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Chapter

# Application of Metal-Organic Framework as Reactive Filler in Bisphenol-A-Based High-Temperature Thermosets

*Chinnaswamy Thangavel Vijayakumar,  
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## Abstract

Excellent thermoset monomers, bisphenol-A-based biscyanate ester (BADCy) and bispropargyl ether (BPEBPA), are synthesized and thermally cured to high-temperature thermosetting polymers. The nanoporous aluminum fumarate (Al\_FA\_A), an interesting Metal-Organic Framework (MOF), is synthesized in an eco-friendly manner and used as a reactive nanoparticle filler. The interaction of fumarate  $\pi$  bonds (*trans*-CH=CH-) in MOF with the reactive end functional groups (-O-C $\equiv$ N) in cyanate ester (CE) and (-CH<sub>2</sub>-C $\equiv$ CH) in bispropargyl (BP) ethers is focused in these hybrid nanocomposites. The % decrease in enthalpy of curing in the organic and the inorganic blends (~60% for CE and ~10% for BP) indicates the interaction existing between the MOF and the organic component. The addition of the aluminum fumarate MOF increases the glass transition temperature of the polymers. The amount of heat released for every increase in 1°C during the temperature window of curing ( $\Delta H_c/T_E-T_S$ ) of the neat BADCy resin is approximately 2.4 times higher than the blend (BADCy+Al\_FA\_A). But BPEBPA shows only a 1% higher temperature curing window compared to its blend with MOF. The metal hotspots present in the hybrid nanocomposites may be the reason for the decrease in the thermal stability, and the % char residue is noted at 700°C. The TG-FTIR studies are done to predict the gaseous products (CO<sub>2</sub>) evolved during thermal degradation.

**Keywords:** biscyanate ester, bispropargyl ether, aluminum fumarate MOF, thermal properties, TG-FTIR

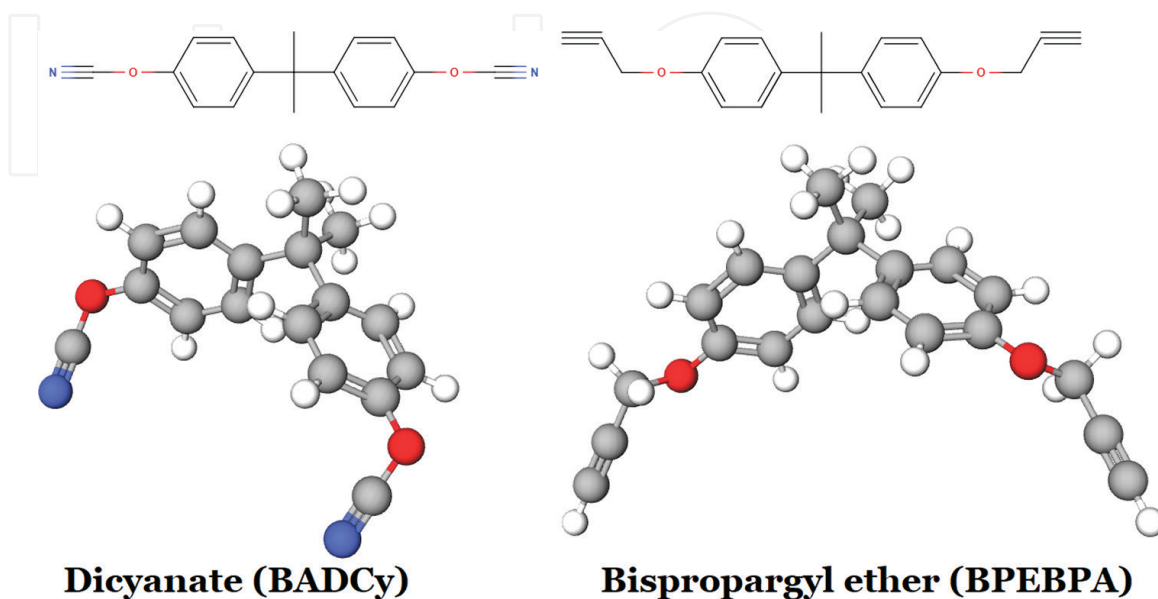
## 1. Introduction

The cyanate ester (CE) and the acetylene terminated (AT) resins are specialty materials and find applications in several fields. Of which, the bisphenol-A-based

dicyanate (BADCy) and the bispropargyl (BPEBPA) resins are advanced thermoset materials due to the formation of triazine [1] (polycyanurate) from BADCy [2] and products such as polyene, phenolic allenes by Claisen rearrangement, and chromene from aromatic bispropargyl ether (BPEBPA). The polycyanurate materials have high strength and toughness, high glass transition temperature, low water absorption, low dielectric constant, and good adhesion to a variety of substrates [3], and they combine the advantages of epoxies, fire resistance of phenolics, and high-temperature performance of polyimides. Several authors studied thermal degradation [4], curing kinetics, and blends of bismaleimides with bispropargyl ethers [5–8]. The authors already have experience in synthesizing the bispropargyl ether with several swivel groups. The most important study is copper-salt-assisted polymerization of bispropargyl of bisphenol-A [9] and the blend of propargyl ether with bismaleimide [10].

