

CYANATE ESTERS WITH IMPROVED FIRE RESISTANCE

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ABSTRACT

Cyanate ester resins are organic polymers and have been used for high temperature applications. Several commercial cyanate esters have been shown to exhibit relatively high onset temperature of degradation in excess of 400 °C with inherent self-extinguishing characteristics. We have been interested in their flame-resistant characteristics and potential utility in aircraft interiors and other area. However, in order for cyanate esters to meet the new stringent requirement for the future aircraft interior applications, further improvements are necessary. Initially, we were interested in phosphorus-containing cyanate esters. Several of such materials were prepared and tested for their flame-resistance. For example, RD 97-169, has exhibited the micro heat release rate of 71 joule/g-°K in the microcalorimetry analysis and heat release rate of 49 kW/m² in the OSU test, which are higher than the new requirement. In our continuing effort, a series of cyanate esters with novel structures were prepared and evaluated for their flame-resistance. Among them, several materials were shown to display relatively low microscale heat release rate in the range of 7 to 25 Joule/g-°K. The cured resin of RD98-228 has exhibited particularly low heat release rate, in the range that is only exhibited by few specialty thermoplastics. This material possesses low viscosity at processing temperature and can be cured in the fashion typical of commercially available cyanate esters. The mechanical properties of this cured resin are characteristics of cyanate esters. Further studies of this material are in progress.

1. INTRODUCTION

The fire-resistant materials currently used in the commercial aircraft cabin do not meet the new goal of generating survivable aircraft cabin condition for 10 to 15 minutes in post-crash fuel fire.¹ This challenging goal translates to a need for the development of new generation of fire-safe materials with low heat release rate (less than 25 kW/m² at 50 kW/m² heat flux using the standard Cone Calorimeter material flammability test ASTM E-1354-92). In order for the new materials to be successful for this type of application, in our opinion, they not only have to fulfill the stringent flame-resistance requirement, but also have to be easily processed at moderate temperature, while generating no volatile products during processing and curing. Potentially, these would reduce the time and the cost associated with the fabrication. Cyanate esters have attracted our attention, because of their greater thermal stability, and the ease of processing. They can be processed similar to epoxies. Since the curing of cyanate esters is through addition polymerization of forming triazine moieties, no volatile would be generated (Figure 1.). They are also known for their good mechanical properties, low moisture

absorption, excellent adhesion, and high onset temperature of degradation in excess of 400 °C. Some cyanate esters have shown to possess self-extinguishing characteristics, such as Arocy F-10 and Arocy T-10. The chemistry, properties, and flammability of cyanate esters have been reviewed in depth.⁴ Another important factor for consideration of fire-safety is the generation of toxic smoke and decomposition products during combustion. The degradation products of polycyanurates have been studied in the 70's. They are mainly carbon monoxide, carbon dioxide and hydrogen.^{2,3} Cyanate esters have been the subject of study for their flame-resistance lately.^{5,6} The fire behavior of trifunctional phenol novolac cyanate esters have also been reported.⁷

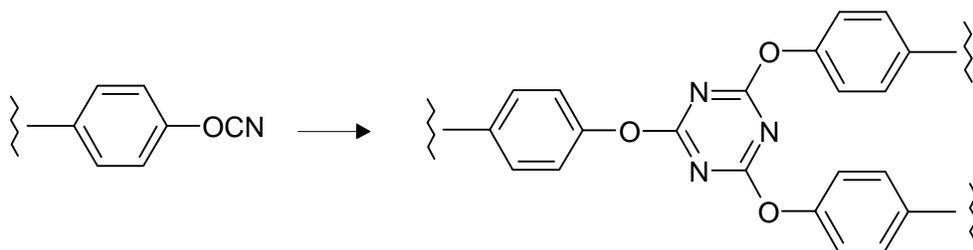


Figure 1. Network formation of triazines from cyanate esters

Phosphorus compounds have been used widely as flame retardant. Initially, we were interested in the flame-resistant effect of phosphorus moiety in the backbone of cyanate ester systems,⁸ although it is known that some phosphorus based fire retardants tend to increase the yield of carbon monoxide and soot formation during combustion. Several cyanate esters of same structural backbone with different percentage of the same phosphorus moiety were prepared and studied for flammability and mechanical properties.

In the mean time, our effort has also been focused on the search for the cyanate esters with novel structures which would potentially offer high flame-resistance and low heat release rate during combustion. A series of cyanate esters have been prepared and screened for the flame resistance with microcalorimetry. The results would help us to get better correlation between the structures and flame resistance of the cyanate esters. Interestingly, some of these cyanate esters with novel aromatic backbones have displayed rather low heat release rate, which should provide better flame resistance. Presented here are some of the results from this on-going study.

2. EXPERIMENTAL

2.1 Materials The precursor for the synthesis, phosphorus-containing polyphenol and the phenolic precursors of the cyanate esters were the product of Ciba's internal effort. Cyanogen bromide, triethylamine and methyl isobutyl ketone (MIBK) were purchased from Aldrich Chemicals. The chemicals were used as received without further purification.

