Thermal behavior and degradation mechanism of phosphate di/triacrylate used for UV curable flame-retardant coatings

Baojun Qu[*] *Hongbo Liang,*

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China.

[*] Corresponding author. Tel: +86-551-3607245. E-mail address: Qubj@ustc.edu.cn

Abstract

Tri(acryloyloxyethyl) phosphate (TAEP) and di(acryloyloxyethyl)ethyl phosphate (DAEEP) as flame retardant multifunctional monomers used for UV curable systems were synthesized with phosphorus oxychloride and hydroxylethyl acrylate. The UV cured TAEP and DAEEP films possess the limiting oxygen index of 36 and 29, respectively. Their thermal behaviors were studied by thermogravimetric analysis, and shows three characteristic degradation temperature regions, attributed to the decomposition of phosphate, thermal pyrolysis of side chains of acrylate, and decomposition of unstable structures in char, respectively. This was further demonstrated by in-situ Fourier-transform in frared and direct pyrolysis/mass spectrometry measurements, and monitored by inductively coupled plasma-atomic emission spectrometry. The flame retardant mechanism was proposed that the degraded products of phosphate form poly(phosphoric acid), which further catalyzes the breakage of carbonyl groups to form an intumescent char for preventing the samples from further burning.

Introduction

The combustion process of a polymer is generally described as three stages: fuel production, ignition and then burning. When a polymeric material is heated with rising temperature, eventually the polymer starts to degrade. During the degradation, small molecules are produced in which the combustible compounds are evaporated and mixed with air, forming a flammable mixture. When the concentration of the mixture and also the temperature reach to the flammability limits, the polymer starts to burn. The exothermic heat from the burning process feeds back to the condensed phase, causing further degradation of the polymer [1]. Therefore, the combustion behavior of a flammable material is strongly affected by the degradation process of its components.

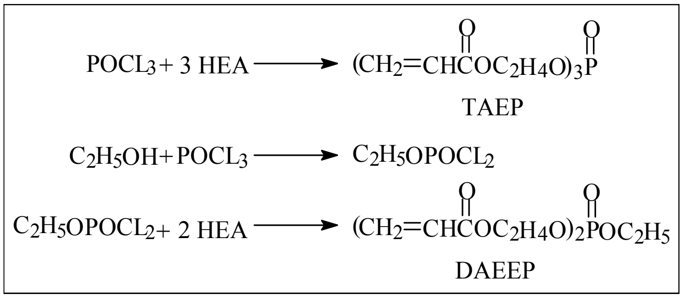
Phosphorus-containing compounds are a family of condensed-phase flame-retardants, which are able to increase the conversion of organic matter to char during burning, and thus decrease the amount of flammable volatile gases reaching the flame zone, and reduce the heat transfer from the flame to the polymer. Therefore, an understanding into the mode of action of phosphorus in a polymer during the degradation and the relationship with the nature of a flame retardant is very important for giving a fundamental basis of flame-retardant materials [2]. The flame-retardant mechanism of phosphate methacrylate polymer investigated by cone calorimeter has been reported by Lindsay [2] and Shi [3].

Direct pyrolysis/mass spectrometry (DP-MS) technique involves the introduction of a polymer sample into a mass spectrometer through a direct insertion probe, and the primary components are then ionized and detected immediately giving the total ion current (TIC) chromatograms. This technique is usually used to study the thermal degradation of polymer materials, especially providing structural information of the thermal degradative volatiles [4-6]. The change of phosphorus content during the thermodecomposition of a polymer can be measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using NaOH aqueous solution as a received solution in an oxygen bottle. Little work has been performed to investigate the thermal degradation mechanism of the UV-cured phosphorus-containing multifunctional acrylate films using DP-MS and ICP-AES.

In this paper, two novel flame retardant multifunctional monomers used for UV curing systems tri(acryloyloxyethyl) phosphate (TAEP) and di(acryloyloxyethyl)ethyl phosphate (DAEEP) based on phosphorus oxychloride and hydroxylethyl acrylate were synthesized. The flame retardancy of their UV cured films of the two monomers, was characterized by the limiting oxygen index. The chemical structure changes during the thermodegradation of the films were monitored by in-situ FTIR. The structures of the pyrolysis products and the changes of phosphorus content during the thermodecomposition were determined by DP-MS analysis and ICP-AES, respectively, allowed a detailed schematization of the thermal degradation pathways and on the reactions leading to the formation of charred residues.

