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Preparation, Cure, and Characterization of Cyanate Ester-Epoxy Blends Containing Reactive Flame Retardants

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PREPARATION, CURE, AND CHARACTERIZATION OF CYANATE ESTER-EPOXY BLENDS CONTAINING REACTIVE FLAME RETARDANTS

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ABSTRACT

Cyanate esters are used in aerospace and microelectronic applications because of their great thermal stability, superior mechanical characteristics, and favorable dielectric properties. Cyanate ester resins are sometimes mixed with lower cost epoxy monomers to modify cost, toughness, and processing capabilities. Despite the high performance of these thermosetting polymers, flame retardancy remains an issue. This study examined blends of three different commercial cyanate ester monomers (LVT-100, LECy, and XU-71787.02) and diglycidyl ether of bisphenol A (DGEBA) at 50/50 wt% of each type. The blends were successfully reacted with two reactive flame retardants (FR): 9,10-dihydro-9-ox-9-phosphaphenanthrene-10-oxide (DOPO) and poly(m-phenylene methylphosphonate) (PMP) at phosphorus contents ranging from 0 to 3 wt%. The curing behavior of EP/CE blends was investigated using differential scanning calorimetry (DSC). It was found that introducing phosphorus into EP/CE blends lowered both the onset reaction temperature and the glass transition temperature T_g for all blends. TGA data revealed that the addition of PMP and DOPO to EP/CE blends resulted in a linear decrease in the onset decomposition temperatures of LVT and LECy blends, with a maximum drop of 36 °C in the EP/XU/DOPO blend compared to the EP/XU baseline blend. In addition, TGA results revealed that the introduction of PMP into EP/CE blends *improved* the char yield of the blends by 24%, while the DOPO *reduced* the char residue of the blend by 24% compared to the baseline EP/CE blends. Incorporating PMP and DOPO as reactive FR into the EP/CE network structure has been successfully investigated.

Keywords: Cyanate ester, Epoxy blend, Flame retardant, Thermal stability, curing behavior

1. INTRODUCTION

In recent decades, epoxy (EP) resin has been extensively used in several industrial sectors because of its exceptional chemical resistance, excellent adhesion, and outstanding mechanical characteristics. However, EP resin's high temperature durability and flammability properties are

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inadequate in some disciplines, including in the electrical and electronic industries [1]–[4]. Polymer blending is a common method for producing materials with an acceptable balance of properties. Polymer blending allows manufacturers to customize the material's qualities to a specific application. Polymer blending enables producers to combine a less expensive material with a higher performance but more costly polymer to develop a material with acceptable properties at a reduced cost [5].

Combining EP resin with other thermosetting resins is a viable strategy for enhancing its heat resistance. Among thermosetting resins, cyanate ester (CE) resin is well suited for enhancing the thermal resistance of EP resin due to its strong heat resistance, minimal moisture absorption, and exceptional dielectric characteristics after curing [3], [5]–[11]. This strategy has been successfully used in several high-performance applications [1], [5].

However, one of the main limitations of CE materials is their flammability, which can be a concern in applications where high fire safety is required. To satisfy application requirements, their flame-retardant capabilities must be increased, but other key features such as mechanical and thermal properties, as well as consideration of environmental problems, must also be maintained. In other words, the key objective is to create multifunctional composites with high-performance mechanical qualities and excellent flame retardancy [12]. Several investigations on introducing different types of flame retardants to enhance the thermal and mechanical characteristics of cyanate ester-epoxy blends have been reported as is discussed next.

In several studies, the addition of a reactive phosphorous-based flame retardant, such as DOPO, to a cyanate ester-epoxy mixture often reduced the thermal resistance (via T_g) of the EP/CE blend [8] [13] [14] . These types of flame retardants react with the thermoset matrix, which minimizes the possibility of the flame retardant leaching from the final material during its lifetime. Although there are various published studies based on DOPO introduced to EP/CE blends and its derivatives, there are none specifically on the reactive phosphorous-based flame retardant PMP with epoxy-cyanate ester. On the other hand, there are a few studies that examined the introduction of PMP into an epoxy resin system and the kinetics of its curing in the presence of a catalyst [4], [15], [16]. For example, Wu et al. found that an epoxy PMP-based system cured at 150 °C after 70 minutes [15].

Mariappan and Wilkie observed that epoxy / Fyrol PMP blends exhibited increased T_g, thermal stability, flame resistance, and reduced smoke production compared to conventional brominated FR and/or DOPO-based flame retardants [4]. In this case, the Fyrol PMP acted as the sole flame retardant *and* curing agent in the epoxy resin [4]. Chen et al. reported that triallyl and triglycidyl isocyanurate compounds were introduced with an equal molar ratio of DOPO, which was then blended with cyanate ester resin to produce ternary flame-retardant modified cyanate ester blends (CEPG and CEPA). In comparison to pure CE, the curing and glass transition temperatures of the CEPG and CEPA blends were found to be lower. However, both CEPG and CEPA blends greatly improve the flame-retardant properties of CE resins, achieving a UL-94 V-0 rating for both CEPG and CEPA[14].

Toldy et al. investigated the use of an epoxy functional adduct of DGEBA and DOPO as a flame retardant in cyanate ester-epoxy resin blends. The results of the study showed that the addition of this flame retardant improved the flame retardancy of the material, as demonstrated by the fact that it passed the UL-94 V-0 test and achieved a limiting oxygen index (LOI) of 48% [17]. In another study, Toldy et al. fabricated CE/EP/DOPO carbon fiber reinforced composites using a similar matrix. The flame-retardant CE/EP blends exhibited a T_g at least 22°C greater than composites with an epoxy-only matrix. Composites fabricated with an epoxy-DOPO matrix resulted in reduced T_g compared to epoxy only. Regarding mechanical properties, the CE/EP composite with 2 wt% P exhibited 25% greater tensile strength than a composite with a CE-only matrix. Furthermore, composites with a DOPO epoxy-cyanate ester matrix resulted in a significant increase in impact resistance compared to a pure CE matrix, although the flexure strength remained the same [18].

Additionally, researchers investigated the addition of DOPO as a flame retardant to a cyanate ester-epoxy combination. They reported that the char yield of cyanate ester-epoxy blends decreased with increasing phosphorus content when exposed to temperatures of 800 °C [8], [14], [18].