Polymer blending with other thermosets (or) with inorganic salts/materials [10, 11] has been studied by different research groups. This created a large scope for investing in the materials through resin modification and reinforcements. The authors work toward the influence of chain extension in BMIM composites and studied the effects of chain extensions on thermal and mechanical properties [12]. In their investigation, Siva Kaylasa Sundari *et al.* [13] studied the influence of nanoporous aluminum fumarate in cyanate ester matrix. It was reported that the double bond of aluminum MOF was involved in triazine formation. The synthesis, characterization, and thermal degradation kinetics by the model free approach of aluminum fumarate were already presented [14]. This study compares the bulk polymerization and polymer thermal properties having different functional group systems (bisphenol-A-based cyanate ester and bispropargyl ether) with aluminum fumarate MOF as particulate reinforcements. The structures of bisphenol-A-based monomers are presented in **Figure 1**.

The exponential increase in the design and development of Metal-Organic Frameworks (MOFs) is due to their tailorable properties and unprecedented functionality. The MOFs have a wide range of advantage and extend applications in several smart fields [15, 16] and also in biomedical applications [17, 18]. MOFs are formed by strong covalent bonds between inorganic metal salts and organic linkers. The author already studied the detailed aspects of synthesis and procedure optimization of aluminum



**Figure 1.**  
Structures of bisphenol-A-based monomers.

fumarate and its isothermal model free [14] and model fitting kinetics. The formation of MOF-polymer composites can be obtained by the in-situ polymerization reaction, MOF construction using polymeric ligands, post-synthetic grafting of polymers onto the reactive ligands, the post-synthetic introduction of pre-formed polymers and MOFs self-assemble around polymers [19]. Markedly, this invention relates to the solvent-free process for preparing the MOF-polymer composite by the post-synthetic grafting of pre-formed polymers on reactive MOFs. The polymerized material contains allenes, phenolic allenes by claisen rearrangement, chromenes from aromatic propargyl ether, and also the linear polyene. The involvement of fumarate  $\pi$ -bonds in MOFs with reactive double bonds of polymerized bispropargyl provides a complex bulk and random hybrid polymer brushes, which makes the material applicable for functionalized applications.

