EVALUATION OF SILICON-CONTAINING PHTHALONITRILE POLYMERS- PROPERTIES, AND DEGRADATIONS

William J. Monzel[a,b], Guo-Quan Lu[a], Timothy L. Pruyn[b], Christopher L. Houser[c], and Gordon T. Yee[c]

a. Department of Materials Science and Engineering, Virginia Tech, Holden Hall, 445 Old Turner St #213, Blacksburg, VA, United States 24060.
b. Polymer Matrix Composites Group, Air Force Research Laboratory, 2941 Hobson Way WPAFB, OH, United States 45433.
c. Department of Chemistry, Virginia Tech, 900 West Campus Drive Blacksburg, VA, United States 24061.

ABSTRACT

Phthalonitrile polymers are of interest as resins for high temperature polymer matrix composites and encapsulation of wide band-gap power modules. However, their long-term use at temperatures above 250 °C is limited by oxidative degradation. The inclusion of organosilicon moieties into the polymer structure may provide higher temperature performance in oxidizing environments while maintaining good processing characteristics. In this work, several phenyl-substituted organosilicon linkages were incorporated to investigate their effect on processing, thermo-mechanical properties, and thermal and oxidative stability. Three silicon-containing phthalonitrile monomers were synthesized incorporating diphenoxydiphenylsilane, tetraphenylsilane, and hexaphenyldisiloxane moieties. Increasing the purity of monomers adversely affected the processing, glass transition, and stability. Processability was highly dependent on catalyst content and an ideal concentration was determined. The impact on glass transition, coefficient of thermal expansion, stability in TGA, and long-term oxidative stability at 250 °C was evaluated. Degradations were examined in more detail via IR-TGA. Results are compared with commercial phthalonitriles and relevant literature.

1. INTRODUCTION

High-performance, hybrid inorganic-organic polymers are increasingly of interest to the aerospace and electronics communities for use in wide band-gap power modules, microelectronics, composites, coatings, and tooling.[1-6] Thus, it is of interest to evaluate the effects of the inclusion of silicon-containing linkages on the properties of polymers such as phthalonitriles. The incorporation of organosilicon moieties into the monomer structure can provide a viable route for improved stability during service at high temperatures in oxidizing environments.[7-12] Siloxy units form from the cleavage of C-Si bonds by oxygen and free radicals. These siloxy units may further react to produce SiO_2, producing a silica-rich surface layer. This layer can act as a barrier for further degradation and diffusion of oxygen.[13]

Phthalonitriles are excellent candidates for hybridization with organosilicon moieties due to their ease of processing and high glass transition temperatures.[1-6, 14] Organic phthalonitrile materials show exceptional thermal stability; however, the long-term, thermo-oxidative stability may require improvement.[2, 15-19] Recently, phthalonitriles with silazane,[20] oxysilane,[21-22] silane,[23]

SAMPE Conference Proceedings. Charlotte, NC, May 20-23, 2019. Society for the Advancement of Material and Process Engineering – North America.

siloxane,[4, 24] and silsesquioxane[25] moieties have been reported. While the materials synthesized by these groups exhibited high thermal and thermo-oxidative stabilities, emphasis was placed on developing resins with low softening points and long-term stability was not characterized. Additionally, a methylene bridge was often used to connect the silicon linkage is to the aromatic backbone. However, due to the lower homolytic C-H bond energy of methylene and benzylic groups, the use of Si-phenylene linkages is reported to result in greater resistance to degradation at temperatures below 550 °C.[26] Si-phenylene linkages and bulky substituents on the silicon also hinder low temperature degradations due to oxidative cross-linking, or chain folding and unzipping or rearrangement mechanisms.[27-30] Instead, the Si-C bond cleavage is reported to occur at temperatures above 300 °C.[9, 28] The incorporation of bulky substituents on the silicon atoms, such as phenyl groups, has also been shown to limit the depression of the glass transition and increase the solubility of resins and thermo-oxidative stability of cured polymers.[26, 28] However, the inclusion of phenyl functional groups and phenylene linkages increases steric hindrance of the organosilicon linkage, reducing its flexibility and increasing the melting point of monomers. Lastly, to the author's knowledge, the effect of purity has not been previously evaluated in silicon-containing phthalonitrile systems. The presence of hydroxyl groups has been shown to result in cleavage of Si-O and Si-C bonds.[26, 29] Additionally, oxidative degradation mechanisms are catalyzed by residual metal, organometallic, ionic, and polar impurities.[29, 31] However extensive purification is not commonly conducted on phthalonitrile resins.[1-6, 14, 21-22]

Recently, the carbosilane-phthalonitrile (CSPN) was first reported by Terraza et al.[32] and its polymer properties characterized by the authors.[33-34] The CSPN monomer exhibited high overall stability. However, this monomer possessed a high melting point and thus small processing window. The inclusion of short siloxane or oxysilane linkages may provide lower melting points, and thus larger processing windows, while simultaneously maintaining high thermo-oxidative stabilities.[21-22] Thus, carbosiloxane (CSOPN) and carboxysilane (COSPN) phthalonitrile materials were evaluated. The structures of CSPN, COSPN, and CSOPN are shown in Figure 1. The performance of purified CSPN and CSOPN materials is compared with as-synthesized CSPN and COSPN materials, as well as several commercial phthalonitriles. Purified materials are given the suffix -P (CSPN-P and CSOPN-P), and as-synthesized materials given the suffix -U (CSPN-U and COSPN-U). Target monomer structures were synthesized, and monomer/catalyst mixtures were prepared and cured. Monomers and b-staged pre-polymers were characterized using differential scanning calorimetry (DSC), parallel plate rheology, thermogravimetric analysis (TGA), and Fourier transform infrared (FTIR) spectroscopy. The glass transition (T_g) of cured polymer samples was evaluated by DSC, thermomechanical analysis (TMA), and torsional dynamic mechanical analysis (DMA). The coefficient of thermal expansion (CTE) was measured using TMA. Thermal and thermo-oxidative stability were evaluated using thermogravimetric analysis (TGA), FTIR, and oxidative aging studies.

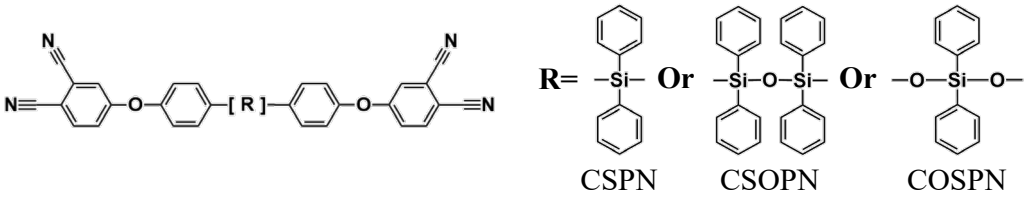

Figure 1: The structures of carbosilane phthalonitrile (CSPN), carbosiloxane phthalonitrile (CSOPN) and carboxysilane phthalonitrile (COSPN).