Results and Discussion

1. Synthesis and characterization of TAEP and DAEEP



$$POCL_3 + 3\ HEA \longrightarrow (CH_2{=}CH\overset{O}{\overset{\|}{C}}OC_2H_4O)_3\overset{O}{\overset{\|}{P}}$$

TAEP

$$C_2H_5OH + POCL_3 \longrightarrow C_2H_5OPOCL_2$$

$$C_2H_5OPOCL_2 + 2\ HEA \longrightarrow (CH_2{=}CH\overset{O}{\overset{\|}{C}}OC_2H_4O)_2\overset{O}{\overset{\|}{P}}OC_2H_5$$

DAEEP

Fig. 1. Schematic outline of the synthesis of TAEP and DAEEP.

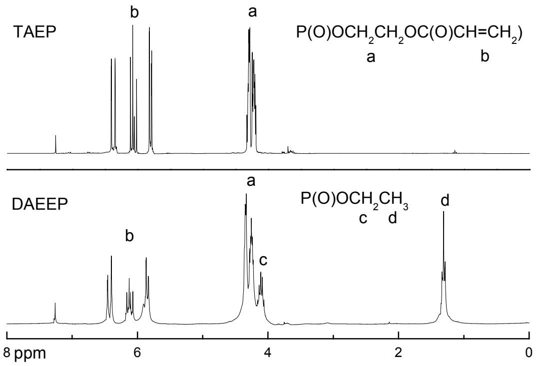


Fig. 2. ^{1}H NMR spectra of TAEP and DAEEP.

The synthesis of TAEP and DAEEP was performed by the reaction of $POCl_3$ and DCEP with HEA, respectively, as schematized in Fig.1. DCEP was prepared by the reaction of ethyl alcohol with $POCl_3$.

The ^{1}H-NMR spectra of TAEP and DAEEP are shown in Fig.2, indicating the expected molecular structures, except for the very small peak at 3.6 ppm corresponding to the (-C**H**$_2$-OH) proton of HEA, which existed in the products as a trace.

2. Thermal degradation behavior

Fig. 3 shows the TGA and the differential weight loss (DTG) curves of the UV cured TAEP and DAEEP films in air. The TGA and DTG data of the films are also are listed in Table 1. It can be seen that two films have the similar thermal behavior, where three characteristic temperature regions are observed. The first region can be assigned to the decomposition of phosphate, whereas the second is due to the thermal pyrolysis of side chains of the acrylate and the formation of char. The third region is attributed to the decomposition of unstable structures in the char [3]. The chemical structural changes during thermodegradation are demonstrated by the following in-situ FTIR and DP-MS measurements.

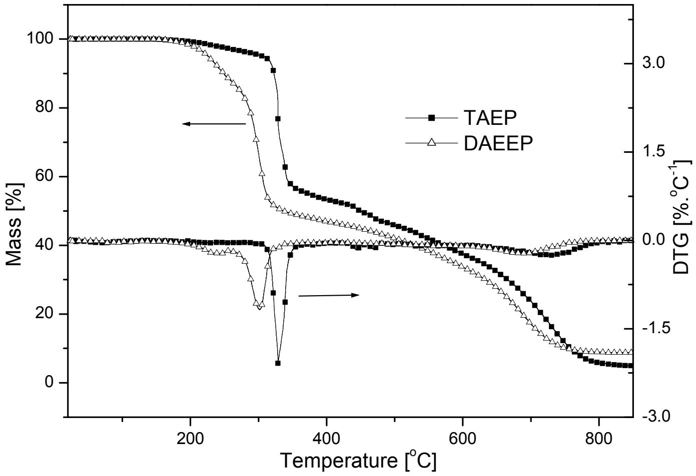


Fig. 3. TGA and DTG curves of the UV cured TAEP and DAEEP films.

Table 1. Thermogravimetric and LOI data of UV cured DAEEP and TAEP.

samples	Specific temperature of Weight loss from TGA (°C)				Char % at	
	5%Loss	Step 1	Step 2	Step 3	800 °C	LOI
DAEEP	226	240	300	686	8.90	29
TAEP	306	-	329	730	5.10	36

As shown in Fig. 3, DAEEP film has more weight loss during the first temperature region and lower onset temperature of the first region than those of TAEP film. The former is because that the degradation products of (P-O-C_2H_5) mainly are C_2H_4 or $(HO)_3POC_2H_5$, which are small molecules and volatilizable [7]. The latter is attributed to its higher phosphorus content [3] and lower crosslinking density [8]. However, TAEP film is more stable than DAEEP film below 700 °C because its higher crosslinking density and lower final char resulting from its lower phosphorus content. Moreover, TAEP has a high LOI value of 36 than 29 of DAEEP though the former has a lower phosphorus content. This is because that the latter is more thermally unstable below 700 °C, and its degradation product (C_2H_4) at a lower temperature is flammable.