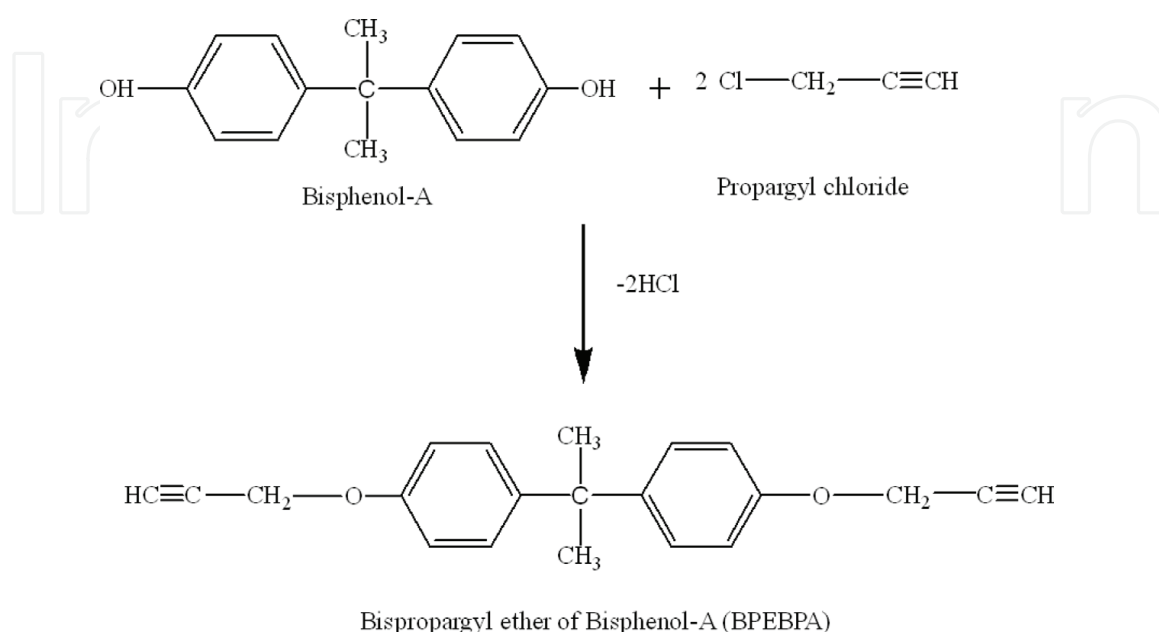
## 2. Materials and methods

### 2.1 Materials

The compounds bisphenol A dicyanate (BADCy), bispropargyl ether (BPEBPA) and the nanoporous aluminum fumarate MOF (Al\_FA\_A) were synthesized. Bisphenol-A, sodium hydroxide, tetra butyl ammonium bromide, and isopropanol were obtained from Merck India Ltd., Mumbai, India, and were used without any further purification. Propargyl chloride obtained from Grauer & Weil (India) Limited, Vapi, India, was distilled (Boiling point: 57°C) before use. The synthesis procedure and the characterizations of bisphenol-A dicyanate [13] and the nanoporous aluminum fumarate MOF [14] were reported in our previous work.

#### 2.1.1 Synthesis of bispropargyl ether of bisphenol-A (BPEBPA)

A mixture of 0.2 mol of bisphenol-A, 200 mL of 20% aqueous sodium hydroxide (NaOH), and 0.01mol of tetrabutyl ammonium bromide was kept at room

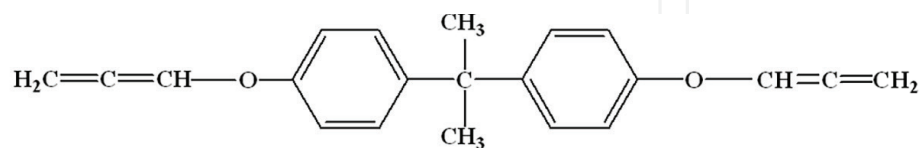


**Figure 2.**  
Synthesis of bispropargyl ether of bisphenol-A.

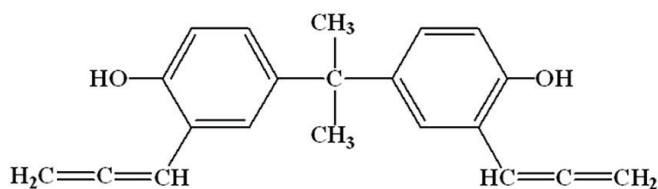
temperature. About 0.6 mol of propargyl chloride was added over 10 min to the above mixture with constant stirring, and the resultant reaction mixture was stirred for 16 h. The resulting white crystals were filtered and washed twice with 200 mL of water and then with 50 mL of isopropanol. This results in a yield of 95% of BPEBPA. The reaction for the synthesis is presented in **Figure 2**.

### 2.1.2 Preparation of hybrid nanocomposites

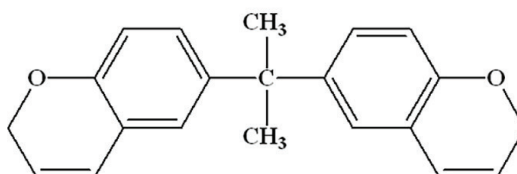
The dried BADCy/BPEBPA and the Al\_FA\_A (99:1, w/w) were taken in an agate mortar, and the mixture was ground repeatedly to have effective mixing. The mixture



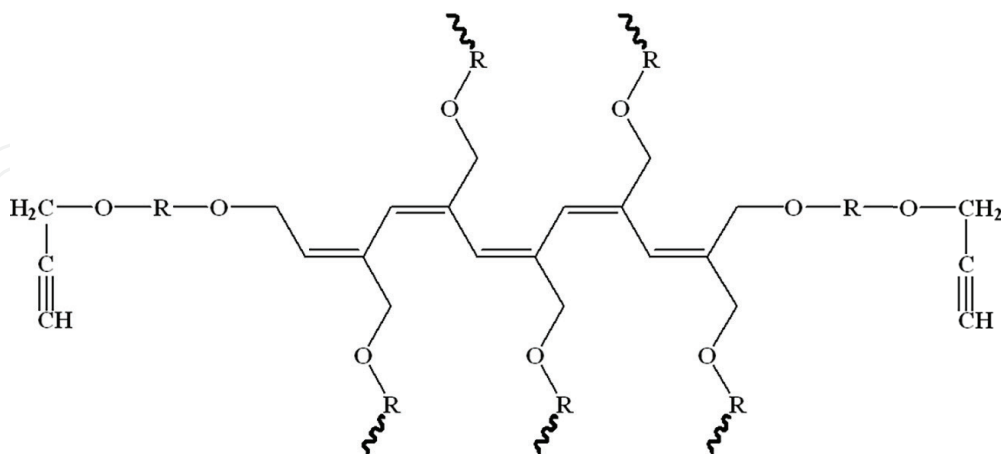
(A) Allene



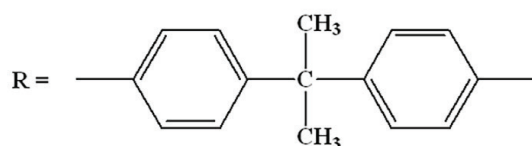
(B) Claisen Rearrangement



(C) Chromene



(D) Polyene



**Figure 3.**

The products formed during the polymerization of bisphenol-A-based bispropargyl ether (BPEBPA).



