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**BISMALEIMIDE/PRECERAMIC POLYMER BLENDS
FOR HYBRID MATERIAL TRANSITION REGIONS:
PART 2. INCORPORATING COMPATIBILIZERS
(POSTPRINT)**

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Interim Report**

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Abstract

The problem of phase separation in polycarbosilane (Starfire resin)–Matrimid thermoset blend structures, designed for thermal protection applications, was addressed in this study. The structural design of the compatibilizers synthesized via a hydrosilylation–deprotection sequence was primarily based on a polymer structure with a nonpolar segment consisting of a carbosilane unit and a polar segment with a bisphenol-type moiety. Besides the homopolymer, block copolymers with varying contents of the polycarbosilane unit and the bisphenol A unit were synthesized and characterized. Curing experiments on the blends of Starfire resin–Matrimid incorporating 1–5% of the compatibilizers were performed followed by morphological characterization of the cured resin plaques. The effectiveness of the compatibilizers was assessed by the StarFire domain size and the distribution of cured specimens was examined in the scanning electron micrographs. Results indicated that the compatibilizers that were more effective in minimizing phase separation were relatively more polar and comprised a larger fraction of the phenolic functional units. In fact, the blend composition incorporating 5% of the homopolymer compatibilizer with the largest fraction of the polar bisphenol A unit was highly effective in providing a homogeneous distribution of very small StarFire domains, that is, fairly uniform domain sizes of the order of 5 μm or less.

Keywords

Preceramic polymer, bismaleimide, hybrid, thermal protection, phase separation, compatibilizers

Introduction

As part of a larger objective of producing an inorganic-to-organic gradient interphase material capable of high temperature stability for thermal protection applications involving surface temperatures in excess of the range of 800–1000°C, a hybrid material approach combining a ceramic component and a high-performance thermoset polymer component has been recently described in the literature.¹ Preceramic materials based on silicones, organic layered silicates, and polyhedral oligomeric silsesquioxane are known to be incorporated in thermosetting resins for increased operating temperatures, improved thermo-oxidative stability, enhanced atomic oxygen resistance, and improved barrier properties. The mode of protection in this case was the formation of a glassy, passivating silicon dioxide layer upon exposure to oxygen at elevated temperatures as well as atomic oxygen.^{2–4} However, for still higher

surface temperature hybrids, a silicon carbide (SiC) outer layer rather than silicon dioxide is desired especially for rocket propulsion and turbine engine components. Preferred hybrid architecture from the standpoint of thermal shock resistance would also embody a gradient interface between the ceramic and the polymer components. In advanced thermostructural composites such as C/C–SiC in

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which the core was made up of C/C composite and the surface was protected by a layer of SiC, problems due to cracking from the different thermal expansions of the two materials was overcome with the use of a gradient composite with SiC present in the matrix phase.⁵ For the fabrication of a non-oxide ceramic such as SiC, the pyrolysis of polymer precursors has been demonstrated to have distinct advantages such as the fabrication of unconventional structures and the generation of ceramics at relatively low temperatures.⁶ Among the precursors of SiC, the allylhydridopolycarbosilane class of polymers is known to be available in ultrahigh purity forms yielding a near stoichiometric ratio on complete pyrolysis.⁷ Their unique processability, high ceramic yield, and low thermal shrinkage are advantageous from the viewpoint of fabricating high-performance SiC composites.⁸ As a precursor of thermally stable SiC, allylhydrido-phenylpolycarbosilane (trade name: Starfire RD-730) potentially combines the dual advantage of the inherently high temperature capability of the ceramic and the polymer/composite-like processability in the range of 200–400°C. The cure temperature of this precursor is reported to be in the range of 150°C and it also has reactive functionalities for combining with commercial bismaleimide (BMI) formulations, making it an ideal preceramic candidate for the fabrication of hybrid ceramic–polymer blends and composites for thermal protection applications. The hybrid formulation would serve as a gradient interphase and a transition layer in an overall architecture that would consist of a polymer matrix composite understructure and an outer layer of SiC. Initial studies of the fabrication by melt mixing and casting of the blends and their characterization after cure have been described in a companion article in this journal.⁹ It was shown that the blends had a two-phase morphology in which the Starfire resin RD-730 was dispersed as spheres within the BMI matrix. It was observed that the number of RD-730 globules increased with increasing weight fraction of RD-730 in the blend. At these higher fractions, RD-730 was also shown to coalesce to produce larger domains in the microstructure. Alleviating this problem to promote the formation of a continuous phase material involving BMI and the carbosilane ceramer would be desirable from the viewpoint of a hybrid material architecture with a gradient morphology.

The main purpose of the current work is to mitigate or even eliminate the morphological issue of phase separation in the preceramic–thermoset transition layer via the incorporation of suitably designed polymeric compatibilizers in the Starfire RD-730-BMI blends. This article describes in detail the design, synthesis, and characterization of polymeric compatibilizers utilized in the formation of the hybrid material; also described are the processing and the cure of the blend systems with the compatibilizers as well as the morphological characterization of the cured resin plaques to assess the extent of phase separation and the uniformity of distribution of the dispersant particles

relative to control specimens that did not contain any compatibilizer in their formulation.

Experimental

Materials

The Starfire resin RD-730 was purchased from Starfire Systems, Malta, New York, USA. The BMI formulation Matrimid[®] BMI A/B was purchased from Huntsman, Freeport, Texas. This two-part Matrimid 5292 system comprised of 4,4'-bismaleimido-diphenylmethane (component A) and 2,2'-diallylbisphenol A (DABA, component B). 2,2'-Diallylbisphenol A was of technical grade (85%) from Aldrich and was purified prior to use. Chlorotrimethylsilane, 1,5-hexadiene, and 2% cross-linked poly(4-vinylpyridine) were purchased from Aldrich (Sigma-Aldrich, St. Louis, Missouri, USA) and used with no further purification. 1,1,4,4-Tetramethyldisilyl ethane and platinum-divinyltetramethyldisiloxane complex were purchased from Gelest, Inc (Gelest Inc., Morrisville, Pennsylvania, USA) and were used without further purification.

Synthesis of polymeric compatibilizers for the Starfire–Matrimid blends

Purification of DABA. DABA was purified according to literature¹⁰ as shown in Figure 1.

Overall, 100 g of commercial DABA was purified by this process with excellent isolated yield (90%).

Bis(O-trimethylsilyl) 2,2'-diallylbisphenol A (trimethylsilyl)-protected DABA or bis(TMS)DABA. The synthesis was conducted according to the following scheme using poly(4-vinylpyridine) as the acid scavenger in the trimethylsilylation procedure (Figure 2).

In a 1.0 L three-necked round-bottomed flask equipped with a Dean-Stark apparatus and a reflux condenser, poly(4-vinylpyridine) was added, 2% cross-linked (33.0 g, 244 mmol of pyridine units). A 150-mL addition funnel containing purified, vacuum-dried DABA (35 g, 113 mmol) was attached. An argon atmosphere was established with the use of needles and septa and then anhydrous toluene (300 mL) was added to the flask by a cannula. The mixture was refluxed with magnetic stirring as about 50 mL of toluene with a few milliliter of water were removed and drained from the Dean-Stark separator. Anhydrous toluene (25 mL) was added to the addition funnel and mixed with the DABA, which was then added to the flask. Then chlorotrimethylsilane (26.5 g, 244 mmol) was added slowly by syringe. The mixture was heated to 80°C for 12 h. Upon cooling, the mixture was filtered through a 500 mL Russet pressure filter under an argon atmosphere to collect the poly(vinylpyridine) hydrochloride, which was washed several times with anhydrous toluene. The combined filtrate and washings were concentrated and kept for 48 h under high vacuum to afford pale yellow oil (49 g, 108 mmol, 96% yield).

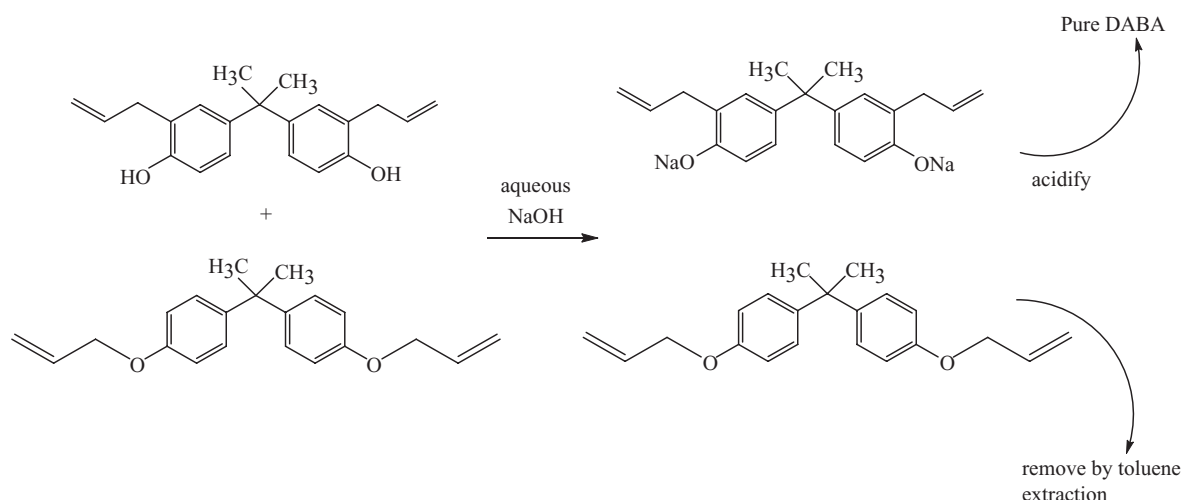


Figure 1. Purification scheme for 2,2'-diallylbisphenol A (DABA).