3.3. Thermal degradation mechanism

The chemical structure changes during the thermodegradation of DAEEP and TAEP films were monitored by in-situ FTIR. The spectra with the wavenumbers from 600 cm^{-1} to 3100 cm^{-1} are shown in Fig. 4 and Fig. 5.

The main peaks and bands of DAEEP and TAEP films are:

1. 2984 cm^{-1}, v_{as} stretching of CH_3; 2956 cm^{-1}, v_{as} stretching of CH_2 of ester; 2926 cm^{-1}, v_s stretching of CH_3, v_{as} stretching of CH_2 of phosphate; 2952 cm^{-1}, v_s stretching of CH_2; 1450 and 1380 cm^{-1}, the deformation vibration of CH; 843 and 753 cm^{-1}, the rocking vibration of CH;”; 2.1733 cm^{-1}, the stretching vibration of C=O bond; 3.1165 cm^{-1}, the stretching vibration of C-O-C bond; 3. 635, 1410 and 810 cm^{-1}, the stretching vibration of C=C bond; 4. 1038, 980 cm^{-1}, the stretching vibration of P-O-C bond; [9] 4.1268 cm^{-1}, the stretching vibration of P=O bond. [10]

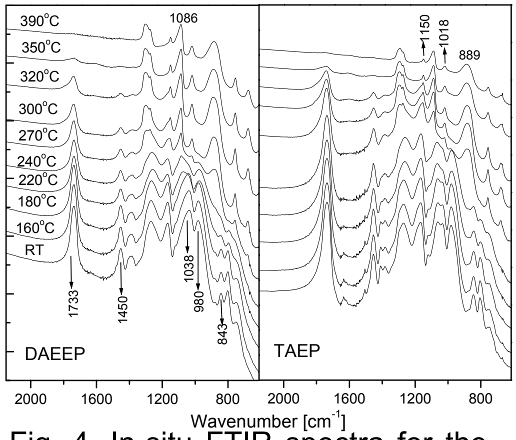


Fig. 4. In-situ FTIR spectra for the degradation process of UV cured TAEP and DAEEP films at 600-2000 cm^{-1}.

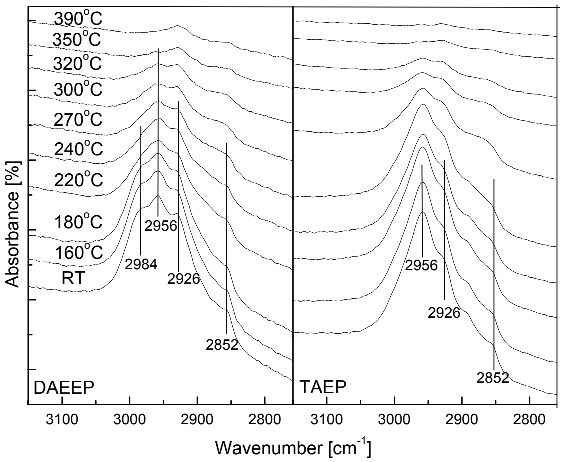


Fig. 5. In-situ FTIR for the degradation process of UV cured DAEEP and TAEP films at 3150-2750 cm^{-1}.

The decomposition of the cured DAEEP and TAEP films can be divided into three parts: the degradation of phosphate groups, the degradation of ester groups and the degradation of alkyl chain. The quickly decreases in relative intensities at 1038 cm^{-1} and 980 cm^{-1} at above 180°C and then disappearance completely at above 270°C (Fig.4) clearly indicate the complete degradation of P-O-C functionality. Furthermore, the peaks at 1150 cm^{-1} and 1018 cm^{-1} assigned to the stretching vibration of P-O-C and PO_2/PO_3 in phosphate-carbon complexes, respectively [11] and the peaks at 1086 cm^{-1} and 889 cm^{-1} assigned to the symmetric and asymmetric stretching vibration of P-O-P band [12,13] appear above 270 °C.