was then dried and preserved for polymerization. The pure BADCy/BPEBPA and their blends with nanoporous aluminum MOF were taken in separate borosilicate glass test tubes and flushed with dry oxygen-free-nitrogen gas and polymerized at 240°C for 6 h. After the polymerization, the samples were allowed to cool to room temperature, removed from the test tubes, ground to a coarse powder, packed, and stored for further analysis. The reaction mechanism for the involvement of fumarate in triazine formation is presented in our previous work [13]. The possible products during the polymerization of bispropargyl ether are presented in **Figure 3**.

## 2.2 Methods

The Fourier Transform Infrared Spectrum (FTIR) of the material was recorded on a Fourier transform infrared-8400S spectrophotometer, Shimadzu, Japan, using the potassium bromide disc technique. The differential scanning calorimetric (DSC) curves were recorded using TA Instruments DSC Q20 using a non-hermetic aluminum pan. The samples were heated from ambient to 350°C at 10°C min<sup>-1</sup> in a nitrogen atmosphere (50 mL min<sup>-1</sup>). The thermal degradation behavior of the material was examined using TGA Model Q50 supplied by TA Instruments, Waters India Pvt., Ltd., Bengaluru – 560,086, India. The measurements were carried out using approximately 3–4 mg of the sample in a high-purity nitrogen atmosphere, and the flow of nitrogen to the balance area was 40 mL min<sup>-1</sup>, and the sample was swept with a nitrogen flow of 60 mL min<sup>-1</sup>. The obtained TG and DTG curves were analyzed using the universal analysis 2000 software provided by TA instruments. The TG-FTIR study of polymerized samples was carried out in a TA Instruments TGA Q5000 V3.10 Build 258 at a heating rate of 10°C min<sup>-1</sup> from ambient to 800°C. Nearly, 3–4 mg samples was used for the analysis in the nitrogen atmosphere (balance flow: 10 mL min<sup>-1</sup> and sample flow: 25 mL min<sup>-1</sup>), and the FTIR spectra of the volatiles formed during the thermal degradation were recorded every 30 s.

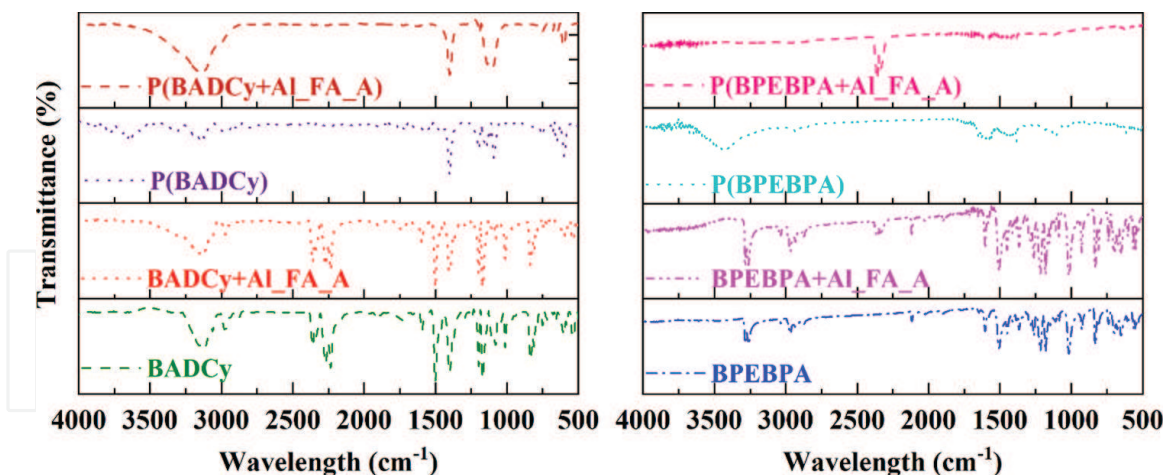
## 3. Results and discussion

### 3.1 Aluminum fumarate

The Fourier Transform Infrared Spectroscopy was done for Al\_FA\_A to find the existence of intermolecular hydrogen bonding between the layers of aluminum fumarate. The Al\_FA\_A shows an onset degradation temperature at 410°C, attains a maximum at 484°C, and ends at 561°C. The material Al\_FA\_A is stable up to 400°C, and the amount of residue noted at 700°C is 33%. The crystallinity of Al\_FA\_A is 89% (Scherrer equation), and the average mean particle diameter of 50 nm. The Brunauer-Emmett-Teller (BET) surface area of Al\_FA\_A was found to be 937 m<sup>2</sup>g<sup>-1</sup>; monolayer volume ( $V_m$ ) of 215.21 cm<sup>3</sup>g<sup>-1</sup>; total pore volume ( $V_{pore}$ ) of 0.38 cm<sup>3</sup>g<sup>-1</sup>; and a mean pore diameter of 1.63 nm. The thermal degradation behavior of the aluminum fumarate by model free kinetics [14] and the curing behavior of BADCy and BADCy+Al\_FA\_A were already presented [13].

