Supplementary Materials

Phosphorus-Containing Silsesquioxane Derivatives as Additive or Reactive Components of Epoxy Resins

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**Table S1.** Results of EDS analysis of unmodified epoxy resin (Ref.) sample

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z   | R   | A   | F   |
|---------|----------|----------|----------|---------|--------|-----|-----|-----|-----|
| C K     | 83.62    | 86.72    | 710.19   | 3.43    | 0.6114 | 1.0004 | 0.9963 | 0.7318 | 1.0000 |
| N K     | 1.94     | 1.74     | 1.65     | 16.12   | 0.6012 | 0.9903 | 1.0062 | 0.0616 | 1.0000 |
| O K     | 14.44    | 11.33    | 45.10    | 19.36   | 0.6128 | 0.9982 | 1.0151 | 0.0916 | 1.0000 |
| ClK     | 0.69     | 0.21     | 45.85    | 3.24    | 0.6054 | 0.8323 | 1.0736 | 1.0496 | 1.0257 |

**Figure S18.** SEM micrograph of unmodified epoxy resin (Ref.) sample.
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**Table S2.** Results of EDS analysis of 1%-8GS sample.

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z | R | A | F |
|---------|----------|----------|----------|----------|--------|---|---|---|---|
| C K     | 81.89    | 85.81    | 740.71   | 3.57     | 0.5919 | 1.0068 | 0.9960 | 0.7178 | 1.0000 |
| N K     | 2.14     | 1.92     | 1.98     | 15.59    | 0.0013 | 0.9864 | 1.0059 | 0.0626 | 1.0000 |
| O K     | 15.24    | 11.99    | 51.75    | 10.28    | 0.0137 | 0.9686 | 1.0149 | 0.0926 | 1.0000 |
| Si K    | 0.19     | 0.08     | 14.65    | 7.05     | 0.0014 | 0.8902 | 1.0571 | 0.8117 | 1.0667 |
| P K     | 0.01     | 0.00     | 0.80     | 55.63    | 0.0001 | 0.8562 | 1.0628 | 0.9242 | 1.0138 |
| S K     | 0.54     | 0.19     | 43.67    | 3.13     | 0.0046 | 0.8327 | 1.0734 | 1.0449 | 1.0254 |

**Figure S21.** SEM micrograph of 1%-8GS sample.
Figure S22. SEM-EDS a) carbon, b) oxygen, and c) silicon atoms distribution maps of 1%-8GS sample.
Figure S23. EDS spectrum of 5%-8GS sample.

Table S3. Results of EDS analysis of 5%-8GS sample.

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z  | R  | A  | F   |
|---------|----------|----------|----------|---------|--------|----|----|----|-----|
| C K     | 80.43    | 84.85    | 593.46   | 4.18    | 0.5334 | 1.0079 | 0.9953 | 0.6579 | 1.0000 |
| N K     | 2.01     | 1.82     | 1.67     | 16.11   | 0.0013 | 0.9675 | 1.0652 | 0.0633 | 1.0000 |
| O K     | 16.04    | 12.70    | 49.12    | 10.29   | 0.0146 | 0.9697 | 1.0142 | 0.0939 | 1.0000 |
| SiK     | 0.91     | 0.41     | 62.52    | 3.59    | 0.0066 | 0.8913 | 1.0565 | 0.8088 | 1.0083 |
| P K     | 0.01     | 0.00     | 0.67     | 56.14   | 0.0001 | 0.6572 | 1.0622 | 0.9054 | 1.0132 |
| CIK     | 0.60     | 0.22     | 43.37    | 2.98    | 0.0053 | 0.8337 | 1.0729 | 1.0332 | 1.0238 |

Figure S24. SEM micrograph of 5%-8GS sample.
Figure S25. SEM-EDS a) carbon, b) oxygen, and c) silicon atoms distribution maps of 5%-8GS sample.
Figure S26. EDS spectrum of 10%-8GS sample.

Table S4. Results of EDS analysis of 10%-8GS sample.

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z       | R       | A       | F       |
|---------|----------|----------|----------|----------|--------|---------|---------|---------|---------|
| C K     | 79.27    | 84.05    | 568.17   | 4.58     | 0.4946 | 1.0086  | 0.9647  | 0.6187  | 1.0000  |
| N K     | 2.27     | 2.06     | 1.97     | 15.56    | 0.0014 | 0.9882  | 1.0046  | 0.0639  | 1.0000  |
| O K     | 16.24    | 12.93    | 51.66    | 10.27    | 0.0149 | 0.9705  | 1.0137  | 0.0944  | 1.0000  |
| SiK     | 1.69     | 0.77     | 120.40   | 3.13     | 0.0123 | 0.8900  | 1.0561  | 0.0000  | 1.0077  |
| P K     | 0.01     | 0.01     | 0.96     | 59.94    | 0.0001 | 0.8510  | 1.0610  | 0.0873  | 1.0122  |
| C K     | 0.52     | 0.19     | 38.09    | 3.15     | 0.0045 | 0.8345  | 1.0725  | 1.0217  | 1.0228  |

Figure S27. SEM micrograph of 10%-8GS sample.
**Figure S28.** SEM-EDS a) carbon, b) oxygen, and c) silicon atoms distribution maps of 10%-8GS sample.
Figure S29. EDS spectrum of 1%-4P4GS sample.

