

## Thermal and mechanical evaluation of cyanate ester resin catalyzed by nonylphenol and stannous octoate

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**ABSTRACT:** Nonylphenol (NP), stannous octoate [Sn(Otc)<sub>2</sub>], and a mixture of NP and Sn(Otc)<sub>2</sub> were employed for catalyzing cyanate ester resin. The curing reaction was studied by differential scanning calorimetry. A water-absorption test at 85 °C was utilized to study the resistance to warm and humid conditions. The thermal properties were evaluated through measuring thermal weight loss and the glass-transition temperature ( $T_g$ ), and the mechanical properties were evaluated through three-point bending tests and tensile tests. The results show that the mixture of NP and Sn(Otc)<sub>2</sub> exhibits the best catalytic efficiency by decreasing the exothermic peak temperature by almost 148 °C. The mixture of NP and Sn(Otc)<sub>2</sub> has unfavorable effects on the thermal stability. Nevertheless, all catalyst systems have good water-absorption resistance. The mechanical investigation confirms that the tensile properties show a little reduction that is due to the plasticization of the catalyst, while the excellent flexural properties are maintained. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43959.

**KEYWORDS:** adsorption; catalysts; mechanical properties; resins; thermal properties

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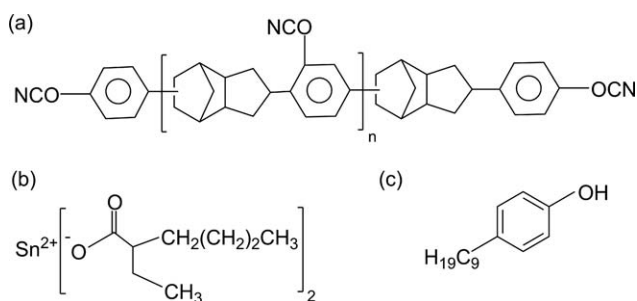
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### INTRODUCTION

The development of astronautic precision optical instruments includes various aspects of space optical cameras, optical reflectors, and lens barrels for space optical remote sensors.<sup>1,2</sup> These applications have stringent requirements for the precision and dimensional stability of the optical elements. Carbon fiber composites can satisfy the need for lightweight designs to reduce launch costs, so applying carbon fiber composites of high stiffness to highly precise space optical instruments has been an urgent need. However, residual stress might be contained due to the stand and fall of the dimensional stability of optical instruments made from carbon fiber composites, and the higher the curing temperature of the resin, the more serious the curing residual stress and the deformation.<sup>3</sup> Furthermore, when composite materials serve in humid conditions, water vapor could be absorbed because of the diffusion of free water derived by a kinetic process involving water molecules jumping between molecular-sized gaps in the polymer network or through the interface between the fiber and the matrix resin under the driving force of the water concentration gradient. The absorbed water vapor may cause dimensional deformation of the instruments, so water absorption of the resin is the factor needing evaluation.<sup>4,5</sup> In other words, the dimensional accuracy requirements of the optical instruments lead to the challenge of balancing the reduction of curing temperature of the resin matrix with maintainance of good water resistance.

Cyanate ester resins are a new group of high-performance thermosetting resin matrix, and they have the absolute advantages of good water resistance, low coefficient of thermal expansion, excellent mechanical properties, low dielectric constant, and high temperature stability.<sup>6–8</sup> Because of these outstanding properties, they are substituted for epoxy and bismaleimide resins and are widely used in electronics, electrical appliances, aerospace materials, and prepreg preparation.<sup>9–11</sup> Although pure cyanate ester resin has low water absorption, the high curing temperature exceeding 250 °C brings difficulty in the composite processing and hinders its application.

To optimize the process performance of cyanate ester resins, they are usually doped with appropriate catalysts. To date, some important experiments in catalyzing cyanate ester resin have been carried out. Previous work has demonstrated organometallic salts (e.g., copper acetylacetonate, cobalt acetylacetonate, organotin, stannous octoate), active hydrogen compounds (e.g., nonylphenol, triethylamine), and UV activation as effective catalysts for polymerization of cyanate resins.<sup>8,12–15</sup> It also has been established that the combination of active hydrogen compounds and organometallic salts could lead to improved curing efficiency; the former, especially nonylphenol,<sup>6,16,17</sup> generally acts as a cocatalyst to dissolve the latter. Our research has proved that the combination of stannous octoate and nonylphenol is a highly effective group for catalyzing the curing reaction of cyanate resins, and it could be



**Figure 1.** Structures of (a) CY-3W, (b) stannous octoate, and (c) nonylphenol.

carried out at temperatures below 100 °C. However, the properties of the cyanate resin and the carbon fiber composites need to be fully investigated in order to evaluate the applicability of these catalysts.

