Flame Retardance and Char Analysis of an Eco-Friendly Polyurethane Hyperbranched Hybrid Using the Sol–Gel Method

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Abstract: This study used the sol–gel method to synthesize a non-halogenated, hyperbranched flame retardant containing nitrogen, phosphorus, and silicon (HBNPSi), which was then added to a polyurethane (PU) matrix to form an organic–inorganic hybrid material. Using 29Si nuclear magnetic resonance, energy-dispersive X-ray spectroscopy of P- and Si-mapping, scanning electron microscopy, and X-ray photoelectron spectroscopy, this study determined the organic and inorganic dispersity, morphology, and flame retardance mechanism of the hybrid material. The condensation density of the hybrid material PU/HBNPSi was found to be 74.4%. High condensation density indicates a dense network structure of the material. The P- and Si-mapping showed that adding inorganic additives in quantities of either 20% or 40% results in homogeneous dispersion of the inorganic fillers in the polymer matrix without agglomeration, indicating that the organic and inorganic phases had excellent compatibility. In the burning test, adding HBNPSi to PU made the material pass the UL-94 test at the V2 level, unlike the pristine PU, which did not meet the standard. The results demonstrate that after non-halogenated flame retardant was added to PU, the material’s flammability and dripping were lower, thereby proving that flame retardants containing elements such as nitrogen, phosphorus, and silicon exert an excellent flame-retardant synergistic effect.

Keywords: flame retardant; organic–inorganic hybrid; polyurethane; sol–gel method; synergistic effect

1. Introduction

Polyurethane (PU) can appear in many forms, such as foam, adhesive, paint, and elastomer. Because of its favorable mechanical properties and resistance to chemicals and wear, PU is widely used in the automobile, textile, sports equipment, shoe sole, and paint industries, among others [1–3]. PU is the most common commercial polymer material in daily life. However, it has some weaknesses, such as low thermal stability and high flammability. For example, when PU is heated to 80–90 °C, its mechanical properties rapidly deteriorate. When the PU matrix is heated to over 200 °C, severe pyrolysis occurs and it becomes flammable, increasing the risk of a fire hazard. Therefore, improving the flame retardance of PU is a critical task in the development of polymer materials [1,4,5].

Compared with halogenated flame retardants, non-halogenated flame retardants have attracted great attention because during their combustion a lower amount of hazardous gases or smoke is produced, which is safer for the people in the fire and will not destroy the ozone layer in the atmosphere. These are called eco-friendly flame retardants. Flame retardants can play a role in the gas phase or condensed phase. Halogenated flame retardants are typically in the gas phase, whereas flame retardants containing phosphorus and nitrogen can be in either phase [4,6,7]. Flame retardants containing siloxane have a main chain of Si–O. The energy of the Si–O bond is high and the Si–O chain is resilient when
forming SiO$_2$; as a result, these flame retardants exhibited outstanding thermal stability under high temperatures [8]. Rao et al. [9] reported an organic–inorganic phosphorus–nitrogen–silicon flame retardant that was synthesized by the Kabachnik–Fields reaction and the sol–gel method, and then it was used as a reactive flame retardant to prepare flame-retardant and smoke-suppressant epoxy resins (EPs). The results certified the charring effect of the phosphaphenanthrene group and the enhancing effect of the silicon group. Subsequently, the flame inhibition effect and lesser combustible gases release enhanced the flame-retardant properties of the EP.

In the last few decades, the hyperbranched hybrid has gained more attention due to its special structure. Many hyperbranched materials have been synthesized and used in many fields, including flame retardants. Yang et al. [10] reported a novel hyperbranched phosphorus/nitrogen-containing flame retardant (HPNFR) that was facilely synthesized via the transesterification reaction of dimethyl methylphosphonate and tris (2-hydroxyethyl) isocyanurate. The sample with 4 wt% HPNFR can achieve a V-0 rating in the UL-94 test and possesses a limiting oxygen index (LOI) value as high as 34.5%. HPNFR would not significantly damage the transparency of EP thermosets; consequently, it reserved its application value in some special fields. Hu et al. [11] showed a phosphorus/nitrogen-containing hyperbranched polymer (PN-HBP) that was synthesized via the esterification reaction of 2-carboxyethyl (phenyl) phosphinic acid (CEPPA) and tris (2-hydroxyethyl) isocyanurate (THEIC). A higher LOI and a V-0 rating in the UL-94 vertical burning test were realized, which indicated an apparent synergistic effect. The peak heat release rates (PHRRs) of composites were reduced significantly compared with that of PU.

