

## Research paper

# Specific heat, thermal conductivity, and magnetic susceptibility of cyanate ester resins – An alternative to commonly used epoxy resins



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## ABSTRACT

In low temperature experiments, resins have many applications as glues or thermal and electrical insulators. Cyanate ester resins (CEs) are a high-temperature compatible thermoset resin whose glass-transition temperature  $T_g$  is  $\approx 300$  °C. Recently, we found that CEs also withstand low temperatures without microcracking by measuring  $^4\text{He}$  permeability. Here, we measured specific heat  $C$ , thermal conductivity  $\kappa$ , and magnetic susceptibility  $\chi$  of different kinds of CEs in the wide temperature range from room temperature to 0.5 K for  $C$  and 2 K for other two. The thermal properties,  $C$  and  $\kappa$ , of different kinds of CEs are surprisingly coincident with each other. We discuss chemical structures and crystallinity of CEs and their blends based on the measured thermal properties. Compared to Stycast 1266, a commonly-used epoxy resin in low temperature experiments,  $C$  of CEs is larger by a factor of 3 ( $\leq 30$  K),  $\kappa$  is lower by a factor of 4 ( $\leq 10$  K), indicating the small thermal diffusivity. The  $\chi$  values are as small as Stycast 1266, indicative of their high purity. Our results show that cyanate esters are a new option for cryogenic resins with thermal insulative properties in/for low temperature experiments.

## 1. Introduction

Cyanate ester resins (CEs) are a strong and stiff thermoset resin, which offers advantages as a matrix resin of FRPs (fiber reinforced composites) because of their high thermal stability, low water absorption, low outgassing properties, small dielectric loss, and high radiation resistance [1]. Since the late 1970s, FRPs of CEs or their copolymers have widely been used in the electronic and aerospace industries under severe environmental conditions such as extremely high/low temperature and/or in vacuum. They are also attracting attention for their excellent cryogenic durability to microcracking [2] and additional functions as a thermal management material [3] in space applications.

On the other hand, neat resins of CEs (without fibers or fillers) are not commonly used at cryogenic temperature. As a casting resin or glue for low temperature, epoxy resins (EPs) are widely used so that we can access the vast database of their cryogenic properties [4–6]. Unlike EPs, limited measurements have been reported for CEs at low temperature [7]. To our knowledge, even the thermal conductivity or specific heat have not been measured yet.

In principle, CEs can take the place of EPs in most applications

because they share a number of pre- and post-cure qualities with common EPs. CEs have the following features which have benefits over EPs and thus could see new applications: higher glass-transition temperature ( $T_g \approx 300$  °C), lower dielectric loss, and absence of irritant or allergic reactions [1]. Recently, we suggest that CEs are an excellent alternative to EPs especially in surface-sensitive experiments at low temperature based on our measurements of  $^4\text{He}$  permeation properties at 77–340 K and  $\text{H}_2\text{O}$  uptake at room temperature [8]. However, the lack of vast materials database of various kinds of CEs on much more common thermal and magnetic properties, such as  $\kappa$ ,  $C$ , and magnetic susceptibility  $\chi$ , particularly below room temperature still discourages the broad use of CEs in low temperature experiments. Especially,  $C$  is important to verify the existence/absence of structural transitions which may cause drastic change in other material properties, along with its technical importance to estimate heating/cooling time required to change the temperature.

Here, we measured the  $C$  (0.5–300 K),  $\kappa$  (2–300 K), and  $\chi$  (2–400 K) of several kinds of CEs at wide temperature ranges indicated in the parentheses. We also discuss the crystallinity and chemical structures based on amorphous contributions in the  $C$  and  $\kappa$  below 10 K, and

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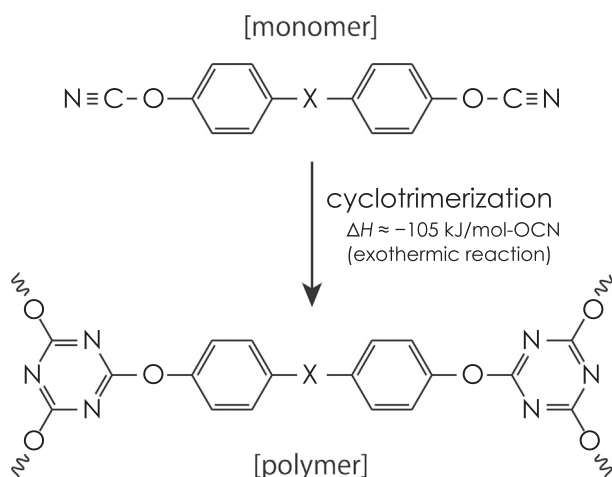


Fig. 1. Typical chemical structures of monomer and polymer of aromatic cyanate ester resins.

impurity concentrations based on diamagnetic and paramagnetic components of the  $\chi$ .

## 2. Experiments

### 2.1. Sample details

Cyanate monomers contain multiple  $-\text{O}-\text{C}\equiv\text{N}$  groups. After repeating cyclotrimerization of three  $-\text{O}-\text{C}\equiv\text{N}$  groups, rigid triazine rings form a strong three-dimensional polymer network. Typical chemical structures of the monomer and polymer are illustrated in Fig. 1.

