Phenylethynyl-Terminated Polyimides Containing Siloxane Structures and Their Thermal Stability

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Abstract: A series of phenylethynyl-terminated polyimides containing siloxane structures were prepared aiming at development of polyimide matrix resins with good balance of the processibility and thermal properties. The effect of siloxane structure on the processability of oligoimides and the thermal stability of cured polyimdies was investigated. The results indicated that the oligoimides have lower melt viscosity and broader processing window with the incorporation of flexible siloxane segment. The thermal stability of the cured polyimides can be significantly enhanced by high temperature postcuring due to the oxidative crosslinking of siloxane. The polyimide with siloxane structure gave the glass transition temperature even over 550°C. The T800 carbon fiber reinforced composites prepared from these polyimide matrix resins exhibited excellent mechanical properties at the temperature as high as 500°C.

1. INTRODUCTION

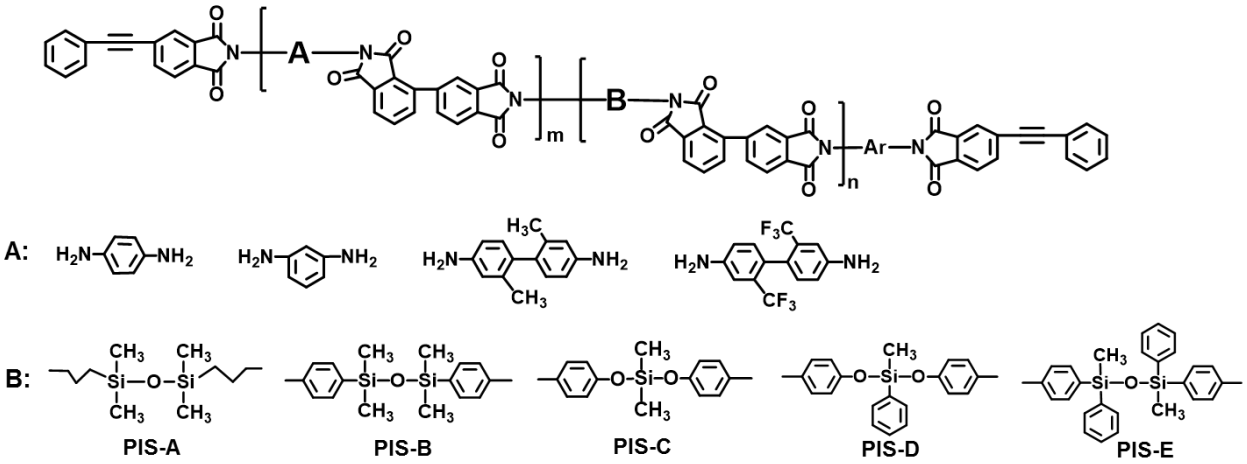
Polyimide matrix composites are widely used as structural or sub-structural components in aeronautic and aerospace applications because of their excellent combination of thermal and mechanical properties [1]. The most important requirements for the polymer materials in the high temperature applications is their high temperature resistance, *i.e.*, high glass transition temperature (T_g), good thermal stability at harsh environment, and excellent mechanical properties at elevated temperature [2]. An ideal polyimide matrix should possess not only high thermal durability but also good processability. The former determines the performance of composites as serving at elevated temperature; the latter ensures the fabrication of composites with low void content. However, it is difficult to take a good balance between the heat resistance and processability of polyimides. In general, the thermoset polyimides with rigid backbone and low molecular weight exhibit high thermal stability with high T_g due to the restricted molecular mobility and high crosslinking density [3]. On the other hand, the polyimides with rigid backbone usually exhibit poor processability with high melting viscosity [4, 5] that often lead to create voids in the composites. In addition, thermoset polyimides prepared from oligoimides with low molecular weight usually exhibit great brittleness [6].

In this research, a series of phenylethynyl-terminated polyimides containing siloxane structures were prepared, aiming at development of polyimide matrix resins with good balance of the processibility and thermal properties. The effect of siloxane structure on the processability of oligoimides and the thermal stability of cured polyimdies was investigated. The thermal stability of polyimide resins after postcuring at elevated temperature and the correlation with the microstructure and morphology was discussed. The mechanical properties of T800 carbon fiber reinforced composites prepared from these polyimide matrix resins at elevated temperature were evaluated.

2. RESULTS AND DISCUSSION

The phenylethynyl-terminated oligoimides containing different siloxane structures were prepared *via*

PMR process. The chemical structures of these oligoimides were shown in Scheme 1. The complex viscosity of the oligoimides with different siloxane structures was investigated by the dynamic rheological method and illustrated in Figure 1. It is found that these oligoimides exhibited good processability with the minimum melt viscosities no more than 120 Pa·s. Moreover, the oligoimides with longer siloxane chain exhibited lower melt viscosity and broader processing window.



Scheme 1. Chemical structures of phenylethynyl-terminated oligoimides

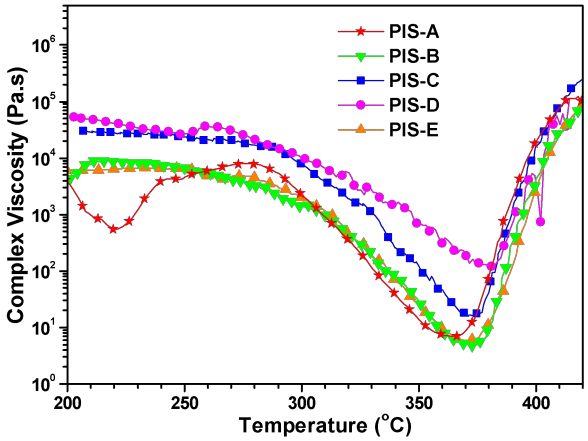


Figure 1. Complex viscosity of oligoimides with different siloxane structures

The thermal properties of polyimides containing siloxane structure are affected by the curing temperature. From the DMA curves depicted in Figure 2, it can be seen that the glass transition (tanδ) shifted to the higher temperature region combined with an enhancement of storage modulus for the polyimides after