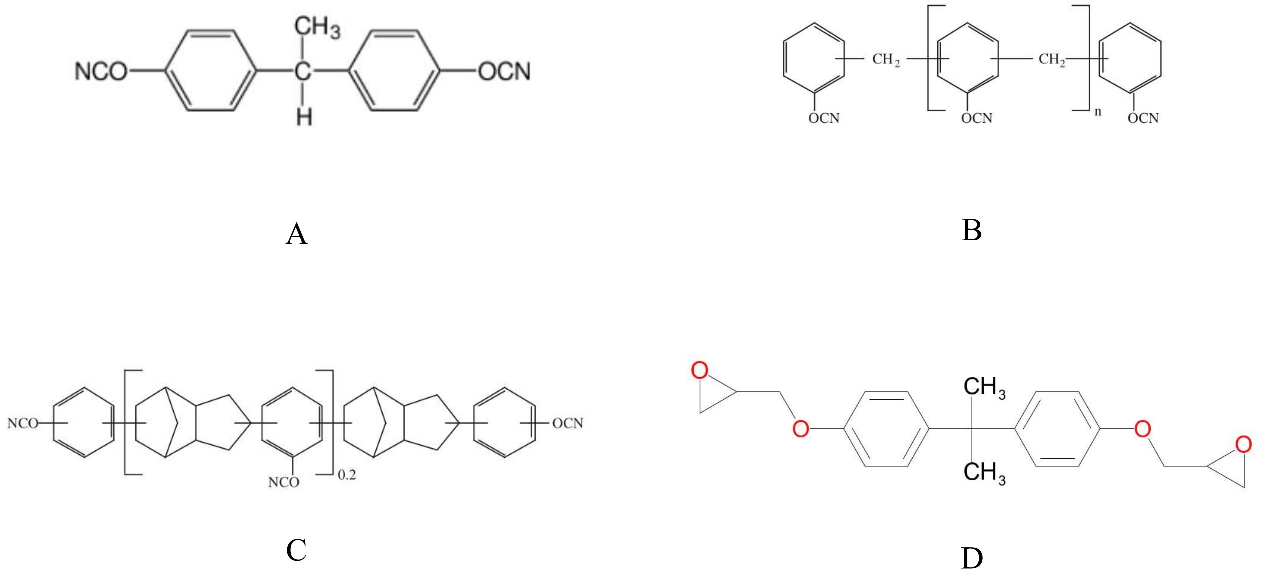
In summary, the literature demonstrates that the glass transition temperature (T_g) and the char yield of the EP/CE/DOPO combinations are often reduced when the phosphorous content is increased. Although there are several publications on reactive phosphorus flame retardants based on DOPO introduced to EP/CE blends and their derivatives, there are none on the PMP epoxy-cyanate ester combination. Thus, the objective of the current study is to formulate three cyanate ester monomer types (LVT-100, LECy, and XU) with 50 wt% DGEBA epoxy resin (EPON 825). The flame retardants Fyrol® PMP and DOPO were incorporated into EP/CE blends. The impact of increasing the phosphorus concentration from 0 to 3wt% on the curing behavior, glass transition temperature, and thermal stability of epoxy-cyanate ester blends was investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). This work was undertaken as a screening study that will eventually lead to composite fabrication.

2. EXPERIMENTAL WORK

2.1. Materials

Two cyanate ester resins, Primaset LECy and Primaset LVT-100, were generously donated by Arxada (formerly Lonza). Figure 1A. & 1B. illustrates the chemical structures of LECy and LVT-100 respectively. According to the material safety data sheet for Primaset LVT-100, it is a combination of polyphenol cyanate and LECy (as shown in Figure 1B, where n is unknown). A third CE monomer AroCy XU-71787.02 (Huntsman) was donated by the University of Dayton Research Institute. Figure 1C shows the chemical structure of the XU monomer. Both LECy and LVT-100 have low viscosities and are solvent-free; at 25 °C, their viscosities were measured by Klosterman to be 0.077 and 0.307 Pa-sec [19], respectively, while XU-71787.02 is solid at ambient temperature. The epoxy resin system employed as the basis for this study was bisphenol A epichlorohydrin epoxy resin (EPON 825). EPON 825 had a theoretical epoxide equivalent weight (EEW) of 170 g/equiv (DGEBA, see Figure 1D). This epoxy is suitable for vacuumassisted resin transfer molding (VARTM), which is used to fabricate large composite structures in infrastructure, transportation, and marine applications where flame retardancy is an important requirement. This paper will refer to the cyanate ester monomers as LECy, LVT, and XU. The epoxy will be referred to as EPON 825, EP, or epoxy.

The first flame retardant used in this study, Poly (m-phenylene methylphosphonate) (PMP), is sold commercially as Fyrol® PMP and was donated by ICL Industrial Products. This is a relatively newly developed reactive flame retardant with 17.5 wt% P content (see structure in Figure 2A). The second reactive flame retardant, 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-Oxide (DOPO) (14.35 wt% P content) was purchased from TCI America (see structure in Figure 2B). Fyrol® PMP is a solid glassy yellowish material at room temperature with a melting point of 100 °C, whereas DOPO is a white powder with a melting point of 120 °C.



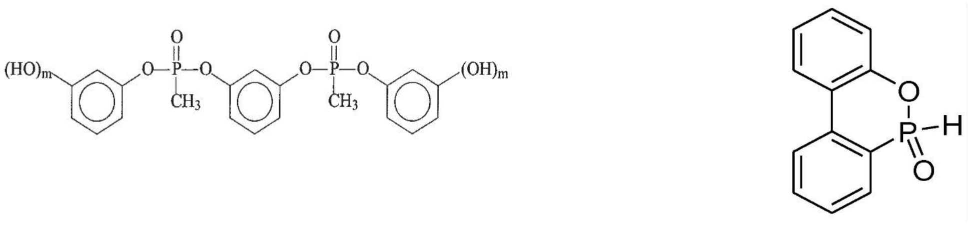
A

B

C

D

Figure 1: chemical structure of monomers used in this study: A) LECy (CAS 47047-92-7), B) polyphenol cyanate (CAS 87397-54-4), C) XU-71787.02, D) DGEBA (CAS 2905-03-6)



A

B

Figure 2: chemical structure of flame retardants monomers used in this study: A) Fyrol PMP, B) DOPO.