2. EXPERIMENTATION

2.1 Materials and Methods

4-Nitrophthalonitrile (98%) was obtained from Accela Chembio Co. Ltd. Dichlorodiphenylsilane, *n*-butyllithium (*n*-BuLi, 2.5 M in hexanes), and palladium on carbon (Pd/C, 10 wt.%) were purchased from Sigma Aldrich. Hydroquinone (99.5%) was purchased from Acros Organics. From Gelest Inc. was obtained 1,3-dichlorotetraphenyldisiloxane. From Oakwood Chemical was purchased 4-benzyloxybromobenzene (low moisture, >99%). Potassium carbonate (K_2CO_3, 99%) and 4-benzyloxyphenol (>98%) were purchased from Alfa Aesar. Magnesium sulfate ($MgSO_4$, anhydrous, >98%) was obtained from MP Biomedicals. Triethylamine (TEA), tetrahydrofuran (THF), dimethylformamide (DMF), dichloromethane (DCM), ethyl acetate, hexane, and chloroform were purchased from Fisher Chemical. Ethanol was purchased from Decon Laboratories. Toluene was purchased from Spectrum Chemical MFG Corp. Silica gel (40-60 μm, 60 Å) was obtained from VWR International. Bis(4-(4-aminophenoxy)phenyl)sulfone (*p*-BAPS, >98%) was purchased from TCI America. Samples of commercial phthalonitriles, denoted here as PN1, PN2, and PN3, were supplied by the Air Force Research Laboratory Polymer Matrix Composites Group. THF and toluene were each distilled over sodium/ benzophenone ketyl and stored over 4A molecular sieves under nitrogen. DMF was dried with 4A molecular sieves. K_2CO_3 was dried under vacuum at 80 °C for 24 hours. All other materials were used as received. ^{1}H, ^{13}C, and ^{29}Si nuclear magnetic resonance (NMR) spectra were recorded on an Agilent U4-DD2 instrument with DMSO-d_6, $CDCl_3$, or acetone-d_6 as the solvent, and tetramethylsilane (TMS) as an internal standard. Correlation spectroscopy (COSY), heteronuclear single-quantum correlation spectroscopy (HSQC), and heteronuclear multiple-bond correlation spectroscopy (HMBC) were used to assign protons and carbons. Melting point and glass transition data were obtained by DSC using a TA Instruments Q1000 or Q20 with a ramp rate of 5 °C/min. Elemental analysis was performed by Atlantic Microlab Inc. FTIR spectroscopy was conducted using a Thermo Scientific Nicolet 6700 with Spectra Tech Inc. attenuated total reflection (ATR) and Thermo Electron Corp. TGA/FTIR accessories. Parallel plate rheology and DMA were performed on a TA Instruments Ares G2 with a ramp rate of 5 °C/min. A TA Instruments Q400 was used for TMA with a ramp rate of 5 °C/min. TGA of powder samples in air and nitrogen was performed using a TA Instruments Q500, with a ramp rate of 10 °C/min and a flow rate of 90 mL/min. A model 10444 (30 ton) Wabash hydraulic press was used to compression mold resin plaques. Panels were c-scanned at AFRL/RXAS, Wright Patterson Air Force Base. For thermo-oxidative stability (TOS) characterization, 12.7 mm x 12.7 mm x 3.3 mm samples were aged in air at 250 °C

2.2 Synthetic Information

General synthetic information for the carboxysilane-phthalonitrile and carbosiloxane-phthalonitrile monomers are provided in the following sections. Synthesis and purification of the carbosilane-phthalonitrile monomer has been previously reported.[33-34]

2.2.1 Synthesis of the Carboxysilane-Phthalonitrile Monomer

To produce the carboxysilane-phthalonitrile monomer, hydroxyphenoxy-phthalonitrile (HOPOPN) was first synthesized, and then reacted with dichlorodiphenylsilane to produce the desired monomer.

2.2.1.1 4-(4-Hydroxyphenoxy)phthalonitrile (HOPOPN)

The reaction vessel was flame-dried under vacuum and purged with nitrogen. To the vessel was added 80 mL of dry dimethylformamide (DMF) and an excess of hydroquinone (36.9 g, 335 mmol). To the solution was added pulverized, dried potassium carbonate (23.2 g, 168 mmol). The reaction vessel was chilled in an ice water bath and allowed to stir for fifteen minutes. A solution of DMF (95 mL) and 4-nitrophthalonitrile (14.5 g, 83.8 mmol) was added dropwise slowly over approximately one hour. The reaction was allowed to warm to room temperature overnight and then heated to 80 °C for 7 hours. The reaction contents were removed and poured into 1000 mL of 0.1 M HCl. Brown precipitate of the desired product was separated by vacuum filtration through a coarse frit and washed with 200 mL deionized water. The product was then dissolved in 600 mL of DCM and washed with water four times (1.6 L water total). The organic layer was separated and dried with $MgSO_4$. The $MgSO_4$ was removed by vacuum filtration and the solvent was removed by rotary evaporation. The orange/brown product was purified by silica column chromatography (5:12 ethyl acetate: hexane) to produce white powder. The product was dried in a vacuum oven (48 torr at 70-80°C for 24 hours). Extended drying at 70-80 °C caused the product to turn a bluish-green. Yield: 16.1 g, 68.2 mmol, 81%. R_f: 0.36 (SiO_2, hexanes/ethyl acetate, 3:1). mp: 152 °C (lit. mp 150-151 °C [35]). ^{1}H NMR (400 MHz, DMSO-d6, δ, ppm): 6.80 – 6.89 (m, 2H), 6.97 – 7.06 (m, 2H), 7.28 (dd, J = 8.8, 2.6 Hz, 1H), 7.67 (dd, J = 2.7, 0.4 Hz, 1H), 8.05 (dd, J = 8.8, 0.4 Hz, 1H), 9.62 (s, 1H). ^{1}H NMR in $CDCl_3$, ppm: 6.94 (4H,m), 7.21 (2H, m), 7.70 (1H, d).^{13}C NMR (101 MHz, DMSO-d6, δ, ppm): 107.31 (ArC), 115.46 (R-C≡N), 116.00 (R-C≡N), 116.54 (ArC), 116.71 (ArC), 120.92 (ArC), 121.72 (ArC), 121.82 (ArC), 136.22 (ArC), 145.30 (ArC), 155.33 (ArC), 162.19 (ArC). IR (ATR, cm^{-1}): 3413, 3107, 3077, 3041, 2235, 1592, 1503, 1484, 1442, 1308, 1251, 1197, 1096, 1081, 950, 880, 833, 792. Anal. calcd for $C_{14}H_8N_2O_2$: C, 71.18; H, 3.41; N, 11.86; O, 13.55. Found: C, 71.53; H, 3.41; N, 11.84.

2.2.1.2 4,4'-((((Diphenylsilanediyl)bis(oxy))bis(4,1-phenylene))bis(oxy))diphthalonitrile (COSPN)

The reaction vessel was flame dried under vacuum and purged with nitrogen. HOPOPN (2.36 g, 10.0 mmol), dry THF (7 mL), dry toluene (1 mL), and TEA (3.8 mL, 27.5 mmol) were added to the vessel. The reaction vessel was placed under nitrogen in an ice water bath. The HOPOPN/THF/ Toluene/TEA solution was stirred for 20 minutes. A solution of dichlorodiphenylsilane (1.05 mL, 5.0 mmol), THF (8.75 mL) and toluene (1.25 mL) was added slowly dropwise. The reaction contents were allowed to warm to room temperature and stirred for 24 hours. Additional dichlorodiphenylsilane (0.53 mL, 2.5 mmol), diluted with THF (7 mL) and toluene (1 mL) was added dropwise. The reaction mixture was heated to 75 °C for 6 hours. The reaction vessel was then allowed to cool to room temperature under nitrogen in a glove box. An additional 100 mL of THF was added. After fifteen minutes contents were filtered to remove triethylammonium salts. The reaction vessel was removed from the glove box and the solvents were removed by rotary evaporation. The yellowish solid product was heated under vacuum (24 torr at 80 °C. for 24 hours to remove solvents and residual impurities. The product was then stored under dry nitrogen. Yield: 3.10 g, 4.70 mmol, 78%. Purity (LCMS): 80%, mp: 168-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.88 – 6.93 (m, 4H), 7.02 – 7.07 (m, 4H), 7.13 – 7.20 (4H, m), 7.44 – 7.47 (4H, m), 7.50 – 7.56 (m, 2H), 7.69 (dd, J = 8.7, 0.5 Hz, 2H), 7.76 – 7.81 (4H, m). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 108.78 (ArC), 115.11 (R-C≡N), 115.51 (R-C≡N), 117.73 (ArC), 121.01, 121.35 (ArC), 121.68 (ArC), 122.05 (ArC), 128.46 (ArC), 130.30 (ArC), 131.60 (ArC), 135.07 (ArC), 135.48 (ArC), 148.12 (ArC), 152.08 (ArC), 162.23 (ArC).

IR (ATR, cm^{-1}): 3042, 2929, 2232, 1650, 1584, 1498, 1486, 1429, 1259, 1229, 1214, 1150, 1126, 1103-1012, 1103-1012, 933, 833, 718, 696.

2.2.2 Synthesis of the Carbosiloxane-Phthalonitrile Monomer

To produce the CSOPN monomer, a synthetic route similar to that used to produce the CSPN monomer[33] was utilized. First a benzyl protected compound was produced, BODSO. The protecting groups were removed to produce the bisphenol, DPDSO. The bisphenol was then reacted with 4-nitrophthalonitrile to produce the desired monomer. The structures of BODSO, DPDSO, and CSOPN are given in Figure 2.

