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ORIGINAL ARTICLE

Thermal degradation and evolved gas analysis: A polymeric blend of urea formaldehyde (UF) and epoxy (DGEBA) resin

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Abstract A polymeric blend has been prepared using urea formaldehyde (UF) and epoxy (DGEBA) resin in 1:1 mass ratio. The thermal degradation of UF/epoxy resin blend (UFE) was investigated by using thermogravimetric analyses (TGA), coupled with FTIR and MS. The results of TGA revealed that the pyrolysis process can be divided into three stages: drying process, fast thermal decomposition and cracking of the sample. There were no solid products except ash content for UFE during combustion at high temperature. The total mass loss during pyrolysis at 775 °C is found to be 97.32%, while 54.14% of the original mass was lost in the second stage between 225 °C and 400 °C. It is observed that the activation energy of the second stage degradation during combustion (6.23×10^{-4} J mol^{-1}) is more than that of pyrolysis (5.89×10^{-4} J mol^{-1}). The emissions of CO_2, CO, H_2O, HCN, HNCO, and NH_3 are identified during thermal degradation of UFE.

1. Introduction

Urea-formaldehyde (UF) resin is a major commercial adhesive, especially within the forest product industry. Approximately one million metric tons of UF resin are produced annually and more than 70% of this resin is used by the wood industries as an adhesive for bonding particleboard, medium density fiberboard, hardwood plywood and as a laminating adhesive for bonding due to its several strong positive aspects such as very low cost, non-flammable, very rapid cure rate, and a light color (Girods et al., 2008; Daisy et al., 2011; Pierre et al., 2008). The major disadvantage associated with UF adhesives is their poor water resistance; UF polymer can be depolymerized by the heat and moisture, resulting in continuous emission of formaldehyde (Guru et al., 2006; Zhongkai et al., 2012; Siimer et al., 2003) during production and indoor application. The release of formaldehyde (a suspected carcinogen) from products bonded with urea formaldehyde adhesives is a major concern that has come under close scrutiny by State and Federal Regulatory Agencies (OASA, 1992). The emission of formaldehyde can be reduced by using polymeric blend of UF with some other polymers such as alkyds, acrylics and

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epoxy resins (Boran et al., 2011). Epoxy resins are also used as adhesive and coating materials in various fields because of their good environmental resistance and the ability to bond to wood, metals, plastics, ceramics, and concrete (Jintao et al., 2011a,b; Rosu et al., 2011). The most common epoxy resin is the diglycidyl ether of bisphenol A (DGEBA), which is not commonly used in wood industries because of its higher cost compared to other adhesives. The segregation of minor component such as flow agent, in an industrial coil coating based on epoxy resins cross-linked with UF resin and applied to a hot dipped galvanized steel substrate, has been investigated (John et al., 2001). Furthermore, the increasing focus on the health and environmental compatibility of house hold furniture or coating materials has drawn the attention to toxic and corrosive gases evolved during their thermal degradation. The effects of evolved gases are often more harmful than those of fire. Eighty-five percent of deaths in a fire are due to inhaling evolved toxic gases (Kok et al., 2004). Thermogravimetry (TG) is widely used in polymer chemistry due to its ability to evaluate thermal resistant and determine the quantity of components in polymers. Moreover, in recent years, multi-purpose thermal analysis coupled with gas analyzers (TG–FTIR, TG–MS) has become very popular (Marisa et al., 2011; Sikorska and yszczek, 2004; Anca et al., 2010) that can be used to carry out further analysis of evolved gases during thermal treatment of polymers, which in turn facilitates estimation of sample structure and composition. The evolved gas analysis method has been used in the different research fields; in our previous study we have used the TG–FTIR–MS technique for evolved gas analysis of thiourea formaldehyde polymer and tobacco bidi powder (Tansir and Alshehri, 2012a, b). However, evolved gas analysis during thermal degradation of UF/DGEBA blend has been seldom studied. So it is urgent to investigate deeply the evolved gas analysis during pyrolysis or combustion process of UFE blends. In the present study, a polymeric blend has been prepared using urea formaldehyde and epoxy resin in 1:1 mass ratio and the thermal properties and evolved gas analysis of this polymeric blend have been carried during pyrolysis and combustion process. The mass loss of the sample was recorded by TG, and the volatile products were directly introduced into the gas cell for FTIR and MS, and the changes of the products with the temperature rising were monitored by the FTIR and MS spectrometry.