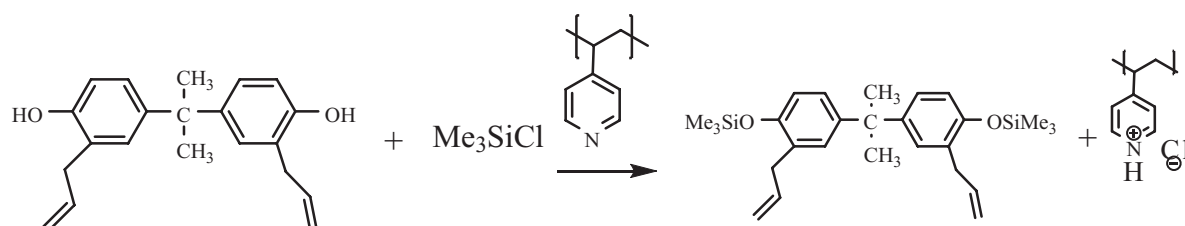


Figure 2. Synthetic scheme for bis(O-trimethylsilyl) 2,2'-diallylbisphenol A (bis(TMS)DABA).

*Block copolymer comprising tetramethyldisilylethyl units with hexyl and bis(*n*-propyl), bis(O-trimethylsilyl)bisphenol A linkers with approximately same number of repeat units in each block.* In a 500 mL round-bottomed flask equipped with a water-cooled Friedrich condenser, 125 mL addition funnel, and adapters for argon atmosphere, tetramethyldisilylethane (3.5 g, 23.9 mmol) and platinum-divinyldisiloxane complex (2.0–2.5% in xylene, 100 μ L) were added. An argon atmosphere was established and anhydrous methylene chloride (20 mL) was added by syringe. In the addition funnel, 1,5-hexadiene (1.746 g, 21.25 mmol), platinum-divinyldisiloxane complex (2.0–2.5% in xylene, 200 μ L), and methylene chloride (20 mL) were added. The contents of the addition funnel were mixed well under argon by bubbling with argon through a needle. Under argon, the contents of the addition funnel were slowly added in drops to the magnetically stirred reaction flask over a period of 30 min. (Initially, the mixture became warm enough to boil slightly.) After the addition was complete, the mixture was stirred at room temperature (RT) for a period of 4 h at RT. While maintaining an argon atmosphere in the reaction flask, the addition funnel was removed and charged with more tetramethyldisilylethane (3.29 g, 22.51 mmol) and bis(TMS)DABA (11.46 g,

25.31 mmol). The addition funnel was reattached and methylene chloride (20 mL) was added to the addition funnel and the contents were mixed well under argon by bubbling with argon through a long needle. The contents of the addition funnel were added to the reaction flask under argon over a period of 30 min. The mixture was then stirred under argon at RT for 72 h.

The volatiles were then evaporated in a stream of argon while warming the flask in a 50°C water bath affording clear brown oil. With stirring, the oil was triturated with 3 $\times$ 50 mL of methanol resulting in a milky white suspension. The suspension was centrifuged and the nearly clear supernatant was decanted leaving behind sticky oil that was stripped of volatiles under vacuum to afford a total mass of 20 g of white oil, designated as compatibilizer 1 precursor.

Deprotection of compatibilizer 1 precursor. The trimethylsilyl-protected block copolymer (Compatibilizer 1 precursor, 10.4 g) was transferred into a 1.0-L single-necked round-bottomed flask with about 100 mL of toluene. A solution of 11.0 mL of concentrated hydrochloric acid (HCl) in 489 mL of denatured ethanol was added to the flask and the mixture was stirred at RT overnight. The reaction mixture was added to 400 mL of methylene chloride and 200 mL of water in a 2.0 L separatory funnel. After mixing and

separating the layers, the upper layer was further extracted with 2×150 mL of methylene chloride. The combined methylene chloride extracts were extracted with distilled water (2×200 mL) until the extract comes to a neutral pH. The methylene chloride layer was dried (anhydrous sodium sulfate), concentrated, and finally dried under vacuum (<1 mm Hg) to afford 7.22 g of a slightly sticky foam, which was ground into an off-white powder (compatibilizer 1).

Block copolymer comprising tetramethyldisilylethyl units with hexyl and bis(*n*-propyl) bis(*O*-trimethylsilyl)bisphenol A linkers with unequal numbers of the two block repeat units. In a 500-mL round-bottomed flask equipped with a water-cooled Friedrich condenser, 125 mL addition funnel, and adapters for argon atmosphere, tetramethyldisilylethane (6.56 g, 44.8 mmol) and platinum-divinyldisiloxane complex (2.0–2.5% in xylene, 100 μ L) were added. An argon atmosphere was established and anhydrous methylene chloride (20 mL) was added by syringe. In the addition funnel, 1,5-hexadiene (3.46 g, 42.2 mmol), platinum-divinyldisiloxane complex (2.0–2.5% in xylene, 200 μ L) and methylene chloride (20 mL) were added. The contents of the addition funnel were mixed well under argon by bubbling with argon through a needle. Under argon, the contents of the addition funnel were slowly added in drops to the magnetically stirred reaction flask over a period of 30 min. After the addition was complete, the mixture was stirred at RT for a period of 7 h at RT. While maintaining an argon atmosphere in the reaction flask, the addition funnel was removed and charged with tetramethyldisilylethane (1.929 g, 13.18 mmol) and bis(TMS)DABA (7.16 g, 15.81 mmol). The addition funnel was reattached and methylene chloride (20 mL) was added by syringe to the addition funnel and the contents were mixed well under argon by bubbling with argon through a long needle. The contents of the addition funnel were added to the reaction flask under argon over a period of 30 min. The mixture was then stirred under argon at RT for 72 h. The contents of the reaction flask were transferred to a single-necked round-bottomed flask and stripped of volatiles (rotary evaporator, 24 h at <1.0 mm Hg vacuum) to afford clear light brown oil (compatibilizer 2 precursor, 19.0 g, 100% yield).

Deprotection of compatibilizer 2 precursor. The trimethylsilyl-protected block copolymer (compatibilizer 2 precursor, 19.0 g) was transferred into a 1.0-L single-necked round-bottomed flask in about 150 mL of toluene. A solution of 11.0 mL of concentrated HCl in 489 mL of denatured ethanol was added to the flask and the mixture was stirred at RT overnight. The reaction mixture was added to 500 mL of methylene chloride and 300 mL of water in a 2.0 L separatory funnel. After mixing and separating the layers, the upper layer was further extracted with 3×200 mL of methylene chloride. The combined methylene chloride extracts were extracted with distilled water

(3×200 mL) until the extract comes to neutral pH. The methylene chloride was dried (anhydrous sodium sulfate), concentrated, and finally dried under vacuum (<1 mm Hg) to afford a light brown gum (compatibilizer 2, 16.7 g, 99.5% yield).

Homopolymer comprising tetramethyldisilylethyl and bis(*n*-propyl) bis(*O*-trimethylsilyl)bisphenol A units. In a 500-mL round-bottomed flask equipped with a water-cooled Friedrich condenser, 125 mL addition funnel, and adapters for argon atmosphere, tetramethyldisilylethane (5.12 g, 35.0 mmol) and platinum-divinyldisiloxane complex (2.0–2.5% in xylene, 100 μ L) were added. Bis(TMS)DABA (15.85 g, 35.0 mmol) and platinum-divinyldisiloxane complex (2.0–2.5% in xylene, 200 μ L) were added to the funnel. An argon atmosphere was established and anhydrous methylene chloride (20 mL) was added by syringe to the flask. Methylene chloride (20 mL) was also added to the addition funnel by syringe and the contents were mixed well under argon by bubbling with argon through a long needle. The contents of the addition funnel were added to the contents of the magnetically stirred reaction flask under argon over a period of 30 min. The mixture was then stirred under argon at RT for 72 h. The contents of the reaction flask were transferred to a single-necked round-bottomed flask and stripped of volatiles (rotary evaporator and under vacuum for 24 h at <1.0 mm Hg) to afford clear light brown oil (compatibilizer 3 precursor, 21.0 g, 100% yield).

Deprotection of compatibilizer 3 precursor. The trimethylsilyl-protected polymer (compatibilizer 3 precursor, 21 g) was transferred into a 1.0-L single-necked round-bottomed flask in about 150 mL of toluene. A solution of 11.0 mL of concentrated HCl in 489 mL of denatured ethanol was added to the flask and the mixture was stirred at RT overnight. The reaction mixture was added to 500 mL of methylene chloride and 300 mL of water in a 2.0 L separatory funnel. After mixing and separating the layers, the upper layer was further extracted with 3×200 mL of methylene chloride. The combined methylene chloride extracts were extracted with distilled water (3×200 mL) until the extract comes to a neutral pH. The methylene chloride was dried (anhydrous sodium sulfate), concentrated, and finally dried under vacuum (<1 mm Hg) to afford a light brown gum (compatibilizer 3, 15.5 g, 97% yield).

Characterization of polymers. The molecular weights of the homo and block copolymers prepared in this study were characterized by gel permeation chromatography. The analysis was carried out in *N*-methylpyrrolidone (NMP) as solvent at 70°C. Structural characterization was accomplished with the help of infrared spectra using Nicolet 4700 FT-IR, taken in the reflectance mode for the isolated (neat) polymer either as powder or as light brown gum. Both

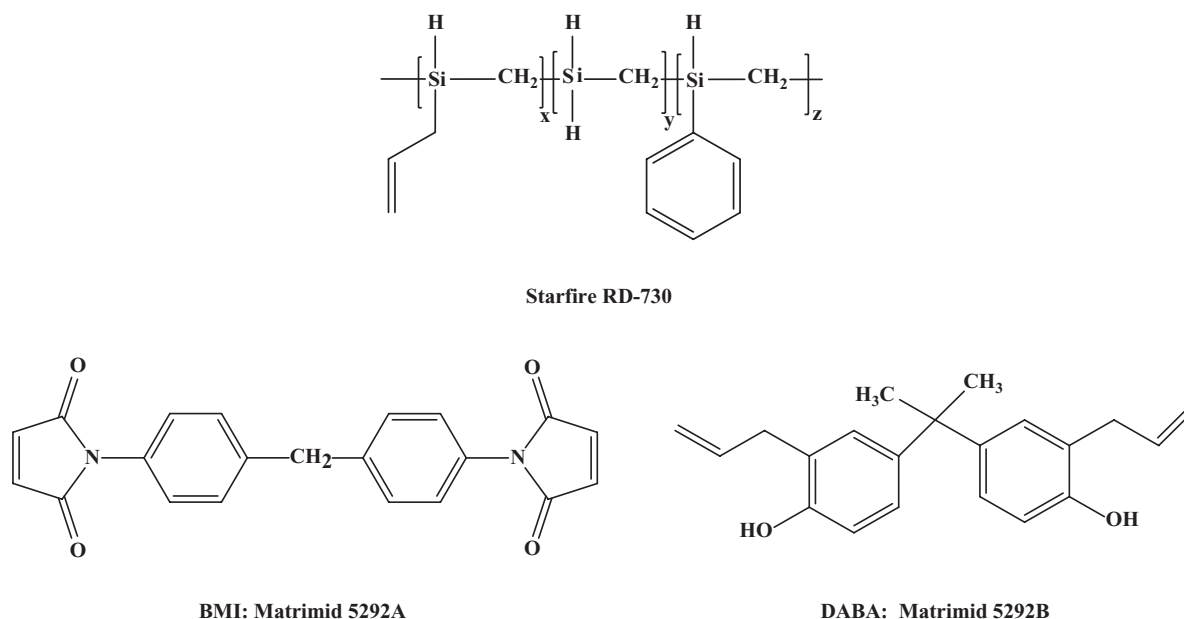


Figure 3. Chemical structures of Starfire RD-730 and Matrimid resin 5292 A and B.