This indicates that some phosphate groups link to each other by sharing one oxygen atom, leading to the formation of poly(phosphoric acid), such as P_2O_5 and P_4O_{10}. Indeed, the presence of poly(phosphoric acid) is demonstrated by the following DP-MS measurements. The decomposition of P-O-C groups is also confirmed by the disappearance of strong peak at 1268 cm^{-1} and the appearance of two new peaks at 1300 cm^{-1} and 1274 cm^{-1} in the FTIR spectra [3]. These imply that the phosphate group deviates from the aliphatic structure and forms poly(phosphoric acid) or re-links to the aromatic structures at the temperatures over 270 ^oC. The formation of aromatic structures is approved by the appearance of two new peaks at 755 cm^{-1} and 679 cm^{-1} [14].

Because there are interferential peaks of phosphate at around 753, 840 and 1380 cm^{-1}, the peaks around 2800-3000 and 1450 cm^{-1} are selected to studying the decomposition of CH bonds. The peak at 2984 cm^{-1} for $–CH_3$ of DAEEP film disappears completely at above 220 ^oC, as shown in Fig. 5. This is due to the fast decomposition of $P-O-C_2H_5$. Furthermore, the peaks at 1635 cm^{-1}, 1410 cm^{-1} and 810 cm^{-1} for C=C bond disappears at above 270 ^oC. This is because the double bonds are thermally cured or volatize as the product of the decomposition of phosphate.

Fig. 6 shows the changes of relative intensities of the peaks at 1733 cm^{-1} for C=O bond and 1450 cm^{-1} for C-H bond in the FTIR spectra of the cured TAEP and DAEEP films with raising the temperature. It is very clear that the absorbance at 1450 cm^{-1} for C-H bond of DAEEP film decreases rapidly with raising the temperature from 150 ^oC to 220 ^oC followed by decreasing further at a lower rate, while the absorbance at 1450 cm^{-1} for TAEP film decreases slowly with raising the temperature from 150 ^oC to 240 ^oC followed by decreasing further at a higher rate. The sharp decrease of C-H bond of DAEEP film can be interpreted as due to the fast decomposition of unstable $P-O-C_2H_5$ at lower temperatures.

From the relative intensities of the absorbance at 1733 cm^{-1} for C=O bond of the films, the same tendency of the degradation with the degradation of C-H bond can be seen. However, there is an obvious different tendency between DAEEP and TAEP films with their degradation of C=O bond and C-H bond, which due to the different crosslinking density resulting from their different functionality. The new peaks for carboxylic acid, ketone, lactone or anhydride resulted from the degradation of phosphate methacrylate oxidation products [3, 15] are not observed. This implies that the degradation process of phosphate acrylate polymer is different from that of phosphate methacrylate, which is further investigated by DP-MS measurements.

Fig. 7 shows the total ion current (TIC) chromatograms by DP-MS for the cured DAEEP and TAEP films. It can be observed that TAEP film has three peaks at 150, 310 and 490 ^oC, whereas DAEEP film has a broad band from 160 ^oC to 280 ^oC except for three peaks at 140, 300 and 470 ^oC. The mass spectra corresponding to the TICs at different temperatures are presented in Fig. 8 and the products identified are given in Table 2. TAEP film at 150 ^oC and DAEEP

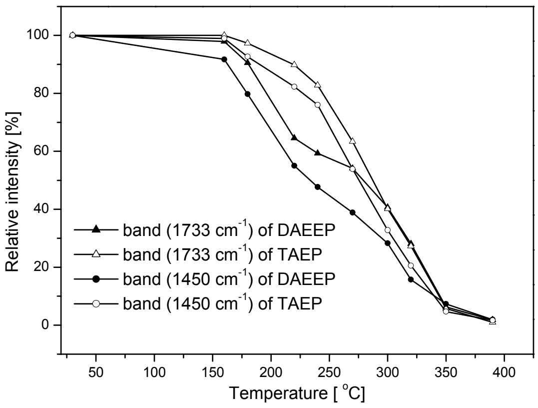


Fig. 6. Relative peak intensity at 1733 cm^{-1} for C=O bond and 1450 cm^{-1} for C-H bond in the FTIR spectra for the UV cured DAEEP and TAEEP films as a function of temperature.