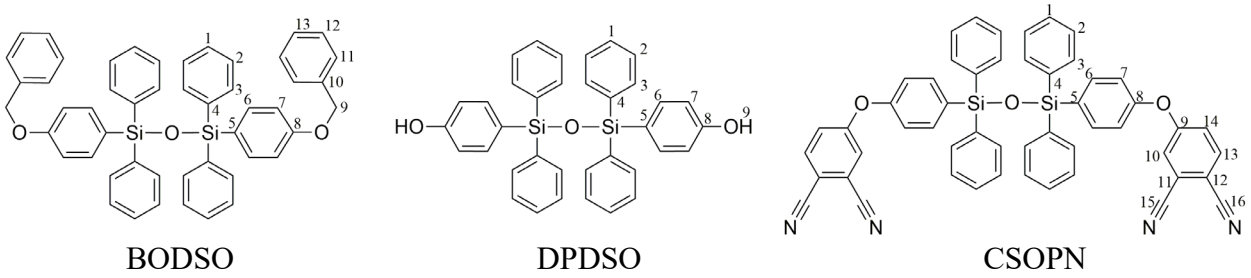

Figure 2: The structures of BODSO, DPDSO, and CSOPN with numbered carbons for NMR.

2.2.2.1 1,3-Bis(4-(benzyloxy)phenyl)-1,1,3,3-tetraphenyldisiloxane (BODSO)

The reaction vessel was flame dried under vacuum and purged with nitrogen. To the vessel, 190 mL THF and 4-benzyloxybromobenzene (10 g, 38.0 mmol) was added. The vessel was placed in a dry ice/acetone bath. To the solution, *n*-BuLi (16.8 mL, 38.0 mmol) was added slowly dropwise. The reaction mixture was stirred at -78 °C for thirty minutes. Then 1,3-dichlorotetraphenyldisiloxane (6.53 mL, 7.8 g, 17.3 mmol), diluted with 65 mL THF, was added slowly dropwise. The reaction contents were allowed to warm up to room temperature over a period of four hours. The solvent was removed by rotary evaporation. The product was then dissolved in 300 mL DCM and washed with deionized water four times (approximately 2.0 L of water total). The organic layer was separated and dried with $MgSO_4$. The drying agent was removed by vacuum filtration and the solvents were removed by rotary evaporation. The resulting product was purified by silica column chromatography (3:1 Hexane/ DCM) to yield a white powder. Yield: 8.73 g, 38.3 mmol, 68%. mp: 164°C. R_f: 0.19 (SiO_2, Hexane/$CHCl_3$, 2:1). ^{1}H NMR (400 MHz, Acetone-d_6, δ, ppm) δ 5.11 (s, 4H(9)), 6.99 – 6.94 (m, 4H(7)), 7.34 – 7.27 (m, 10H(2,13)), 7.44 – 7.34 (m, 12H(1,6,12)), 7.49 – 7.44 (m, 4H(11)), 7.53 – 7.49 (m, 8H(3)). ^{13}C NMR (101 MHz, Acetone-d_6) δ 70.20 (C9), 115.26 (C7), 127.31 (C5), 128.47 (C11), 128.63 (C2), 128.66 (C13), 129.28 (C12), 130.75 (C1), 135.79 (C3), 136.72 (C4), 137.55 (C6), 138.14 (C10), 161.40 (C8). ^{29}Si NMR (79 MHz, Acetone-d_6) δ -18.41. IR (ATR, cm^{-1}): 3067-3019 (w), 2936 (w; -CH_2-), 2875 (w; -CH_2-), 1593 (s), 1560 (w), 1503 (m), 1465 (w; -CH_2-), 1456 (w), 1430 (m; Si-ϕ), 1273 (m), 1247 (m), 1182 (m), 1112 (s; Si-ϕ), 1095 (s; Si-O-Si), 1026 (w), 1011 (m), 998 (w), 861 (w), 831 (w), 821 (w), 741 (m), 700 (s). Anal. calcd for $C_{50}H_{42}O_3Si_2$: C, 80.39; H, 5.67; O, 6.42; Si, 7.52). Found: C, 80.18; H, 5.62.

2.2.2.2 4,4'-(1,1,3,3-Tetraphenyldisiloxane-1,3-diyl)diphenol (DPDSO)

The reaction vessel was flame dried under vacuum and purged with dry nitrogen. BODSO (23.4 g, 31.4 mmol), 351 mL THF, 117 mL ethanol, and 2.34 g Pd/C were added to the flask. The reaction vessel was then purged with hydrogen via balloon. The mixture was stirred at room temperature for 1 hour. The reaction contents were then heated to 70 °C for four days. The Pd/C was removed by filtration. The solvents were removed via rotary evaporation. The product was purified by flash silica column chromatography using 19:1 DCM/ethyl acetate. Solvents were removed via rotary evaporation. The resulting white powder was dried under vacuum (48 torr at 50 °C for 24 hours). Yield: 15.2 g, 26.8 mmol, 86%. A small amount was further purified by recrystallization from toluene for analytical characterization. *Rf*: 0.08 (SiO_2, DCM/ethyl acetate, 19:1). mp: 217 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 6.79 – 6.83 (m, 4H(7)), 7.29 (m, 8H(2)), 7.32 – 7.36 (m, 4H(6)), 7.36 – 7.41 (m, 4H(1)), 7.48 – 7.55 (m, 8H(3)), 8.56 – 8.60 (m, 2H(9)). ^{13}C NMR (101 MHz, Acetone-d_6) δ 115.86 (C7), 125.69 (C5), 128.52 (C2), 130.59 (C1), 135.78 (C3), 137.01 (C4), 137.65 (C6), 160.03 (C8). ^{29}Si NMR (79 MHz, Acetone-d_6) δ -18.38. IR (ATR, cm^{-1}): *ν* = 3536 (w, br; OH), 3200-3400 (m, br; OH), 3067-2974 (m), 1598 (m), 1581 (m), 1504 (m), 1428 (m; Si-ф), 1372 (w; ф-OH), 1263 (m), 1243 (m), 1179 (m), 1114 (s; Si-ф), 1091 (s; Si-O-Si), 1047 (m), 828 (m), 738 (w), 712 (m), 699 (s); Anal. calcd for $C_{36}H_{30}O_3Si_2$: C, 76.29; H, 5.34; O, 8.47; Si, 9.91. Found: C, 76.41; H, 5.38.

2.2.2.3 4,4'-(((1,1,3,3-Tetraphenyldisiloxane-1,3-diyl)bis(4,1-phenylene))bis(oxy)) diphthalonitrile (CSOPN)

The reaction vessel was flame dried under vacuum and purged with dry nitrogen. DPDSO (15.2 g, 26.8 mmol) was dissolved in 112 mL of dry DMF. K_2CO_3 (11.12 g, 80.5 mmol) was stirred into solution. The mixture was allowed to stir for fifteen minutes. Then, 4-nitrophthalonitrile (9.28 g, 53.6 mmol) was added. The reaction was stirred at room temperature overnight and was then heated to 80 °C for 8 hours. The reaction contents were poured into 700 mL of 0.1 M HCl. Precipitate of the desired product was separated by filtration and washed with deionized water. The product was then dissolved in 500 mL DCM and washed with deionized water 4 times (2 L total). The organic layer was separated and dried with $MgSO_4$. The $MgSO_4$ was removed by filtration, and the solvent was removed by rotary evaporation. The product was purified by flash silica column chromatography using 10:1:10 hexane/ethyl acetate/chloroform. Yield: 15.4 g, 18.8 mmol, 70 %. For analytical characterization, a small amount was further purified by recrystallization from acetonitrile. *Rf*: 0.23 (SiO_2, hexane/ethyl acetate/chloroform, 10:1:10). mp: 190-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.95 – 7.01 (m, 4H(7)), 7.23 – 7.28 (m, 4H(10,14)), 7.30 – 7.35 (m, 8H(2)), 7.41 – 7.46 (m, 4H(1)), 7.48 – 7.53 (m, 8H(3)), 7.54 – 7.58 (m, 4H(6)), 7.71 – 7.76 (m, 2H(13)). ^{13}C NMR (101 MHz, $CDCl_3$, δ, ppm): 109.14 (C12), 114.92 (C15), 115.32 (C16), 117.65 (C11), 119.77 (C7), 121.60 (C14), 121.90 (C10), 127.96 (C2), 130.29 (C1), 133.65 (C5), 134.55 (C4), 135.08 (C3), 135.43 (C13), 137.64 (C6), 155.13 (C8), 161.24 (C9). ^{29}Si NMR (79 MHz, $CDCl_3$) δ -18.50. IR (ATR, cm^{-1}): ν = 3098-3000 (w), 2233 (m; C≡N), 1580 (s), 1563 (w), 1495 (m), 1485 (s), 1428 (m; Si-ф), 1311 (s), 1281 (s), 1252 (s; O-ф), 1213 (m), 1175 (m), 1138 (s; Si-ф), 1107 (s; Si-ф), 1086 (s; Si-O-Si), 1054 (w, br; Si-O-Si), 897 (w), 853 (w), 837 (m), 830 (m), 739 (m), 712 (m), 699 (m). Anal. calcd for $C_{52}H_{34}N_4O_3Si_2$: C, 76.26; H, 4.18; N, 6.84; O, 5.86; Si, 6.86. Found: C, 76.04; H, 4.23; N, 6.73.