The PU used in this study has a wide range of applications. However, it has fatal disadvantages such as flammability and dripping. This study employed the sol–gel method to prepare a reactive flame retardant containing nitrogen, phosphorus, and silicon and classified the flame retardance of the organic–inorganic polyurethane hybrid.

2. Experimental
2.1. Materials

Isophorone diisocyanate (IPDI) and dibutyltin dilaurate (DBTDL) were purchased from Alfa Aesar Co., Shore Road, Heysham LA3 2XY, UK. ARCOL POLYOL 1021 (Polyol) was purchased from Bayer Material Science Taiwan Limited Taipei, Taiwan. The purchase of 1,4-Butanediol (1,4-BD) was from Acros Chemical Co., Morristown, NJ, USA. The purchase of 3-Isocyanatopropyliethoxysilane (IPTS) was from GELEST, Inc., 11 steel Rd. EAST, Morrisville, PA, USA. Triglycidyl isocyanurate (TGIC) was purchased from TCI, Tokyo, Japan. The purchase of 10-(2,5-Dihydroxyphenyl)-10H-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-BQ) was from Sigma-Aldrich Co. Ltd., Taipei, Taiwan. Anhydrous stabilized tetrahydrofuran (THF) was obtained from Lancaster Co., Morecambe, Lancashire, UK. Hydrogen chloride (HCl) was purchased from ECHO Chemical Co., Ltd., Toufen, Taiwan.

2.2. Preparation of DOPOBQ-IPTS-TGIC

First, DOPO-BQ (7.58 g) and IPTS (5.78 g) were added into a 100 mL serum bottle, and then 80 mL of THF solvent and 0.2 g of metal catalyst DBTDL were added. The aforementioned reactants were stirred at 60 ℃ and the substances were allowed to react for 2 h. Subsequently, we added 0.72 mL of deionized (DI) water into THF, instilled HCl, and adjusted the pH value to 4; the product of the sol–gel reaction was hyperbranched phosphorous–silicon (HBPSi). Additionally, TGIC (6.95 g) was dissolved in THF and a sol–gel reaction was conducted for 2 h on HBPSi. After the temperature reached 60 ℃, TGIC was slowly added into HBPSi and allowed to react at 60 ℃ for 2 h. This formed hyperbranched nitrogen-phosphorous-silicon (HBNPSi) flame retardant that was dissolved in THF and then the addition reaction took place with prepolymer to form nanocomposites. This reaction is presented in Scheme 1.
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Scheme 1. The reaction of hyperbranched nitrogen–phosphorous–silicon (HBNPSi).
2.3. Preparation of PU/HBNPSi Hybrid

IPDI (9.88 g) and Polyol (20 g) were added into a four-necked bottle in a nitrogen environment; the mixture was stirred by a magnetic stirrer (PC 410 D, Corning Incorporated, Corning, NY, USA), at 60 °C. Subsequently, DBTDL catalyst (0.3 g) was added into the four-necked bottle for a simultaneous reaction to form a prepolymer. Following 2 h of reaction, HBNPSi was slowly dripped into the four-necked bottle. After 2 h of reaction, 1,4-BD (0.8 g) was also allowed to react for 2 h and we observed whether the viscosity increased. After the viscosity increased for any sample, that sample was poured into a polytetrafluoroethylene mold and placed into a vacuum oven (DOV-40, Dengyng Co., New Taipei City, Taiwan) for 24 h of de-aeration. After the temperature reached 60 °C, it was placed in another circulating oven (OV-80, Firstek Scientific Co., Hsin Chuang City, Taiwan) for 24 h. When the temperature reached 60 °C, the finished product was withdrawn and stored at room temperature for cooldown, thereby completing the preparation of PU/HBNPSi. Its reaction formula is presented in Scheme 2. The schematic diagram for the experimental part is shown in Scheme 3.