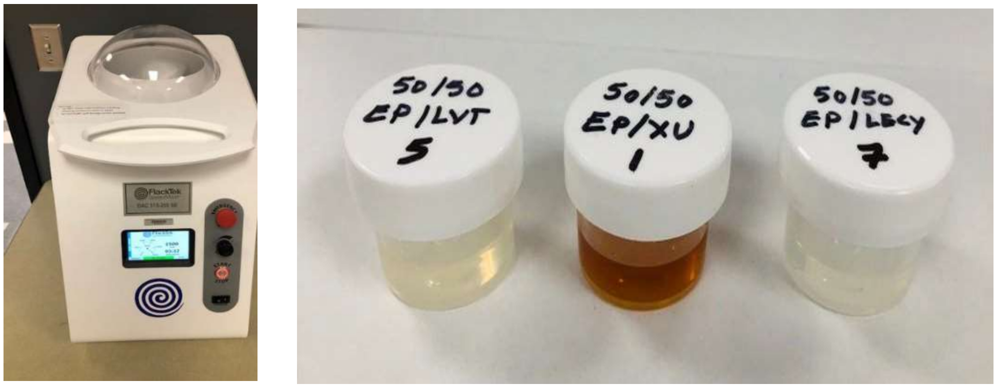
2.2. Formulations and processing conditions

The first step was to blend each of the three cyanate ester types (LVT, LECy and XU) separately with EPON 825 at a level of 50/50 wt%. The next stage was to investigate the addition of two commercial types of reactive phosphorus flame retardants by applying different levels of phosphorous in each sample. The phosphorous loadings investigated were 1, 2 and 3 wt.% for both PMP and DOPO flame retardants as shown in **Table 1** which summarizes all these combinations. Before mixing, both flame retardants were placed in a convection oven for 1 hour at 120°C to ensure there was no trace of moisture and to facilitate mixing in the liquid phase. Each sample was mixed in a double planetary mixer (Flacktek SpeedMixer DAC 515-200 SE) using a Flacktek max 10 g cup (see **Figure 3**). The sample size for this study was 6 grams, and the mixing speed was set at 2500 RPM for 5 minutes. The details of the mixing procedures are as follows. First, the cyanate ester monomer and EPON 825 was added to the cup at 50/50 wt.%, and then the mixture was heated to 100 °C in an oven. The preheated flame retardant was then added to the cup at the appropriate loading. The samples were then manually mixed with the stirring stick and placed back in the oven for 2 minutes prior to being automatically blended with the Flacktek mixer for 5 minutes. The contents of the cup remained warm and liquid throughout mixing. After mixing and cooling to room temperature, all samples appeared to be homogenous, clear liquids free of phase separation and air bubbles (see **Figure 3B).**

Table 1. Composition of the CE, EP and CE/EP blends with flame retardants (total of 21 unique formulations produced).

Sample composition [wt%]				
Baseline samples				
Sample	EPON	CE	Fyrol PMP	DOPO
EP/CE*	50.00	50.00	--	--
Flame retardant combinations using Fyrol PMP				
EP/CE* 1%P	47.00	47.00	6.00	--
EP/CE* 2%P	44.30	44.30	11.40	--
EP/CE* 3%P	41.43	41.43	17.15	--
Flame retardant combinations using DOPO				
EP/CE* 1%P	46.50	46.50	--	7.00
EP/CE* 2%P	43.00	43.00	--	14.00
EP/CE* 3%P	39.51	39.51	--	20.98

*CE: Cyanate ester type LVT, LECy and XU



A

B

Figure 3: A Flacktek mixer, B) Samples in mixing cups.

Each sample was examined using DSC twice: first immediately after mixing (i.e., in the freshly mixed liquid condition) to evaluate curing behavior. The second test was performed after post-curing each formulation in a convection oven to determine the glass transition temperature for each sample and to ensure that no residual cure remained in each sample. DSC testing was used to evaluate all EP/CE blends at a heating rate of 10 °C/min. A sample of each freshly mixed formulation was transferred to an aluminum dish and cured with a curing cycle as follows: 1 hour at 150 °C, 2 hours at 220 °C. The heating rate was kept very low at 1 °C/min to control the high exothermic reaction of the cyanate ester. After being cured in the oven and cooled to room temperature, all samples were post-cured at 240 °C for 1 hour using the same heating rate.

Before curing, the color of the samples varied depending on the color of the cyanate ester: LVT blends were a light rose-colored liquid, LECy blends were a light yellowish liquid, and XU blends were a red, highly viscous liquid. Throughout the curing procedure, the samples gradually darkened; however, the average weight loss was 0 to 1 wt% for PMP samples and 1 to 3 wt% for DOPO samples. The thermal stability of post-cured samples was evaluated using thermogravimetric analysis (TGA); all samples were evaluated in their solid condition. The post cured samples were easily removed from the aluminum dish.

2.3. Characterization

All samples were evaluated using a differential scanning calorimeter (DSC) model Q2000 from TA Instruments to determine curing behavior and glass transition temperature (T_g). The heat-flow curves of liquid samples were acquired using dynamic DSC measurements in 50 mL of flowing nitrogen at a ramp rate of 10 °C/min from 40 to 375 °C. Each sample weighed between 4 and 6 mg and was put in a low mass T-zero aluminum pan with hermetic lid. The T_g of all post-cured samples was measured using the same procedure, which included heating the cured samples to a maximum temperature of 350 °C at a rate of 10 °C/min.

To investigate the thermal stability of cured samples, thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 unit with an evolved gas analysis (EGA) furnace. The samples were tested in platinum pans with sample sizes ranging from 10 to 15 mg. The temperature was raised from room temperature to 800 °C at a rate of 10 °C/min in flowing nitrogen (90 mL/min to furnace, 10 mL/min to thermobalance).

3. RESULTS AND DISCUSSION

3.1. DSC results: curing characteristics

A DSC test with a heating rate of 10 °C/min was performed to examine the curing behavior of EP/CE/FR blends. Exothermic peaks were observed at relatively high temperatures for all three types of cyanate ester/epoxy combinations, as shown in **Figure 4**: 300 °C for LVT, 290 °C for LECy, and 304 °C for XU. The total enthalpy of their exothermic peaks for EP/CE blends is 903 J/g for LVT, 847 J/g for LECy, and 726 J/g for XU. The onset temperature in this study was taken as the temperature at which the first deviation from baseline was recorded.