Among several types of cyanate ester resins, dicyclopentadienyl bisphenol cyanate ester oligomer (CY-3W) has the same good thermal stability but relatively low viscosity that is advantageous for its composite processing. In this article, CY-3W was employed, and the catalytic effect of NP and  $\text{Sn}(\text{Otc})_2$  on CY-3W was investigated. The integrated performances, especially the thermal and mechanical properties, of cyanate ester resins (CY-3W) catalyzed by nonylphenol (NP), stannous octoate [ $\text{Sn}(\text{Otc})_2$ ], and the mixture of NP and  $\text{Sn}(\text{Otc})_2$  were compared. To the best of our knowledge, it is the first report for the evaluation of catalyzed CY-3W properties. It has important significance for the modification and further application of CY-3W as a high-performance resin matrix for fabricating carbon fiber composites used in such areas as optical precision instruments.

## EXPERIMENTAL

### Materials

Trifunctional CY-3W with purity exceeding 92% was supplied by Jiangsu Jiangdu Wuqiao Resin Factory (China). Stannous octoate (AR) was provided by Aladdin Chemistry Co. Ltd (China), and nonylphenol (AR) was provided by Chengdu Xiya Reagent Co. Ltd (China). The structures of CY-3W and catalysts are shown in Figure 1.

### Sample Preparation

The resins mixed with catalysts were prepared as CY-3W/6%NP, CY-3W/0.8% $\text{Sn}(\text{Otc})_2$ , and CY-3W/6%NP/0.8% $\text{Sn}(\text{Otc})_2$ , then stirred at 60 °C in a water bath until a homogeneous mixture was obtained. Parts of the resin mixtures were for differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) measurement and the others were for casting preparation. The homogeneous mixture was poured into the preheated mold and degassed at different temperatures (according to the initial curing temperature of each catalyst system) for 1 h under vacuum. Then the samples were cured in an oven and furnace-cooled to room temperature. For comparison, casting samples of pure resin were also prepared.

As a function of the DSC results, the curing processes of the pure resin and the different catalytic systems were determined as shown in Figure 2, where  $T_i$ ,  $T_p$ , and  $T_e$  are the initial temperature, peak

temperature, and end temperature of the reaction, respectively. The specific temperatures are listed in the section on the curing characteristics for the different catalyzed resins.

### Differential Scanning Calorimetry

The curing curves and glass-transition temperatures ( $T_g$ ) were obtained with a DSC 200 F3 differential scanning calorimeter (Netzsch, Shanghai, China). The testing temperature ranged from 30 to 400 °C with a temperature ramping rate of 10 °C  $\text{min}^{-1}$  in a  $\text{N}_2$  atmosphere, and the weight of the samples was about  $8 \pm 0.5$  mg.

### Thermogravimetric Analysis

The thermogravimetric analysis (TGA) curves were measured with an STA 449 F3 Simultaneous DSC-TG. The test temperature ranged from 30 to 800 °C with a temperature ramping rate of 10 °C  $\text{min}^{-1}$  in a  $\text{N}_2$  atmosphere.

### Fourier Transform Infrared Spectroscopy

The infrared spectra of the cyanate resins at different stages were recorded on an FTIR-8700 (Netzsch, Shanghai, China). The FTIR spectra ranged from 4800 to 500  $\text{cm}^{-1}$  with a resolution of 1  $\text{cm}^{-1}$ . The liquid resins were directly measured, while the cured resins were blended with KBr for compression into slices.

### Water-Absorption Measurements

In order to accelerate the test, the casting samples were put in a water bath at  $85 \pm 1$  °C for 434 h, and filter paper was used to absorb water on the surface every day to measure the weight of the castings. The final water absorption value was the average of five samples, and the water-absorption values  $M(t)$  were calculated according to the following equation:

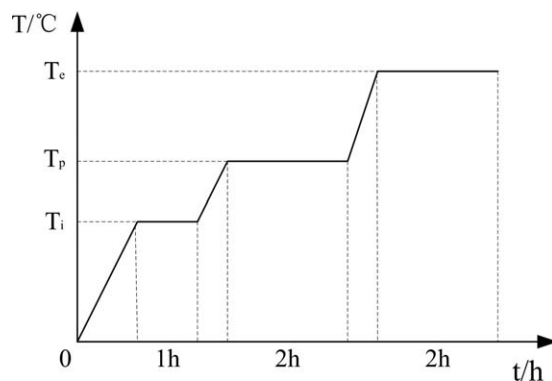
$$M(t) = (W_t - W_0) / W_0 \times 100\% \quad (1)$$

where  $W_t$  is the weight after water absorption at time  $t$  (g), and  $W_0$  is the initial weight before the water absorption test (g).