Scheme 2. The reaction of polyurethane (PU)/HBNPSi.
3.1. Measurements

To observe the condensation density, $^{29}\text{Si}$ nuclear magnetic resonance (NMR) was used and performed by a Bruker DSX-400WB, Bremen, Germany. The samples were treated at 180 °C for 2 h and then ground into a fine powder. The vertical burning test was done inside a fume hood. The UL-94 standard was then used to evaluate the flame retardance of the hybrid material. Samples were held vertically with tongs at one end and burned from the free end. Three samples were prepared for every test. Samples were exposed to an ignition source for 10 s. Then, they were allowed to burn above cotton wool until both the sample and cotton wool were extinguished. Observable parameters were recorded to assess fire retardance. The UL-94 test classifies the materials as V-0, V-1, and V-2 according to the period needed before self-extinction and the occurrence of flaming dripping after removing the ignition source. V-0 is the most ambitious and desired classification. X-ray photoelectron spectroscopy (XPS) was adopted to determine the char composition to observe the mechanism of burning. The process for using the high-resolution X-ray photoelectron spectrometer (HR-XPS, ULVAC-PHI, Inc., Kanagawa-ken, Japan) is as follows: the sample is crushed into powder and then adhered to the aluminum sheet with small round holes. This sheet is mainly used for detecting the sample’s surface as well as its elemental composition and distribution in vertical directions, in addition to implementing analysis on the links of elemental substances. The morphology of the fractured surface of the composites was studied under a scanning electron microscope (SEM) (JEOL JSM 840A, Tokyo, Japan). Energy-dispersive X-ray spectroscopy (EDX) was used to observe the distributions of Si and P atoms in the hybrid, which were obtained from SEM EDX mapping (JEOL JSM 840A, Tokyo, Japan).

3. Results and Discussion

3.1. $^{29}\text{Si}$ NMR

Solid-state $^{29}\text{Si}$ NMR spectrometry was used to determine the structure of the PU/HBNPSi hybrid material, and the DOPO-BQ-IPTS reaction process and its degree of hydrolysis condensation.
sation was obtained using the sol−gel method. Because one end of IPTS was terminated with three tri-alkoxy groups (T), the end of the prepolymer had a T-shaped structure. The other end was terminated with an organic chain—an –NCO functional group—that reacted with the –OH functional group in DOPO-BQ. The T-end further hydrolyzed and condensed to form a network structure of Si–O–Si, which was more stable. According to the degree of hydrolysis and condensation, the single-, double-, and triple-replacement absorption peaks located at −45 to −48 ppm, −56 to −62 ppm, and −66 to −69 ppm indicate the T1[12,13], T2[12,14], and T3[12,13] structures, respectively.

Figure 1 presents the solid-state 29Si NMR spectra of the PU/HBNPSi hybrid material. The hybrid material had the T-structure, primarily T3. Using peak separation treatments, the T1, T2, and T3 areas could be identified. Then, the following equation was used to calculate the condensation density (Dc(%)) [13].

\[
Dc(\%) = \frac{1 \times (\text{area}T1) + 2 \times (\text{area}T2) + 3 \times (\text{area}T3)}{3}
\]

The Dc(%) of the hybrid material PU/HBNPSi was calculated to be 74.4%. Higher Dc(%) indicates that a material has a denser network structure. The Si–O–Si bonded into an excellent network structure, and the Si–O bond had high bond energy. The hybrid material thus had high thermal stability and flame retardance. The results are summarized in Table 1.

### Table 1. Distribution of area proportion.

| Sample NO.     | Area (%) |
|----------------|----------|
| PU/HBNPSi 40%  | T1 24.3  | T2 44.3  | T3 36.8  |

3.2. P- and Si-Mapping of EDX

This study determined the compatibility of pristine PU and HBNPSi. Two phases were obtained and demonstrated differences under different interaction forces. The P- and
Si-mapping of energy-dispersive X-ray spectroscopy was utilized to determine whether the dispersibility and homogeneity were favorable or whether agglomeration occurred when the inorganic phase was mixed with the organic phase. Favorable dispersibility indicates that the two phases have excellent compatibility, which is crucial in a hybrid material.

