

Facile, efficient synthesis of a phosphinated hydroxyl diamine and properties of its high-performance poly(hydroxyl imides) and polyimide–SiO₂ hybrids†

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Introduction

It has been reported that the incorporation of well dispersed inorganic particles into polymers is an effective approach to improve their thermal and mechanical properties. In this work, we report our strategy to enhance the thermal properties of phosphinate polyimides. We designed and prepared a hydroxyl diamine monomer, (1), by a facile one-pot procedure. A series of poly(hydroxyl imides) (2a–2e) based on 1 were prepared, and the effect of the hydroxyl groups on the thermal properties was investigated. We also prepared polyimide–SiO₂ hybrids based on the poly(hydroxyl imide) 2e in order to further enhance the thermal and optical properties.

Results and Discussion

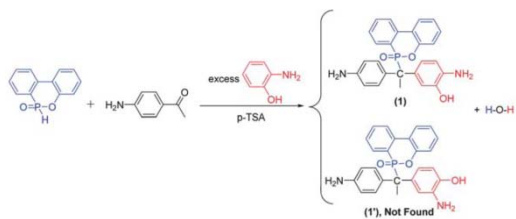
The dynamic mechanical properties of the resulting poly-(hydroxyl imides) were evaluated by DMA. [Figure. 1] shows the DMA thermograms of 2c and 2c'. This result demonstrates the contribution of the hydroxyl structure in enhancing thermal properties. We speculated that the hydroxyl groups, which interact with the imide linkage, lead to poly-(hydroxyl imides) having a higher modulus, glass transition temperature, and dimensional stability. [Figure. 2] shows the TGA thermograms of 2c and 2c'. It is speculated that the thermal cyclization of the poly(hydroxyl imide) to polybenzoxazole during the TGA heating scan at temperatures higher than 400°C might be responsible for the better thermal stability. [Figure. 3] shows the UV-vis spectra of 2e and 2e16 (both with 25 mm thickness). 2e16 displays a lower cutoff wavelength and higher transparency than 2e does, demonstrating the optical benefits resulting from the incorporation of silica. DMA and TMA were applied to evaluate the thermomechanical properties and dimensional stability of the polyimide–SiO₂ hybrid films. [Figure. 4] shows the DMA thermograms of several polyimide–SiO₂ hybrid films. The T_g values measured by DMA ranged from 354 to 364°C for 2e3–2e16, and increased with the content of SiO₂. The storage moduli also significantly increased with the increase in SiO₂ content. The phenomena could be attributed to the restricted mobility of T_g by the SiO₂ clusters. [Figure. 5] shows the TMA curves of 2e, and 2e3–2e16. The CTE of the hybrid films was reduced from 47 ppm °C⁻¹ for 2e to 27 ppm °C⁻¹ for 2e16, corresponding to a 43% reduction. This result demonstrates that the incorporation of SiO₂ efficiently reinforced the polyimide matrix and decreased the CTE. Fig. 8 shows typical TEM micrographs of the different concentrations of SiO₂ particles in the polyimide matrix. Several nanorods were aggregated into a cluster (as indicated by white arrows in [Figure. 6] (a)), and these clusters were well dispersed in the polyimide–SiO₂ hybrids.

Conclusions

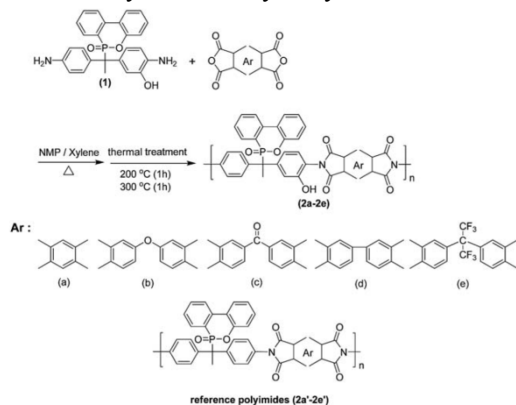
We have successfully prepared a series of poly(hydroxyl imides) (2b–2e) based on a hydroxyl diamine (1), which was prepared by a facile, efficient procedure. The structure of 1 was well characterized by single crystal X-ray diffraction and NMR data. Poly(hydroxyl imides) 2 display higher T_g, thermal stability, and dimensional stability than the reference polyimides 2'. The result demonstrates the contribution of the hydroxyl structure in enhancing the thermal properties. Polyimide–SiO₂ hybrids were prepared based on 2e and various amounts of TEOS via a sol–gel process. The hydroxyl groups of the poly(hydroxyl imides) provided the organic–inorganic bonding sites with the TEOS. Light-yellow, transparent and flexible polyimide–SiO₂ films with a maximum SiO₂ content of 16 wt% can be obtained without the addition of coupling agents. UV-vis data show that optical properties, such as cutoff wavelength and transparency of the polyimide–SiO₂ hybrids, were improved by the incorporation of SiO₂. DMA, TMA, and TGA thermograms show that the polyimide–SiO₂ hybrids exhibit higher moduli, higher T_g, lower CTE, and better thermal stability than 2e. TEM micrographs show that several nanorods were aggregated into a cluster, and these clusters were well dispersed in the polyimide–SiO₂ hybrids.