2. Experiments

2.1. Materials

Epoxy resin (diglycidyl ether of bisphenol A, DGEBA) with epoxy equivalent 180 (Ciba Speciality Chemicals, India) was used. Urea-formaldehyde resin was synthesized as follows: in a three necked round bottom flask 6 g of urea was dissolved in 10 ml of distilled water and mixed with 15 ml formaldehyde. The pH of the solution was maintained at 8.5 using aqueous NaOH solution. The mixture was stirred at 80 °C for 5 h; resulting transparent viscous product was washed with diluted HCl solution, distilled water, ethanol and acetone and dried in a vacuum oven under reduced pressure at 60 °C for 10 h (Nishat et al., 2006). UFE was prepared by mixing DGEBA and UF resin in 1:1 mass ratio with continuous stirring at room temperature for 20 min as shown in Scheme 1. The cured material UFE were crushed and pulverized into a size of lower than 0.2 mm for further analysis.

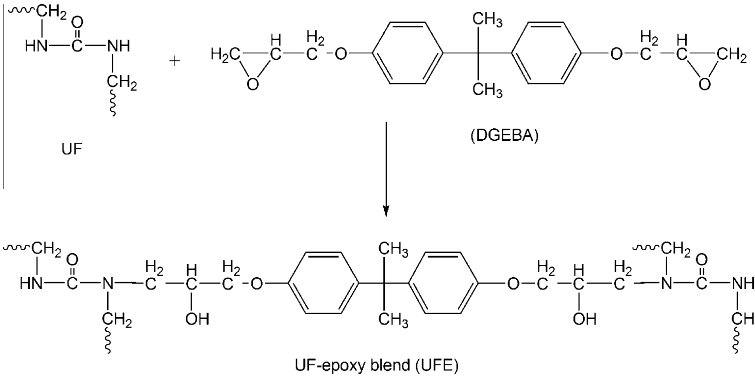
2.2. Method

The TG–FTIR–MS experiments were performed using simultaneous thermogravimetry (STD 600 TA Instrument) coupled with FTIR (Bruker Tensor 27) and ThermoStar quadrupole mass spectrometer. FTIR measurements were carried out with a high sensitivity MCT detector in a specifically developed low-volume gas cell with a 123 mm path length. Helium and oxygen (99.99 %) was used as carrier gas with a flow rate of 100 ml/min during pyrolysis and combustion, respectively. The coupling system between TG, FTIR and MS was heated at 200 °C to prevent condensation of evolved gases. Approximately 10 mg sample was heated from room temperature to 800 °C in TG equipment with heating rate of 10, 20, 30, and 50 °C/min. It was found that the intensity of the thermal decomposition and the emission of gaseous products were slowed down at lower heating rates, but similar components of gaseous products and evolution with temperature at different heating rates were observed. So the heating rate of 30 °C/min was adopted for thermal decomposition of UFE. During TG/FTIR/MS experiments, spectral data are repeatedly collected in the form of interferograms and then processed to build up a Grame Schmidt reconstruction, each point of which corresponds to the total IR absorbance of the evolved components in the range of 4000–500 cm^{-1}. The mass spectrometer was operated at 70 eV electron energy. A scan of the m/z was carried out from 1 to 100 amu to determine which m/z has to be followed during the TG experiments. The single ion curves close to the noise level were omitted. Finally, only the intensities of 22 selected ions (m/z = 12, 14, 15, 16, 17, 18, 20, 26, 27, 28, 30, 31, 32, 40, 42, 43, 44, 59, 60, 64, 76, and 78) were monitored with the thermogravimetric parameters.