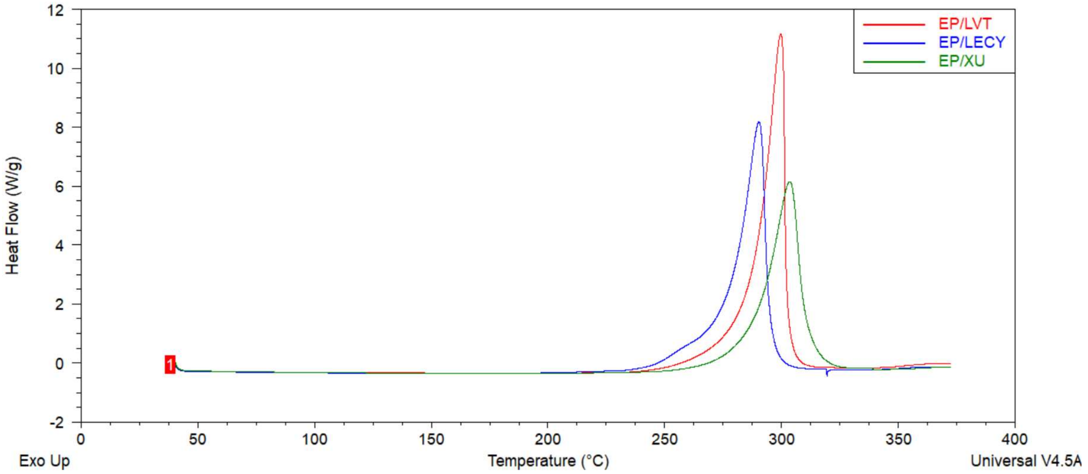
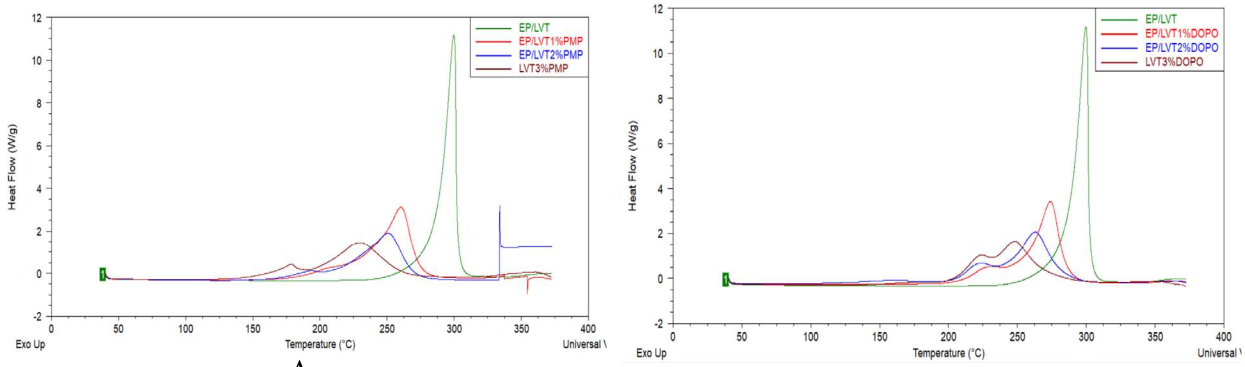


Figure 4: DSC curves showing the heat flow for the three baseline blends of EP/CE at 50/50 wt.%.

Figure 5, which illustrates DSC heat flow curves for EP/LVT blends *with flame retardant*, shows that the exothermic curing peak temperatures gradually decreased with increase of phosphorus content using both PMP and DOPO. When the phosphorus content was 1 wt% of the EP/LVT blend, the exothermic peaks for the curing reaction were reduced by 39 °C in the presence of PMP and by 25 °C in the case of DOPO. As observed, when the phosphorus content increased to 2.0 wt% and 3.0 wt% of the blend, the appearance of the two exothermic peaks became clearer and the peak temperatures were reduced further. Those exothermic peaks are attributed to the reactions among the flame retardant with the epoxide group at a range of 150°C to 200°C and the epoxy group with the cyanate group at a higher temperature range of 200°C to 250°C.

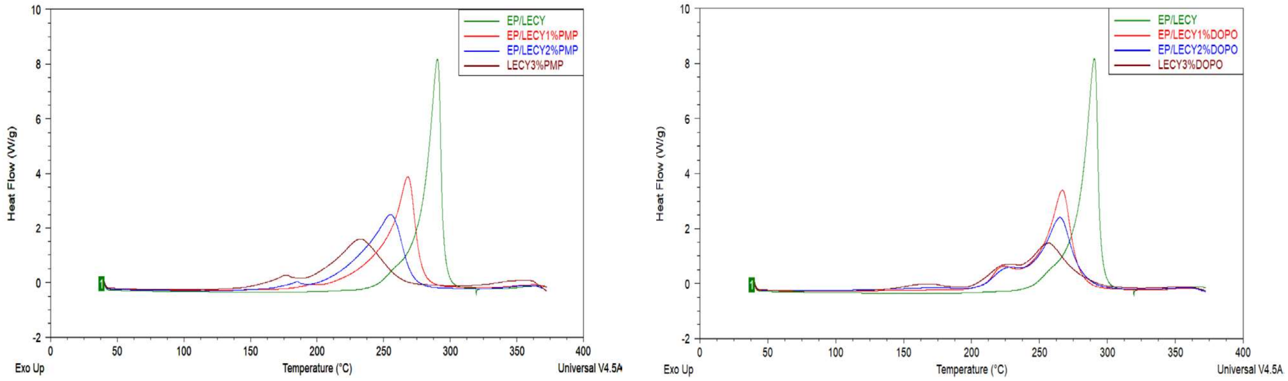
The total enthalpy value of the exothermic peak for EP/LVT at 1 wt% PMP was 731.7 J/g, which is 81.0% of that of neat EP/LVT. The decrease in total heat of reaction values as phosphorus content increased had an identical effect when using PMP and DOPO for LVT blends, which lowered the total heat of reaction by 40% at 3% P level compared to neat EP/LVT. This tendency is comparable with the findings of Chen et al., where flame-retardant system was similarly based on DOPO [9], [16]. The main exothermic peak temperatures for both systems were reduced by adding more phosphorus, and an additional second peak became more noticeable and larger. In comparison to LVT baseline samples (no FR), the onset reaction temperature dropped by an average of 76 °C for PMP and 87 °C for DOPO as phosphorus concentrations increased.



A B

Figure 5: DSC curves showing the heat flow for EP/LVT samples with different loading of phosphorus content A) PMP B) DOPO.