film at 140 °C have the same mass spectra. The peaks at 105.0345 m/z and 59.0510 m/z correspond to C_6H_5CO and $(CH_3)_2C(OH)$ (in Table 2), respectively, which are the decomposition products of photoinitiator Darocur 1173. The remaining peaks in the mass spectra at 39.0244, 51.0239, 77.0387 m/z are assigned to the fragment ions of C_6H_5CO (105.0345), and those at 43.0187, 42.0467, 29.0030, 26.0165 and 17.0040 m/z are attributed to the fragment ions of $(CH_3)_2C(OH)$ (59.0510). The peak at 122.0826 m/z is attributed to the fragment ions of C_6H_5COOH, which was formed by the reaction of C_6H_5CO (105.0345) with OH (17.0040). Therefore, these small peaks in the spectra of both polymers are mostly due to the volatilisation of thephotoinitiator.

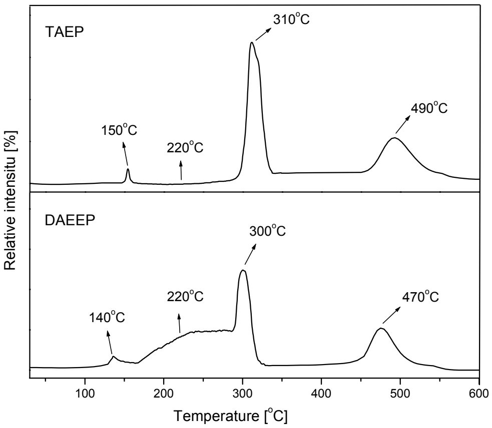


Fig. 7. Total ion current (TIC) curves of the decomposition process of UV cured DAEEP and TAEP films.

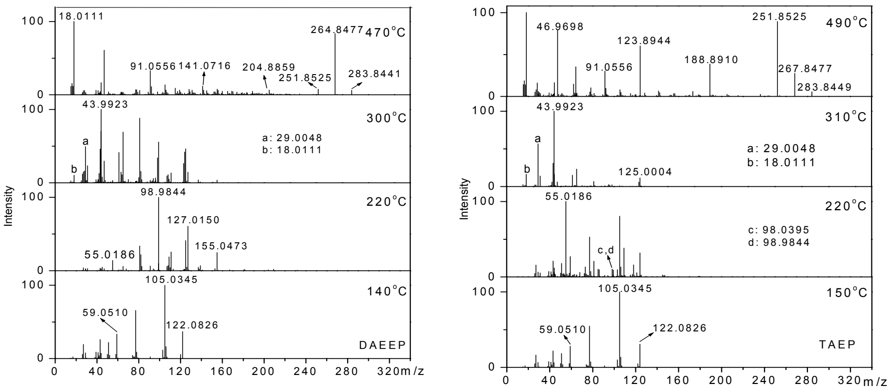


Fig. 8. EI ms spectra of compounds evolved from DAEEP and TAEP films at the different temperatures.

Table 2. Structural assignment in the DP-MS of UV cured DAEEP and TAEP.

m/z	Structure	m/z	Structure
17.0040	OH	105.0345	Ar-C=O
18.0110	H_2O	122.0826	Ar-COOH
29.0048	CHO	123.8944	P_4
43.0207	CH_2=CH-O	125.0004	$C_2H_3OP(OH)_3$
43.9923	CO_2	126.0065	$C_2H_5OP(O)(OH)_2$
46.9715	OP	127.1500	$C_2H_5OP(OH)_3$
55.0186	CH_2=CHC=O	141.0716	$C_{11}H_9$
59.0510	$(CH_3)_2C(OH)$	155.4780	$(C_2H_5O)_2P(OH)_2$
63.9731	HO_2P	172.8969	O_5P_3
64.9797	H_2O_2P	188.8916	O_6P_3
80.9763	H_2O_3P	204.8859	O_7P_3
81.9818	H_3O_3P	235.8989	O_7P_4
82.9906	H_4O_3P	251.8525	O_8P_4
91.5560	Ar-CH_2^+	267.8477	O_9P_4
98.0395	CH_2=CHCOOCH=CH_2	283.8441	$O_{10}P_4$
98.9840	H_4O_4P		

In the mass spectra of DAEEP and TAEP films at 220 °C (Fig.8), the peaks at 98.0395 m/z and 98.9844 m/z appear, corresponding to CH_2=CHCOOCHCH$_2$ and H_4O_4P. However, the peaks at 127.0150 m/z for $C_2H_5OP(OH)_3$ and 155.0473 m/z for $(C_2H_5O)_2P(OH)_2$ appear only in the DAEEP spectrum. The remaining peaks at 43.0207 m/z and 55.0186 m/z are attributed to the fragment ions of CH_2=CHCOOCHCH$_2$ (98.0395), whereas the peaks at 46.9715, 63.9731 and 80.9763 m/z are assigned to the fragment ions of phosphate. Therefore, the products at this temperature range for DAEEP film are mainly resulted from the degradation of phosphate.