Table S5. Results of EDS analysis of 1%-4P4GS sample.

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio  | Z   | R   | A   | F   |
|---------|----------|----------|----------|----------|---------|-----|-----|-----|-----|
| C K     | 82.28    | 86.15    | 678.31   | 3.55     | 0.5967  | 1.0067 | 0.9961 | 0.7202 | 1.0000 |
| N K     | 1.94     | 1.74     | 1.62     | 16.17    | 0.0012  | 0.9963  | 1.0060 | 0.9023 | 1.0000 |
| O K     | 15.09    | 11.86    | 46.50    | 10.32    | 0.0135  | 0.9655  | 1.0149 | 0.9925 | 1.0000 |
| Si K    | 0.07     | 0.03     | 4.95     | 18.71    | 0.0005  | 0.8901  | 1.0571 | 0.8123 | 1.0089 |
| P K     | 0.02     | 0.01     | 1.42     | 54.88    | 0.0002  | 0.6561  | 1.0028 | 0.9275 | 1.0141 |
| Cl K    | 0.60     | 0.21     | 44.40    | 3.10     | 0.0953  | 0.6326  | 1.0735 | 1.0469 | 1.0254 |

Figure S30. SEM micrograph of 1%-4P4GS sample.
Figure S31. SEM-EDS a) carbon, b) oxygen, c) silicon and d) phosphorus atoms distribution maps of 1%-4P4GS sample.
**Figure S32.** EDS spectrum of 5\%-4P4GS sample.

**Table S6.** Results of EDS analysis of 5\%-4P4GS sample.

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z    | R    | A    | F    |
|---------|----------|----------|----------|---------|--------|------|------|------|------|
| C K     | 80.40    | 84.70    | 615.78   | 3.90    | 0.5566 | 1.0075| 0.9956| 0.0085| 1.0000|
| N K     | 2.39     | 2.15     | 1.96     | 15.56   | 0.0015 | 0.9871| 1.0055| 0.0035| 1.0000|
| O K     | 16.10    | 12.73    | 48.87    | 10.29   | 0.0146 | 0.9693| 1.0145| 0.0035| 1.0000|
| Si K    | 0.40     | 0.18     | 27.17    | 4.86    | 0.0029 | 0.8969| 1.0567| 0.0075| 1.0087|
| P K     | 0.10     | 0.04     | 6.32     | 12.84   | 0.0008 | 0.8569| 1.0024| 0.9100| 1.0134|
| CJK     | 0.56     | 0.20     | 40.27    | 3.22    | 0.0050 | 0.6334| 1.0731| 1.0386| 1.0246|

**Figure S33.** SEM micrograph of 5\%-4P4GS sample.
Figure S34. SEM-EDS a) carbon, b) oxygen, c) silicon and d) phosphorus atoms distribution maps of 5%-4P4GS sample.
Figure S35. EDS spectrum of 10%-4P4GS sample.

Table S7. Results of EDS analysis of 10%-4P4GS sample.

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z    | R    | A     | F
|---------|----------|----------|----------|---------|--------|------|------|-------|---
| C K     | 70.04    | 82.70    | 633.24   | 4.32    | 0.5008 | 1.0085 | 0.9949 | 0.0439 | 1.0000
| N K     | 3.99     | 3.82     | 3.83     | 13.31   | 0.0026 | 0.9881 | 1.0048 | 0.0050 | 1.0000
| O K     | 16.33    | 12.99    | 55.93    | 10.25   | 0.0148 | 0.9704 | 1.0139 | 0.0934 | 1.0000
| Si K    | 0.88     | 0.40     | 67.49    | 3.48    | 0.0063 | 0.8919 | 1.0503 | 0.8037 | 1.0085
| P K     | 0.25     | 0.10     | 18.39    | 8.61    | 0.0020 | 0.8579 | 1.0600 | 0.0021 | 1.0126
| Cl K    | 0.52     | 0.19     | 41.56    | 3.15    | 0.0045 | 0.8343 | 1.0727 | 1.0277 | 1.0235

Figure S36. SEM micrograph of 10%-4P4GS sample.
Figure S37. SEM-EDS a) carbon, b) oxygen, c) silicon and d) phosphorus atoms distribution maps of 10%-4P4GS sample.
Figure S38. EDS spectrum of 1%-8PS sample.