Figure 2 displays P- and Si-mapping of 20% and 40% PU/HBNPSi. The images show the dispersion of the inorganic elements P and Si in their organic phases. Each bright dot represents P or Si. The Figure reveals that the inorganic substances in both the 20% and 40% PU/HBNPSi were dispersed favorably in the matrix and that the material was homogeneous. No agglomeration was observed, which indicated that the compatibility between the organic and inorganic phases was excellent. The amount of P and Si in the material increased as the HBNPSi content was increased.

![Figure 2](image_url)

**Figure 2.** Mapping photograph of the P- and Si-containing hybrid PU/HBNPSi.

### 3.3. Flame Retardance Analysis

In the UL-94 test, a standardized ignition specimen is combusted and the total burning duration (the sum of two burning durations) must meet the standard; additionally, during the burning process, dripping, which could ignite the cotton beneath the specimen, must not occur. The flame retardance of polymeric material is classified into the V-0, V-1, and V-2 levels. Figure 3 and Table 2 reveal that the pristine PU failed and did not achieve any level. Dripping was observed, and the drips ignited the cotton below. As the concentration of HBNPSi in the material was increased to 40%, the two flame burning durations of the PU/HBNPSi hybrid material were 0.7 and 16.1 s, respectively. The sum of these two burning durations was 16.8 s. However, because dripping occurred, the material was graded as V-2. HBNPSi had excellent flame retardance because during pyrolysis the N and P in the structure became gaseous, capturing free radicals and playing a role in the condensed phase, thereby catalyzing the formation of char. Additionally, Si migrated across the surface [14,15] and formed a dense SiO₂ structure that protected the interior of the materials. The benzene ring of DOPO-BQ provided the source for char formation, and the char layer resisted burning under high temperature.
3.4. Morphology Analysis

SEM was used to observe the morphology of the hybrid material and determine its surface microtopography, particle size, and surface nucleation. Figure 4a shows that the surface of the pristine PU was smooth and homogeneous before burning, without phase separation. Figure 4b displays the surface of the burned pristine PU. Because pristine PU is highly flammable and molten after burning, some wave patterns can be observed in the SEM image. Figure 4c shows the surface of the 20% PU/HBNPSi before burning; it was generally smooth and without phase separation, despite the addition of HBNPSi. Figure 4d displays the surface of 20% PU/HBNPSi after burning. Some Si particles can be seen because Si migrated across the surface during burning. However, because insufficient char was formed, the heat blocking effect was weak, calling to mind UL-94. Therefore, 20% PU/HBNPSi was flammable. Figure 4e shows the surface of 40% PU/HBNPSi before burning and that the surface had discrete HBNPSi particles. Although the additional loading was 40%, no phase separation was observed. Figure 4f shows the surface of 40% PU/HBNPSi after burning. A dense char layer covered this surface because P was dehydrated and catalyzed into char and Si migrated across the surface while burning to form a dense char layer through the condensed phase. Both P and Si covered the material surface [13–15], which blocked the transmission of gas and flame and increased thermal stability.

3.5. XPS Char Analysis

XPS was used to examine the changes in chemical bonds in the PU/HBNPSi hybrid material at room temperature and after being burned at 800 °C in a high-temperature furnace. Additionally, after flame retardant was added to the PU the functional group changes, before and after the hybrid was burned, were observed. The peak separation method was used to calculate the material's anti-oxidation characteristics. The results are presented in Figures 5–10 and Tables 3 and 4.
Figure 4. SEM micrographs of composites (a) pristine PU (before burning) (×1 K), (b) pristine PU (after burning) (×1 K), (c) PU/HBNPSi 20% (before burning) (×1 K), (d) PU/HBNPSi 20% (after burning) (×1 K), (e) PU/HBNPSi 40% (before burning) (×1 K), (f) PU/HBNPSi 40% (after burning) (×1 K).