2.3 Polymer Sample Fabrication

COSPN-U monomer and a catalytic amount (4 wt. %) of *p*-BAPS were co-dissolved in anhydrous THF and the mixture cast into aluminum weighing boats. The THF was removed under nitrogen at 110 °C for 3.5 hours. The temperature was then slowly increased to 200 °C under vacuum over three hours. The samples were then cured in an oven under nitrogen at 300 °C for four hours, 350 °C for four hours, and 375 °C for four hours. The cured COSPN-U samples were then ground for TGA and DSC measurements. For CSPN-P, The 6 wt. % *p*-BAPS sample was dry-mixed and melted at 220-230 °C. For CSPN-P with 3.5-4 wt. % *p*-BAPS, the monomer and catalyst were co-dissolved in 1:1 DCM/chloroform mixture and then the solvent was removed by rotary evaporation. The mixture was dried and degassed under vacuum at room temperature for 4 hours, 230 °C for 30 minutes, and 240-250 °C for 25 minutes. The resin was then b-staged under nitrogen atmosphere at 250-260 °C until viscosity increased. CSOPN-P samples were melted at 200 °C under nitrogen. The catalyst, *p*-BAPS (2.7 or 4 wt. %) was added. The mixture was stirred for two minutes. Vacuum was applied, and the resin was degassed for 30 minutes at 200 °C, 30 minutes at 220-230 °C, and 25 minutes at 240-250 °C. The resin was then b-staged under nitrogen atmosphere at 250-260 °C for until viscosity increased. CSPN-P and CSOPN-P resin panels were fabricated by compression molding at 300 °C for four hours (130-170 psi) and 350 °C for four hours (290 psi). Acoustic c-scan data provided information on the porosity content of each panel. The qualitative hardness and strength of the materials was observed during de-molding panels, cutting samples for TMA, DMA, and TOS, and grinding powder samples for TGA and DSC characterizations. Additional curing of some CSOPN-P samples was accomplished in an oven under nitrogen at 375 °C for 1-3 hours.

3. RESULTS

The COSPN monomer showed a high sensitivity to hydrolysis. The re-formation of HOPOPN was confirmed by NMR and FTIR. Due to this hydrolytic sensitivity, practical application of the resin was implausible. Thus, only limited processing and characterization of the of the carboxysilane (COSPN-U) monomer was performed, and the highly purified monomer was not evaluated. Focus was placed on evaluating CSPN-P and CSOPN-P and comparing results to commercial phthalonitriles and previously published data on CSPN-U.

3.1 DSC of Monomer/p-BAPS Mixtures

The COSPN-U/ 4 wt.% p-BAPS mixtures exhibited melting endotherms between 131-158 °C. Exothermic curing peaks occurred between around 265-277 °C. The melting point of the CSPN-P/ 4 wt.% *p*-BAPS mixture was observed at 220 °C, very close to the melting point of CSPN-P without *p*-BAPS (223 °C). The CSPN-P/*p*-BAPS mixture displayed exothermic curing peaks at 275-300 °C. In contrast, in the CSPN-U/*p*-BAPS mixture the curing reaction occurred at lower temperatures, 255-278 °C. With the addition of the 4 wt.% *p*-BAPS, the melting temperature of CSOPN-P resin decreased from 191 °C to 181 °C. Exothermic peaks corresponding to the curing reaction were observed in the CSOPN-P/*p*-BAPS resin at 285-327 °C.

3.2 Processing of Resins

In contrast with CSPN-U/*p*-BAPS, which softened beginning at 130 °C, CSPN-P/*p*-BAPS softened beginning at 190 °C. The minimum viscosity dropped sharply to 0.2 Pa·s at 220 °C. CSOPN-P/*p*-BAPS samples began to soften at 100 °C and showed a gradual decrease in

viscosity. The viscosity was observed as low as 0.09-0.1 Pa·s beginning at 170 °C. Table 1 provides the time until viscosity visibly increased and resulting resin panel quality as a function of *p*-BAPS content. Approximately 3.5-4 wt. % (5.0-5.6 mol%) *p*-BAPS was required to achieve visible increase in viscosity within a reasonable amount of time. Resin panels were compression molded with different amounts of *p*-BAPS. At lower concentrations of *p*-BAPS (<3.5 wt.%), resins took substantially longer to cure and resulted in lower panel quality. Panels with lower qualitative strength, lower hardness, cracks, and higher porosity exhibited a cloudy, mat finish. In contrast, higher quality panels possessed a glossy finish.

Table 1: Working time at 250-260 °C and resin panel results for CSPN and CSOPN resins.[33]

Sample	*p*-BAPS, wt.% (mol%)	Time Until Gelation (Hr.) at 250-260 °C	Qualitative Panel Result		
			Finish	Hardness/Strength	Porosity
CSPN-U	6.0 (8.4)	~1.0	Good	Good	Low
CSPN-U	4.0 (5.6)	~1.0	Good	Good	Low
CSPN-P	2.1 (3.0)	Did not gel at >12	No panel produced		
CSPN-P	3.5 (5.0)	~4.0	Mediocre	Good	Low
CSPN-P	4.0 (5.6)	~0.7	Good	Good	Low
CSPN-P	6.0 (8.4)	Cured while melting	Bad	Low	High
CSOPN-P	1.6 (3.0)	Did not gel at >12	No panel produced		
CSOPN-P	2.7 (5.0)	~13	Bad, cracks	Low	NA
CSOPN-P	4.0 (7.3)	~1.5	Good	Good	Low

3.2.1 FTIR of CSOPN-P Monomer and Cured Polymers

The IR spectra (ATR) of the CSOPN-P monomer was compared to compression molded CSOPN-P polymers. After curing with 4 wt.% *p*-BAPS to 350 °C for 4 hours, the formation of triazine peaks are observed at 1356-1360 cm^{-1} and 1520-1532 cm^{-1}.[3, 14, 36] Peaks for isoindoline or phthalocyanine structures at 1580-1590 cm^{-1} and 1015-1016 cm^{-1} overlapped with peaks present in the monomer. Additional curing at 375 °C did not result in observable changes to the IR spectra.

3.3 Polymer Properties

Figure 3 provides a summary of glass transition measurements from DSC, DMA, and TMA for CSPN-U, CSPN-P, and CSOPN-P, and commercial phthalonitrile PN2. The T_g of purified CSPN-P and CSOPN-P are observed in the same range. A significant difference of 99-174 °C is observed between purified CSPN-P or CSOPN-P polymers and the as-synthesized CSPN-U, depending on sample and measurement method.

A summary of CTE data for CSPN-U, CSOPN-P, and several reference materials is provided in Figure 4. The CTE between 50-150 °C was measured in the range of 77.7-79.7 (µm/(m °C)) for CSOPN-P and 72.1-78.4 (µm/(m °C)) for CSPN-U. Commercially available phthalonitriles and reference polyimides showed lower CTE values than CSPN-U and CSOPN-P materials. This may be due to a possible lower degree of cure, or greater free volume due to bulky phenyl pendant groups and longer Si-C and Si-O bonds.

