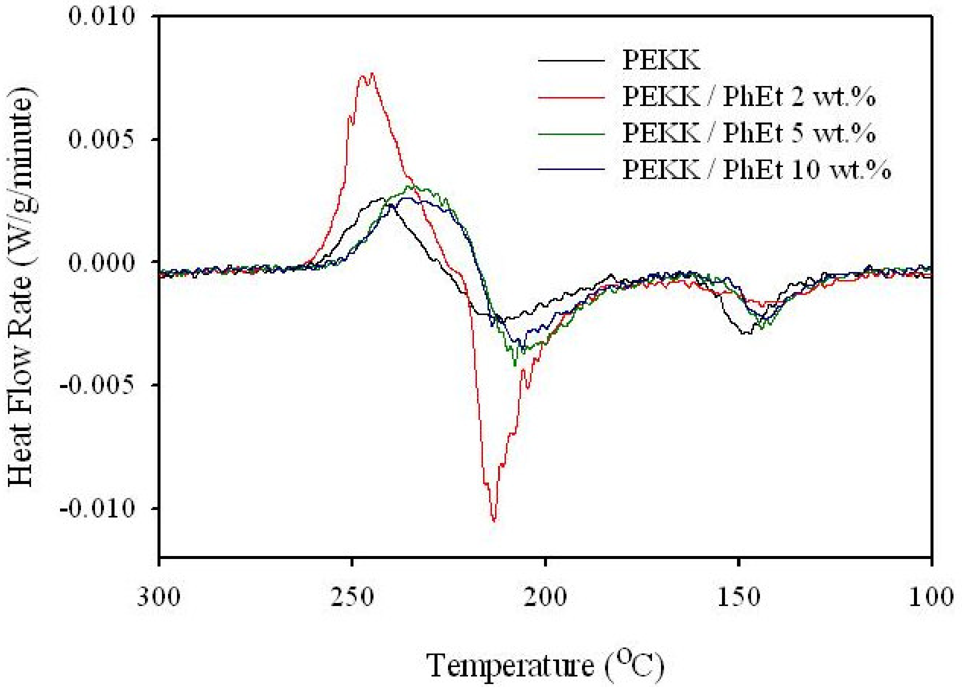

Figure 7. Rates of heat flow of PEKK / PhEt8T8 blends monitored by DSC during cooling, plotted against temperature.

3.4 Monitoring Crystallization Kinetics through Isothermal Viscometry Complex rheological experiments provide a convenient means towards monitoring the crystallization rates of polymers and is complimentary to DSC analyses. By decoupling the complex moduli measured during isothermal annealing experiments one may monitor the growth of the elastic modulus with time as crystallization proceeds. As fractions of ordered polymer chains grow in the material, emerging crystallites effectively act as tie points restricting polymer flow and thereby increasing the elastic response of the material. Such rheological characterization also yields insight into the developing mechanical properties of the material.

The evolution of the storage (elastic) modulus of PEKK / Aerosil R150 blends with annealing time at 238°C are depicted in Figure 8 where it is apparent that the elastic moduli of the blends not only develop more rapidly in comparison with the neat PEKK control, but also achieve much higher values. These observations suggest that the crystallization kinetics are enhanced through the incorporation of the nanoparticles, but of equal importance, that higher levels of crystallinity are achieved in the hybrid materials.