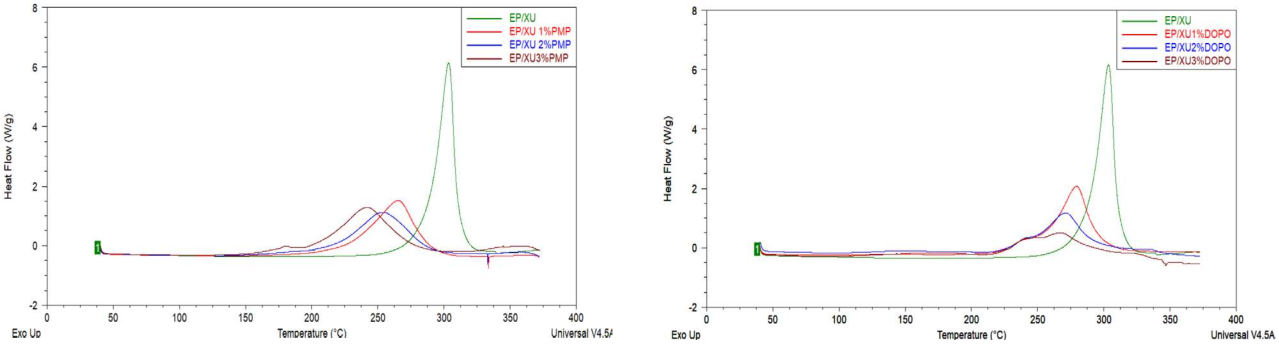
Figure 6 depicts DSC curing behavior curves for EP/LECy blends and demonstrates the similar tendency as the LVT type: the exothermic peaks of the curing reactions rapidly decreased as phosphorus content increased with both PMP and DOPO. When the phosphorus concentration of the EP/LECy blend was 1 wt%, the exothermic peak temperatures were lowered by the same amount of 23 °C in the presence of both PMP and DOPO. According to the DSC data in Table 2, the LECy type has comparable curing behavior to the LVT type, with both having the same tendency toward reduced onset cure temperature and total heat of reaction when phosphorous content was increased.



A B

Figure 6: DSC curves showing the heat flow for EP/LECy samples with different loading of phosphorus content A) PMP B) DOPO.

As expected, both **Figure 7** and data in Table 2 indicate that the DSC curing behavior for EP/XU blends show the identical trend of curing characteristics for LVT and LECy types. However, among the two types of cyanate ester, EP/XU revealed the highest curing temperature at 303 °C and the lowest total heat of reaction at 725.7 J/g.



A B

Figure 7: DSC curves showing the heat flow for EP/XU samples with different loading of phosphorus content A) PMP B) DOPO.

Table 2. DSC results for CE/EP blends with flame retardants.

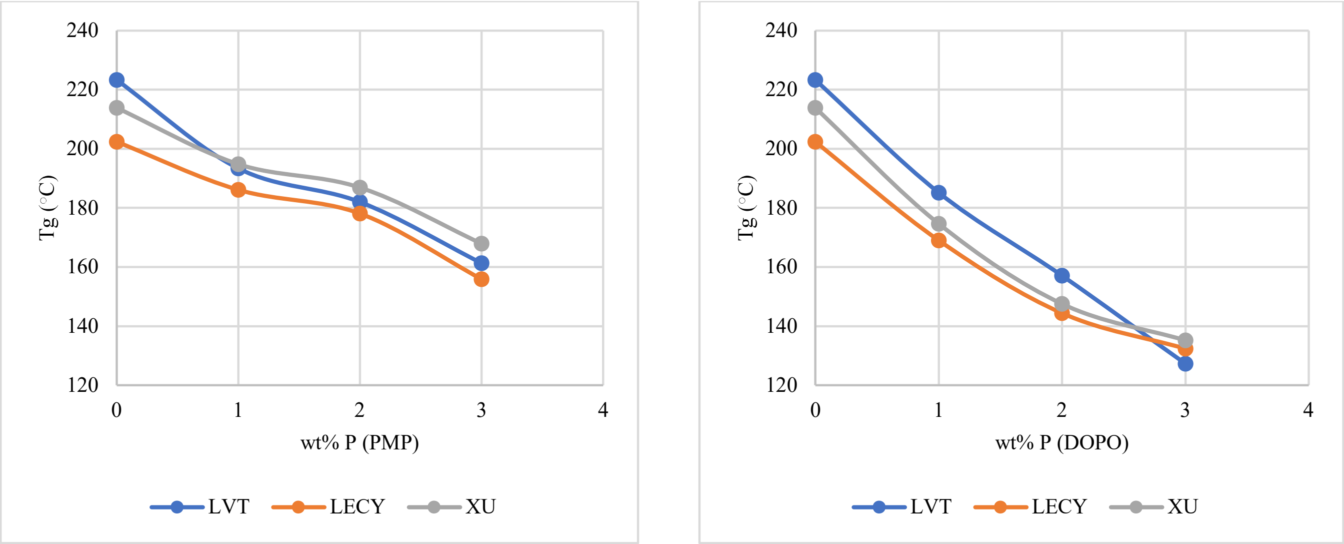
Sample	%wt. P	PMP				DOPO			
		ΔH_{rxn} (J/g)	Onset temp. (°C)	Peak temp. (°C)	Tg (°C)	ΔH_{rxn} (J/g)	Onset temp. (°C)	Peak temp. (°C)	Tg (°C)
EP/LVT	0	904	245	300	223	904	245	300	223
	1	732	182	260	193	660	207	274	185
	2	575	167	251	182	599	125	263	157
	3	544	157	230	161	538	143	249	127
EP/LECy	0	847	243	290	202	847	243	290	202
	1	722	198	268	186	666	208	267	169
	2	652	183	255	178	606	135	265	144
	3	543	155	233	156	562	133	257	132
EP/XU	0	726	261	304	214	726	261	304	214
	1	477	198	266	195	489	205	279	175
	2	435	186	255	187	315	148	272	148
	3	481	184	242	168	261	156	268	135

In accordance with all published investigations, it has been determined that the curing characteristics of all epoxy-cyanate ester blends change significantly as the phosphorus levels increase, namely a reduction in cure onset temperature, peak temperature, and total heat of reaction [9], [17], [18], [20]. This implies that the network is affected profoundly by the reaction of the flame retardants with the baseline monomers. As expected, the addition of a small dose (1 wt%) of phosphorus resulted in the smallest reduction in peak temperature compared to EP/CE blends at baseline, as was the case with the glass transition temperature which will be discussed next. The effects of the two reactive flame retardant types on the curing behavior of EP/CE blends were comparable; however, the PMP flame retardant type had a lesser influence on the glass transition temperature of all epoxy cyanate ester combinations.

3.2. DSC results: Effect of flame retardants on EP/CE Tg.

Figure 8 summarizes the findings of the glass transition temperatures of both flame-retardant systems, PMP and DOPO. In all systems, the glass transition temperature decreased fairly linearly as the phosphorus level increased. In this investigation, the amount of epoxy with cyanate ester was held constant, whereas the type of cyanate ester and level of two different flame retardants were modified to deliver 1, 2, or 3 wt% P. For most formulations the LVT type had the greatest glass transition temperature, while the XU type exhibited the lowest reduction in T_g with the PMP flame retardant. However, overall, the T_g values and trends are comparable within each flame retardant type. Other interesting results observed from the study are that the average T_g reduction in PMP systems was lower than that of DOPO-based flame retardants, which are 16 to 30 °C for 1 wt% P (PMP) and 33 to 39 °C for 1 wt% P (DOPO).