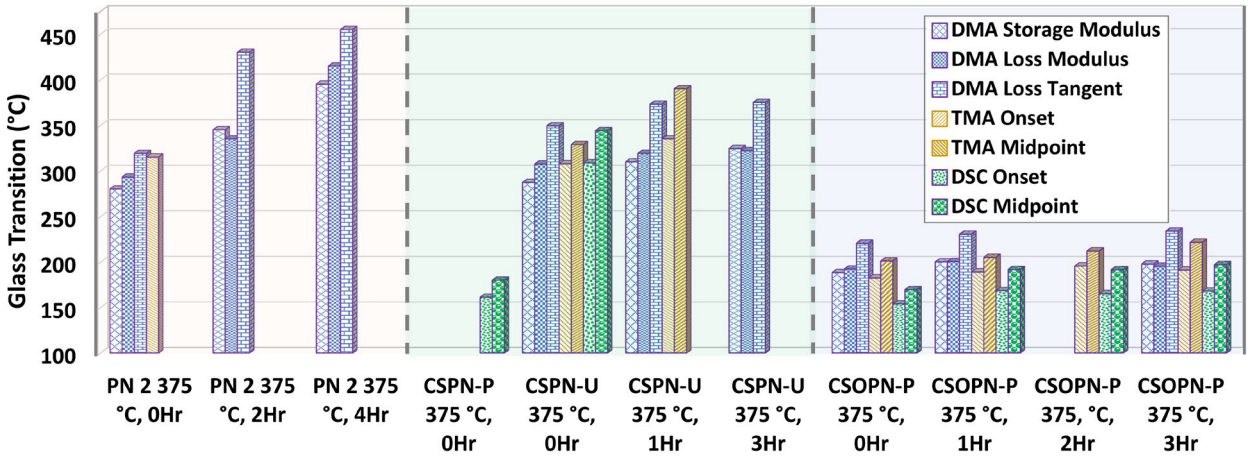

Figure 3: Glass transition data for CSPN-U, CSPN-P, and CSOPN-P, and commercial phthalonitrile PN2. Data on PN2 is included from Koerner and Gibson et al.[19]

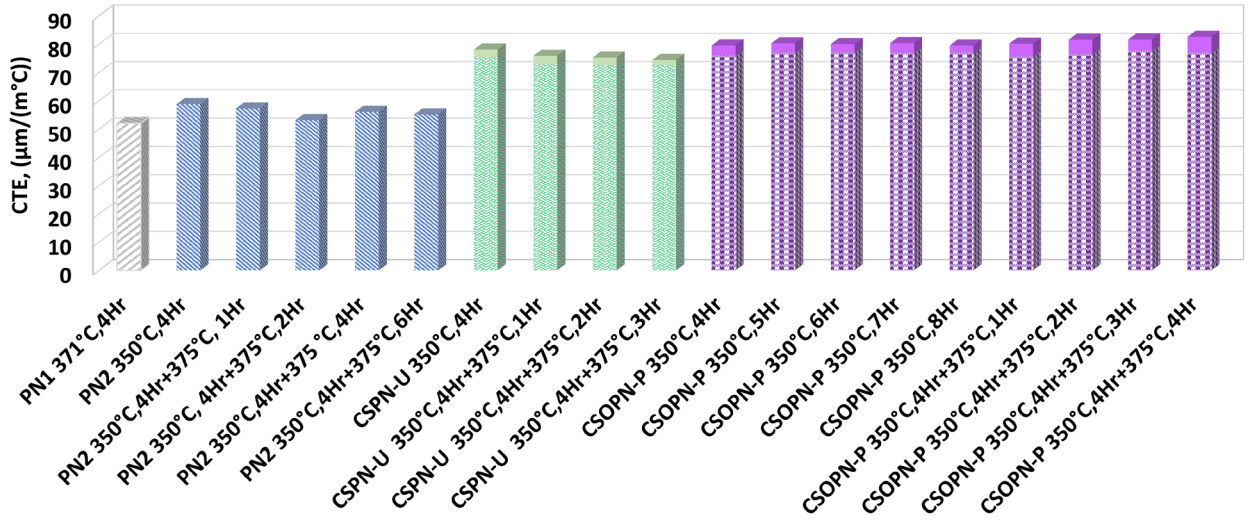

Figure 4: CTE data for CSPN-U, CSOPN-P and two commercial phthalonitrile resins (PN1 and PN2). Data is included from Koerner and Gibson et al.[19]

3.3.1 Thermal and Thermo-Oxidative Stability from TGA

The TGA results for COSPN-U, CSPN-U, CSPN-P, and CSOPN-P with 4 wt.% p-BAPS are compared in Figure 5. For silicon-containing polymers stability followed the trend CSPN-U > CSOPN-P > COSPN-U > CSPN-P. Stability increased with additional curing time at 375 °C. To better understand the degradation routes of CSOPN-P, FTIR was performed on gases evolved during TGA. The intensity of IR peaks is compared with weight loss and derivative TGA curves in nitrogen and air respectively in Figure 6 and Figure 7 respectively. The degradation peaks of CSOPN-P were nearly identical to those observed in CSPN-U in both air and nitrogen.[33] In nitrogen, four overlapping degradations were observed in IR spectra at 520 °C, 590 °C, 601 °C, and 745 °C. The first degradation correlated with IR peaks corresponding to HCN (714 cm^{-1}) and what is plausibly isoindoline structures or other nitrogen-containing aromatics (1342, 1379, and 1601 cm^{-1}). The second degradation at 590 °C correlated with the evolution of benzene (654,

672, 687, 1483, and 3059 cm^{-1}) from cleavage of Si-phenyl bonds. The evolution of ammonia (930, and 965 cm^{-1}) and hydrogen cyanide (714 cm^{-1}) in the third and fourth degradations were likely from the decomposition of triazine and phthalocyanine structures.

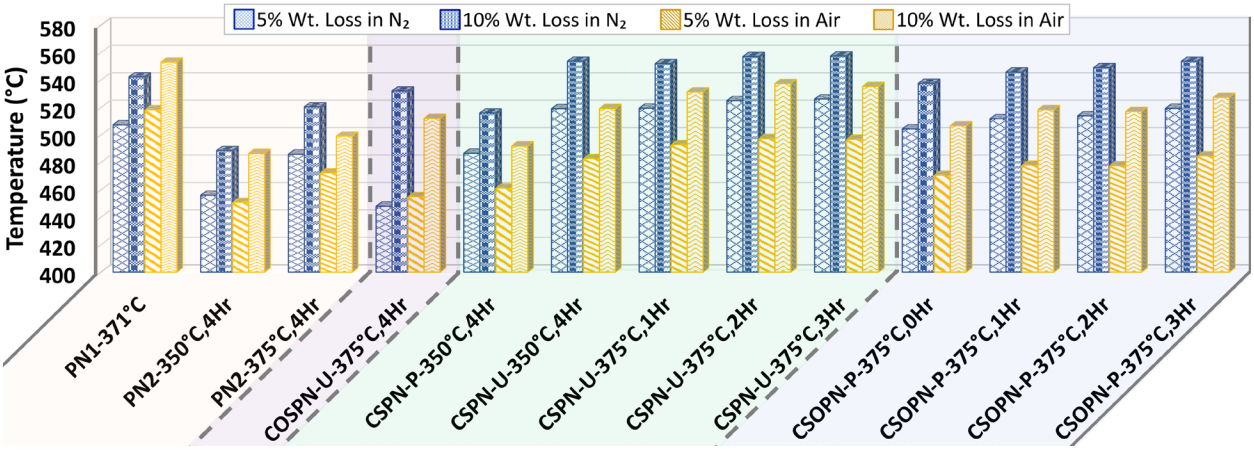

Figure 5: TGA data in N2 and air for COSPN-U, CSPN-U, CSPN-P, and CSOPN-P polymers.