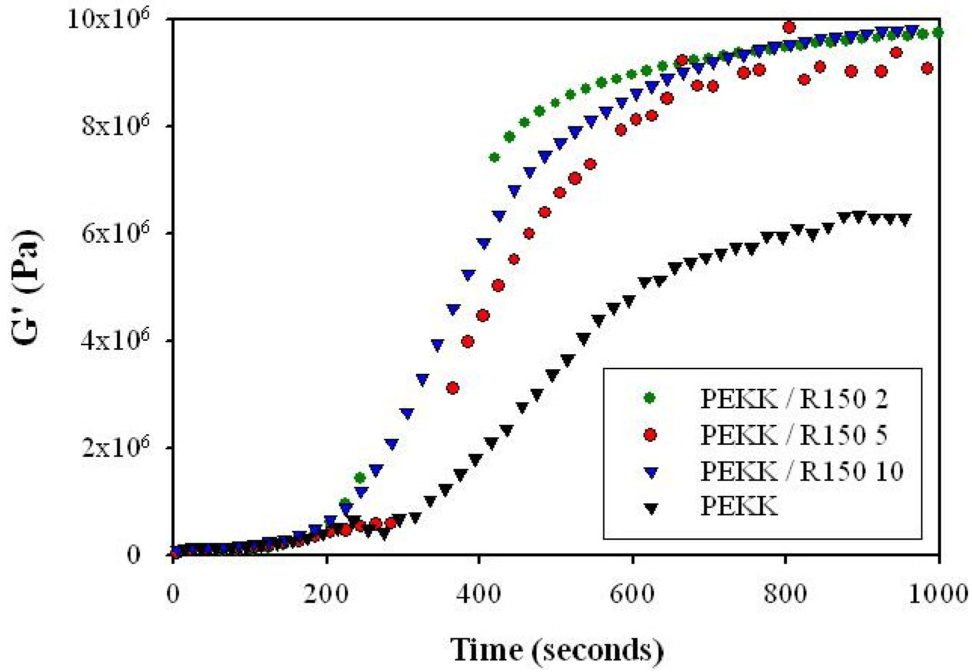

Figure 8. Development of elastic moduli during crystallization annealing time at 238°C of the PEKK / Aerosil R150 blends as monitored through parallel plate rheological experiments.

3.5 Thermal Stability of Hybridized Materials As the aim of this study is to qualify PEKK / nanoparticle hybrid blends for processes to fabricate a variety of aerospace components, it is imperative to investigate their thermal stability through thermogravimetric analysis (TGA). The incorporation of Aerosils imposes a minimal effect on the thermal stability of the blends in comparison with the PEKK control, with the Aerosil R150 blends performing slightly better than the R202 blends due to the PDMS surface treatment of the R202 nanosilicate particles. The weight loss curves of PEKK / PhEt8T8 POSS blends are shown in Figure 9. PEKK exhibits exceptional thermo-oxidative stability for an organic species, losing five weight percent at approximately 560°C and maintaining 80 percent of its original weight at 600°C. On the other hand, PhEt8T8 POSS demonstrates significantly lower thermo-oxidative stability. The dashed lines in the plot represent the theoretical predictions of weight loss with temperature as calculated by the rule of mixtures. The incorporation of PhEt8T8 POSS into PEKK is more damaging to the weight loss profiles than what is theoretically predicted. Since weight loss commences well beyond the melting point of the crystalline phase of PEKK, it is valid to assume that the blends in this temperature regime are amorphous in nature and presumably uni-phasic, or alternatively speaking, above the coexistence curve of the phase diagram for this system. With this in mind, it is reasonable that PhEt8T8 POSS, owing to its relatively large size (neglecting the organic periphery, the Si-O core cage structure alone is 1.5 nm) disrupts polymer inter-chain interactions and increases the free volume of the mixture. As such, oxygen should maintain greater permeability in the material thereby having greater access to polymer chains thus accelerating decomposition mechanisms. As it has been demonstrated that the hybrid containing two weight percent PhEt8T8 POSS exhibits the most rapid crystallization kinetics, the reduction in thermal stability for this blend is marginal as compared to the PEKK control.