proton nuclear magnetic resonance spectroscopy (^1H NMR) and ^{13}C carbon nuclear magnetic resonance (^{13}C NMR) spectra were obtained on polymer solutions in deuteriochloroform (CDCl_3). The glass transition temperatures of the synthesized polymers were determined by differential scanning calorimetry (DSC; TA Instruments Q1000) and their thermal stabilities were assessed by thermogravimetric analysis (TGA; TA Instruments Q5000) at a heating rate of $20^\circ\text{C min}^{-1}$.

Blending of compatibilizers with Starfire RD-730–Matrimid 5292 and further cure

Control specimen containing Starfire and Matrimid 5292. Mixing experiments incorporating the compatibilizers 1, 2, and 3 in the Starfire/DABA/BMI system were performed followed by high temperature cure of the resulting blends. Control or reference sample (without the compatibilizer) was 20 g of a 10 wt% Starfire blend that comprised 2.0 g of Starfire and 18 g Matrimid 5292. Matrimid 5292 was made up of 7.7 g DABA and 10.3 g BMI. The typical procedure was as follows. Starfire resin was taken up in a beaker and warmed on the hot plate, DABA (a viscous liquid) was added to the softened resin, and the mixture was magnetically stirred in a 150°C oil bath. To the stirred mixture, BMI powder was added in small installments to ensure thorough mixing. After ~ 10 min, the homogeneous mixture was poured into silicone molds to be further cured in the autoclave.

Mixing of compatibilizers 1–3 in the Starfire–Matrimid 5292 resin system. The composition of the resin mixture was comparable with the control sample except that 5 wt% of the

compatibilizer (relative to the 20 g mass of Starfire + Matrimid) was added. The general procedure is described below. After the Starfire resin and DABA were thoroughly mixed/stirred in a beaker heated in a 150°C oil bath, 1 g of the compatibilizer was added to the hot mixture. BMI powder was added in parts to the hot mixture. After the addition was complete, the hot mixture was poured into silicone molds. While all the compatibilizers seemed to dissolve in the hot liquid comprising Starfire and DABA, the addition of the compatibilizer 1 to the mixture was accompanied by some foaming that persisted during the addition of BMI as well. The mixing of 5 wt% of the compatibilizers 2 and 3 into the Starfire/DABA mixture, on the other hand, was quite smooth and no foaming was observed.

Besides the samples described above, two Starfire–Matrimid blends containing 1 wt% of compatibilizers 2 and 3 (0.20 g of the compatibilizer in each case) were also fabricated. The hot mixtures were poured into silicone molds and autoclaved overnight at 200°C to effect curing.

Morphological characterization of cured Starfire–Matrimid resin systems. The morphology of the cross-sections of the cured resin specimens was examined by scanning electron microscopy (SEM; Quanta 600F SEM). Several images of the sample cross-section were taken in each case.

Results and discussion

Design of compatibilizers

The chemical structures of the Starfire RD-730 resin, Matrimid 5292A (BMI), and Matrimid 5292B (DABA) are shown in Figure 3.

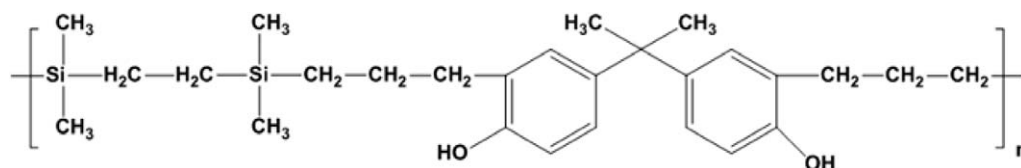


Figure 4. Homopolymer containing carbosilane and bis(n-propyl)bisphenol A structural units.

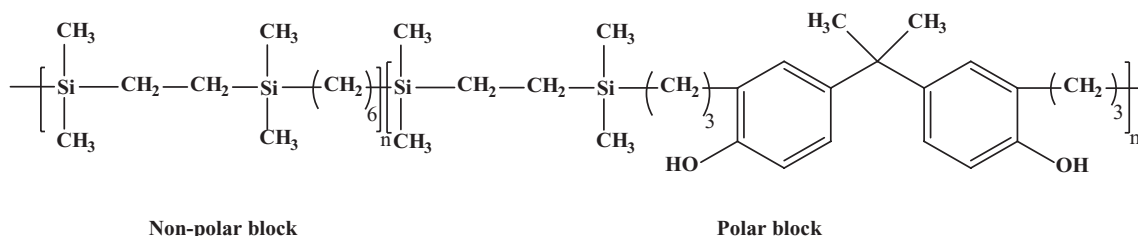


Figure 5. Carbosilane block copolymer containing hexyl and bis(n-propyl)bisphenol A linkers.

A likely explanation for the observed phase separation is that the nonpolar polycarbosilane is sparingly miscible or even immiscible with the relatively polar Matrimid system (containing phenolic and imide groups) during the mixing stage and, consequently, phase separation is promoted during and after the cure. Perhaps secondarily, the phase separation phenomenon may be explained by differing rates of reaction between BMI and (1) allyl groups on DABA and the (2) allyl groups on the Starfire resin. Accordingly, if the DABA/BMI system cures rapidly, during the typical Matrimid 5292 heating profile, then very few reactive maleimide groups will be present in the system for co-reaction with the Si-allyl groups on the Starfire polymer.

The cure mechanism of the Matrimid resin system discussed by Phelan and coworkers¹¹ invokes "ene" reaction of DABA with BMI as the first step in the cure followed by Diels-Alder reaction and rearomatization in the subsequent steps of the cure. While the Diels-Alder addition that occurs in the second step between the "ene" adduct formed in the first step and BMI is favored by the presence of the electron-rich phenolic group, the role of the phenolic group and its effect on reaction rates is not entirely clear. Nevertheless, if the Starfire can be made more miscible with the Matrimid components and if, as a result, early Starfire phase separation can be slowed, and then this may cause the Starfire domains to be much smaller than what was previously observed. This could result in the production of a BMI/Si-C hybrid, or at least, a material that is compatible with BMI-type processes but is converted to SiC during heat exposure/end-use conditions.

The approach we describe in this article for improving the homogeneity and the miscibility of Starfire-Matrimid blends consists of incorporation of small amounts of suitably designed compatibilizers in the blend system followed by the cure of the blend. The molecular design of the

compatibilizers was based on the combined structural similarity to two of the components in the Starfire resin-Matrimid blends, that is, polycarbosilane and DABA. We envisaged that a simple homopolymer backbone structure consisting of a nonpolar carbosilane unit and a polar bisphenol A-type unit would be representative of such a compatibilizer. The structure of such a homopolymer containing dipropyl-substituted bisphenol A and tetramethyldisilylthane units can be readily prepared from commercially available starting materials and will be used as one of the compatibilizers in this study (Figure 4).

We have also extended this structural motif by exploring similar methodology to that described above for synthesizing well-designed block copolymers consisting of a nonpolar segment as well as a relatively more polar phenolic block that may result in well-defined polar and nonpolar domains for enhanced compatibilization and miscibility of Starfire and Matrimid systems. The structure of such a block copolymer for utilization as a compatibilizer in this study contains a nonpolar block in which a carbosilane is attached to a hydrocarbon chain and a polar block that has the repeat unit of the homopolymer backbone shown above. The nonpolar block can be considered a "carbosilane-modified paraffin" analogous to the siloxane modification of a long chain hydrocarbon 1,9-decadiene via hydrosilylation reaction, reported in the literature.¹² The chemical structure of the carbosilane block copolymer compatibilizer containing hexyl and dipropyl-substituted bisphenol A linkers is shown above (Figure 5).