### Three-Point Bending Tests

Three-point bending tests were conducted on a SANS universal testing machine (Shenzhen, China). The speed of the crosshead was set to 2  $\text{mm min}^{-1}$ , and the span length was 64 mm. The flexural strength  $\sigma_f$ , flexural strain  $\epsilon_f$ , and flexural modulus  $E_f$  were calculated using eqs. (2–4), and each value was the average of five samples for each catalytic system. A schematic illustration of the three-point bending tests is shown in Figure 3(a).

$$\sigma_f = (3P \cdot L) / (2b \cdot d^2) \quad (2)$$



**Figure 2.** Curing schedule of the different resin systems.

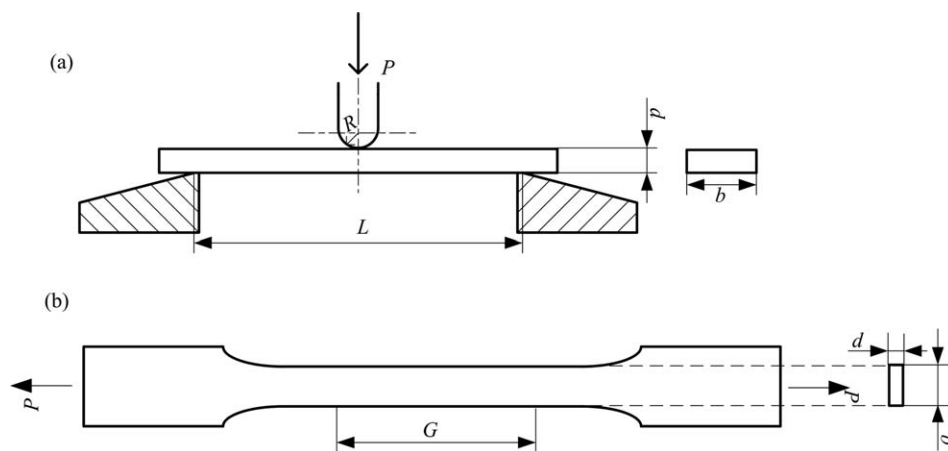


Figure 3. Schematic illustrations of (a) three-point bending tests and (b) tensile tests.

$$\varepsilon_f = (6D \cdot d) / L^2 \quad (3)$$

$$E_f = (L^3 \cdot m) / (4b \cdot d^3) \quad (4)$$

where  $P$  is the load at a given point on the load-deflection curve (N),  $L$  is the span length (mm),  $b$  is the width of the beam tested (mm),  $d$  is the depth of the beam tested (mm),  $D$  is the maximum deflection of the center of the beam (mm), and  $m$  is the slope of the tangent to the initial straight-line portion of the load-deflection curve ( $\text{N mm}^{-1}$ ).

#### Tensile Tests

The tensile tests were conducted on the SANS universal test machine. The speed of the crosshead was set to  $2 \text{ mm min}^{-1}$ , and the gap length ( $G$ ) was 50 mm. The tensile strength  $\sigma_t$  and tensile modulus  $E_t$  were calculated using eqs. (5 and 6). Each value was the average of five samples for each catalytic system. The schematic tensile tests are illustrated in Figure 3(b).

$$\sigma_t = P / (b \cdot d) \quad (5)$$

$$E_t = (G \cdot \Delta P) / (b \cdot d \cdot \Delta G) \quad (6)$$

where  $P$  is the load at a given point on the load-deflection curve (N),  $b$  is the width of the narrow section (mm),  $d$  is the depth of the narrow section (mm), and  $G$  is the gap length (mm).

## RESULTS AND DISCUSSION

### Curing Characteristics for Different Catalyzed Resins

Figure 4 and Table I exhibit the DSC results of both pure resin and catalyzed resins. It is found that the curing reaction of the pure resin starts at about  $226.08^\circ\text{C}$ , then the peak temperature is  $265.66^\circ\text{C}$ , and the reaction finishes at  $313.96^\circ\text{C}$ . The DSC trace shows a single sharp exothermic peak. When the resin was doped with the catalyst, the main exothermic peak was shifted to a lower temperature, clearly indicating that the catalyst can accelerate the curing reaction effectively.

NP can provide its phenolic group as an excellent hydrogen donor. Considering too much catalyst may result in thermal oxidative degradation under high post-curing temperatures,<sup>18,19</sup> the composition of NP was chosen to be 6%.<sup>17</sup> As shown in Figure 4, upon adding 6% NP into CY-3W, the exothermic

peak temperature is reduced by  $55^\circ\text{C}$ , and the exothermic peak is broader than that of the pure resin. This may be due to the formation of the intermediate imidocarbonate<sup>16,17</sup> because of the nucleophilic reaction between the hydroxy with the atom N of the group  $-\text{O}-\text{C}\equiv\text{N}$ . CY-3W with 0.8% stannous octoate reduces the  $T_p$  to  $178.99^\circ\text{C}$  and sharpens the exothermic peak, demonstrating a narrow temperature range for gelation.