Figure 5. XPS survey spectra of (a) pristine PU, (b) PU/HBNPSi 10% at RT, (c) PU/HBNPSi 40% at RT, (d) PU/HBNPSi 40% at 800 °C.
Figure 6. C1s spectra of PU/HBNPSi 10%: (a) RT; (b) under an air atmosphere at 800 °C for 30 min.

Figure 7. C1s spectra of PU/HBNPSi 40%: (a) RT; (b) under an air atmosphere at 800 °C for 30 min.

Figure 8. O1s spectra of PU/HBNPSi 40%: (a) RT; (b) under an air atmosphere at 800 °C for 30 min.

Figure 9. P2p spectra of PU/HBNPSi 40%: (a) RT; (b) under an air atmosphere at 800 °C for 30 min.
Figure 10. Si2p spectra of PU/HBNPSi 40%: (a) RT; (b) under an air atmosphere at 800 °C for 30 min.

Table 3. Binding energy (eV) and relative peak intensities (%) of the various components of Cls peak-fitted signals.

| Sample NO. | Cls | C–C/C–H | C–Si | C=C | C–N | C–O | C=O |
|------------|-----|-------|------|-----|-----|-----|-----|
| PU/HBNPSi 10%—RT | C–O | 0.31 | 0.16 | 0.11 | 0.12 | 0.15 | 0.08 |
| PU/HBNPSi 10%—800 °C | C–O | 0.11 | 0.20 | 0.37 | 0.11 | 0.09 | 0.10 |
| PU/HBNPSi 40%—RT | C–O | 0.38 | 0.15 | 0.10 | 0.15 | 0.13 | 0.08 |
| PU/HBNPSi 40%—800 °C | C–O | 0.14 | 0.38 | 0.48 | 0.12 | 0.05 | 0.07 |

Table 4. The values of Cox/Ca of composites at room temperature (RT) and 800 °C.

| Sample NO. | Temperature |
|------------|-------------|
|             | RT          | 800 °C     |
| PU/HBNPSi 10% | 0.33        | 0.24       |
| PU/HBNPSi 40% | 0.27        | 0.11       |

Figure 5 displays XPS rough scans illustrating the elemental composition of the pristine PU, 10% PH/HBNPSi at room temperature, 40% PH/HBNPSi at room temperature, and 40% PU/HBNPSi after being burned at 800 °C. The scan in Figure 5a indicates three elements: C, O, and N. For the hybrid material containing 10% flame retardant (Figure 5b), P and Si were observed in addition to C, O, and N. The XPS rough scan, obtained after DOPO-BQ and IPTS were reacted, verifies that the hybrid material contained P and Si. Figure 5c presents the rough scan for the hybrid material containing 40% of HBNPSi. Because the additive content was higher than for the 10% hybrid material, the P and Si content were higher. Figure 5d shows that the hybrid material was 40% HBNPSi after being burned. Burning at a high temperature led to a slight increase in the amount of P and Si in the hybrid material because during the burning process P was dehydrated and formed char and Si migrated across the surface [14,15]. Together, these elements formed a layer of char containing P and Si that protected the material. Nitrogen mainly exerts a flame-retardant effect in the gas phase, which can dilute the oxygen concentration and capture free radicals in the gas phase, so in the XPS spectrum, the nitrogen element disappears in Figure 5d.

Figures 6–10 present scans showing Cls, O1s, P2p, and Si2p bonds in the materials at room temperature and after being burned at 800 °C. Six functional groups can be observed in the Cls spectra: those at 284 eV (C–C and C–H) [16], 285.4 eV (C–N) [17], 288.5 eV (C=O) [18], 284.5 eV (C–C) [19], and 286 eV (C–O) [20]. Because the material additive contained silicide, the spectrum contains a peak at 282.9 eV (C–Si) [21]. After heat oxidation at 800 °C, the material was mostly graphitized. The C=C content was higher, as illustrated in Figures 6 and 7. The formation of graphitized carbon–carbon double bonds is very
important for the improvement of thermal stability. It takes more than 3000 degrees to destroy its structure and form a high thermal stability protective layer on the surface of the material.