The main peaks in the spectrum in TAEP film at 310 °C at 18.0111 m/z for H_2O, 29.0048 m/z for CHO and 43.9923 m/z for CO_2, and a small peak at 125.0004 m/z for $C_2H_3OP(OH)_3$ are observed (Fig.8). However, the peaks at 98.9844 m/z for H_4O_4P, 127.0150 m/z for $C_2H_5OP(OH)_3$, and 155.0473 m/z for $(C_2H_5O)_2P(OH)_2$ are observed in the mass spectrum of DAEEP film at 300 °C except for the same peaks observed in the spectrum of TAEP film. These products are due to the breakage of carbonyl groups and the degradation of the remaining phosphate.

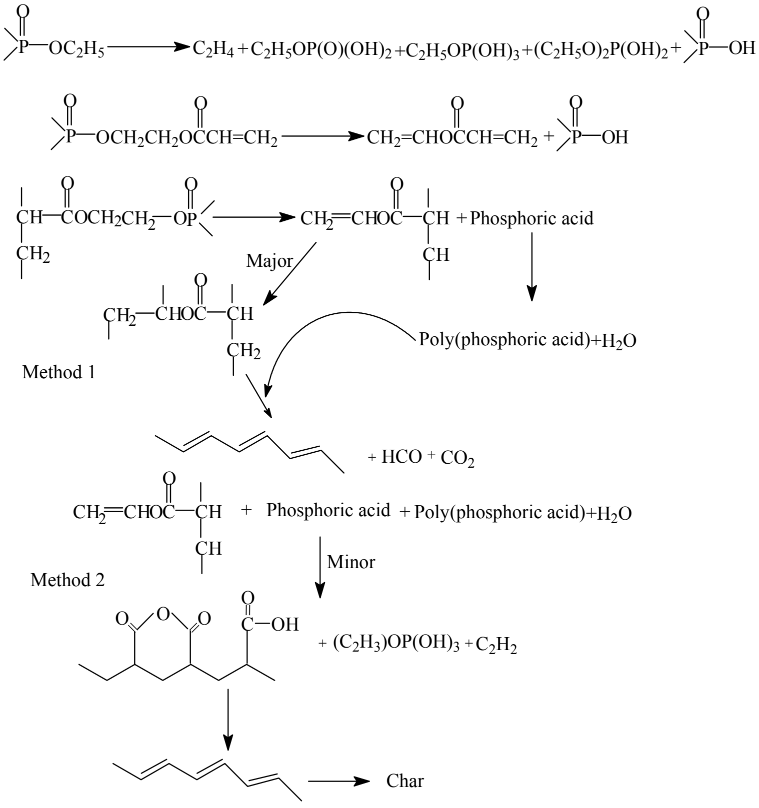


Fig. 9. Schematic outline for he degradation of UV cured DAEEP and TAEP films.

In the mass spectra of DAEEP film (470 °C) and TAEEP film (490 °C) (Fig. 8), the main peaks at 18.0111 m/z for H_2O, 91.0556 m/z for C_7H_7 ,141.0716 m/z for $C_{11}H_9$, 123.8944 m/z for P_4, 204.8859 m/z for O_3P_7, and 283.8441 m/z for $O_{10}P_4$ are observed. The remaining peaks at 46.9698, 62.9656, 63.9727, 172.8969, 188.8910, 235.8589, 251.8525 and 267.8477 m/z can be assigned to the fragment ions of poly(phosphoric acid), and the other peaks at 77.0412, 78.0483 m/z can be attributed to the fragment ions of aromatic structure.