For the resin catalyzed with 6% NP and 0.8%  $\text{Sn}(\text{Otc})_2$ , the DSC curve shows double peaks, and the first peak is much sharper. This phenomenon can be attributed to the acceleration of a certain reaction because of the catalyst, separating it from other exothermic peaks. The  $T_p$  is reduced by about  $148^\circ\text{C}$  compared with the pure resin, and  $E_a$  shows a dramatic decrease from 116.18 to 66.89 KJ/mol, showing an admirable synergistic effect. As seen in Figure 1, the structures of  $\text{Sn}(\text{Otc})_2$  and CY-3W constitute the clathrate, and CY-3W provides a lone pair of electrons, and the  $\pi$  bond interacts with the hybrid orbital of  $\text{Sn}^{2+}$ , promoting the cyclotrimerization of mono-mer cyanate ester resin.<sup>20</sup>  $\text{Sn}(\text{Otc})_2$  plays the main role before

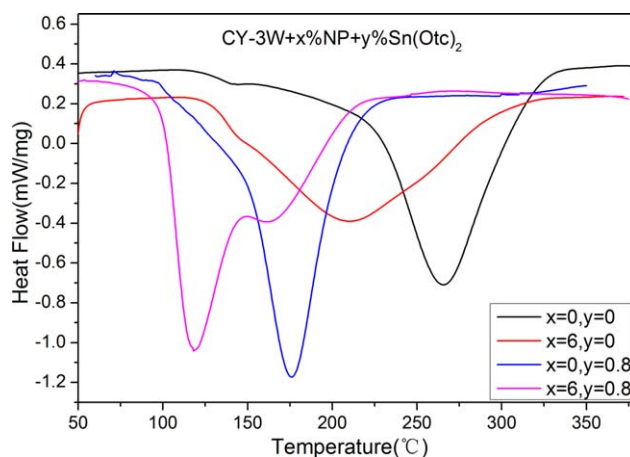
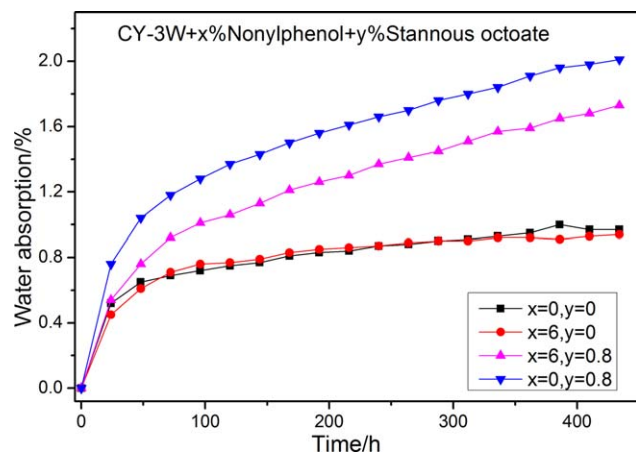


Figure 4. DSC thermograms of both pure resin and catalyzed resins. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table I.** Three Characteristic Temperatures and Activation Energy ( $E_a$ ) for Pure Resin and Catalyzed Resins

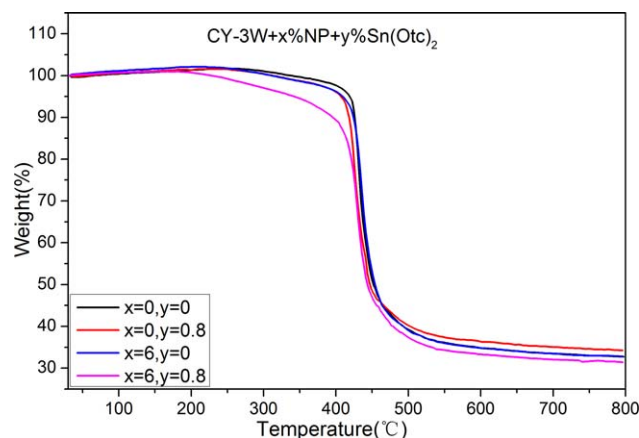
Formulas	$T_s$ (°C)	$T_p$ (°C)	$T_f$ (°C)	$E_a$ (KJ/mol)
CY-3W	226.08	265.66	313.96	116.18
CY-3W/6%NP	128.46	210.24	297.78	90.49
CY-3W/0.8%Sn(Otc) <sub>2</sub>	110.71	178.99	239.60	84.44
CY-3W/6%NP/ 0.8%Sn(Otc) <sub>2</sub>	100.41	118.07	231.86	66.89

**Figure 5.** Water-absorption curves for CY-3W samples of different catalyst systems conditioned for 434 h in an 85°C water bath. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