3. Results and discussion

3.1. TG data analysis

The TG/DTG profiles for UFE as a function of temperature at the heating rate of 30 °C min^{-1} are given in Figs. 1 and 2 during combustion and pyrolysis, respectively. The combustion process of UFE can be subdivided into four stages based on the DTG profile. The first stage shows a mass loss of 12.47% for drying the sample between 25 and 225 °C; surface moisture and inherent moisture are emitted in this stage (Jingai et al., 2008). The second stage is fast thermal decomposition for UFE between 200 and 400 °C; the maximum mass loss (about 49.93 wt.% of the total weight) occurs in this stage. The third stage shows 27.90 wt.% of the total mass loss due to further decomposition of polymeric blend. The last stage has a wide temperature range, from 575 °C to the end of this experiment (775 °C). There are no other solid products except ash content for UFE combustion at high temperature in oxidizing atmosphere. During the combustion of UFE, there are four peaks of the DTG curve (mass loss rate) at 186.59, 289.17, 517.29 and 632.84 °C in first, second third and last stage degradation, respectively. The maximum mass loss rate of 19.27%/min occurred at 289.17 °C. The thermogram of



Scheme 1

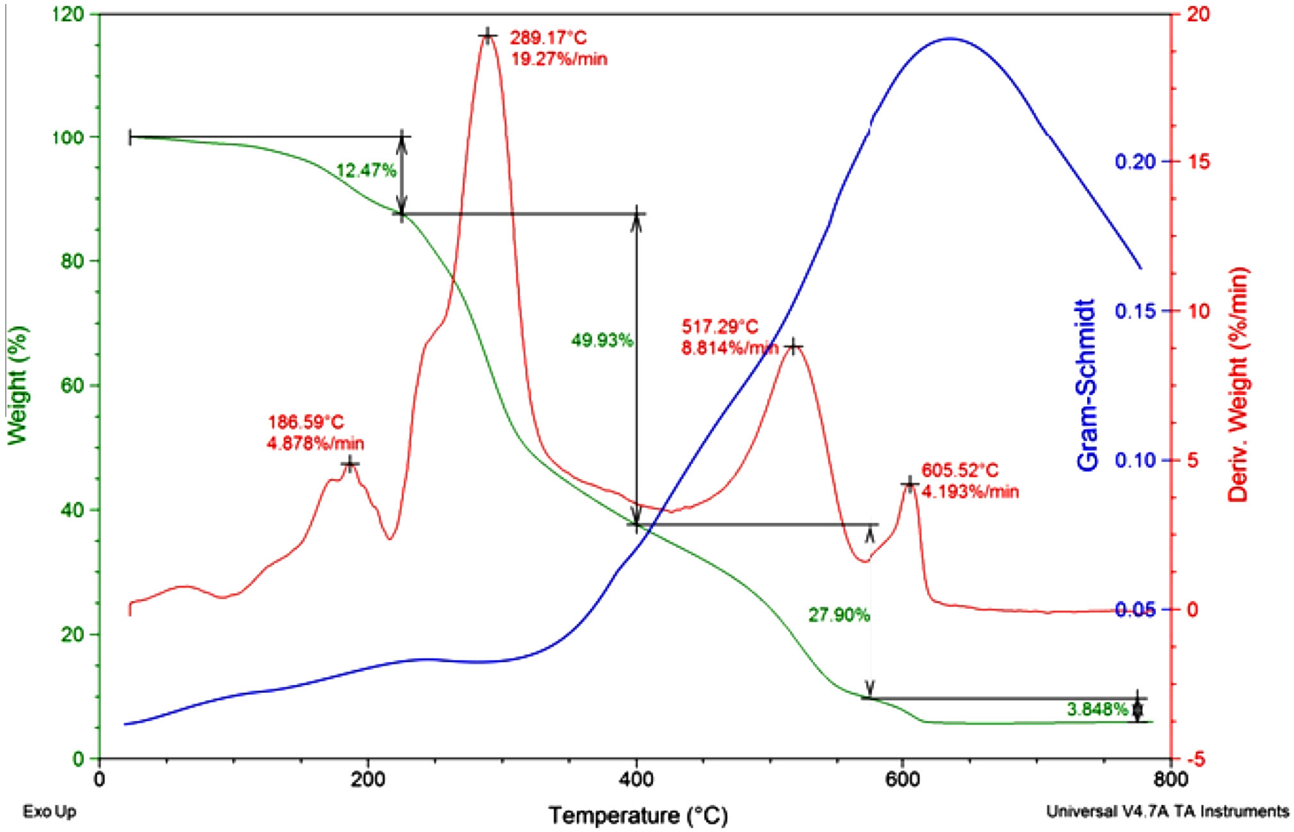


Figure 1 Tg/DTG of UFE during combustion.