Reference

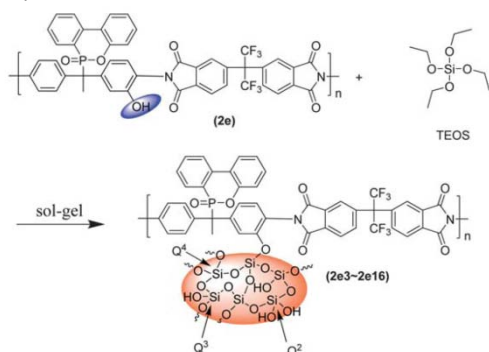
1. H. Zou, S. Wu and J. Shen, *Chem. Rev.*, **108**, 3893–3957(2008).
2. A. Morikawa, Y. Iyoku, M.-A. Kakimoto and Y. Imai, *J. Mater. Chem.*, **2**, 679–689(1992).
3. C. Xenopoulos, L. Mascia and S. J. Shaw, *J. Mater. Chem.*, **12**, 213–218(2002).
4. H. Wang, W. Zhong, Q. Du, Y. Yang, H. Okamoto and S. Inoue, *Polym. Bull.*, **51**, 63–68(2003).



Scheme 1 Synthesis of hydroxyl diamine.



Scheme 2 Synthesis of poly(hydroxyl imides) 2 and structures of the reference polyimides 2'.



Scheme 3 Synthesis of PI-SiO₂ hybrids

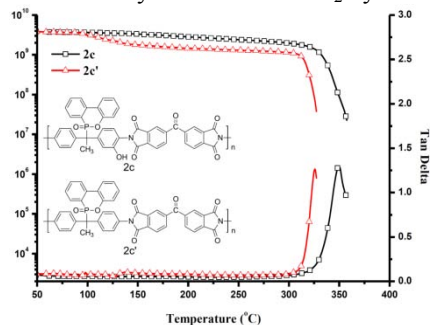


Figure 1 DMA thermograms of 2c and 2c'.

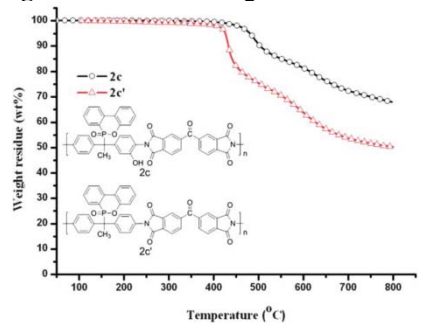


Figure 2 TGA thermograms of 2c and 2c'.

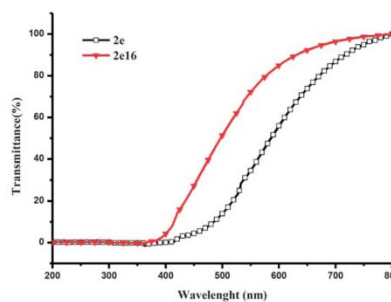


Figure 3 UV-vis spectra of 2e and 2e16.

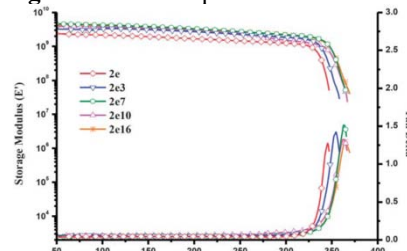


Figure 5 DMA thermograms of 2e, and 2e3–2e16

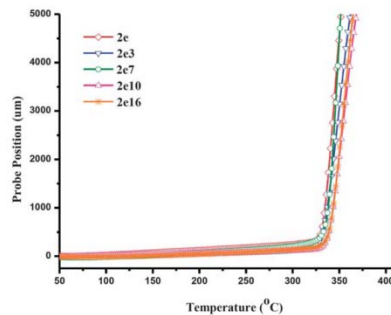


Figure 6 TMA curves of 2e, and 2e3–2e16.

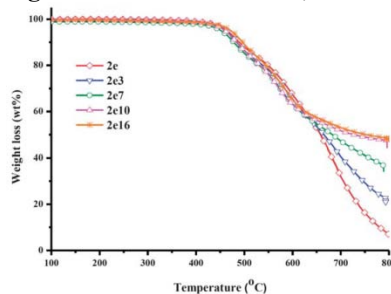


Figure 7 TGA thermograms of 2e, 2e3–2e16 in a N₂ atmosphere.

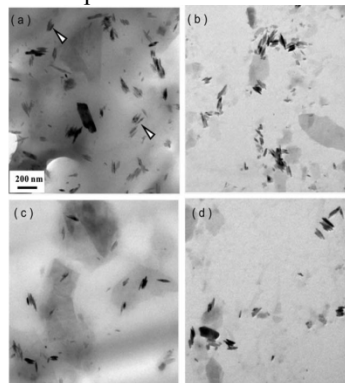


Figure 8 TEM micrographs of olyimide-SiO₂ hybrids: (a) 2e16 (b) 2e10 (c) 2e7 and (d) 2e3.