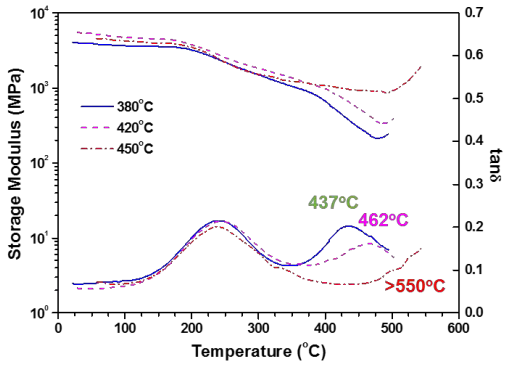


Figure 2. DMA curves of polyimides after curing at different temperatures

curing at relatively higher temperatures. The T_g enhanced from 437 to 462 °C for the polyimides after curing at 380 and 420 °C, respectively. It is unexpected that the glass transition peak of tanδ even exceeding the testing temperature range of 550°C, when the curing temperature was further increased to 450 °C.

In order to clarify how the curing temperature affects the thermal stability of polyimides containing siloxane structure, the microstructure and morphology of polyimides at elevated temperatures were investigated. Figure 3 shows the Si 2p XPS spectra of oligoimide after curing at 370 °C as well as further postcuring at 420, 450 and 500 °C, respectively. It is found that the Si 2p peak was centered at 102.03 eV for the oligoimide after thermally curing at 370 °C, which shifted to the higher binding energy after postcuring due to the siloxane oxidation. The Si 2p XPS peak can be resolved into three components, such as D [$(CH_3)_2SiO_{2/2}$], T [$CH_3SiO_{3/2}$] and Q [$SiO_{4/2}$] siloxy units, indicating the number of oxygen atoms attached to the silicon atom [7]. The curve fitting results of the Si 2p peaks indicated that the oligoimide cured at 370°C only gave the D and T components with the concentration of 92.4 and 7.6 at.%, respectively. After it was postcured at 420 and 450°C, the Q component was appeared with the concentration of 54.2 and 76.9 at.%, respectively. Meanwhile, a decrease of D component accompanied with T component was observed. The Si 2p peak shifted to 103.64 eV and only gave the Q component for the polyimide after postcuring at 500 °C, implying the completed oxidative crosslinking of siloxane.

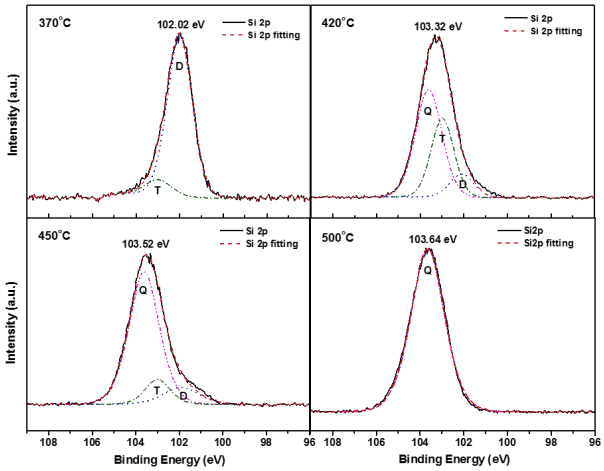


Figure 3. Si 2p XPS spectra of polyimides after thermally curing at different temperatures.

The flexural strength and interlaminar shear strength of the T800/PIS composite were measured at room temperature and elevated temperature, respectively (Figure 4). The composite gave the flexural strength of 1910 MPa and interlaminar shear strength of 106 MPa at room temperature, respectively, suggesting the excellent mechanical properties. The flexural strength and interlaminar shear strength of composite measured at 500 °C were 1440 MPa and 54.6 MPa, respectively, which gave the corresponding retention ratio of 75.4% and 51.5%. The flexural modulus of the composite only exhibited a slight drop from 158 GPa to 145 GPa as measured at 25 °C and 500 °C, which gave the retention ratio as high as 91.8%. The results indicated that the T800/PIS composite have good thermal oxidative stability even at the temperature as high as 500 °C. The respectable mechanical properties of the composite at elevated temperature are related to good melt processability and improved thermal stability of matrix resin. As the testing temperature increased to 550 °C, the flexural strength decreased to 634 MPa, implying the matrix resin degradation. However, the interlaminar shear strength of composite still maintained at 40.8 MPa as measured at 550 °C. This may be due to the good fluidity of resin in curing processing which provides a strong interface between matrix resin and fiber.

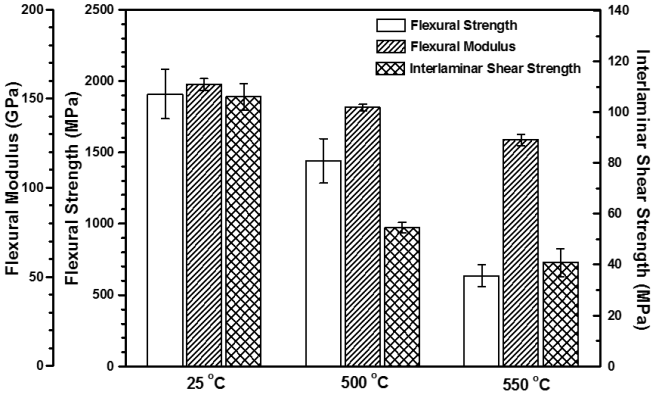


Figure 4. Mechanical properties of T800/PIS composite.

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