### 3.2 FTIR studies

The FTIR spectra for synthesized and polymerized materials are given in **Figure 4**, and the bands were reported in **Table 1**. The FTIR bands for the pre and



**Figure 4.**  
FTIR spectra for monomers and polymers.

S.No.	Frequency (cm <sup>-1</sup> )	Bands (BADCy)	Bands (BPEBPA)
1.	3259	—	≡C-H stretching
2.	3100	Phenolic -OH stretching	—
3.	2970	C-H stretching in CH <sub>3</sub>	C-H stretching in CH <sub>3</sub>
4.	2120	—	C ≡ C stretching
5.	2240 to 2260	C ≡ N stretching	—
6.	1510	C=N-C stretching of triazine ring	—
7.	1400	O-C=N stretching of triazine ring	—
8.	1100 to 1200	C-O-C stretching	C-O-C stretching
9.	820	C-H out of plane deformation	C-H out of plane deformation

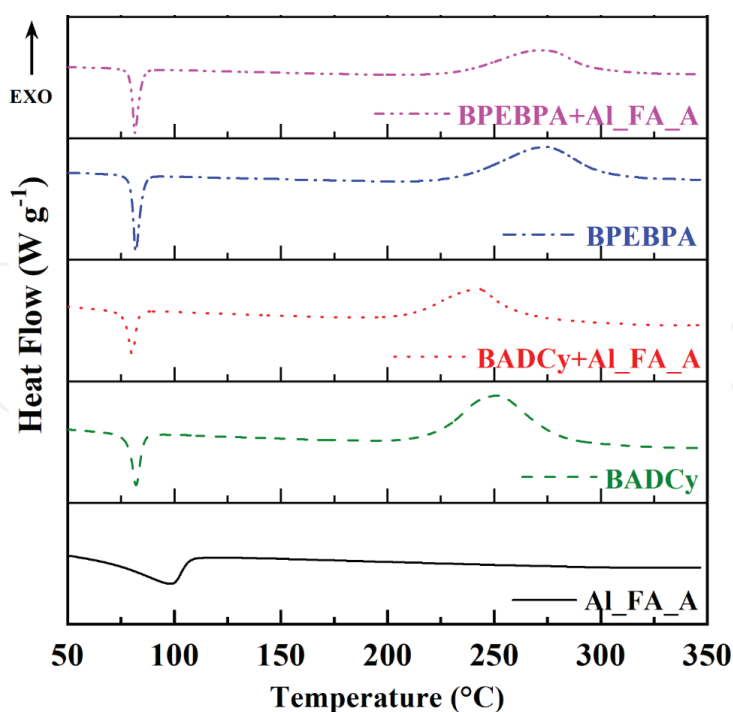
**Table 1.**  
The frequency and corresponding bands of cyanate ester and bispropargyl system.

post-polymerization of BADCy and BADCy+Al\_FA\_A at different temperatures were discussed in detail in our previous work [13]. The compound BPEBPA shows a characteristic band at 2120 cm<sup>-1</sup> for C ≡ C stretching, 3259 cm<sup>-1</sup> for ≡C-H stretching, and 700cm<sup>-1</sup> for ≡C-H deformation. The blending of fumarate MOFs in BPEBPA showed similar spectra to monomers. The polymerization that happened via the claisen polymerization was confirmed by the presence of the ketone group in IR spectra. The propargyl/bispropargyl involved in allene rearrangement then follows the claisen rearrangement to form keto-allene, which undergoes enolization for phenolic allene. The keto-allene further reacts to form the chromene structure [8], which shows a band at 1630 cm<sup>-1</sup> and a cyclic ether group at 1150 cm<sup>-1</sup>.

### 3.3 DSC studies

The DSC thermograms for the monomers and the blends are given in **Figure 5**. The details regarding the melting and curing behavior values for materials are given in **Table 2**.