Purification and protection of DABA. DABA was purified by preparing the corresponding disodium salt, followed by toluene extraction of impurities, such as diallyloxy bisphenol A, followed by reacidification to regenerate DABA. Protection of the phenolic OHs of DABA by bis O-trimethylsilylation was effected by reaction of DABA

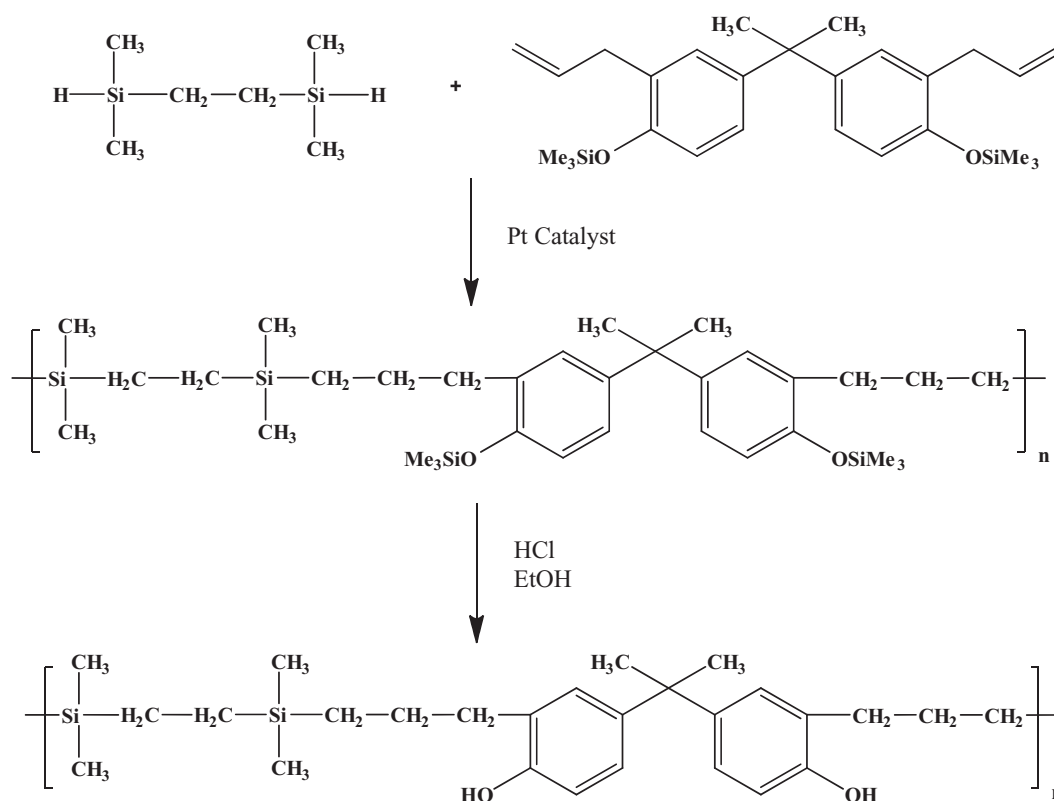


Figure 6. Schematic representation of the synthesis of homopolymer comprising carbosilane and bis(*n*-propyl) bisphenol A units.

with trimethylsilylchloride in the presence of poly(4-vinylpyridine) as acid scavenger as depicted earlier in a scheme in the experimental section. Using our novel procedure, purification was greatly simplified, requiring only filtration to remove the poly(4-vinylpyridine) hydrochloride and then concentration of the filtrate to afford the desired product in 100% yield. The alternative literature procedure requires the use of *N,O*-bis(trimethylsilyl)acetamide in the reaction followed by lengthy purification on silica gel using *n*-pentane/diethylether mixture, affording only 80% yield.¹⁰

Synthesis of compatibilizer based on homopolymer containing tetramethyldisilylethyl and bis(*n*-propyl)bisphenol A units (compatibilizer 3). The scheme for the homopolymer synthesis is shown in Figure 6. It is reported that this type of hydrosilylation can be carried out without noticeable side reactions involving the phenolic $-\text{OH}$ itself.^{13,14} However, to maximize the yields of the desired hydrosilylation product, bistrimethylsilyl-protected DABA, rather than DABA, was hydrosilylated with tetramethyldisilylethane in the presence of a soluble platinum complex as catalyst, followed by deprotection. The hydrosilylation reaction was found to proceed smoothly at RT resulting in the isolation of the product as clear, light brown oil in quantitative yields. The deprotection reaction was carried out using a solution of

concentrated HCl in ethanol at RT. The final product, after solvent extraction and vacuum drying, was isolated in excellent yields (97%).

Synthesis of block copolymers comprising tetramethyldisilylethyl, hexyl and bis(*n*-propyl) bisphenol A units (compatibilizers 1 and 2). The hydrosilylation process followed by deprotection for preparing block copolymers containing nonpolar blocks (with hexyl units) and relatively more polar blocks (with substituted bisphenol A unit) is shown schematically in Figure 7. These block copolymers were synthesized by first reacting 1,5-hexadiene with a slight molar excess of tetramethyldisilylethane in a methylene chloride solution containing platinum–divinylsiloxane complex (2.0–2.5% in xylene). Reaction at RT for 4–7 h resulted in a block with hexane alternating with tetramethyldisilylethane units and terminated with reactive hydridodimethylsilane groups. In the same reaction flask, *O*-trimethylsilyl-protected DABA and tetramethyldisilylethane were added with a slight molar excess of *O*-trimethylsilyl-protected DABA such that the final stoichiometry of the reaction mixture resulted in the other block containing tetramethyldisilylethane unit alternating with *O*-trimethylsilyl-protected bis(*n*-propyl) bisphenol A units. Two block copolymer compositions, one with equal number of repeat units of both blocks ($n = m$, compatibilizer 1) and the other with unequal numbers of

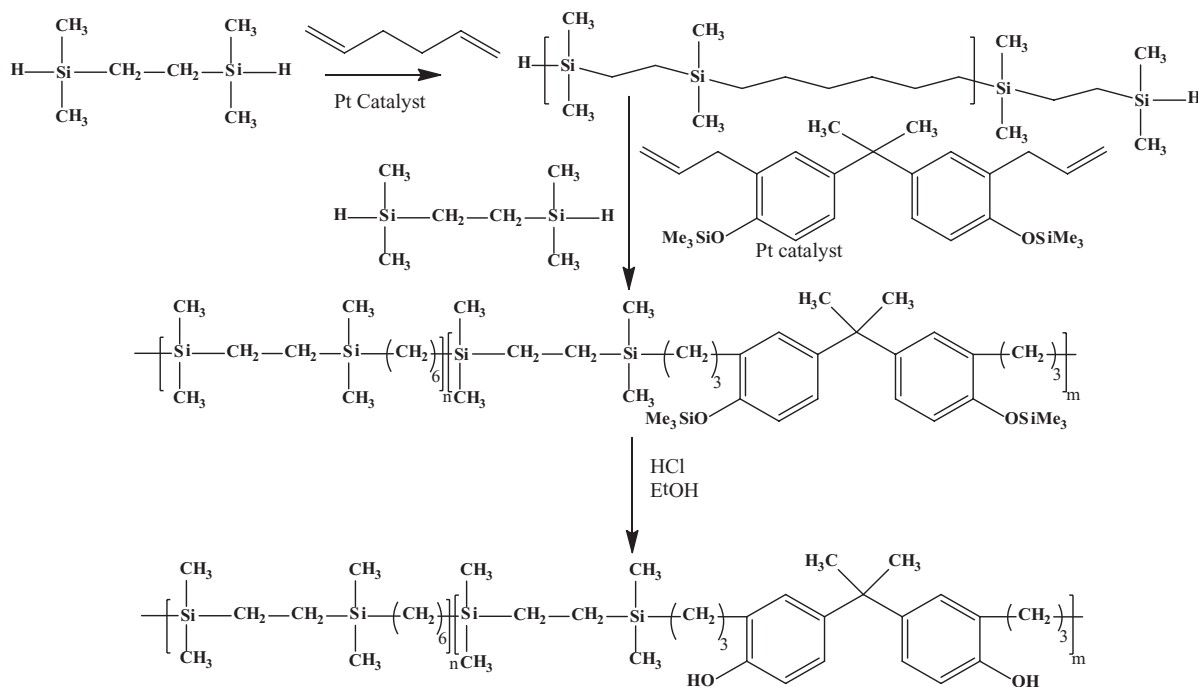


Figure 7. Schematic representation of the synthesis of block copolymers comprising tetramethyldisilylethyl, hexyl, and bis(*n*-propyl) bisphenol A units.

the two repeat units ($n:m = 16:6$, compatibilizer 2) were prepared as described in the Experimental section by varying the relative amounts of tetramethyldisilylethane added in the two hydrosilylation steps as well as the amount of bis(TMS)DABA added in the second hydrosilylation step. Again, the deprotection reaction involving ethanolic HCl to yield the desired copolymer was nearly quantitative.

Characterization of the compatibilizers based on homo and block copolymers in this study

Molecular weight determination. The molecular weights of the block copolymers (compatibilizers 1 and 2) and the homopolymer (compatibilizer 3) were derived from size exclusion chromatography (SEC) measurements. SEC analysis was performed using a Viscotek Model 300 TDA system equipped with refractive index, viscosity, and light scattering detectors operating at 70°C. Two Polymer Laboratories 5 μ m PL gel Mixed C columns were used with NMP (with 0.5% LiBr) as the eluent and a Thermoseparation Model P1000 pump operating at 0.8 mL min⁻¹. Polymer molecular weights were calculated from the Refractive Index (RI) signal and are reported relative to polystyrene standards. The results are listed in Table 1.

All the compatibilizers were synthesized in high molecular weights as evidenced by the Gel Permeation Chromatography (GPC) results and were strongly indicative of the quantitative nature of the polymer-forming reaction. A

Table 1. Polymer molecular weight determination by SEC.

Polymer sample	Mn	Mw	PDI
Compatibilizer 1	23, 300	162, 000	7
Compatibilizer 2 ^a	443, 092	510, 536	1.2
Compatibilizer 3	16,400	145, 100	8.8

PDI: polydispersity index; SEC: size exclusion chromatography.

^aPeaks corresponding to low molecular weight polymers/oligomers were also observed in the chromatogram.

broad molecular weight distribution was obtained for two of the polymers (7–8.8) while the block copolymer compatibilizer 2 showed a much narrower polydispersity index (PDI) of 1.2 for the high molecular weight peak.

IR characterization of the compatibilizers. Infrared spectra of the starting material tetramethyldisilylethane and the homopolymer (compatibilizer 3) are shown in Figure 8. The sharp Si–H at ~ 2150 cm⁻¹ in the starting material is clearly absent in the polymer structure indicating complete consumption of the Si–H groups in the hydrosilylation reaction. In addition, the presence of a broad –OH absorption centered on 3400 cm⁻¹ was evident in the final product due to the presence of the substituted bisphenol A groups. An aromatic C–H stretch at ~ 3025 cm⁻¹, aliphatic C–H stretches in the range of 2950–2870 cm⁻¹ as well as aromatic C=C stretching modes ranging from 1607 to 1500 cm⁻¹ are also indicative of the assigned polymer structure.