2.2 Synthesis Phosphorus-containing polyphenol precursor of RD97-169 and triethylamine were dissolved in MIBK and cooled to -20 °C. Cyanogen bromide in MIBK was added

dropwise into the polyphenol solution with stirring. During the addition, the temperature was kept at about $-20\text{ }^{\circ}\text{C}$. After the addition, the reaction was allowed to stir for 60 minutes, while gradually warming to about $10\text{ }^{\circ}\text{C}$. The whole mixture was washed thoroughly several times with water. The MIBK layer was collected and concentrated in a rotary evaporator. The residual solvent was stripped under vacuum for 2hrs (1 mmHg, $120\text{ }^{\circ}\text{C}$) to afford yellow to light amber viscous resin. The product was characterized with IR and NMR. Its viscosity was measured with an ICI viscometer. Other aromatic cyanate esters were prepared in the similar fashion from the corresponding phenolic precursors.

2.3 Curing Studies and Mold Casting The gel-time of the neat resin and its mixture with catalyst were determined on a hot plate at different temperatures. Neat resin and samples containing various amount of metal catalyst (6% manganese octoate in hex-cem liquid) were cured at different temperature. Differential scanning calorimetry (DSC) was utilized for the study of the total heat release of the uncured and cured samples. The resin with 0.1 to 1.0 % of the manganese catalyst was first degassed at $110\text{ }^{\circ}\text{C}$ for 30 minutes and poured into 1/8-inch thick metal mold and cured at $160\text{ }^{\circ}\text{C}$ for 1hr, and post-cured for 2 hours at $230\text{ }^{\circ}\text{C}$. The cured material was cut to specimens of different sizes for various mechanical and electrical tests.

2.4 Mechanical and Electrical Properties The 1/8-inch thick casting samples were tested for their thermal and mechanical properties. The glass transition temperature (T_g) was determined with Dynamic Mechanical Analysis (DMA) at a heating rate of $2\text{ }^{\circ}\text{C}/\text{min}$ and at 1 Hz. The flexural and tensile test was performed with the test method ASTM D 790-95a and ASTM D-638, respectively, using Instron Model 4505 & 4507. Fracture energy, G_{IC} , was determined by the double torsion method, ASTM D5045. Dielectric constant and dissipation factor of the cured specimens were determined at 1MHz, using the test method ASTM D150.

2.5 Flammability Test Flame-resistance characteristics of the cured material were assessed with several tests. Char-yield of cured specimen was determined with Thermogravimetric Analysis (TGA), from room temperature to $800\text{ }^{\circ}\text{C}$ at the rate of $10\text{ }^{\circ}\text{C}/\text{min}$ under nitrogen and air. Vertical burn test was used to determine the UL flammability rating of the cured samples. Limiting Oxygen Index (LOI) was determined with the test method ASTM D2863-91. Heat release rate was first evaluated with Pyrolysis-Combustion Flow Calorimeter developed by R. Lyon's group of the FAA.⁹ Some of the more promising materials in the study were evaluated further with OSU test for their heat release rate under $35\text{ kW}/\text{m}^2$ of heat flux. The specimens for the OSU test were sandwich panels fabricated either from carbon or glass fabric with the neat resin of the material. The sandwich panels were also studied for smoke density during combustion.

3. RESULTS AND DISCUSSION

The phosphorus-containing cyanate esters that we have prepared, with various percentage of phosphorus content, are all light yellow viscous liquid or semisolid. They possess low viscosity at processing temperature (100 to 200 cps at $100\text{ }^{\circ}\text{C}$). They are soluble in typical organic solvents, such as acetone, MEK, and MIBK. They can be processed and cured similarly to

other typical cyanate esters. The cured materials were evaluated first for their thermal stability and flame-resistance (Table 1). These materials are self-extinguishing and all achieved UL V-0 rating in the vertical burn test. For aircraft interior applications, the heat release rate is probably more indicative of the fire-resistance of the material in the real burning environment. The three phosphorus-containing samples studied all exhibited similar heat release rate of about 70 Joule/g-°K. The different content of phosphorus did not seem to produce any significant difference on the heat release rate. One of the cyanate esters, RD97-169, was further evaluated with the OSU test. The results are shown in Table 2. The specimens either fabricated with glass or carbon fabric have displayed similar heat release rate of about 50 kW/m². However, they have also produced significant smoke density during combustion. The presence of phosphorus probably promoted the smoke formation.