UFE during pyrolysis is lightly similar to combustion up to 400 °C, but it is quite different at higher temperature. The pyrolysis process can be divided into three stages: drying stage up to 225 °C, main pyrolysis stage between 200 and 400 °C and cracking of polymer between 400 and 775 °C. The first mass loss of 15.15% between room temperature and 225 °C corresponds to the vaporization of moisture and desorption of water. In the second stage, 54.14% mass loss of the total mass of the sample was found. The last stage during the pyrolysis of UFE is further cracking process of the polymer in a wide temperature range, from 400 to 775 °C; about 28.22% mass of the total mass loss at a lower rate in this stage. There are four peaks of the DTG curve (mass loss rate) one in the first, two in the second and one in the third stage. The maximum mass loss rate occurred at 300.65 °C (16.43%/min) in the second stage.

3.2. Pyrolysis and combustion kinetics calculation

The first order reaction based Arrhenius theory is commonly assumed in the kinetic analysis during combustion and pyrolysis (Rath and Staudinger, 2001).

$$k = A\exp\left(-\frac{E}{RT}\right) \qquad (1)$$

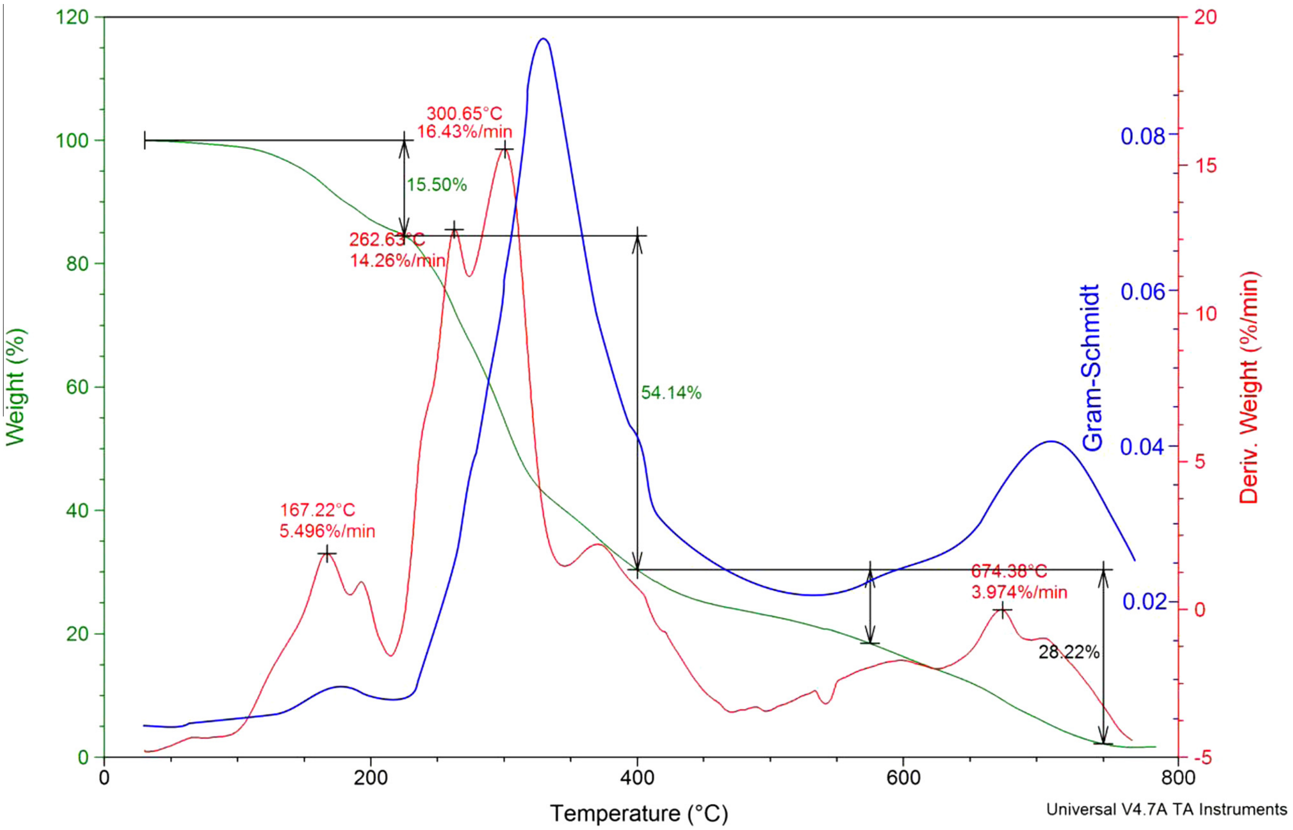


Figure 2 Tg/DTG of UFE during pyrolysis.