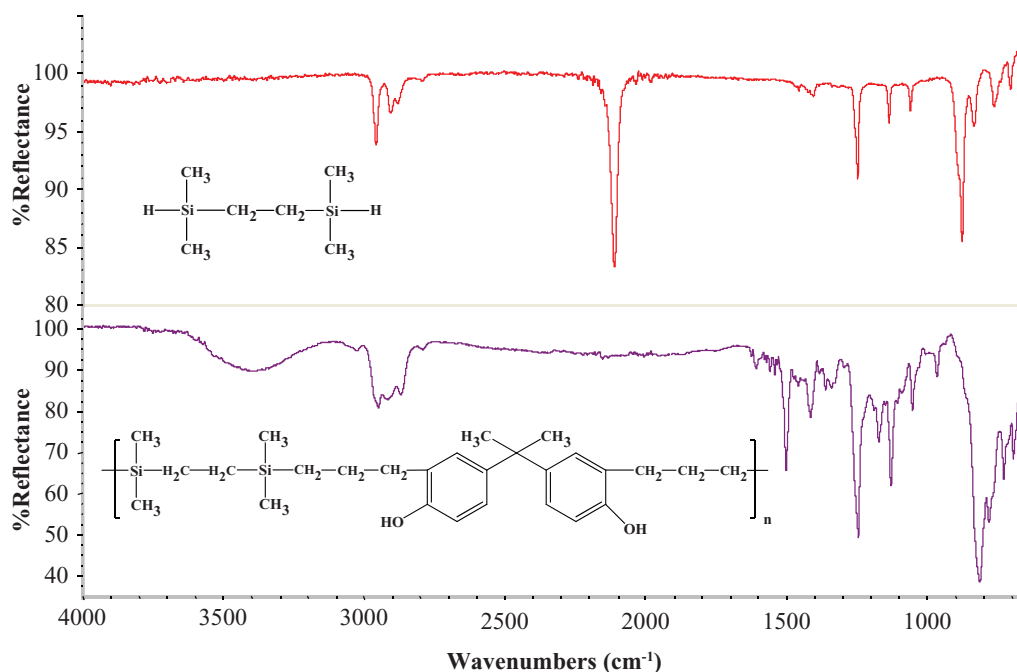


Figure 8. IR spectra of the starting material tetramethyldisilylethane (top) and the homopolymer (compatibilizer 3, bottom).

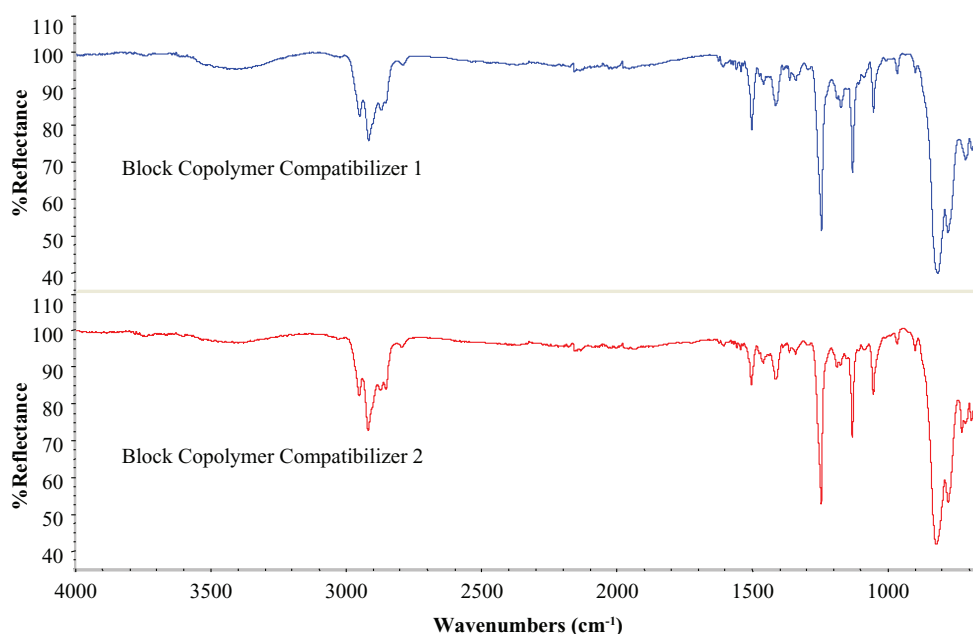


Figure 9. IR spectra of the two block copolymers (compatibilizers 1 and 2) with varying proportions of the polar and nonpolar segments in the backbone.

The IR spectra of the two copolymer compatibilizers 1 and 2 are nearly identical (Figure 9). The infrared spectrum of homopolymer (compatibilizer 3, Figure 8) shows a much stronger $-\text{OH}$ absorption at 3400 cm^{-1} than the IR spectra of the block copolymers (compatibilizers 1 and 2) in Figure 9, which can be attributed to the higher content of substituted bisphenol A content in its structure, which was prepared

without the use of 1,5-hexadiene as the comonomer. It can also be seen that compatibilizer 1 has a slightly stronger OH absorption than compatibilizer 2, reflecting a relatively higher proportion of the polar phenolic block in its structure.

NMR spectral characterization. All the NMR spectra were taken in CDCl_3 without added TMS in order to observe the

upfield resonance due to the methyl groups in the tetramethyldisilyl moiety attached to the polymer backbone.

^1H NMR and ^{13}C solution spectra (CDCl_3) of the two copolymers (compatibilizers 1 and 2) are shown representatively in Figures 10 to 13 depicting the various structural units (tetramethyldisilylethyl moiety linked to the disubstituted bisphenol A unit in the polar block and to the hexamethylene unit in the nonpolar block) in the copolymer architecture. The ^1H NMR spectrum of the block copolymer compatibilizer 1, synthesized with an equal number of repeat units of the nonpolar and polar blocks is shown in Figure 10. The upfield resonances due to the aliphatic protons occur in the -0.064 ppm (due to the methyl groups in the tetramethyldisilyl unit) to 2.6 ppm (due to the methylenes attached to the aromatic carbon) range. The downfield resonances are due to the phenolic $-\text{OH}$ group (broad, at ~ 5 ppm) and the aromatic carbons in the range of 6.3 – 7.0 ppm. The solvent peak (protic impurity in CDCl_3) is observed around 7.26 ppm.

The spectrum is consistent with the assigned copolymer structure, the ratio of the integrated resonances of all the aliphatic protons (-0.06 to 2.6 ppm) to the combined phenolic $-\text{OH}$ and aromatic $\text{C}-\text{H}$ resonances (5 – 7 ppm) is ~ 9.0 , being close to the expected value based on the structure and composition. The assigned structure was also corroborated by the ^{13}C NMR spectrum of the copolymer in CDCl_3 (Figure 11).

The aromatic resonances are observed in the range of 115 – 155 ppm, the most downfield resonance at 151 ppm being assigned to the ipso-aromatic carbon attached to the $-\text{OH}$ group. The aliphatic resonances ranged between approximately -3 to 45 ppm. The most downfield resonance (~ 42 ppm) in this range is assigned to the quaternary carbon in the isopropylidene group of the disubstituted bisphenol moiety while the most upfield resonance (approximately -3 ppm) is due to the methyl carbons attached to Si in the tetramethyldisilylethyl moiety in the copolymer structure. The solvent (CDCl_3) carbon resonance occurred at 77 ppm (not shown in the spectrum).

The ^1H NMR spectrum of block copolymer compatibilizer 2 synthesized with the higher proportion of the nonpolar block relative to the polar block in the copolymer structure ($n:m = 16:6$) is shown in Figure 12. While qualitatively, the spectrum resembles that of the block copolymer compatibilizer 1 shown in Figure 10, the ratio of the aliphatic proton resonances (-0.02 to 2.6 ppm) to the combined aromatic (6.5 – 7.0 ppm) and phenolic OH (broad signal centered around 5 ppm) is expectedly higher than that observed for the compatibilizer 1 (15 vs. 9) and is corroborative of the assigned structure and composition of the copolymer.

The ^{13}C NMR of the copolymer compatibilizer 2 in CDCl_3 is shown in Figure 13. The solvent resonance due to CDCl_3 around 77 ppm serves as the reference. The aromatic resonances in the 120 – 135 ppm range are expanded as an inset in the spectrum. While qualitative similarities in the spectra

of the two block copolymer structures (Figures 11 and 13) are readily seen, a higher intensity of the aliphatic resonances in relation to the aromatic resonances is observed in the compatibilizer 2 copolymer structure compared with the compatibilizer 1 copolymer.

Thermal characterization of the polymers. DSC analysis of the polymer samples was conducted in a nitrogen atmosphere from -50 to 100°C at a rate of $20^\circ\text{C min}^{-1}$. Clear and repeatable glass transition temperatures (T_g s) were found for these materials and the values are summarized in Table 2. The T_g was found to increase with an increase in the content of the polar block containing dipropyl-substituted bisphenol A moiety and was the highest for the homopolymer (compatibilizer 3). An overlay plot of the DSCs of the block copolymer-based compatibilizers 1 and 2 and the homopolymer compatibilizer 3 (Figure 14) reveals T_g s broadening, while shifting to lower temperatures for the copolymers relative to the homopolymer as the substituted diphenol content decreases. Among the two copolymers (compatibilizers 1 and 2), T_g was found to decrease as a function of increasing nonpolar block content.

TGA was conducted in nitrogen and in air. Comparative thermal stability data in nitrogen and in air are shown in Figure 15 for the homopolymer (compatibilizer 3) and for the block copolymers (compatibilizers 1 and 2).

Qualitatively similar thermal degradation profiles were observed for both the homo and the block copolymers when heated up to 800°C in nitrogen. Two weight loss regimes were observed, the minor one (~ 5 wt%) occurring in the range of 200 – 300°C , presumably due to the volatilization of some low molar mass materials in the samples. The second degradation was predominant and occurred in the range of 400 – 500°C for all the polymers with the maximum weight loss occurring around 430 – 445°C for all the three compatibilizers. While small amounts of the residue were left behind after the TGA experiment in nitrogen, larger amounts of residue (10 – 12 wt % in the case of the homo and the copolymers) were found in the TGA conducted in air. This is presumably due to the presence of oxidative products such as silicon dioxide and silicon oxycarbide occurring at the higher temperatures. In contrast to the experiment conducted in nitrogen, TGAs in air show a more complex degradation profile. There were three distinct decomposition stages in the range of 200 – 600°C for all the polymers, with the maximum degradation occurring in the 450 – 550°C region. The compatibilizer 2 containing the highest proportion of the nonpolar (carbosilane-hydrocarbon) block was found to be relatively less thermo-oxidatively stable than the other two.