Table 1. Flammability and Microcalorimetry Tests of Phosphorus-containing Cyanate Esters

	R27K77	RD97-169	R28R52C
% Phosphorus	2.7 %	3.2%	5.2%
LOI	-	35.3 %	-
Vertical Burn	V-0	V-0	-
Microcalorimetry Test			
Micro Heat Release Rate*	70 j/g-K	71 J/g-K	68 J/g-K
Micro Total Heat Release**	11.1 kJ/g	10.9 kJ/g	13.5 kJ/g
Char Yield***	51.5 %	47.0%	42.9 %

* Heat release capacity at 50 kW/m²

** Net heat of complete combustion of pyrolysis volatiles

*** Pyrolysis residue fraction at final temperature (773 °C)

Table 2. Results of OSU and Smoke Density Test of Sandwich Panel with RD97-169

	RD97-169/Carbon fabric	RD97-169/glass fabric
Peak Heat Release Rate	48.6 kW/m ²	49.6 kW/m ²
Total Heat Release*	40.1 kW-min/m ²	49.6 kW-min/m ²
Smoke Density (Ds Value)**	99	155

* Total heat release in two minutes

** Smoke density @ 4 min

The mechanical and electrical properties of cured RD97-169 were also studied. The results are summarized in Table 3. The cured resin exhibited the properties of high mechanical strength, low dielectric constant and low dissipation factor, which are typical of cyanate esters. However, the resin clearly exhibited higher toughness (high G_{1C} value) than typical cyanate esters. The

phosphorus moieties in the backbone of the system probably offer the extra flexibility and toughness.

Table 3. Properties of Cured RD 97-169*

PROPERTY	CURED RD97-169
T _g (DMA)	154 °C
Flexural Strength	16.4 ksi
Flexural modulus	510 ksi
Flexural Elongation	3.4%
G _{1c}	2.1 in-lb/in ²
Dielectric Constant (Dk)	3.02 (1 MHz)
Dissipation Factor (Df)	0.0087 (1 MHz)

* 1/8 inch casting

As a part of our effort to better understand the correlation between the chemical structure and the fire behavior of the cyanate esters, a series of aromatic cyanate esters with various backbones were prepared. These cyanate esters were evaluated for their thermal stability and flame-resistance. Several of them have displayed rather low micro heat release rate (Table 4). Among these, RD98-228 has displayed particularly low heat release rate, which is in the range that is only achieved by some specialty thermoplastics. Currently, this material has been under further evaluation for its flame-resistance, mechanical performance and processing characteristics. RD98-228 is a solid at room temperature and has very low viscosity at processing temperature. It can be processed and cured like typical commercially available cyanate esters. Its low heat release characteristics and good processibility would make this resin potentially a versatile material for various applications where flame-resistance with low heat release rate is a desirable feature.

Table 4. Microscale Heat Release Data of Some Aromatic Cyanate Esters

MATERIAL	PEAK UHRR* (JOULE/G-°K)	TOTAL UHR** (KJ/G)	CHAR YIELD*** (%)
R28R48	23	4.4	68.2
RD98-228	7.2	3.3	62.4
R28R52D	20	2.0	40.9

* Heat release capacity at 50 kW/m²

** Net heat of complete combustion of pyrolysis volatiles

*** Pyrolysis residue fraction at final temperature (773 °C)

Some of the mechanical and thermal properties of the neat resin casting of RD98-228 are listed in Table 5. It has displayed high flexural and tensile strength as well as modulus, which are typical of cyanate esters. More studies are currently undertaken for better understanding of its performance in flame-resistance, processing characteristics, and other properties.

Table 5. Cured State Properties of RD98-228*

PROPERTY	CURED RD98-228
Tg (DMA)	275 °C
Flex Strength	17.7 ksi
Flex Modulus	450 ksi
Flex Elongation	4.8 %
Tensile Strength	8.7 ksi
Tensile Modulus	500 ksi
Tensile Elongation	1.9 %

* Cured cycle: 160 °C 2hrs, 230 °C 2hrs

* With 0.1% by wt. of 6% solution of manganese octoate in hex-cem

4. CONCLUSION

A series of phosphorus-containing cyanate esters with same backbone structure have been prepared and evaluated for their flame resistance. They have exhibited UL V-0 flame resistance. The heat release rate of the materials was studied using microscale pyrolysis-combustion calorimetry and OSU test. The heat release rate was higher than desired. In addition, the increase of the phosphorus content did not seem to reduce the heat release rate further. During burning, significant amount of smoke was generated for these phosphorus-containing cyanate esters.

A series of aromatic cyanate esters were also prepared and screened for thermal stability and heat release rate with microscale pyrolysis-combustion calorimetry. Interestingly, several of these cyanate esters have displayed high char yields and low heat release rates. Especially, RD98-228 has exhibited extremely low heat release rate, in the range only achieved by few specialty thermoplastic materials. This is a significant improvement over commercially available cyanate ester resins and other thermosets. It also offers good mechanical properties. Furthermore, RD98-228 possesses low viscosity at processing temperature and can be processed like regular cyanate esters without generating any volatilize, which would reduce the labor associated with the fabrication. Potentially, this thermoset material could offer the flame resistance, mechanical properties and the processability that the industry is looking for. The OSU test and other flammability evaluation of the material as well as modification of this material are currently in progress.

5. ACKNOWLEDGEMENT

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