Using both PMP and DOPO at higher levels further decreases the T_g. This may imply that the crosslink density decreased, although this is not the only possible explanation, which is consistent with the literature [14]. There is no significant difference in T_g reduction when comparing the results of all samples with the same phosphorus concentration in both PMP and DOPO.



A B

Figure 8: summary of DSC results showing the glass transition of EP/CE blends with different phosphorus contents A) PMP, B) DOPO.

3.3. Thermal stability of EP/CE/FR blends

An example of overlay of TGA graphical results is given in **Figure 9** for EP/LVT, while the numerical results of all epoxy-cyanate ester combinations are given in Table 3. The thermal stability of the cured samples was compared by determining the temperature at which the first sign of decomposition occurs, which was taken as the temperature of 5% weight loss. Also, the char yield was taken as the weight percentage remaining at 780 °C. As expected, the pure EP/CE blends gave the highest onset temperatures and char yields due to the relatively high thermal stability of the epoxy-cyanate network which is consistent with literature [9], [16]. Addition of the reactive flame retardants reduced the thermal stability of the resulting network. The char yield of LVT-100 was moderately higher than that of LECy and XU which was attributed to the presence of some polyphenolic cyanate monomers, which is consistent with the literature as reported [13]. All TGA results for EP/CE, using the two types of flame retardants PMP and DOPO, are summarized in Table 3 and Figures 10-11. As shown in Figure 9, the mass loss curves are an important tool used to investigate the decomposition of polymers.

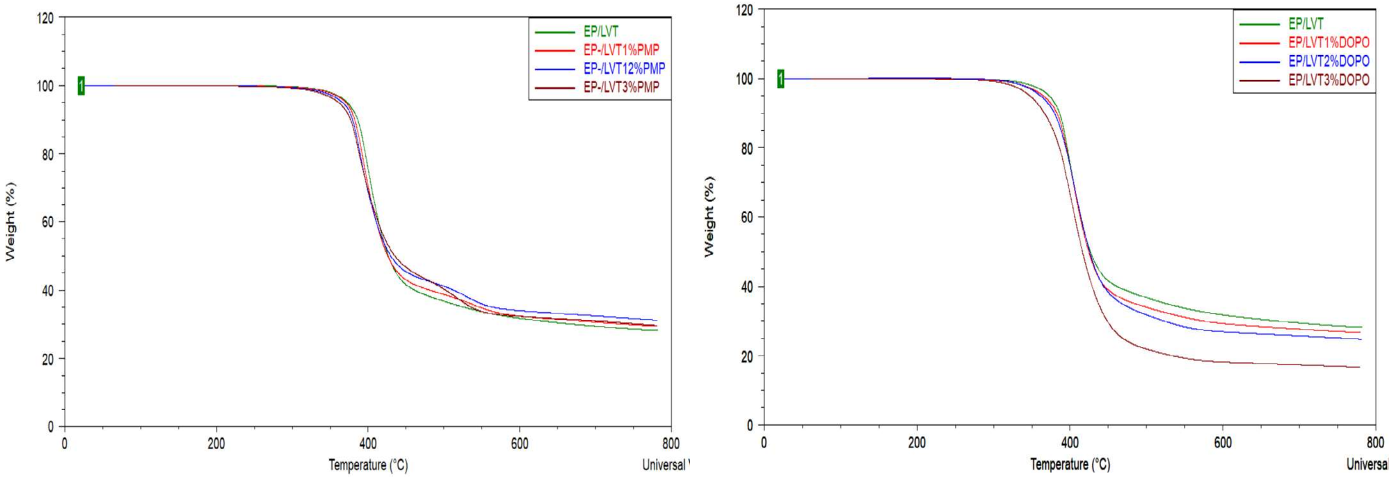


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Figure 9: overlay of TGA results of EP/LVT blends at different phosphorus content (10 °C/min, nitrogen) A) EP/LVT/PMP, B) EP/LVT/DOPO.

Neat EP/CE samples exhibited high thermal stability: the onset decomposition temperature was as high as 387 °C for EP/XU, 381 °C for EP/LVT, and 380 °C for EP/LECy. The highest char yield of neat EP/CE was 28% for the LVT type, while XU exhibited the lowest char yield. As expected, incorporation of the flame retardants into EP/CE blends lead to a decrease in thermal stability by decreasing the onset decomposition temperature by a maximum of 36 °C compared to baseline samples of EP/CE. The effect was very pronounced in the EP/XU formulations containing DOPO. In addition, as phosphorus content increased in all EP/CE samples containing DOPO, the char yield decreased by about 12 wt.% in the case of the EP/LVT blend. A comparison of the average char yield for all EP/EC/DOPO blends demonstrates a linear reduction as the phosphorus content rises. Figure 11B depicts a potential poor reactivity between the DOPO level and the EP/CE blend that results in a weaker crosslinking structure.

Interestingly, when PMP was introduced into all EP/CE blends, the char yields increased steadily with increasing P content. For example, introducing PMP at a concentration of 3 wt% P resulted in the highest char yield, increasing that of EP/XU by 30% (18.29 to 21.61 wt%). Thus, although the EP/XU network exhibited the lowest char yield, the addition of PMP had the greatest effect on increasing it. In contrast, introducing DOPO as a flame retardant by 3 wt% P for the same EP/CE type decreased its char residual by 26% (18.29 to 13.54 wt%) compared to the neat EP/XU char yield value.

Table 3. Thermal decomposition data for EP/CE blends at different levels of PMP and DOPO.

Sample	%wt. P	PMP		DOPO	
		Onset temp. (°C)	Char yield (wt%)	Onset temp. (°C)	Char yield (wt%)
EP/LVT	0	381	28.22	381	28.22
	1	376	29.50	379	26.72
	2	373	31.21	375	24.81
	3	369	30.87	369	16.72
EP/LECy	0	380	25.26	380	25.26
	1	375	26.65	378	22.86
	2	370	27.28	375	20.42
	3	365	27.79	372	21.02
EP/XU	0	388	18.29	388	18.29
	1	378	21.52	384	14.59
	2	371	22.61	361	13.54
	3	364	23.84	351	13.53