Morphology of cured specimens

Control sample containing 10 wt% Starfire resin in the Starfire–Matrimid 5292 blend system. SEMs of a control

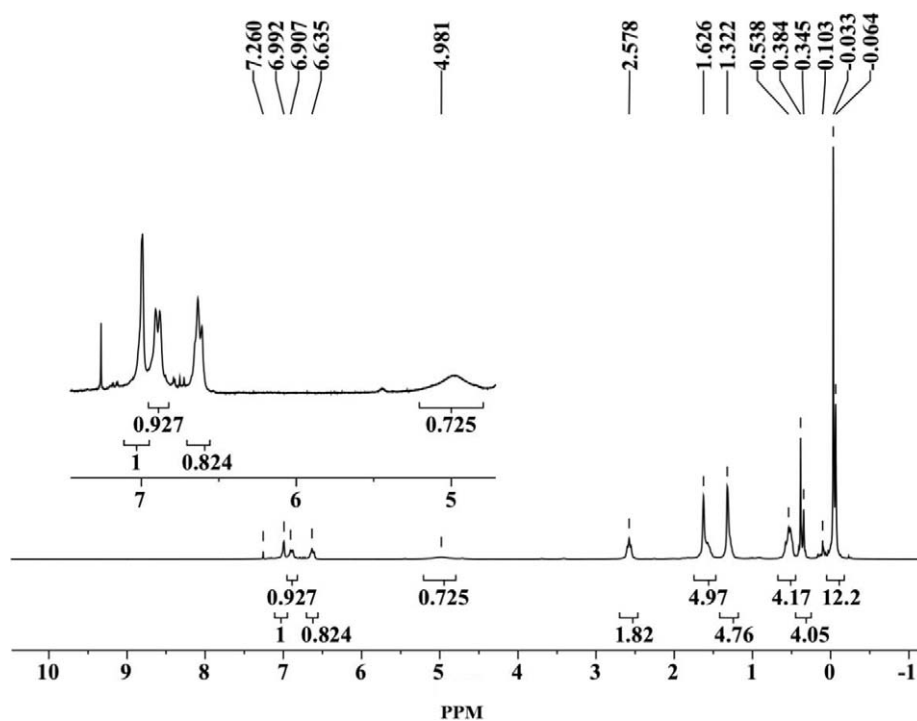


Figure 10. ¹H NMR spectrum of the copolymer (compatibilizer I, with an equal number of the two repeat units in the backbone) containing the tetramethyldisilylethyl unit linked to the dipropyl-substituted bisphenol A unit as well as to the hexamethylene unit.

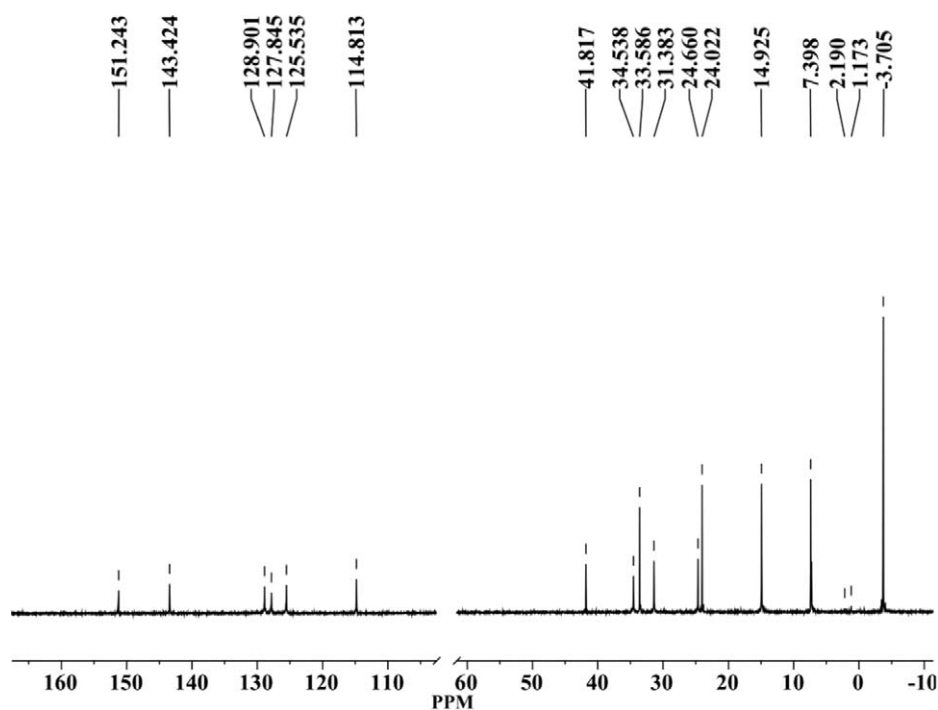


Figure 11. ¹³C NMR spectrum of the copolymer (compatibilizer I, with an equal number of the two repeat units in the backbone) containing the tetramethyldisilylethyl unit linked to the dipropyl-substituted bisphenol A unit as well as to the hexamethylene unit.

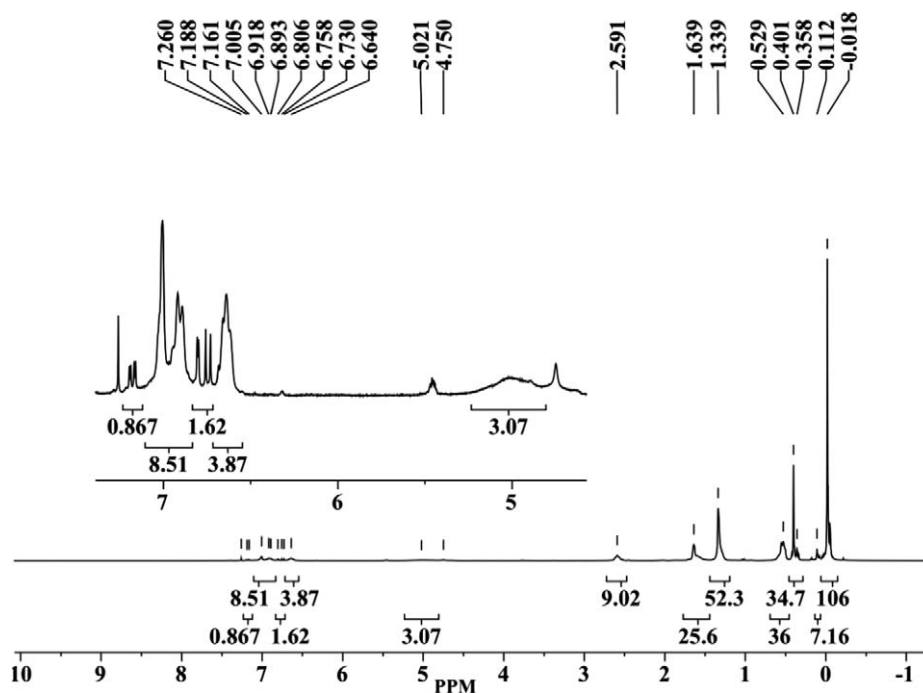


Figure 12. ^1H NMR spectrum of the copolymer (compatibilizer 2, richer in the nonpolar block) containing the tetramethyldisilylethyl unit linked to the dipropyl-substituted bisphenol A unit as well as to the hexamethylene unit.

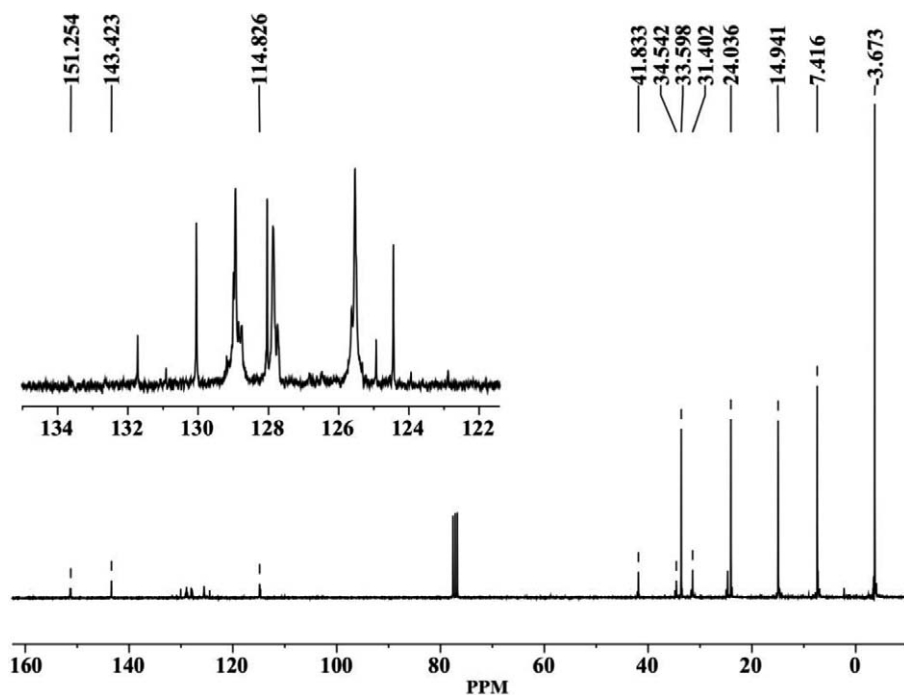


Figure 13. ^{13}C NMR spectrum of the copolymer (compatibilizer 2, richer in the nonpolar block) containing the tetramethyldisilylethyl unit linked to the dipropyl-substituted bisphenol A unit as well as to the hexamethylene unit.

Table 2. Glass transitions temperatures of the compatibilizers as determined by DSC.