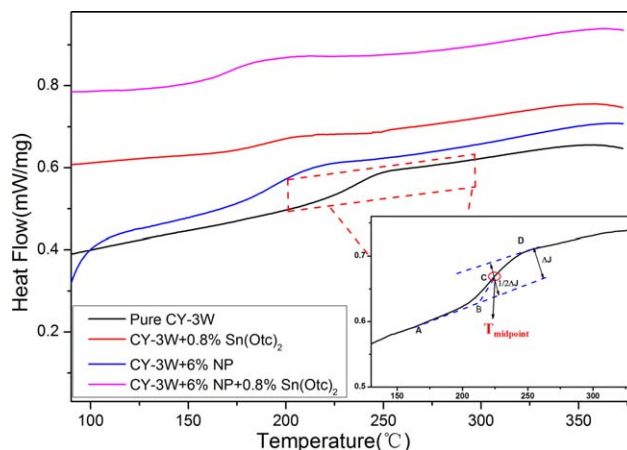
the gel point, while NP as cocatalyst does so after the gel point, owing to the better mobility of NP than Sn(Otc)<sub>2</sub> when forming the three-dimensional mesh structure.<sup>15</sup>

### Water-Absorbing Behaviors

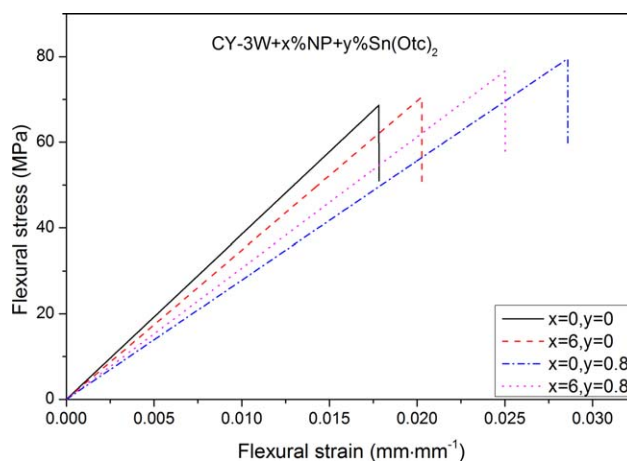
Water-absorption tests can reflect the resistance to warm and humid conditions. Figure 5 shows the effect of different catalysts on water absorption for the CY-3W resin samples. The res-

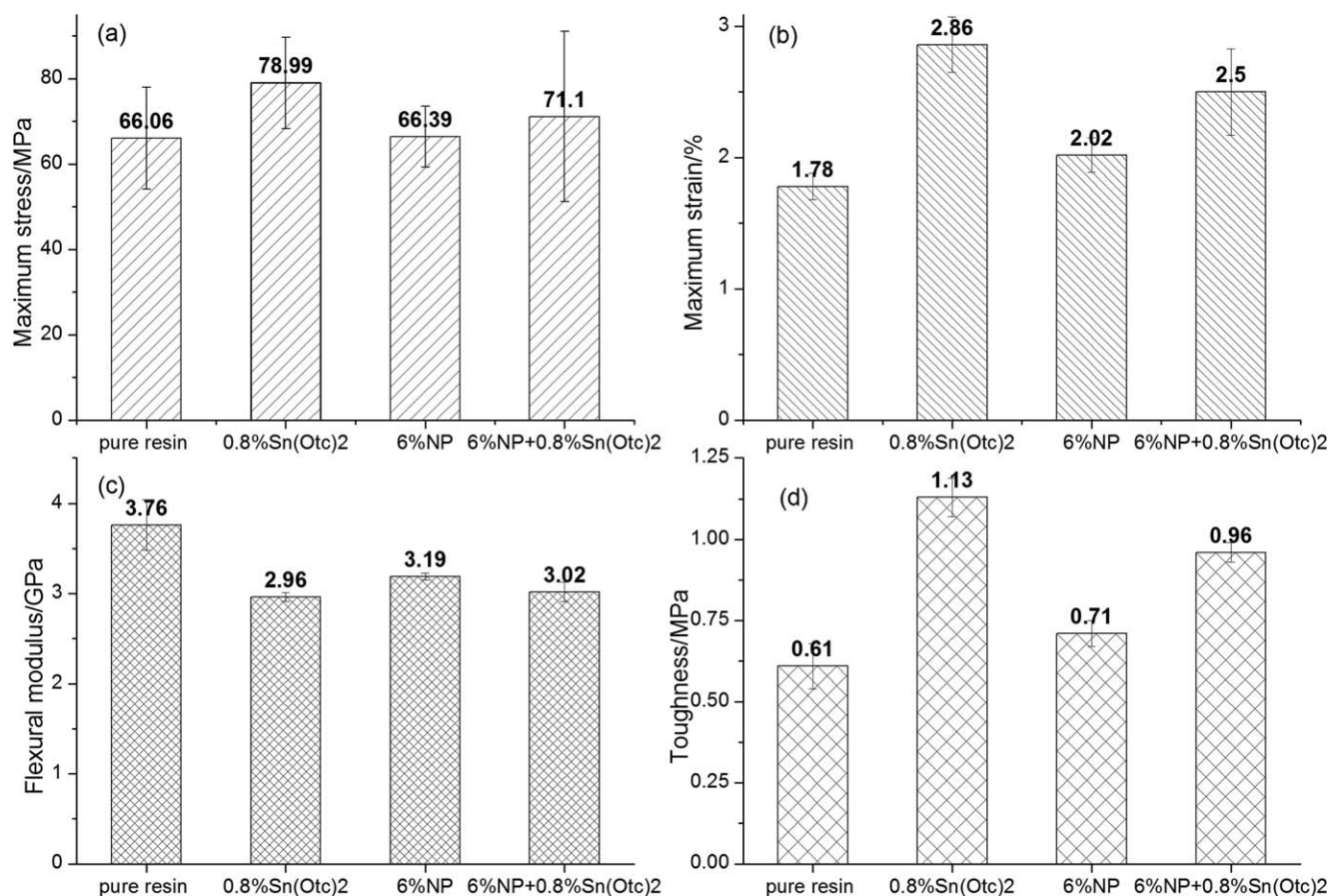
**Figure 6.** TGA thermograms of different systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Table II.** Thermal Properties of Different Systems