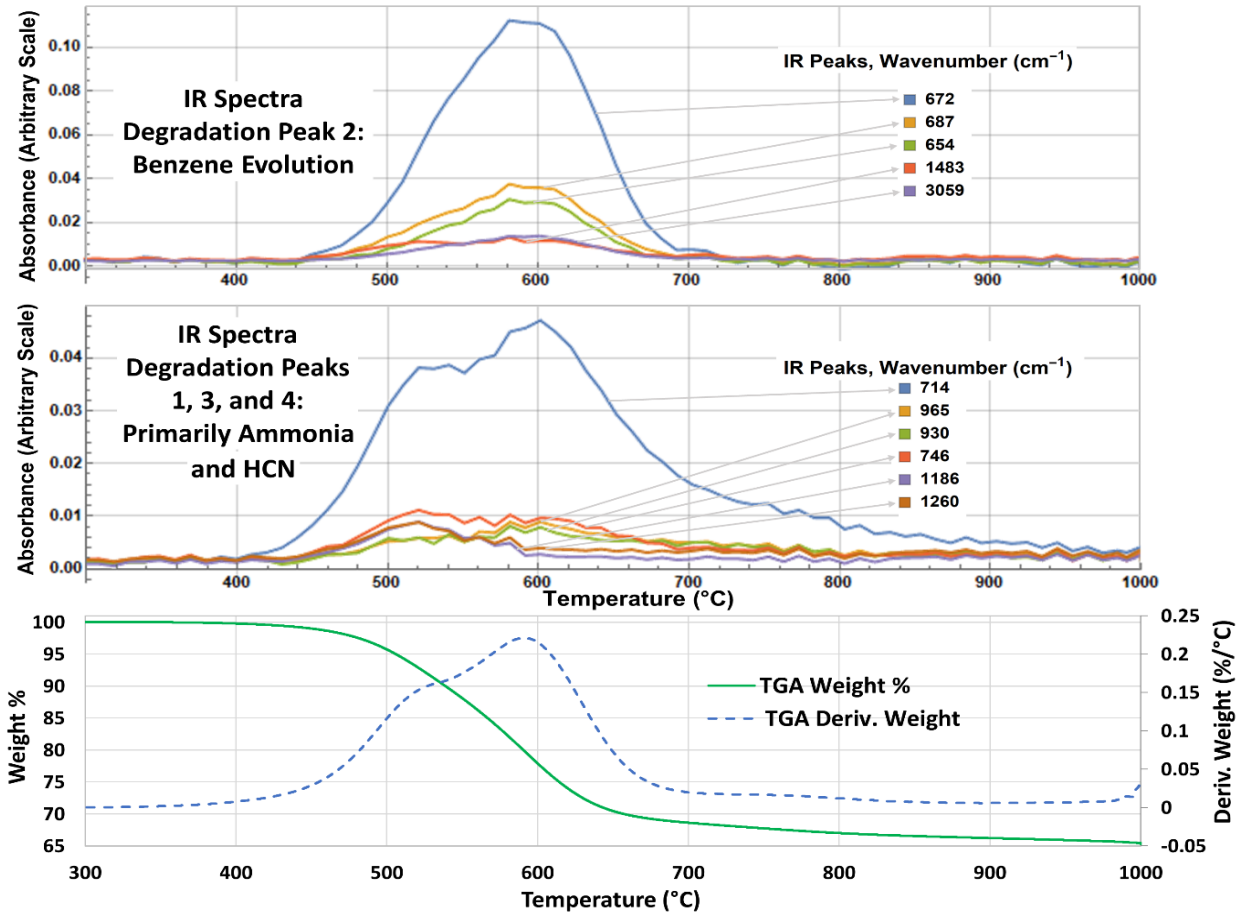

Figure 6: TGA/FTIR in nitrogen of CSOPN-P cured to 350 °C for 4 hours. TGA curves (bottom) correlate with IR peaks of evolved gases (top and middle).

In air, three degradations were observed with peaks at 515°C, 575°C, and 645 °C. All three degradations corresponded primarily with the evolution of CO_2 and H_2O. This result may be expected due to combustion of the organic polymer and degradation products, prior to reaching the IR detector. Hydrogen cyanide was detected in small amounts at 714 cm^{-1}. Trace amounts of benzene were also detected at 500-520 °C.

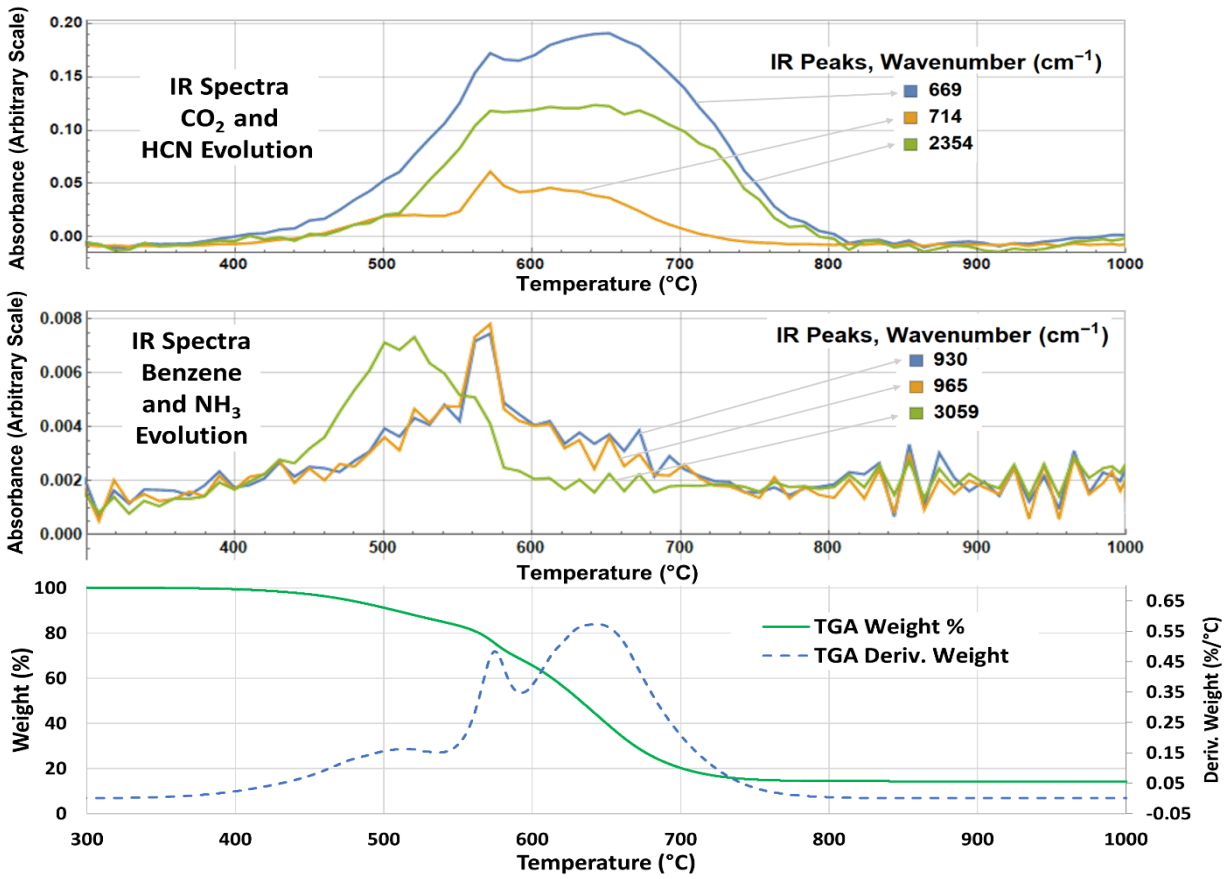

Figure 7: TGA/FTIR in air of CSOPN-P cured to 350 °C for 4 hours. TGA curves (bottom) correlate with IR peaks of evolved CO_2 and HCN (top), and benzene and NH_3 (middle).

3.3.2 Long-Term Thermo-Oxidative Stability (TOS) at 250 °C

The aging temperature of 250 °C was selected based on the needs of the power electronics industry and results of the phthalonitrile aging study performed by Koerner et al.[19] Figure 8 provides weight loss as a function of hours. Overall, CSPN and CSOPN polymers experienced significantly more weight and volume losses than commercial organic resins. For silicon-containing polymers stability followed the trend CSPN-U > CSPN-P > CSOPN-P.