Polymer	T_g first heat ($^{\circ}\text{C}$)	T_g second heat (rescan; $^{\circ}\text{C}$)
Compatibilizer 1	27.2	29.7
Compatibilizer 2	13.1	12.3
Compatibilizer 3	38.4	41.4

DSC: differential scanning calorimetry.

sample of the (10 wt%) Starfire RD-730–Matrimid systems (without the addition of any compatibilizer) are shown in Figure 16 under low and high magnification. The Starfire phase is lighter in color and is dispersed in the dark colored Matrimid matrix. The lower magnification micrograph shows that the Starfire is unevenly distributed in the BMI matrix with more Starfire concentrated near the top of the cross-section (top of the mold) and less near the bottom. As shown in Figure 16, the higher magnification micrograph shows distinct, phase separated domains of the Starfire domains in Matrimid. These domains are mostly spherical and while a distribution of sizes is indicated, they are typically 25 μm and above in diameter. The Starfire domains are also seen to contain dark specks, which may be due to the Matrimid inclusions within the Starfire.

The SEM morphologies of the Starfire–Matrimid systems blended with the compatibilizers (*vide infra*) compared with that of the control sample are discussed in the context of the relative polarities of the homo and block copolymer systems tested as compatibilizers in the cured plaque specimens of Starfire RD-730–Matrimid formulations in this study. The three compatibilizers in the order of increasing polarity in the polymer backbone are as follows: compatibilizer 2 < compatibilizer 1 < compatibilizer 3.

Compatibilizer 2 with the large carbosilane-hydrocarbon block is the least polar among the polymers, whereas the homopolymer (compatibilizer 3) is the most polar due to the large diphenol content in its repeat unit. Compatibilizer 1 was designed to have an approximately equal number of the nonpolar and polar block units and thus has intermediate polarity.

Starfire–Matrimid (10 wt% Starfire resin) blends incorporating compatibilizers 1–3. Examination of the SEMs of Starfire–Matrimid blends incorporating 5 wt% compatibilizer 2 (Figure 17), based on the least polar block copolymer, reveals that the problems of uneven distribution and phase separation of Starfire domains are even more pronounced than in the control sample (*vide supra*). The Starfire domains seem more drastically segregated toward the top of the specimen. At the higher magnification as seen in Figure 17, the Starfire domains, on an average, are as large as or even larger than seen in the control specimen.

In addition, some globular, dark, and grey domains are observed, which may be attributed to the aggregated or partially phase separated compatibilizer.

SEM micrographs of Starfire–Matrimid plaques with 1% added compatibilizer 2 (Figure 18) show qualitatively similar results except that the high magnification SEM shows somewhat well-defined spherical particles of the Starfire-dispersed phase. The average domain size revealed by SEM is similar to that observed for the control sample and thus it is evident that the addition of this compatibilizer did not improve the miscibility of the Starfire and Matrimid components in the mixture. On the other hand, SEMs of Starfire–Matrimid with compatibilizer 1 (5 wt%, Figure 19) indicate that the presence of this compatibilizer with intermediate polarity resulted in distinct improvement in phase separation and in reducing domain size. The micrograph at the higher magnification (Figure 19) shows Starfire domain sizes to be typically of the order of 10 μm compared with larger than 25 μm sizes seen in the control specimen. Besides, several smaller spherical domains are seen as well. Furthermore, several small, dark circles seen around the brighter, white spheres in the SEM may be attributed to the compatibilizer breaking up discrete Starfire domains but nevertheless failing to provide a cured specimen that is completely homogeneous.

In contrast to the blends incorporating compatibilizers 1 and 2, the morphology of a cured blend of Starfire–Matrimid blend containing 5 wt% of compatibilizer 3 (homopolymer in this study) was dramatically different. The SEMs (Figure 20) show a homogeneous distribution of very small Starfire domains.

At 40 $\times$ magnification (Figure 20), a grey field is seen with a homogeneous distribution of the Starfire phase. At 1000 $\times$ magnification, even the larger spherical domains of Starfire are seen as about 5 μm or less in size and all the Starfire domains appear to be uniformly distributed in the sample. SEMs of specimens containing just 1 wt% of compatibilizer 3 show a distribution of Starfire domains with somewhat larger phase-separated domains (~ 10 microns, Figure 21). Evidently, even this sample was found to show an obvious improvement in Starfire distribution as well as in particle size when compared with the control sample (Figure 16).

Thus, it is evident from all the above discussion that the most effective compatibilizer among the ones evaluated for the Starfire RD-730–Matrimid system was the homopolymer consisting of the substituted bisphenol A unit with the carbosilane linker.

Conclusions

The main purpose of the current work was to mitigate or eliminate the morphological issue of phase separation in a preceramic–thermoset transition layer consisting of a Starfire RD-730–Matrimid blend, via the incorporation

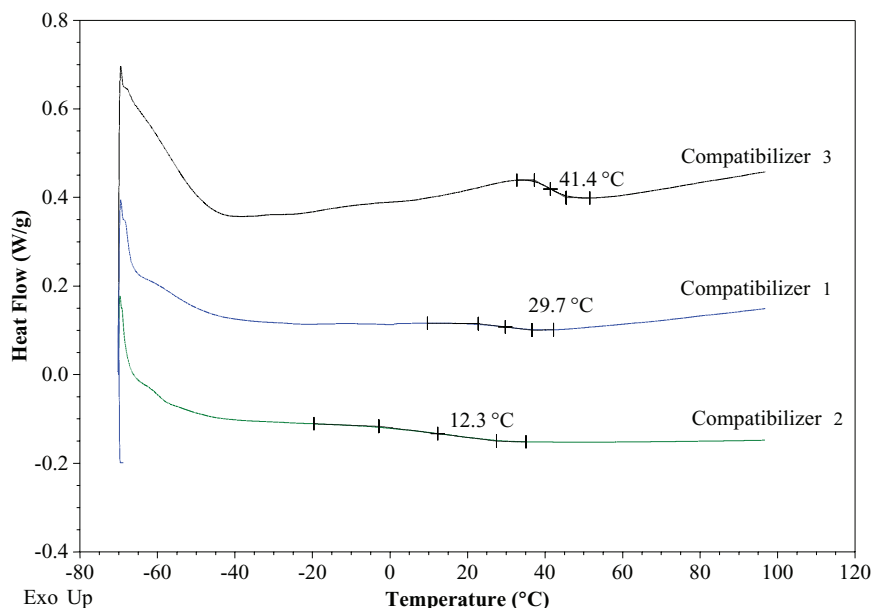


Figure 14. Overlay DSC traces of compatibilizers 3 (top), 1 (middle), and 2 (bottom) showing T_g s during second heating.

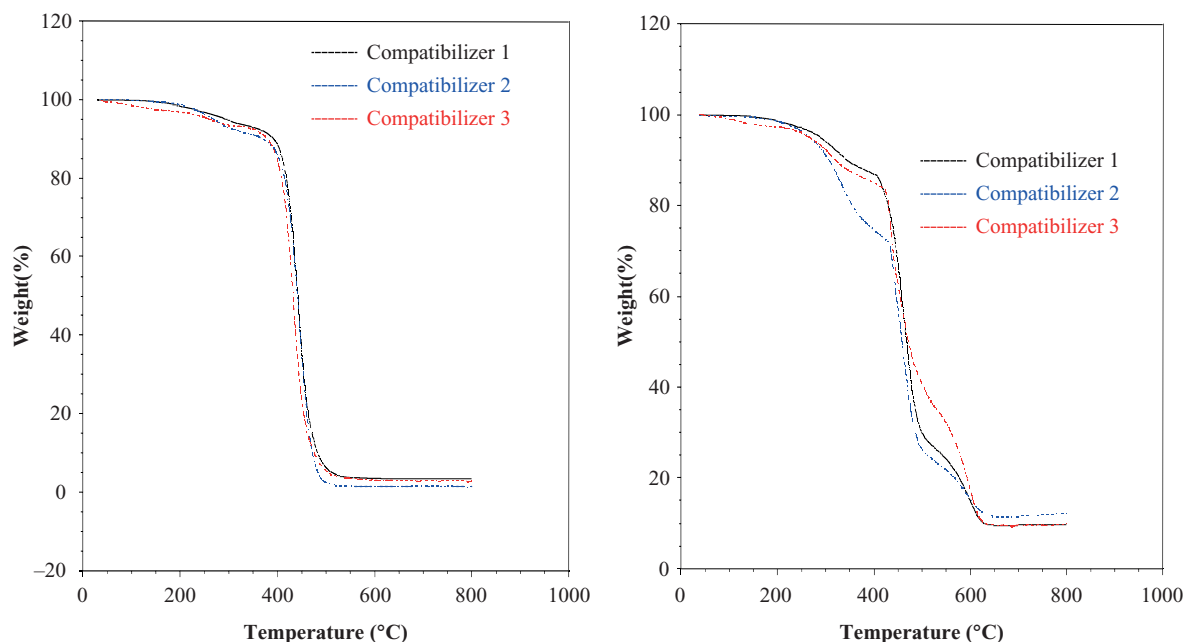


Figure 15. Thermal degradation profiles in nitrogen (left) and in air (right) of the homopolymer (compatibilizer 3) and the block copolymer compatibilizers 1 and 2.

of suitably designed polymeric compatibilizers, followed by cure. The structural motif of the compatibilizers synthesized via a hydrosilylation–deprotection sequence was primarily based on a polymer repeat unit with a nonpolar segment consisting of a carbosilane unit and a polar segment with a bisphenol A-type moiety.