**Cyanate esters.** Three kinds of CE monomers [9] were investigated: TA (2,2-bis(4-cyanatophenyl) propane), P-201 (1,1-bis(4-cyanatophenyl) ethane), and NCN (aralkyl type cyanate ester resin). At room temperature, the appearance of each CE monomer varies dramatically. The monomer of TA is white flakes, P-201 is a yellow liquid, and NCN is a brown solid which is treated as a clear organic solution. The monomers are pretreated by melting them at 120 °C with stirring and having them degass in a vacuum. The CE can then be poured into a mold made of PTFE or surface-treated metals. As the melt viscosity of TA and P-201 is very low ( $\approx 10$  mPa·s at 100 °C), they are suitable for copying fine structures of the mold. Typical curing procedure is 150 °C for 3 h, 180 °C for 5 h, then 250 °C for 5 h in ambient pressure. The stepwise heating is important to prevent runaway reactions due to the topical exothermic polymerization. The cured resins (polymers) are a hard solid whose colors are clear yellow for TA, clear amber for P-201, black for NCN, and intermediate colors for their mixtures. The densities measured at room temperature are 1.17(5) g/cc for TA, 1.20(7) g/cc for P-201, 1.19(2) g/cc for NCN, and 1.17(1) g/cc for copolymer of TA and NCN.

As there are no byproducts from the polymerization, CE polymers rarely include voids, except NCN including the vaporized solvent. To avoid void formation in the NCN sample for thermal conductivity measurements, the first step of the heating at 150 °C was performed in vacuum (at 80 kPa) to pump out the solvent fume. The surface color and void structure varied with curing conditions, but no significant effects on the properties of the solid portion were found when measuring  $C$ ,  $\kappa$ , and  $\chi$ .

**BT resins.** BT resins are blends of CEs and bismaleimides (BMIs) [10]. We prepared two types of BT resins: BT1 is a mixture of TA and BMI70 (bis-(3-ethyl-5-methyl-4-maleimidephenyl) methane), while BT2 is of TA and BMI2300 (phenylmethane maleimide [11]). Both were cured in similar conditions to those for CEs. The mixing ratio of TA and BMI is 3:2 by weight. The densities measured at room temperature are 1.14(2) g/cc for BT1 and 1.15(5) g/cc for BT2.

### 2.2. Magnetization measurements

$\chi$  of CEs (2 samples of TA and one for each of P-201, NCN, and copolymer of TA and NCN), BT resins (BT1, BT2), and Stycast 1266 were measured using Magnetic Property Measurement System (MPMS) [12] with Reciprocating Sample Option (RSO). The samples were 30–50 mg in weight. In the measurements, the samples were inserted to a pair of slits in a straw. The straw has a positive and small  $\chi$  (5–7% of the total signal), which depends very little on the temperature. The  $\chi$  of the straw is subtracted in the results.

### 2.3. Specific heat measurements

The specific heats of the CE samples were measured using Heat Capacity Option of Physical Property Measurement System (PPMS) [12] at temperature ranges 1.8–300 K and 500 mK–50 K (with helium-3 refrigerator). The samples are square plates of  $\approx 4$  mm side and  $\approx 1$  mm in thickness, 10–20 mg in weight. The samples were loaded on the alumina platform of the sample pack using GE 7031 varnish [13].

### 2.4. Thermal conductivity measurements

Thermal conductivity of the CE samples was measured using Thermal Transport Option of PPMS [12] at temperatures between 2 K and 300 K. We mainly used four-terminal method to minimize effects of the contact resistance between the sample and the gold-plated copper leads independently glued to the sample with Stycast 2850FT. The samples were shaped as 4-mm square rod of 12 mm in length, whose thermal relaxation time is too long at higher temperature ( $T > 100$ –200 K). Thus a thin sample of P-201 (5-mm diameter and 2 mm-thick cylinder) was also measured using two-terminal method, and it was found that the data of two samples overlap within 5% discrepancy at temperatures from 4 to 100 K. The effects of the contact resistance in two-terminal method appears at lower temperature.

## 3. Results and discussions

### 3.1. Magnetic susceptibility

Polymers are often used in magnetic fields because normal insulative polymers do not usually have strong ferromagnetic properties. However, when we use them in very strong magnetic fields ( $H \geq 10$  kOe [14]), we should screen the polymer products because coloring agent, catalysts, impurities, and curing residues can have strong magnetic properties. Stycast 1266 [15] is known to have a small magnetic susceptibility  $\chi$  [16], which is one order smaller than other polymers [17].

$M$ - $H$  curves (magnetization  $M$  versus magnetic field  $H$ ) were measured from  $H = -5$  to 5 kOe at  $T = 2$  K and 300 K. They are a featureless straight line for each sample at each temperature as shown in Fig. 2. Thus,  $\chi$  was calculated from the  $M$  measured with a fixed  $H$  ( $= 5$  kOe) at temperatures between 2 and 400 K.

The temperature dependence of  $\chi$  is shown in Fig. 3. The  $\chi$  values are very small ( $|\chi| < 1 \times 10^{-6}$  cm<sup>3</sup>/g) and this polymer family is a potential material to use in high magnetic fields over wide temperature ranges. At room temperature, CEs and BT resins have similar negative values of  $\chi$  to Stycast 1266. Along with this diamagnetic contribution of  $\approx -6 \times 10^{-7}$  cm<sup>3</sup>/g (the intercept in Fig. 3), the paramagnetic component (the slope in Fig. 3) becomes distinguishable at low temperature especially for TA and BT2. The Curie constants correspond to free spin densities ( $g = 2$ ) of  $1.5 \times 10^{17}$ – $4.4 \times 10^{18}$  per gram. As the CEs include  $\approx 2 \times 10^{21}$  triazine rings per gram, it indicates that free spins are found only once or twice for a thousand of triazine rings. The paramagnetic components of P-201, NCN, copolymer of TA and NCN, and BT1 are as small as Stycast 1266.

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