The BADCy shows the onset curing temperature ( $T_s$ ) at 196°C, the temperature at which the curing rate is maximum ( $T_{max}$ ) at 252°C, and the endset temperature



**Figure 5.**  
 DSC thermograms of monomers and blends.

Sample Code	$T_m$ (°C)	$\Delta H_f$ (J g <sup>-1</sup> )	$T_S$ (°C)	$T_{max}$ (°C)	$T_E$ (°C)	$T_E-T_S$ (°C)	$\Delta H_C$ (J g <sup>-1</sup> )	$\Delta H_C/T_E-T_S$ (J g <sup>-1</sup> °C <sup>-1</sup> )
BADCy	82	31	196	252	334	138	211	1.53
BADCy+Al_ FA_A	80	16	192	243	329	137	86	0.63
BPEBPA	82	45	205	274	332	127	207	1.63
BPEBPA+Al_ FA_A	81	43	211	273	335	124	184	1.48

**Table 2.**  
 Parameters from DSC curves.

( $T_E$ ) at 334°C. The addition of nanoporous material decreases the  $T_S$  to 192°C,  $T_{max}$  to 243°C and the  $T_E$  to 329°C. The BPEBPA shows the  $T_S$  at 205°C, the  $T_{max}$  at 274°C, and the  $T_E$  at 332°C. But the addition of Al\_FA\_A increases the  $T_S$  to 211°C for BPEBPA. The enthalpy of curing ( $\Delta H_c$ ) for BADCy is 211 J g<sup>-1</sup>, whereas incorporation of Al\_FA\_A in BADCy drastically decreases the value to 86 J g<sup>-1</sup>, which amounts to a decrease of 59%. The addition of aluminum fumarate in bisphenol-A-based thermoset decreases the enthalpy of fusion (50%) for BADCy and shows a negligible change in the BPEBPA matrix. The addition of aluminum fumarate increases the glass transition temperature ( $T_g$ ) of polymer.

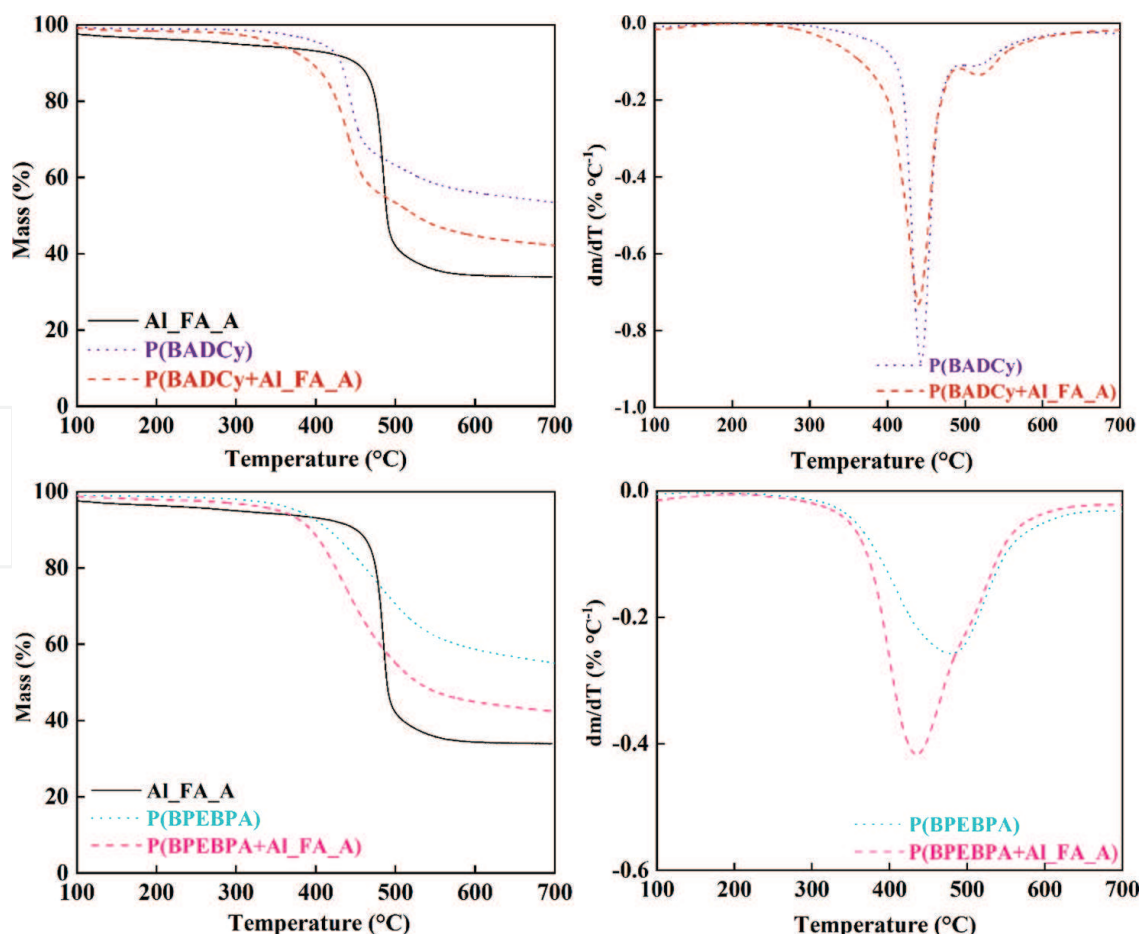
The enthalpy of combustion decreases by 60% for BADCy and by 10% for BPEBPA systems. The reduction in the  $\Delta H_f$  and  $\Delta H_c$  values for the blend indicates the interaction existing between the organic and inorganic components in the blend. The  $T_E-T_S$  values of both the pure resins and the blends show an almost similar rate of curing. The amount of heat released for every increase in 1°C during the temperature window of curing ( $\Delta H_c/T_E-T_S$ ) of the neat BADCy resin is approximately 2.4 times