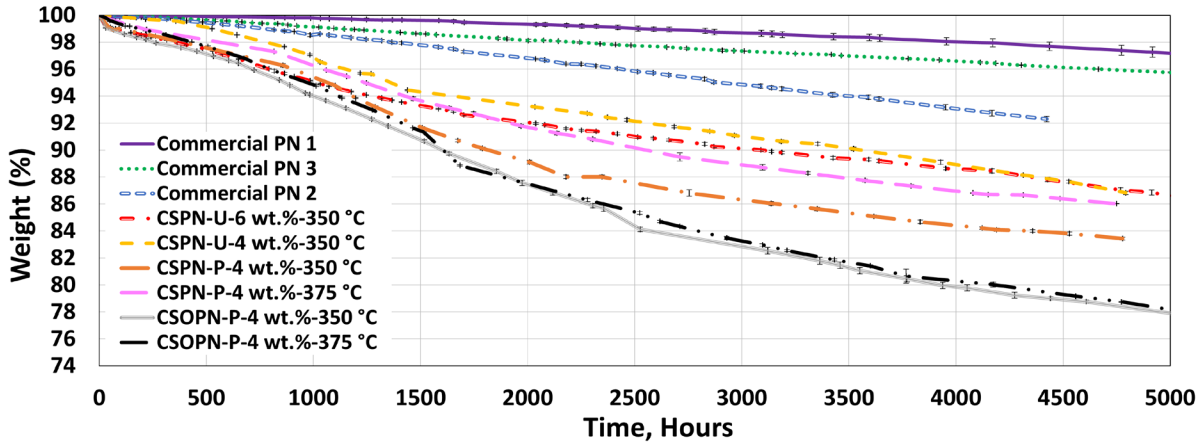

Figure 8: Weight change during aging in air at 250 °C is given as a function of time. CSPN and CSOPN polymers were cured to 350 °C for 4 hours and 0 or 3 hours at 375 °C. Sample nomenclature is as follows: monomer - wt.% p-BAPS- max curing temperature.

4. CONCLUSIONS

Overall polymers presented in this work possessed lower T_g, lower long-term thermo-oxidative stability, and higher CTE and monomer softening points, compared to commercial phthalonitrile polymers. The T_g was also lower than the T_g[20] and T_{hd}[21-22, 24] reported for silicon-containing phthalonitriles in literature. The silicon-containing phthalonitrile polymers did exhibit stabilities in TGA greater than much of organosilicon literature,[26, 28-29, 37-41] and on par with phthalonitriles in literature.[1-6, 14] The lower stability of COSPN compared with CSPN and CSOPN may partially due to hydrolytic degradation, and thus the use of aryloxysilane linkages is not recommended. It was originally assumed that purity would increase stability, and the as-synthesized carbosiloxane (CSOPN-U) materials were not characterized. However, increasing purity was extremely detrimental to the processing, qualitative hardness and strength, glass transition temperature, and stability. This effect may be explained by several considerations. First, the softening point increased with purity, resulting in higher initial processing temperatures and smaller processing windows. Volatile entrapment and monomer degradation are more likely. Simultaneously, many impurities, including metal salts, amines, and compounds with hydroxyl groups, catalyze the phthalonitrile curing reaction.[20, 23] All polymers considered performed well in oxidative testing. However, the expected higher thermo-oxidative stability of silicon-containing polymers was not achieved compared with commercial systems. This decreased performance may be due to several reasons: 1) homolytic cleavage of Si-phenyl bonds occurred at lower temperatures than C-C bonds due to the lower Si-C bond energy, 2) the loss of a phenyl group results in greater weight loss and volume change, compared with the loss of a methyl or hydrido group, 3) while oxidative crosslinking through siloxane and subsequently silica formation occurred,[33] it is likely the silicon content of these polymers is insufficient to form an effective barrier layer, and 4) the polymers likely exhibited a lower degree of cure with less triazine and phthalocyanine formation. One plausible explanation for this lower degree of cure may be steric hindrance from the high degree of aromatic substitution. Tri- or tetra-phenyl-substituted systems are known to have difficulties reaching full conversion.[7-8] This is expecially critical for such polymer systems, where three or four reactive end groups must interact to from the desired curing products. An alternative explanation may be incompatability of the amine catalyst and silicon-containing monomer. If

phase separation occurred, the catalyst would exhibit a lower effective reactivity. However, further work is requred to identify any potential phase separation and quantify the degree of cure.

5. REFERENCES

1. Keller, T. M.; Price, T. R., "Amine-Cured Bisphenol-Linked Phthalonitrile Resins." *Journal of Macromolecular Science: Part A - Chemistry 18* (1982), 931-937 http://dx.doi.org/10.1080/00222338208077208.
2. Laskoski, M.; Dominguez, D. D.; Keller, T. M., "Synthesis and properties of a bisphenol A based phthalonitrile resin." *Journal of Polymer Science Part A: Polymer Chemistry 43* (2005), 4136-4143 http://dx.doi.org/10.1002/pola.20901.
3. Laskoski, M.; Neal, A.; Keller, T. M.; Dominguez, D.; Klug, C. A.; Saab, A. P., "Improved synthesis of oligomeric phthalonitriles and studies designed for low temperature cure." *Journal of Polymer Science Part A: Polymer Chemistry 52* (2014), 1662-1668 http://dx.doi.org/10.1002/pola.27161.
4. Laskoski, M.; Neal, A.; Schear, M. B.; Keller, T. M.; Ricks-Laskoski, H. L.; Saab, A. P., "Oligomeric aliphatic–aromatic ether containing phthalonitrile resins." *Journal of Polymer Science Part A: Polymer Chemistry 53* (2015), 2186-2191 http://dx.doi.org/10.1002/pola.27659.
5. Tong, L.; Jia, K.; Liu, X., "Novel phthalonitrile-terminated polyarylene ether nitrile with high glass transition temperature and enhanced thermal stability." *Materials Letters 128* (2014), 267-270 http://dx.doi.org/10.1016/j.matlet.2014.04.132.
6. Liu, Y. "Packaging of Silicon Carbide High Temperature, High Power Devices - Processes and Materials." Auburn University, Auburn, Alabama, 2006.
7. Guenthner, A. J.; Yandek, G. R.; Wright, M. E.; Petteys, B. J.; Quintana, R.; Connor, D.; Gilardi, R. D.; Marchant, D., "A New Silicon-Containing Bis(cyanate) Ester Resin with Improved Thermal Oxidation and Moisture Resistance." *Macromolecules 39* (2006), 6046-6053 http://dx.doi.org/10.1021/ma060991m.
8. Guenthner, A. J.; Vij, V.; Haddad, T. S.; Reams, J. T.; Lamison, K. R.; Sahagun, C. M.; Ramirez, S. M.; Yandek, G. R.; Suri, S. C.; Mabry, J. M., "Silicon-containing trifunctional and tetrafunctional cyanate esters: Synthesis, cure kinetics, and network properties." *Journal of Polymer Science Part A: Polymer Chemistry 52* (2014), 767-779 http://dx.doi.org/10.1002/pola.27052.
9. Yilgör, E.; Yilgör, I., "Silicone containing copolymers: Synthesis, properties and applications." *Progress in Polymer Science 39* (2014), 1165-1195 http://dx.doi.org/10.1016/j.progpolymsci.2013.11.003.
10. Xi, K.; Meng, Z.; Heng, L.; Ge, R.; He, H.; Yu, X.; Jia, X., "Polyimide–polydimethylsiloxane copolymers for low-dielectric-constant and moisture-resistance applications." *Journal of Applied Polymer Science 113* (2009), 1633-1641 http://dx.doi.org/10.1002/app.30154.
11. Saxena, K.; Bisaria, C. S.; Kalra, S. J. S.; Saxena, A. K., "Synthesis of some novel silicone-imide hybrid inorganic–organic polymer and their properties." *Progress in Organic Coatings*, http://dx.doi.org/10.1016/j.porgcoat.2014.08.016.
12. Damaceanu, M.-D.; Musteata, V.-E.; Cristea, M.; Bruma, M., "Viscoelastic and dielectric behaviour of thin films made from siloxane-containing poly(oxadiazole-imide)s." *European Polymer Journal 46* (2010), 1049-1062 http://dx.doi.org/10.1016/j.eurpolymj.2010.01.020.
13. Zhuo, D. X.; Gu, A. J.; Liang, G. Z.; Hu, J. T.; Cao, L.; Yuan, L., "Flame retardancy and flame retarding mechanism of high performance hyperbranched polysiloxane modified