Formulas	$T_{onset}$ (°C)	$T_d^5$ (°C)	Char yield (%)	$T_g$ (°C)
CY-3W	339.81	419.81	32.73	243.43
CY-3W/6%NP	313.48	410.10	32.79	195.01
CY-3W/0.8%Sn(Otc) <sub>2</sub>	313.28	408.28	34.26	197.59
CY-3W/6%NP/ 0.8%Sn(Otc) <sub>2</sub>	231.12	343.62	31.41	175.20

**Figure 7.** Determination of  $T_g$  for different catalyst systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ins show different water-absorbing behaviors for different systems. The water absorption of the catalyzed resins with Sn(Otc)<sub>2</sub> obviously increases compared with that of the pure resin. However, the nonylphenol did not distinctly improve the water absorption of the resin, which can be seen from the same behavior of uncatalyzed resin and resin catalyzed with NP. Also, the resin catalyzed with the mixture of Sn(Otc)<sub>2</sub> and NP shows

**Figure 8.** Typical three-point bending test results for CY-3W samples with different catalyst systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

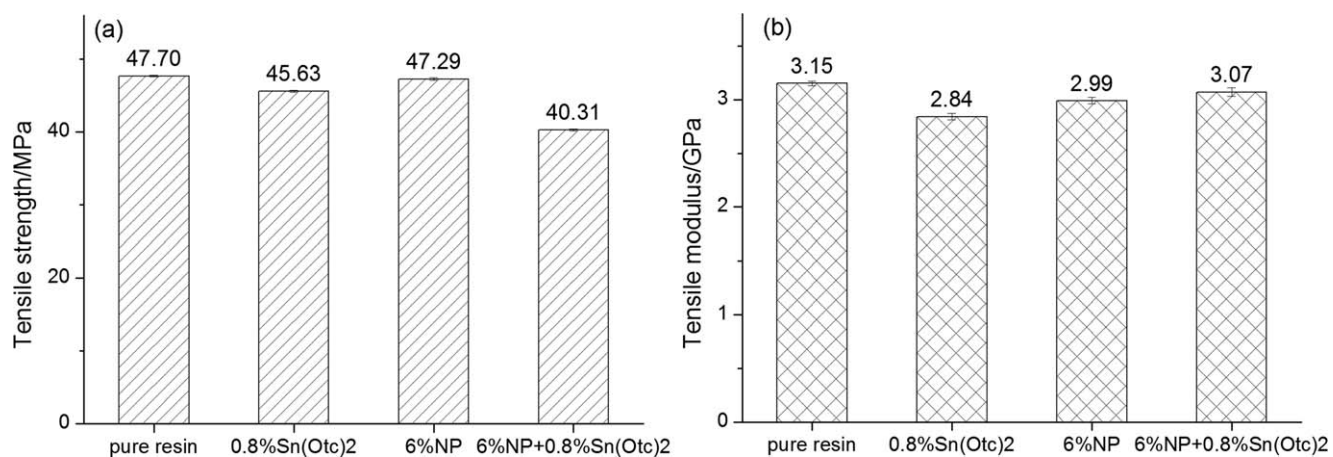


**Figure 9.** Mechanical properties of pure resin and cured resin modified by catalyst: (a) maximum stress; (b) maximum strain; (c) flexural modulus; (d) toughness.