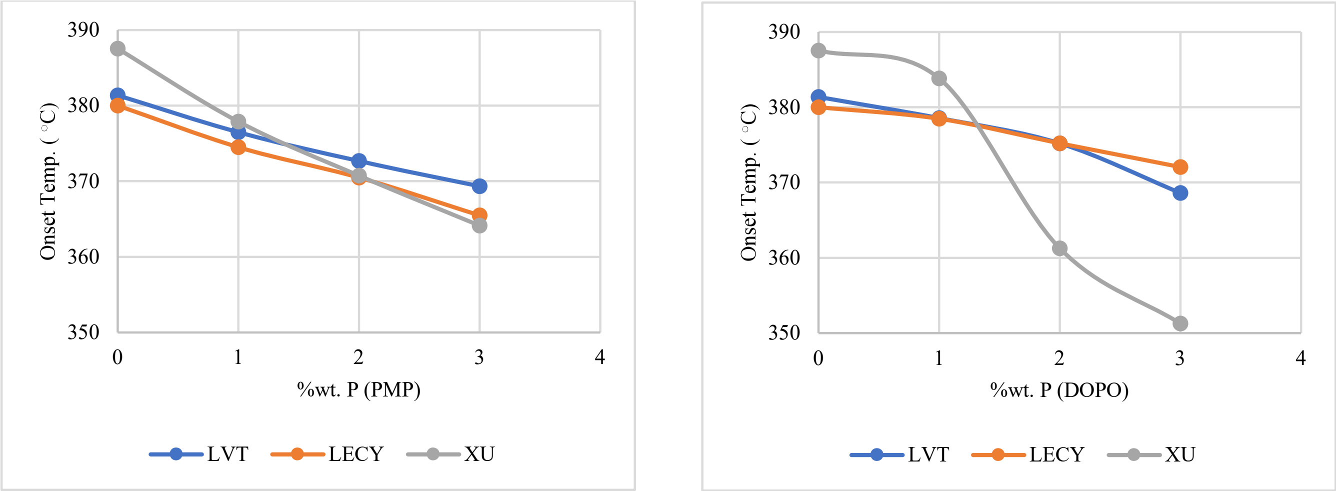

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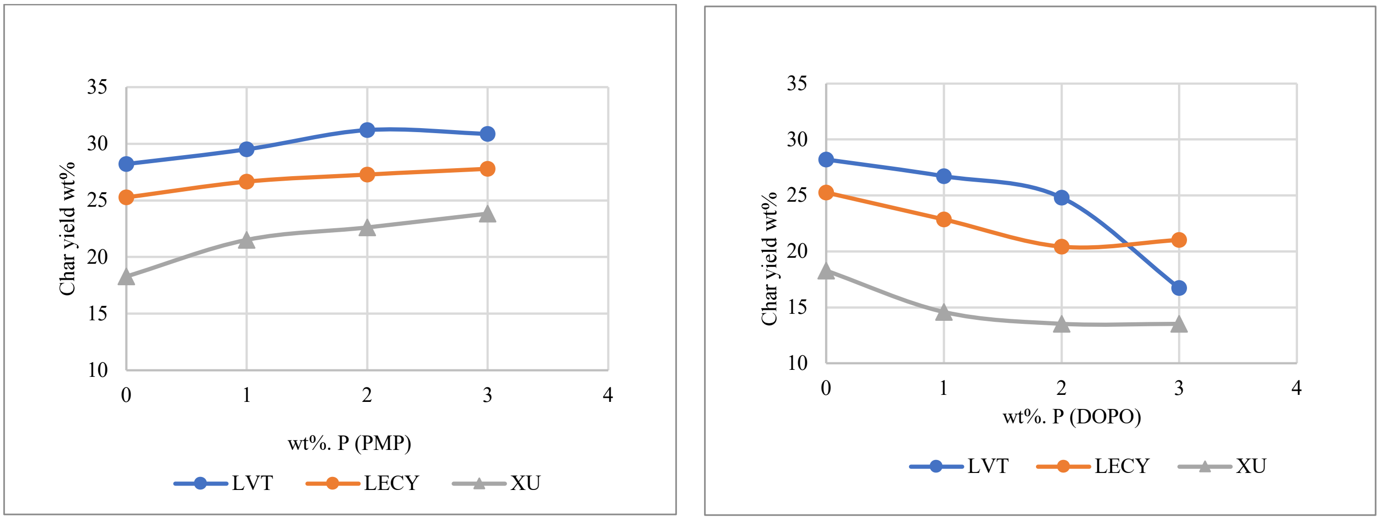
Figure 10: Comparison of the onset decomposition temperatures of EP/CE blends with different loading of phosphorus content A) PMP, B) DOPO.



A

B

Figure 11: Char yield of EP/CE blends with different loading of phosphorus content A) PMP, B) DOPO.

4. CONCLUSION

In this study, three cyanate ester types (LVT-100, LECy, and XU) were combined with epoxy resin (EPON825) at 50/50 wt%. Flame-retardant EP/CE blends were prepared by adding Fyrol® PMP and DOPO, and the effect of phosphorus content from 0 to 3 wt% on thermal stability was investigated. Both the LVT-100 and LECy monomers were liquids at ambient temperature, while XU was solid in the same condition, which gave LVT and LECy a notable advantage in terms of processing and handling. Without flame retardants the EP/LVT blend had a higher T_g and greater thermal stability compared to both the EP/LECy and EP/XU blends. This effect was attributed to the presence of the high functionality polyphenol cyanate monomers in LVT-100, which were expected to result in a higher crosslink density than the similar bifunctional LECy and XU.

Introducing both flame retardants into each type of EP/CE system significantly reduced the average DSC onset temperature and peak temperature of the blends by 35% compared to the EP/CE samples used as a baseline. Furthermore, as the phosphorus concentration increased, two DSC curing peaks became more visible, with a linear decrease in the total heat of reaction. This indicates that the reactive flame retardants had a powerful effect on changing the curing mechanisms and presumably the resulting network structure. TGA results revealed that the char yield of the EP/CE blend increased significantly when PMP was introduced into the blend, with the highest increase of 30% observed at a concentration of 3 wt% PMP with EP/XU. In contrast, the introduction of DOPO into the EP/CE blends *decreased* the char yield by an average of 24% compared to the char yields of the neat EP/CE blends. In addition, the research found that the flame retardants reduced the T_g of the blends. The average T_g reduction for EP/CE/PMP systems was lower than that for EP/CE/DOPO blends (16-30 °C @1%P (PMP) vs. 33-39 °C @ 1%P (DOPO)).

In conclusion, this study successfully demonstrated and quantified the effect of the multi-level introduction of two reactive phosphorus flame retardants on the thermal stability of the epoxy/cyanate ester blends. Further study is required to evaluate if these FRs can improve both mechanical and flame retardancy properties in epoxy/cyanate ester blends, as well as their behavior in fiber-reinforced systems.