The thermodecomposition of polyacrylate has been reported by Haken JK [16, 17]. The main degradation products were monomers, dimonomers, trimonomers and longer chains. However, these products are absent in the compounds detected by DP-MS in this study. The results from DP-MS and in-situ FTIR spectra of the cured DAEEP and TAEP films suggest the occurrence of different degradation processes, as shown in Fig. 9. From the spectra of both films shown in Fig. 8, it is found that no C_2H_2 (m/z= 26.0176) as a degradation product could be detected by DP-MS at 310 °C. Moreover, the peaks for carboxylic acid, ketone, lactone or anhydride during the degradation of C=O bond are absent in the in-situ FTIR spectra. It is concluded that the C=O bond mainly degrades in the method 1.

From TGA and TIC measurements as described above, the degradation of DAEEP and TAEP films can be divided into three steps. However, the TIC peaks are shifted to lower temperatures compared with the corresponding DTG peak temperatures. This is due to the high pressure in the ms instrument and the similar behavior was observed earlier for other polymers [6, 18]. From 160 °C to 270°C, the degradation is mainly attributed to the fast degradation of phosphate groups. From 270 °C to 350°C, poly(phosphoric acid) is formed, which catalyzes the breakage of carbonyl groups to form polynuclear aromatic structures. When raising the temperature over 500 °C, some unstable structures in the char are decomposed, resulting in the formation of poly(phosphoric acid) and some volatilizable aromatic molecules. The main difference in the degradation of DAEEP and TAEP films is that DAEEP film releases C_2H_4, and $(HO)_3POC_2H_5$ during the first step, greatly resulting in the reduction in flame retardant property of DAEEP film. From LOI value, DAEEP film has a lower LOI of 29 compared with 36 of TAEP film.

Fig. 10 shows the phosphorus contents and the weight loss of phosphorus measured by ICP-AES in DAEEP and TAEP films after treated at 180, 300, 400, 500, and 600°C. It can be seen from Fig. 10 that when raising the temperature from 180 °C to 300 °C, the phosphorus contents of both polymers increase quickly and DAEEP film has a 20 % weight loss of phosphorus, while TAEP film has only 3 % loss. In this temperature range, a large amount of carbon releases as CHO and CO_2, whereas poly(phosphoric acid) is hard to volatilise, resulting in the increase of phosphorus content. However, a small amount of $(HO)_3POC_2H_5$ might release from DAEEP film in the temperature range, resulting in a 20% weight loss of phosphorus. When raising the temperature over 300 °C, the trends of the phosphorus contents and the weight loss of phosphorus in two films are very similar. From 300 to 400 °C, poly(phosphoric acid) catalyzes the breakage of the remaining carbonyl groups to release CO_2 and H_2O, resulting in the increase of phosphorus content. When raising the temperature over 400 °C, the phosphorus content decreases because some phosphorus oxides volatilize, which has been confirmed by the DP-MS measurements.

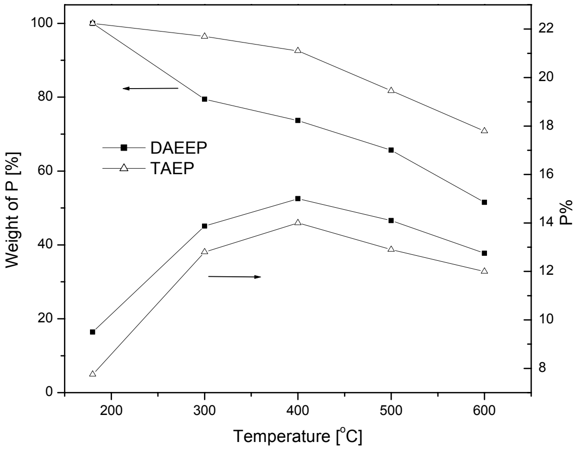


Fig. 10. Phosphorus contents and weight loss of UV cured DAEEP and TAEP films during the degradation.

Conclusions

The results indicate that the degradation of the UV cured DAEEP and TAEP films can be divided into three steps. From 160 °C to 270°C, the degradation is mainly attributed to the fast degradation of phosphate groups. From 270 °C to 350°C, poly(phosphoric acid) is formed, which catalyzes the breakage of carbonyl groups to form polynuclear aromatic structures. When raising the temperature over 500 °C, some unstable structures in the char are decomposed, resulting in the formation of poly(phosphoric acid)s and some volatilizable aromatic molecules.

The main difference in the degradation of DAEEP and TAEP films is that DAEEP film releases C_2H_4, and $(HO)_3POC_2H_5$ during the first step, greatly resulting in the reduction in flame retardant property of DAEEP film. From LOI value, DAEEP film has a lower LOI of 29 compared with 36 of TAEP film.

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