Table S8. Results of EDS analysis of 1%-PS sample.

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z      | R      | A      | F      |
|---------|----------|----------|----------|----------|--------|--------|--------|--------|--------|
| C K     | 81.75    | 85.70    | 052.21   | 3.63     | 0.5865 | 1.0069 | 0.9960 | 0.7124 | 1.0000 |
| N K     | 2.20     | 1.98     | 1.81     | 15.80    | 0.0014 | 0.9865 | 1.0056 | 0.0620 | 1.0000 |
| O K     | 15.28    | 12.03    | 46.13    | 19.32    | 0.0137 | 0.9687 | 1.0148 | 0.0926 | 1.0000 |
| Si K    | 0.12     | 0.06     | 8.58     | 11.79    | 0.0009 | 0.8903 | 1.0570 | 0.8112 | 1.0089 |
| P K     | 0.07     | 0.03     | 4.56     | 19.81    | 0.0006 | 0.8563 | 1.0627 | 0.9253 | 1.0139 |
| C K     | 0.58     | 0.20     | 41.75    | 3.18     | 0.0051 | 0.8328 | 1.0734 | 1.0447 | 1.0252 |

Figure S39. SEM micrograph of 1%-8PS sample.
Figure S40. SEM-EDS a) carbon, b) oxygen, c) silicon and d) phosphorus atoms distribution maps of 1%-PS sample.
Figure S41. EDS spectrum of 5%-8PS sample.

Table S9. Results of EDS analysis of 5%-PS sample.

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z     | R     | A     | F     |
|---------|----------|----------|----------|----------|--------|-------|-------|-------|-------|
| C K     | 81.30    | 85.42    | 631.42   | 3.86     | 0.5647 | 1.0873| 0.9957| 0.6895| 1.0000|
| N K     | 2.32     | 2.09     | 1.93     | 15.65    | 0.0014 | 0.9889| 1.0056| 0.0028| 1.0000|
| O K     | 15.31    | 12.38    | 46.53    | 10.32    | 0.0138 | 0.9691| 1.0146| 0.0927| 1.0000|
| Si K    | 0.30     | 0.14     | 20.96    | 5.21     | 0.0022 | 0.8906| 1.0568| 0.8107| 1.0090|
| P K     | 0.17     | 0.07     | 11.66    | 8.55     | 0.0014 | 0.8566| 1.0625| 0.9209| 1.0136|
| C K     | 0.59     | 0.21     | 42.94    | 3.16     | 0.0052 | 0.8331| 1.0732| 1.0405| 1.0246|

Figure S42. SEM micrograph of 5%-PS sample.
Figure S43. SEM-EDS a) carbon, b) oxygen, c) silicon and d) phosphorus atoms distribution maps of 5%-PS sample.
**Figure S44.** EDS spectrum of 10%-8PS sample.

**Table S10.** Results of EDS analysis of 10%-PS sample.

| Element | Weight % | Atomic % | Net Int. | Error % | Kratio | Z     | R     | A     | F     |
|---------|----------|----------|----------|---------|--------|-------|-------|-------|-------|
| C K     | 80.52    | 85.01    | 583.24   | 4.27    | 0.5273 | 1.0080| 0.9952| 0.6496| 1.0000|
| N K     | 1.55     | 1.49     | 12.18    | 17.90   | 0.0010 | 0.9876| 1.0051| 0.9632| 1.0000|
| O K     | 16.28    | 12.91    | 40.18    | 10.28   | 0.0149 | 0.9099| 1.0141| 0.0944| 1.0000|
| Si K    | 0.73     | 0.33     | 49.88    | 3.68    | 0.0053 | 0.8914| 1.0564| 0.8084| 1.0089|
| P K     | 0.41     | 0.17     | 20.30    | 4.99    | 0.0032 | 0.8574| 1.0622| 0.9092| 1.0126|
| Cl K    | 0.51     | 0.18     | 36.31    | 3.38    | 0.0045 | 0.8339| 1.0729| 1.0297| 1.0236|

**Figure S45.** SEM micrograph of 10%-8PS sample.
Figure S46. SEM-EDS a) carbon, b) oxygen, c) silicon and d) phosphorus atoms distribution maps of 10%-PS sample.
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Figure S50. Graphs of a) TG and b) DTG curves of epoxy resin samples modified with 1, 5 and 10% of 4P4GS derivative in air atmosphere.
Figure S51. Graphs of a) TG and b) DTG curves of epoxy resin samples modified with 1, 5 and 10% wt. of 8PS derivative in N₂ atmosphere.
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**Figure S56.** DSC cooling curves for epoxy resins modified with 10%wt. of 8GS, 4P4GS and 8PS derivatives