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6. REFERENCES

[1] C. P. Reghunadhan Nair, D. Mathew, and K. N. Ninan, “Cyanate ester resins, recent developments,” *Advances in Polymer Science*, vol. 155. pp. 1–99, 2001, doi: 10.1007/3-540-44473-4_1.

[2] J. D. Sudha, S. Pradhan, H. Viswanath, J. Unnikrishnan, P. Brahmbhatt, and M. S. Manju, “Studies on the cure parameters of cyanate ester-epoxy blend system through rheological property measurements,” *J. Therm. Anal. Calorim.*, vol. 115, no. 1, pp. 743–750, Jan. 2014, doi: 10.1007/s10973-013-3273-2.

[3] P. Ren, G. Liang, and Z. Zhang, “Epoxy-modified cyanate ester resin and its high-modulus carbon-fiber composites,” *Polym. Compos.*, vol. 27, no. 4, pp. 402–409, Aug. 2006, doi: 10.1002/PC.20207.

[4] T. Mariappan and C. A. Wilkie, “Flame retardant epoxy resin for electrical and electronic applications,” *Fire Mater.*, vol. 38, no. 5, pp. 588–598, 2014, doi: 10.1002/fam.2199.

[5] A. Salunke, S. Sasidharan, J. C. Gopinathapanicker, B. Kandasubramanian, and A. Anand, “Cyanate ester epoxy blends for structural and functional composites,” *Industrial and Engineering Chemistry Research*, vol. 60, no. 8. pp. 3260–3277, 2021, doi: 10.1021/acs.iecr.0c05008.

[6] B. Szolnoki, A. Toldy, P. Konrád, G. Szebényi, and G. Marosi, “Comparison of additive and reactive phosphorus-based flame retardants in epoxy resins,” *Periodica Polytechnica Chemical Engineering*, 2013. https://pp.bme.hu/ch/article/view/2175/1309 (accessed Sep. 13, 2021).

[7] J. Ueyama, R. Ogawa, K. Ota, Y. Mori, A. Tsuge, and T. Endo, “Rapid Curing System of a Cyanate Ester Resin/Epoxy Resin with a Thermal Latent Polymeric Hardener Based on a Phenol–Amine Salt,” *ACS Appl. Polym. Mater.*, vol. 4, no. 1, pp. 84–90, Jan. 2022, doi: 10.1021/acsapm.1c00995.

[8] Z. Wang, X. Gao, and W. Li, “Epoxy resin/cyanate ester composites containing DOPO and wollastonite with simultaneously improved flame retardancy and thermal resistance,” *High Perform. Polym.*, vol. 32, no. 6, pp. 710–718, 2020, doi: 10.1177/0954008319897095.

[9] T. H. Ho, H. J. Hwang, J. Y. Shieh, and M. C. Chung, "Thermal, physical and flame-retardant properties of phosphorus-containing epoxy cured with cyanate ester," *React. Funct. Polym.*, vol. 69, no. 3, pp. 176–182, Mar. 2009, doi: 10.1016/j.reactfunctpolym.2008.12.019.

[10] J. Li, Z. Wu, C. Huang, and L. Li, "Multiscale carbon nanotube-woven glass fiber reinforced cyanate ester/epoxy composites for enhanced mechanical and thermal properties," *Compos. Sci. Technol.*, vol. 104, pp. 81–88, Dec. 2014, doi: 10.1016/j.compscitech.2014.09.007.

[11] Z. Li, J. Hu, L. Ma, and H. Liu, "Shape memory CTBN/epoxy resin/cyanate ester ternary resin and their carbon fiber reinforced composites," *J. Appl. Polym. Sci.*, vol. 137, no. 22, Jun. 2020, doi: 10.1002/APP.48756.

[12] A. Toldy, B. Szolnoki, and G. Marosi, "Flame retardancy of fibre-reinforced epoxy resin composites for aerospace applications," *Polym. Degrad. Stab.*, vol. 96, no. 3, pp. 371–376, Mar. 2011, doi: 10.1016/j.polymdegradstab.2010.03.021.

[13] C. H. Lin, "Synthesis of novel phosphorus-containing cyanate esters and their curing reaction with epoxy resin," *Polymer (Guildf).*, vol. 45, no. 23, pp. 7911–7926, 2004, doi: 10.1016/J.POLYMER.2004.09.023.

[14] X. Chen, J. Wang, S. Huo, S. Yang, B. Zhang, and H. Cai, "Study on properties of flame-retardant cyanate esters modified with DOPO and triazine compounds," *Polym. Adv. Technol.*, vol. 29, no. 10, pp. 2574–2582, Oct. 2018, doi: 10.1002/pat.4368.

[15] T. Wu, A. M. Piotrowski, Q. Yao, and S. V. Levchik, "Curing of epoxy resin with poly(m-phenylene methylphosphonate)," *J. Appl. Polym. Sci.*, vol. 101, no. 6, pp. 4011–4022, Sep. 2006, doi: 10.1002/app.22966.

[16] S. Levchik, A. Piotrowski, E. Weil, and Q. Yao, "New developments in flame retardancy of epoxy resins," in *Polymer Degradation and Stability*, Apr. 2005, vol. 88, no. 1, pp. 57–62, doi: 10.1016/j.polymdegradstab.2004.02.019.

[17] A. Toldy, Szlancsik, and B. Szolnoki, "Reactive flame retardancy of cyanate ester/epoxy resin blends and their carbon fibre reinforced composites," *Polym. Degrad. Stab.*, vol. 128, pp. 29–38, Jun. 2016, doi: 10.1016/j.polymdegradstab.2016.02.015.

[18] A. Toldy, P. Niedermann, G. Szebényi, and B. Szolnoki, "Mechanical properties of reactively flame retarded cyanate ester/epoxy resin blends and their carbon fibre reinforced composites," *Express Polym. Lett.*, vol. 10, no. 12, pp. 1016–1025, Jun. 2016, doi: 10.3144/expresspolymlett.2016.94.

[19] D. A. Klosterman, "PREPARATION, CURE, AND CHARACTERIZATION OF CYANATE ESTER-EPOXY BLENDS," in *International SAMPE Technical Conference*, 2022, vol. 2022-May, Accessed: Dec. 30, 2022. [Online]. Available: https://ecommons.udayton.edu/cme_fac_pub/209/.

[20] C. H. Lin, K. Z. Yang, T. S. Leu, C. H. Lin, and J. W. Sie, "Synthesis, characterization, and properties of novel epoxy resins and cyanate esters," *J. Polym. Sci. Part A Polym. Chem.*, vol. 44, no. 11, pp. 3487–3502, Jun. 2006, doi: 10.1002/POLA.21453.