Besides the homopolymer, two block copolymer systems with varying proportions of a nonpolar block containing a carbosilane with an aliphatic hydrocarbon linker and a relatively more polar block containing a bisphenol A unit linked to a carbosilane were also synthesized and characterized. The effectiveness of the compatibilizers,

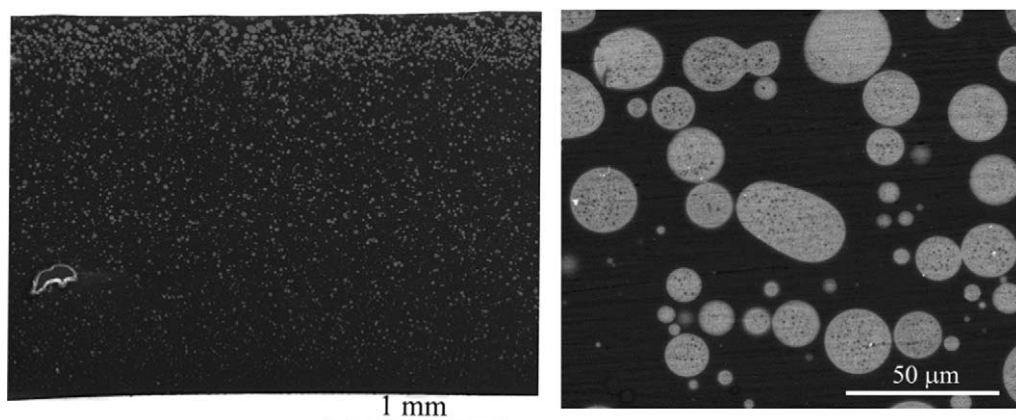


Figure 16. SEMs of control specimens of a cured (10 wt% Starfire) Starfire-Matrimid blend under $\times 50$ (left) and $\times 1000$ (right) magnifications.

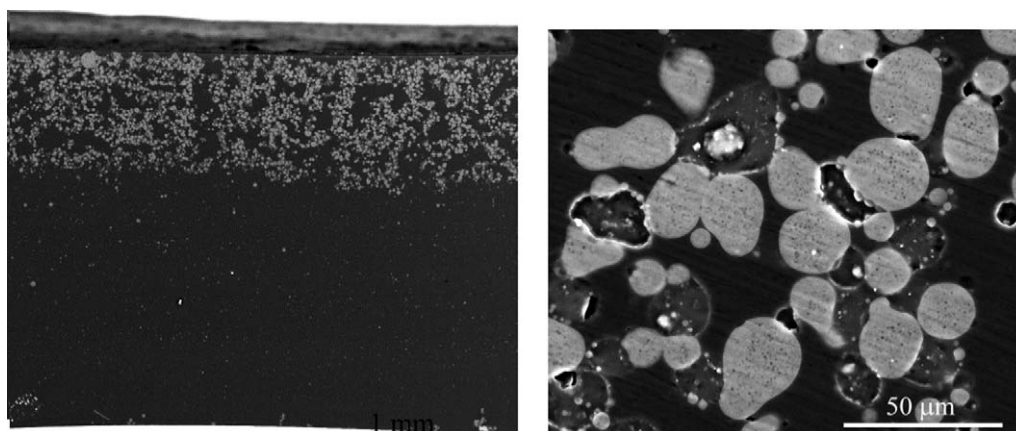


Figure 17. SEM of Starfire-Matrimid (10 wt% Starfire) blends incorporating 5 wt% compatibilizer 2 with $\times 40$ (left) and $\times 1000$ (right) magnification.

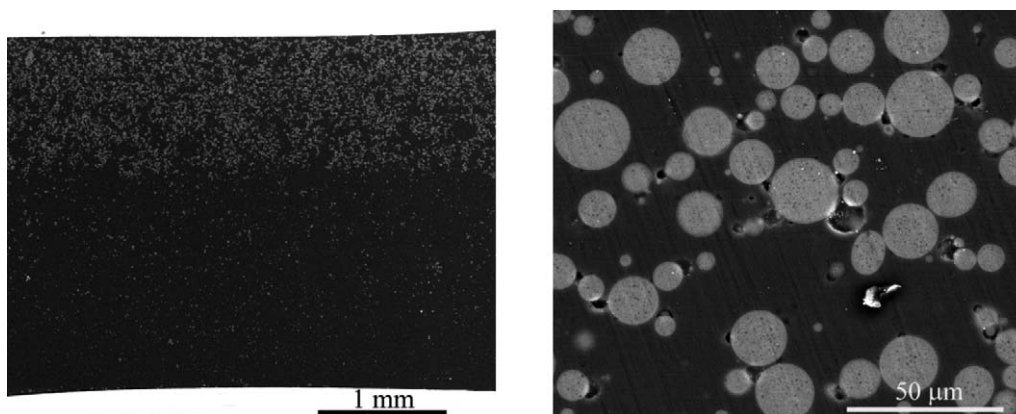


Figure 18. SEM of Starfire-Matrimid (10 wt% Starfire) blends incorporating 1 wt% compatibilizer 2 with $\times 40$ (left) and $\times 1000$ (right) magnification.

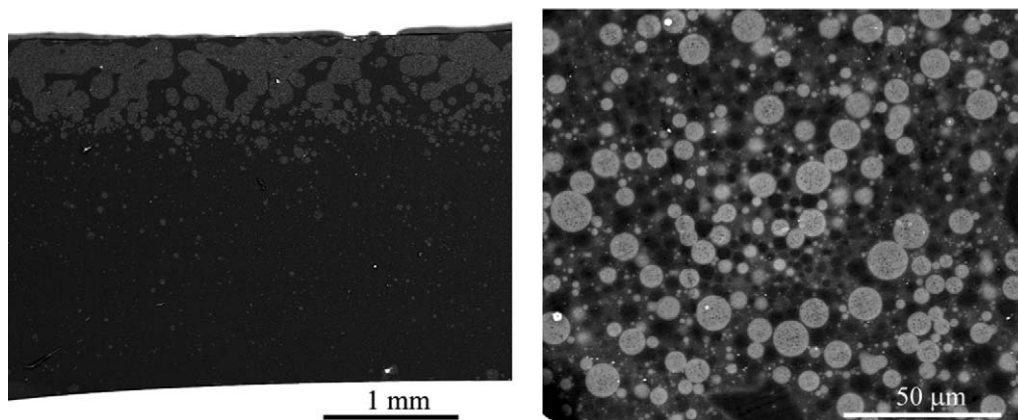


Figure 19. SEM of Starfire-Matrimid (10 wt% Starfire) blends incorporating 5 wt% compatibilizer 1 with ×40 (left) and ×1000 (right) magnification.

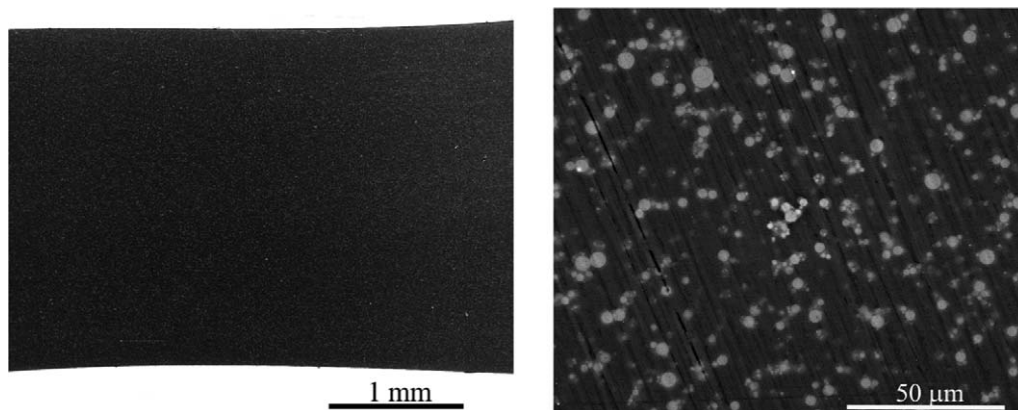


Figure 20. SEM of Starfire-Matrimid (10 wt% Starfire) blends incorporating 5 wt% compatibilizer 3 with ×40 (left) and ×1000 (right) magnification.

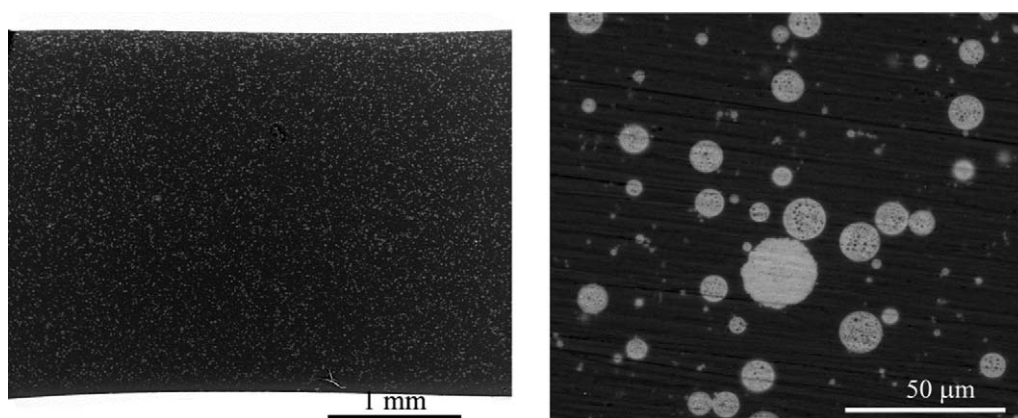


Figure 21. SEM of Starfire-Matrimid (10 wt% Starfire) blends incorporating 1 wt% compatibilizer 3 with ×40 (left) and ×1000 (right) magnification.

incorporated in small quantities for alleviating phase separation in the blends, was assessed by the Starfire domain size and distribution observed in the SEM of

cured specimens. The block copolymer, designed to have an equal number of the nonpolar and polar block repeat units, was found to be reasonably effective in

mitigating phase separation. However, the incorporation of the homopolymer that was most polar due to the highest phenolic content in its structure resulted in a dramatic reduction of the Starfire domain size, down to ≤ 5 μm in diameter, in the cured Starfire–Matrimid blend. The presence of this compatibilizer was also found to result in the uniform distribution of Starfire domains in the samples examined.

Based on the discussion above, the compatibilizers can be assessed as follows in terms of decreasing effectiveness in minimizing phase separation of the Starfire domains as well as promoting homogeneity in the cured resin plaques, in accordance with decreasing polarity from the homopolymer compatibilizer 3 to block copolymer compatibilizer 2: compatibilizer 3 (5 wt%) > compatibilizer 3 (1 wt%) > compatibilizer 1 (5 wt%) > control > compatibilizer 2 (5 wt%).

Further work in this area will involve molecular design of compatibilizer structures in which various polar phenolic moieties will be attached via flexible spacer groups as side chains to a polycarbosilane backbone using hydrosilylation methodology reported for such reactions.¹⁵

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