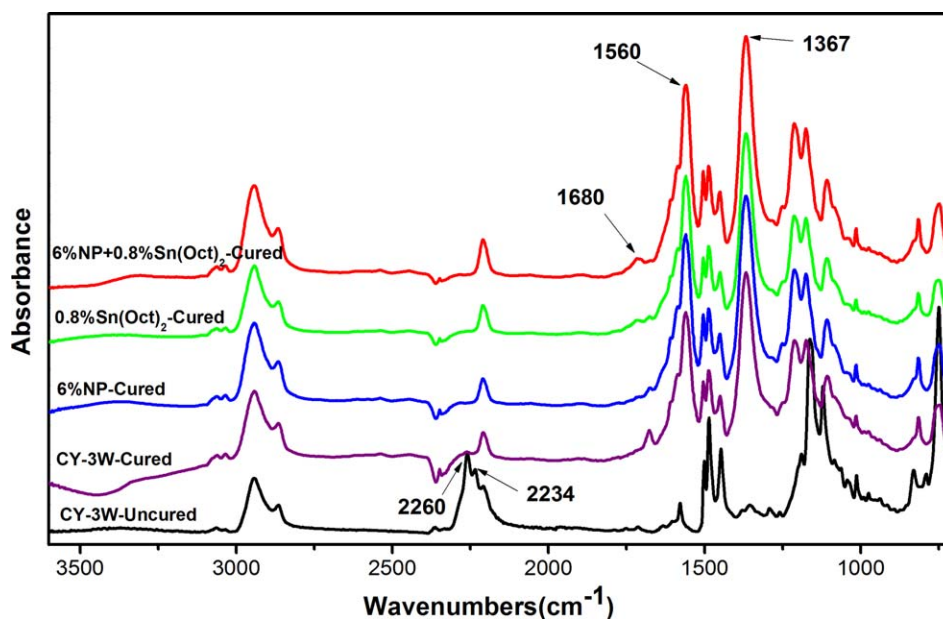
a lower water absorption compared with the resin catalyzed with Sn(Otc)<sub>2</sub> alone. Therefore, from the point of view of resistance to warm and humid conditions, NP is a good candidate as a catalyst for cyanate ester resin.

The water-absorption mechanism mainly includes physical adsorption and chemical adsorption. Physical adsorption con-

sists of two aspects. On one hand, it is distributed in the free volume, cracks, or voids in the resin in the form of free water molecules. On the other hand, the water residing in cracks and voids will accelerate the propagation of cracks, causing additional damage. In chemical adsorption, water molecules are distributed in the resin in the form of hydrogen bonds interacting with the polar group of the resin, which is determined by the



**Figure 10.** Tensile properties of pure resin and cured resin modified by catalyst: (a) tensile strength; (b) tensile modulus.



**Figure 11.** FTIR spectra of the resins cured with different catalyst systems. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

aggregation structure (including molecular shape, crosslinking density, and two-phase structure).<sup>21</sup>

The water absorption conforms to Fick's law. At the initial reaction stage, there is a sharp water absorption that is mainly caused by physical adsorption, producing the osmotic pressure in the resin matrix because of water diffusion. This makes tiny cracks and crazes that accelerate the water absorption. With the prolongation of the water absorption time, the rate gradually slows down. The diffusion of water molecules is seriously hindered by the molecular structure of cured cyanate ester resin, which contains a large number of benzene rings and triazine rings. They have apparent characteristics of relatively big space steric hindrance and thus have good resistance to warm and humid conditions. The water absorption of pure cured resin is about 0.97% after 434 h because of the compact structure of cured resin and the large crosslinking density, combined with hardly any water absorption groups of CY-3W; thus cured cyanate ester resin has good water resistance.<sup>22</sup> When the resin is catalyzed by the mixture of 6% nonylphenol and 0.8% stannous octoate, the water-absorption value can reach 1.73%, which is between those of 6% nonylphenol and 0.8% stannous octoate. This is because the cocatalysis of nonylphenol and stannous octoate results in a stronger compact structure and larger crosslinking density.

#### Thermal Properties

The TGA thermograms for CY-3W in the presence of different catalyst systems and pure resin are shown in Figure 6, and Table II shows the specific data of different catalyst systems. The initial weight-loss peaks are above 300 °C, except that of CY-3W/6%NP/0.8%Sn(Otc)<sub>2</sub> (231.12 °C). The decomposition temperatures at 5 wt % weight loss ( $T_d^5$ ) of both CY-3W/6%NP and CY-3W/0.8%Sn(Otc)<sub>2</sub> are 410.10 and 408.28 °C, respectively,

which are close to the pure resin (419.81 °C). Then the char yields at 800 °C are above 30 wt % (31–35 wt %) because there are abundant thermal-resistant triazine rings in the cured resin. However, it should be noted that the mixture of Sn(Otc)<sub>2</sub> and NP would deteriorate the thermal stability of the cyanate ester resin when the temperature is just above 200 °C. This might be because NP and Sn(Otc)<sub>2</sub> catalyze the hydrolysis reaction of triazine at the same time, resulting in the decline of the thermal stability of the cured resin.<sup>18,19</sup>