higher than the blend (BADCy+Al\_FA\_A). But BPEBPA shows only a 1% higher-temperature curing window compared to its blend with MOF. From the DSC curves, a profound effect was observed during the physical blending of aluminum fumarate in bisphenol-A-based thermosets.

### 3.4 TG studies

The thermal analyses of the polymerized samples are presented in **Figure 6**. The polymers are less stable than the nanoporous aluminum MOFs. The details regarding the onset and endset degradation temperatures,  $T_E$ - $T_S$  value, mass loss (%) and the residue (%) at 700°C are given in **Table 3**. Compared to the BADCy, the BPEBPA matrix shows broad degradation. The influence of nanoporous material does not affect the degradation pattern in BADCy, but it shows a drastic difference in the BPEBPA polymer. The effect of copper salts (CuCl: cuprous chloride;  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ : cupric chloride dihydrate;  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ : copper sulfate pentahydrate;  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ : basic copper carbonate;  $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$ : cupric acetate monohydrate; CuO: cupric oxide) in the BPEBPA matrix reported that the addition of copper salts decreases the onset degradation temperature [9]. Similarly, the addition of Al\_FA\_A decreases the thermal stability in both cyanate (BADCy) and the bispropargyl (BPEBPA) systems. The limiting oxygen



**Figure 6.**  
TG and DTG curves of polymers.

Sample Code	First Degradation Stage					Second Degradation Stage				Residue (%) at 700°C	LOI
	T <sub>s</sub>	T <sub>max</sub>	T <sub>E</sub>	T <sub>E</sub> -T <sub>S</sub>	Mass Loss (%)	T <sub>s</sub>	T <sub>max</sub>	T <sub>E</sub>	Mass Loss (%)		
Al_FA_A	410	484	548	138	65	—	—	—	—	33	0.31
P(BADCy)	376	443	623	247	45	—	—	—	—	53	0.39
P(BADCy+Al_FA_A)	327	439	658	331	55	—	—	—	—	42	0.34
P(BPEBPA)	220	476	672	452	42	672	751	797	4	52	0.38
P(BPEBPA+Al_FA_A)	206	435*	662	456	55	—	—	—	—	40	0.34

\*Overlapped degradation.

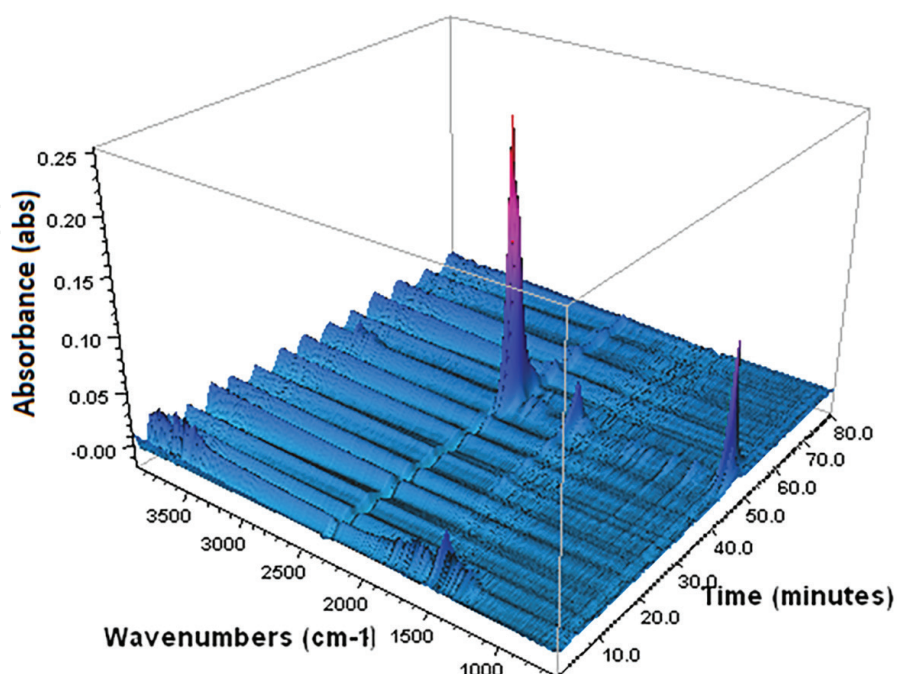
**Table 3.**  
 Degradation parameters of Al\_FA\_A and polymers.

index (LOI) for the nanoporous MOF and the polymers was calculated using Van Krevelen method [20] eq. (1).