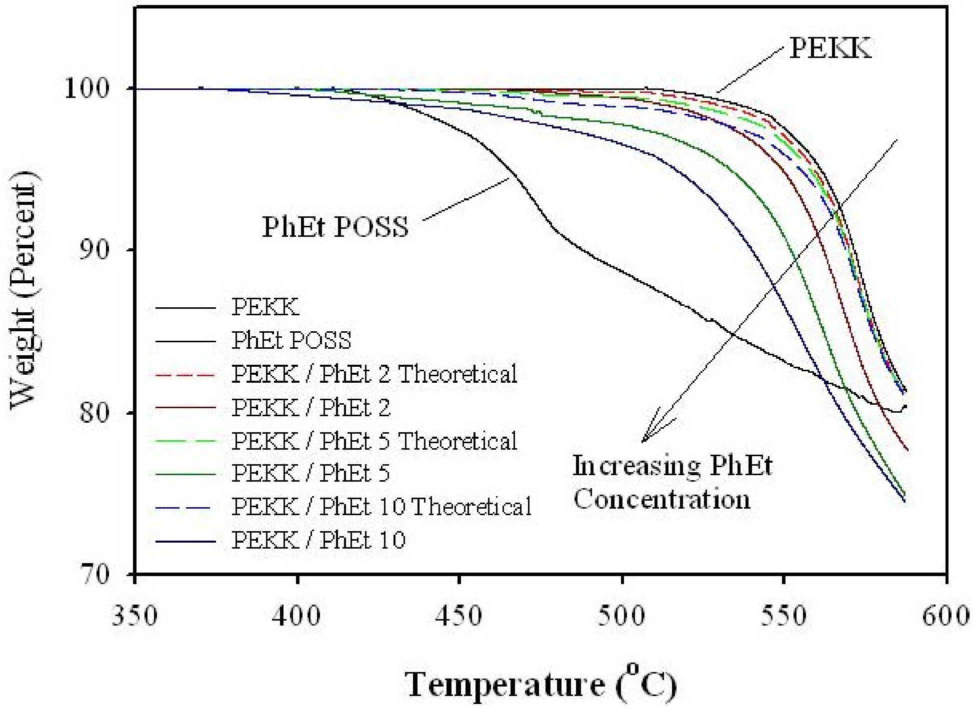

Figure 9. Weight loss curves of PEKK / PhEt8T8 POSS blends in air as determined from TGA analyses (scan rate 10°C / minute). The dashed lines represent theoretical weight losses calculated from the rule of mixtures.

4. Conclusions

The observed micro-scale dispersion of phenyl8T8 and phenyl12T12 crystallites exerts negligible if not negative effects on the organizational rate of PEKK. In contrast, the crystallization kinetics of PEKK are accelerated through the incorporation of phenethyl8T8 POSS and Aerosils R150 and R202 nanosilica particles most likely due to the nanoscale level of dispersion of the additives. Achieved fractions of crystallinity in the hybridized materials exceed those observed in the thermoplastic control, which may have profound consequences as to how this thermoplastic is utilized in aerospace applications. Losses in mechanical properties beyond the glass-rubber transition may be mitigated with enhanced crystalline fractions and is currently under investigation. Increases in crystallinity may also improve not only various mechanical properties of engineering thermoplastics but also solvent resistance to jet fuel, water, etc. Investigations are currently underway to elucidate the underlying physics and mechanisms behind the observed improvements in macromolecular organization of PEKK using optical techniques including polarized optical microscopy, atomic force microscopy, and polarized two-dimensional time-resolved laser light scattering methods. It is conceivable that the successful solution to this problem is synergistic in molecular weight tailoring, processing parameter modification, and nanoparticle selection.

5. Acknowledgements

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6. References

1. S. H. Kim, S. H. Ahn, and T. Hirai, Polymer, 44(19), 5625 (2003).
2. J. Qian and P. He, Journal of Materials Science, 38(11), 2299 (2003).
3. M. S. Sreekala, B. Lehmann, K. Friedrich, and M. Z. Rong, International Journal of Polymeric Materials, 55(8), 577 (2006).
4. T.-M. Wu, S.-F. Hsu, C.-F. Chien, and J.-Y. Wu, Polymer Engineering and Science 44(12), 2288 (2004).
5. Q. Zhang, M. Yu, and Q. Fu, Polymer International, 53(12), 1941 (2004).
6. S. D. Wanjale and J. P. Jog, Journal of Macromolecular Science, Physics, B42(6), 1141 (2003).
7. P. Maiti, and M. Okamoto, Macromolecular Materials and Engineering, 288(5), 440 (2003).
8. T. G. Gopakumar, J. A. Lee, M. Kontopoulou, and J. S. Parent, Polymer, 43(20), 5483 (2002).
9. A. Fina, D. Tabuani, A. Frache, and G. Camino, Polymer, 46, 7855 (2005).
10. J.-H. Chen and Y.-D. Chiou, Journal of Polymer Science: Part B: Polymer Physics, 44, 2122 (2006).
11. T. A. Ezquerra, E. Lopez-Cabarcos, B. S. Hsiao, and F. J. Balta-Calleja, Physical Review E, 54(1), 989 (1996).