The heat-resistant quality of resin can also be characterized by the glass-transition temperature ( $T_g$ ). The high  $T_g$  of cyanate ester is due to the formation of the rigid triazine rings by the polymerization reaction of the cyanate ester groups.<sup>26</sup> For this work, we chose the  $T_{midpoint}$  as the  $T_g$  to compare the heat resistance of pure resin and the different catalyst systems. As shown in Figure 7 and Table II, catalysts can reduce the  $T_g$  of cyanate ester resin: the  $T_g$  of cured resin doped with 0.8% Sn(Otc)<sub>2</sub> is 46 °C lower than for pure resin. Cured resin with 6% NP decreases the  $T_g$  to 195.01 °C. When the resin was catalyzed by the mixture of 6% NP and 0.8% Sn(Otc)<sub>2</sub>, the  $T_g$  is reduced by 60 °C compared with pure resin, due to plasticization.<sup>7</sup> Although a relative decline of the hydrothermal stability of cured resin occurred, the high catalytic activity of the mixture of NP and Sn(Otc)<sub>2</sub> leading to a low curing temperature is very important for the applications in space optical instruments that our research focuses on. Also, the  $T_g$  of 175.20 °C still maintains a relatively high thermal property that is superior to the  $T_g$  (143 °C) of the thermoplastic poly(ether ether ketone) with super performance.

#### Mechanical Properties

Three-point bending tests and tensile tests were utilized to evaluate the mechanical properties of the samples. Figure 8 shows

the stress–strain curves for samples with different catalysts. Pure resin and all catalyzed resin systems exhibit typical brittle behavior. The flexural toughness is defined as the total area under the stress–strain curve.<sup>24</sup> All the systems show enhanced flexural toughness because of the addition of catalysts. This is reasonable because catalysts can lead to the plasticization of the cyanate ester resin. The resin catalyzed by 0.8% Sn(Otc)<sub>2</sub> shows an increase in toughness by about 85.2% from 0.61 MPa to 1.13 MPa that is due to the improvement in flexural strain. Compared with Sn(Otc)<sub>2</sub>, NP did not show much enhancement of the flexural toughness of the cyanate ester resin. The flexural toughness of the resin catalyzed with the mixture of Sn(Otc)<sub>2</sub> and NP lies between Sn(Otc)<sub>2</sub> and NP.

Figure 9 and Figure 10 show the mechanical properties of the pure resin and the catalyzed resin systems. In terms of maximum strain and maximum stress, the resin catalyzed by 0.8% Sn(Otc)<sub>2</sub> shows the best result, with a 19.6% enhancement in maximum stress and 60.7% enhancement in maximum strain compared with the pure resin. While flexural modulus had a little reduction, that means the reduction for stiffness. The tensile strength and tensile modulus of all catalyzed systems also showed a little reduction. These phenomena can be explained by Figure 11. In the FTIR spectra, the characteristic peaks of the cyano group (2260, 2234 cm<sup>-1</sup>) appear before the curing reaction, and they disappear completely after the curing reaction whether catalyzed or not, followed by the absorption peaks of triazine rings at 1367 cm<sup>-1</sup> (N=C–O) and 1560 cm<sup>-1</sup> (C=N–O), clearly demonstrating the similar spectra in different catalyst systems. Thus it is reasonable for all the resin samples to show similar behaviors of flexural modulus and tensile modulus. In addition, some triazine rings are inserted into other groups, which can form isocyanurates with the observation of the small peak of the isocyanuric group at 1680 cm<sup>-1</sup>. This also implies that all catalysts can only accelerate the reaction rate but not change the reaction mechanism during the curing reaction.

## CONCLUSIONS

The curing characteristics of cyanate ester resins catalyzed with nonylphenol (NP), stannous octoate [Sn(Otc)<sub>2</sub>], and the mixture of NP and Sn(Otc)<sub>2</sub> were investigated, and the thermal and mechanical properties were evaluated. The mixture of NP and Sn(Otc)<sub>2</sub> shows an obvious synergistic effect and exhibits excellent catalytic efficiency by decreasing the  $T_p$  by around 148 °C. Although the mixture of Sn(Otc)<sub>2</sub> and NP deteriorates the thermal stability of the cyanate ester resin more or less at below 400 °C, a similar char yield at high temperature remained. NP shows a better resistance to humidity, so the mixture of Sn(Otc)<sub>2</sub> and NP shows lower water absorption compared with the resin catalyzed with Sn(Otc)<sub>2</sub> alone. The mechanical investigation confirms that the tensile properties showed a little reduction due to the plasticization of the catalyst, while the excellent flexural properties are maintained. The resin catalyzed by 0.8% Sn(Otc)<sub>2</sub> shows an increase in toughness by about 85.2% from 0.61 MPa to 1.13 MPa.

In conclusion, different catalyst systems show different water-absorption, thermal, and mechanical behaviors. Generally, NP as a cocatalyst can help to reduce the curing temperature and the low humidity absorption of cyanate ester resins, which are beneficial for the dimensional stability of precise optical instruments made from carbon fiber composites. Of course, the outgassing properties of the composites should be further evaluated to determine the practical applicability of CY-3W with different catalysts for optical instrument applications. For those applications under high temperature, the mixture of Sn(Otc)<sub>2</sub> and NP should be cautiously considered because of the deterioration of the thermal stability.

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