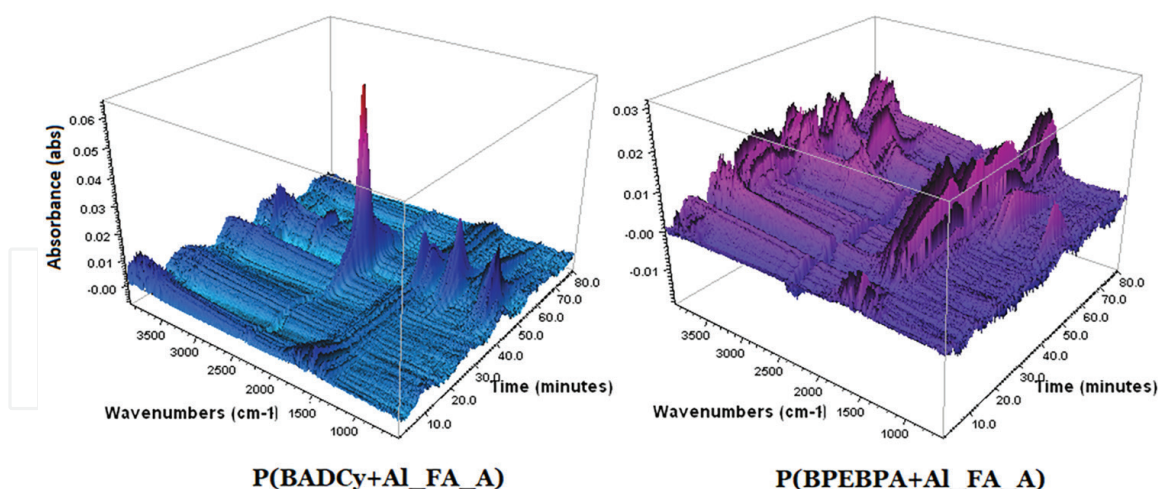
$$LOI = \frac{17.5 + (0.4 * Char Residue)}{100} \quad (1)$$

### 3.5 TG-FTIR studies

The 3D TG-FTIR spectrum of aluminum fumarate is presented in **Figure 7**. The major compounds released from the Al\_FA\_A were water (H<sub>2</sub>O), carbon



**Figure 7.**  
 3D: TG-FTIR spectra of aluminum fumarate.



**Figure 8.**  
3D: TG-FTIR spectra of polymer blends.

dioxide ( $\text{CO}_2$ ), carbon monoxide (CO), and acetylene. A detailed discussion regarding the bond dissociation energies of the aluminum fumarate is provided in the previous work [14]. The 3D TG-FTIR spectra for polymer blends are presented in **Figure 8**.

Compared to P(BADCy) and P(BADCy+Al\_FA\_A), the polymers P(BPEBPA) and P(BPEBPA+Al\_FA\_A) release more carbon dioxide ( $\text{CO}_2$ ) at  $2350\text{ cm}^{-1}$  at all temperatures. The intensity of  $\text{CO}_2$  evolution in P(BADCy) and P(BPEBPA) decreases due to the addition of nanoporous MOF, it indicates that the  $\text{CO}_2$  can be captured in the tunnels of the MOF. Vinayagamoorthy *et al.* [6] and Dhanalakshmi *et al.* [9] studied the off-line pyrolysis and the evolved gas analysis technique of the bispropargyl ethers, and they concluded that the obtained gaseous degradation products should be able to liberate by cleavage at an activated benzylic (or) propargylic site in BPEBPA system. The thermal, mechanical, and electrical effects of Al MOFs in the di/trifunctional epoxies of epoxy resin composites were studied in our previous work [21, 22].

#### 4. Conclusion

The nanoporous aluminum fumarate (Al\_FA\_A), bisphenol-A-based cyanate ester (BADCy), and bispropargyl ether (BPEBPA) were synthesized. The high-temperature thermoset polymers were obtained from the monomers and blended with Al\_FA\_A. The addition of aluminum fumarate MOF decreases the onset curing temperature ( $T_s$ ) for BADCy and increases  $T_s$  for the BPEBPA system without affecting the melting point. The influence of  $\pi$ -fumarate bonds of Al\_FA\_A in the polymer matrix was observed from the drastic changes in the enthalpy of fusion and enthalpy of combustion values. The onset thermal degradation temperature of polymers was decreased by the influence of MOF. The influence of nanoporous material does not affect the degradation pattern in BADCy, but it shows a substantial difference in the BPEBPA matrix. The major products released from the polymers are water ( $\text{H}_2\text{O}$ ), carbon dioxide ( $\text{CO}_2$ ), carbon monoxide (CO), and acetylene.

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## Conflict of interest

The authors have no relevant financial or non-financial interests to disclose.

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