bismaleimide/cyanate ester resin." *Polymer Degradation and Stability 96* (2011), 505-514 http://dx.doi.org/10.1016/j.polymdegradstab.2011.01.006.
14. Augustine, D.; Mathew, D.; Nair, C. P. R., "Phenol-containing phthalonitrile polymers - synthesis, cure characteristics and laminate properties." *Polymer International 62* (2013), 1068-1076 http://dx.doi.org/10.1002/pi.4393.
15. Dominguez, D. D.; Keller, T. M., "Properties of phthalonitrile monomer blends and thermosetting phthalonitrile copolymers." *Polymer 48* (2007), 91-97 http://dx.doi.org/10.1016/j.polymer.2006.11.003.
16. Keller, T. M.; Dominguez, D. D.; Laskoski, M., "Oligomeric bisphenol A-based PEEK-like phthalonitrile-cure and polymer properties." *Journal of Polymer Science Part A: Polymer Chemistry 54* (2016), 3769-3777 http://dx.doi.org/10.1002/pola.28276.
17. Laskoski, M.; Dominguez, D. D.; Keller, T. M., "Synthesis and properties of aromatic ether phosphine oxide containing oligomeric phthalonitrile resins with improved oxidative stability." *Polymer 48* (2007), 6234-6240 http://dx.doi.org/10.1016/j.polymer.2007.08.028.
18. Keller, T. M.; Dominguez, D. D., "High temperature resorcinol-based phthalonitrile polymer." *Polymer 46* (2005), 4614-4618 http://dx.doi.org/10.1016/j.polymer.2005.03.068.
19. Hilmar Koerner, T. G., G. P. Tandon, & Heritage Weems. "Phthalonitriles (PN): Thermo-Oxidative Stability (TOS) Study." *High Temple Workshop.* Charleston, SC, January 23-26.
20. Zhang, Z. B.; Li, Z.; Zhou, H.; Lin, X. K.; Zhao, T.; Zhang, M. Y.; Xu, C. H., "Self-Catalyzed Silicon-Containing Phthalonitrile Resins with Low Melting Point, Excellent Solubility and Thermal Stability." *Journal of Applied Polymer Science 131* (2014), http://dx.doi.org/10.1002/app.40919.
21. Babkin, A. V.; Zodbinov, E. B.; Bulgakov, B. A.; Kepman, A. V.; Avdeev, V. V., "Low-melting siloxane-bridged phthalonitriles for heat-resistant matrices." *European Polymer Journal 66* (2015), 452-457 http://dx.doi.org/10.1016/j.eurpolymj.2015.03.015.
22. Bulgakov, B. A.; Babkin, A. V.; Dzhevakov, P. B.; Bogolyubov, A. A.; Sulimov, A. V.; Kepman, A. V.; Kolyagin, Y. G.; Guseva, D. V.; Rudyak, V. Y.; Chertovich, A. V., "Low-melting phthalonitrile thermosetting monomers with siloxane- and phosphate bridges." *European Polymer Journal 84* (2016), 205-217 http://dx.doi.org/10.1016/j.eurpolymj.2016.09.013.
23. Wang, M.; Ning, Y., "Oligosilylarylnitrile: The Thermoresistant Thermosetting Resin with High Comprehensive Properties." *ACS Applied Materials & Interfaces 10* (2018), 11933-11940 http://dx.doi.org/10.1021/acsami.8b00238.
24. Dzhevakov, P. B.; Korotkov, R. F.; Bulgakov, B. A.; Babkin, A. V.; Kepman, A. V.; Avdeev, V. V., "Synthesis and polymerization of disiloxane Si–O–Si-linked phthalonitrile monomer." *Mendeleev Communications 26* (2016), 527-529 http://dx.doi.org/10.1016/j.mencom.2016.11.023.
25. Li, X.; Yu, B.; Zhang, D.; Lei, J.; Nan, Z., "Cure Behavior and Thermomechanical Properties of Phthalonitrile–Polyhedral Oligomeric Silsesquioxane Copolymers." *Polymers 9* (2017), 334 http://dx.doi.org/10.3390/polym9080334.
26. Yang, Z.; Han, S.; Zhang, R.; Feng, S.; Zhang, C.; Zhang, S., "Effects of silphenylene units on the thermal stability of silicone resins." *Polymer Degradation and Stability 96* (2011), 2145-2151 http://dx.doi.org/10.1016/j.polymdegradstab.2011.09.014.
27. Camino, G.; Lomakin, S. M.; Lazzari, M., "Polydimethylsiloxane thermal degradation Part 1. Kinetic aspects." *Polymer 42* (2001), 2395-2402 http://dx.doi.org/10.1016/S0032-3861(00)00652-2.

28. Sun, J. T.; Huang, Y. D.; Cao, H. L.; Gong, G. F., "Effects of ambient-temperature curing agents on the thermal stability of poly(methylphenylsiloxane)." *Polymer Degradation and Stability 85* (2004), 725-731 http://dx.doi.org/10.1016/j.polymdegradstab.2004.03.018.
29. BEATTIE, S. R. "The Thermal Decomposition of Some Silphenylene Siloxane Polymers." University of Glasgow, 1981.
30. Coutant, W. R. L., Arthur "A Kinetic Study of the Thermal Decomposition of Selected Cyclohexyl and Phenylsilanes." Battelle Memorial Inst Columbus Ohio Columbus Labs: Air Force Research Laboratories, Office of Aerospace Research, Wright Patterson Air Force Base, Ohio, 1969.
31. Cella, J.; Rubinsztajn, S., "Preparation of Polyaryloxysilanes and Polyaryloxysiloxanes by B(C6F5)3 Catalyzed Polyetherification of Dihydrosilanes and Bis-Phenols." *Macromolecules 41* (2008), 6965-6971 http://dx.doi.org/10.1021/ma800833c.
32. Terraza, C. A.; Tagle, L. H.; Tundidor-Camba, A.; Gonzalez-Henriquez, C. M.; Sarabia-Vallejos, M. A.; Coll, D., "Synthesis and characterization of aromatic poly(ether-imide)s based on bis(4-(3,4-dicarboxyphenoxy)phenyl)-R,R-silane anhydrides (R = Me, Ph) - spontaneous formation of surface micropores from THF solutions." *RSC Advances 6* (2016), 49335-49347 http://dx.doi.org/10.1039/C6RA00188B.
33. Monzel, W. J.; Lu, G.-Q.; Pruyn, T. L.; Houser, C. L.; Yee, G. T., "Thermal and oxidative behavior of a tetraphenylsilane-containing phthalonitrile polymer." *High Performance Polymers 0* (2018), 0954008318811481 https://doi.org/10.1177/0954008318811481.
34. Monzel, W. J. "Synthesis, Processing, and Properties of Silicon-Containing Phthalonitrile Resins." Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, VA, 2018.
35. Liu, X.-Q.; Jikei, M.; Kakimoto, M.-a., "Synthesis and Properties of AB-Type Semicrystalline Polyimides Prepared from Polyamic Acid Ethyl Ester Precursors." *Macromolecules 34* (2001), 3146-3154 http://dx.doi.org/10.1021/ma001862n.
36. Zhao, F.; Liu, R.; Kang, C.; Yu, X.; Naito, K.; Qu, X.; Zhang, Q., "A novel high-temperature naphthyl-based phthalonitrile polymer: synthesis and properties." *Rsc Advances 4* (2014), 8383-8390 http://dx.doi.org/10.1039/c3ra46638h.
37. Gardelle, B.; Duquesne, S.; Vu, C.; Bourbigot, S., "Thermal degradation and fire performance of polysilazane-based coatings." *Thermochimica Acta 519* (2011), 28-37 http://dx.doi.org/10.1016/j.tca.2011.02.025.
38. Hamciuc, E.; Hamciuc, C.; Cazacu, M.; Ignat, M.; Zarnescu, G., "Polyimide–polydimethylsiloxane copolymers containing nitrile groups." *European Polymer Journal 45* (2009), 182-190 http://dx.doi.org/10.1016/j.eurpolymj.2008.10.028.
39. Adhikari, R.; Dao, B.; Hodgkin, J.; Mardel, J., "Synthesis, structures and membrane properties of siloxane-imide co-polymers produced by aqueous polymerization." *European Polymer Journal 47* (2011), 1328-1337 http://dx.doi.org/10.1016/j.eurpolymj.2011.02.018.
40. Ku, C.-K.; Lee, Y.-D., "Microphase separation in amorphous poly(imide siloxane) segmented copolymers." *Polymer 48* (2007), 3565-3573 http://dx.doi.org/10.1016/j.polymer.2007.04.028.
41. Othman, M. B. H.; Ramli, M. R.; Tyng, L. Y.; Ahmad, Z.; Akil, H. M., "Dielectric constant and refractive index of poly (siloxane–imide) block copolymer." *Mater. Des. 32* (2011), 3173-3182 http://dx.doi.org/10.1016/j.matdes.2011.02.048.