Figure 8 shows the Ols spectra, in which four functional groups can be observed, namely 531.2 eV (C=O), 532.2 eV (C–O), 531.5 eV (P=O), and 530.6 eV (Si–O) [22–27]. This indicates the change in bonding type after high-temperature heat oxidation. In Figure 8a, the Si–O–Si bonds are formed by the sol–gel reaction. In Figure 8b, it can be clearly seen that a large number of Si–O bonds are formed, mainly to form silicon dioxide, which is resistant to high temperatures. The heat-resistant layer will protect the polymer matrix on the surface of the material.

Figure 9 shows that the P2p spectrum has peaks at 131.5 eV (P–C) [28] and 133 eV (P–O–C) [27]. The corresponding bonds formed because of the addition of DOPO-BQ flame retardant. After high-temperature deep oxidation, the peaks were at 135 eV (P2O5) and 133.1 ± 0.3 eV (P2O74−) [29], corresponding to inorganic phosphides, forming char protective material. The two aforementioned inorganic phosphides were converted from the bonds before burning. P2O5 is a kind of glass, which is a non-combustible material. It will melt and cover the surface of the material to achieve insulation resistance and material transfer, which can improve the flame-retardant properties of the material.

The Si2p spectra presented in Figure 10a,b, obtained before and after burning, respectively, have considerable differences in bonding strength. Figure 10a reveals that the siloxane coupling agent caused the hydrolysis condensation reaction. Three bonds were identified: those corresponding to peaks at 100.7 eV (Si–C), 101.6 eV (Si(–O1)), and 102.2 eV (Si(–O2)). After burning and oxidation, the Si–C peak has disappeared whereas peaks have appeared at 101.6 eV (Si(–O1)), 102.2 eV (Si(–O2)), and 103.5 eV (Si(–O4)) [30]. Because silicide was converted into SiO2, the peak intensity of Si(–O4) increased. This result indicates that after burning, the hybrid material PU/HBNPSi had char layers that covered and protected the matrix. Silica is an inorganic glass that will not burn and will melt at high temperatures, covering the surface of the material to resist high-temperature attacks.

We further analyzed the differences between PU/HBNPSi 10% and PU/HBNPSi 40% at room temperature and 800 °C for 30 min under an air atmosphere. After calculating the area ratio of each bond species individually using the Cls spectrum from Figure 6 to Figure 7, the Cox (oxidized carbons)/Ca (aliphatic, aromatic carbons) ratio was obtained to show the antioxidant effect of the material [31]. The results are shown in Tables 3 and 4. The ratio of Cox/Ca at room temperature of the mixed material with 10% and 40% concentration are 0.33 and 0.27, respectively. After high-temperature combustion, the ratio decreases to 0.24 and 0.11, respectively. In summary, the higher the concentration, the better the oxidation resistance, thus improving the thermal stability of hybrid materials.

4. Conclusions

This study used 29Si NMR to determine that the siloxane condensation degree of the PU/HBNPSi was 74.4%. High condensation density indicates superior material properties. P- and Si-mapping revealed that the additive HBNPSi was well dispersed and homogeneously distributed in the polymer matrix. When the HBNPSi concentration was increased, aggregation did not occur, showing that the materials and additives were compatible. The UL-94 standard was used to determine the flame retardancy of the hybrid material. Pristine PU failed to meet the standard. The 40% PU/HBNPSi, however, achieved the V-2 level, proving that the flame retardant effectively improved the flame retardancy of the pristine PU. Using XPS, char analysis was conducted on the hybrid material PU/HBNPSi to determine the correlation between char formation and the material’s thermal property. Cls, Ols, and Si2p XPS spectra revealed that the phosphide and siloxane formed by burning had the effect of protecting the material. A higher concentration of HBNPSi resulted in a stronger effect, achieving high thermal stability and an antioxidation effect. The organic–inorganic hybrid material prepared by the sol–gel method has good compatibility and flame resistance, and has great potential for future applications in coating applications.
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