where k is constant of reaction rate, T is thermodynamic temperature (K), R is universal gas constant ($R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$), E is activation energy and A is a pre-exponential factor. The rate of decomposition may be expressed by:

$$\frac{d\alpha}{dt} = k(1 - x) \tag{2}$$

where α is mass loss fraction and defined as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f}$$

where m_0 is the initial mass sample, m_t is mass sample at the time during thermal degradation and m_f is the final mass when the experiment is finished. Taking into account that temperature is a function of time and increases with constant heating rate β the following expression derives:

$$T = \beta t + T_0 \tag{3}$$

Differentiating the above correlation, it derives:

$$dT = \beta dt$$

Eq. (2) could be written as

$$\frac{d\alpha}{1 - \alpha} = \frac{k}{\beta} dT \tag{4}$$

An integration function of the above Eq. (4) is shown below

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{dt} = \frac{A}{\beta} \int_0^{t} \exp\left(-\frac{E}{RT}\right) dT \tag{5}$$

where $g(\alpha) = -\ln(1-\alpha)$

Eq. (5) is integrated by using the Caots–Redfern method:

$$\ln\frac{g(\alpha)}{T^2} = \ln\left(\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right]\right) - \frac{E}{RT} \tag{6}$$

where $g(\alpha)$ is the kinetic mechanism function in integral form. As the term of $2RT/E$ can be neglected since it is much less than 1, Eq. (6) could be simplified as

$$\ln\frac{g(\alpha)}{T^2} = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{R}\frac{1}{T} \tag{7}$$

The term of $\ln(g(\alpha)/T^2)$ varies linearly with $1/T$ at a slope $-E/R$. Meanwhile, the intercept of the line with y-axis is related to the pre-exponential factor A. Both the activation energy E and pre-exponential factor A can be determined by the slope and intercept of the line and presented in Table 1. It is observed that the activation energy of the first step during combustion is little more than that of pyrolysis in the first step while the activation energy in the second step for fixed carbon combustion is larger than the first step for volatile material combustion.

3.3. FTIR measurement

The FTIR absorption intensity of evolved gases detected by the spectrometer is depicted by Gram–Schmidt thermogram, plotted against mass and derivative mass in Figs. 1 and 2. The detector signal has been plotted as a function of sample temperature and qualitatively approximates DTG curves

Table 1 Kinetic parameters (activation energy and Arrhenius pre-exponential factors) and coefficient of determination for the thermal degradation of UFE blend.

Temperature (°C)	Activation energy (J mol^{-1})	Pre-exponential factor	R^2
Pyrolysis in second stage (300.65)	5.89×10^{-4}	5.62E + 00	0.945
Combustion in second stage(289.17)	6.23×10^{-4}	4.36E + 01	0.969
Combustion in third stage (517.29)	4.42×10^{-4}	3.25E + 02	0.942

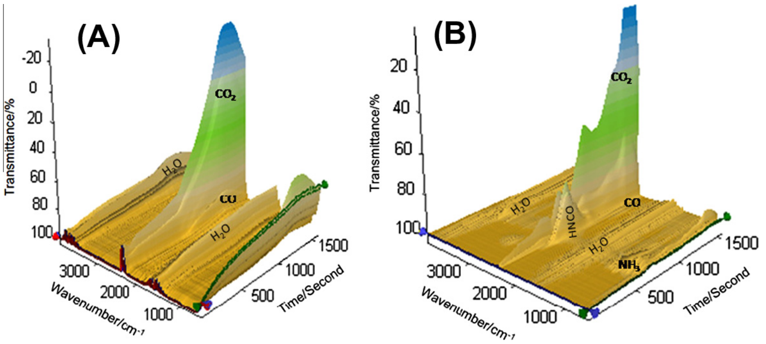


Figure 3 3D FTIR plot during thermal degradation of UFE (A) combustion (B) pyrolysis.

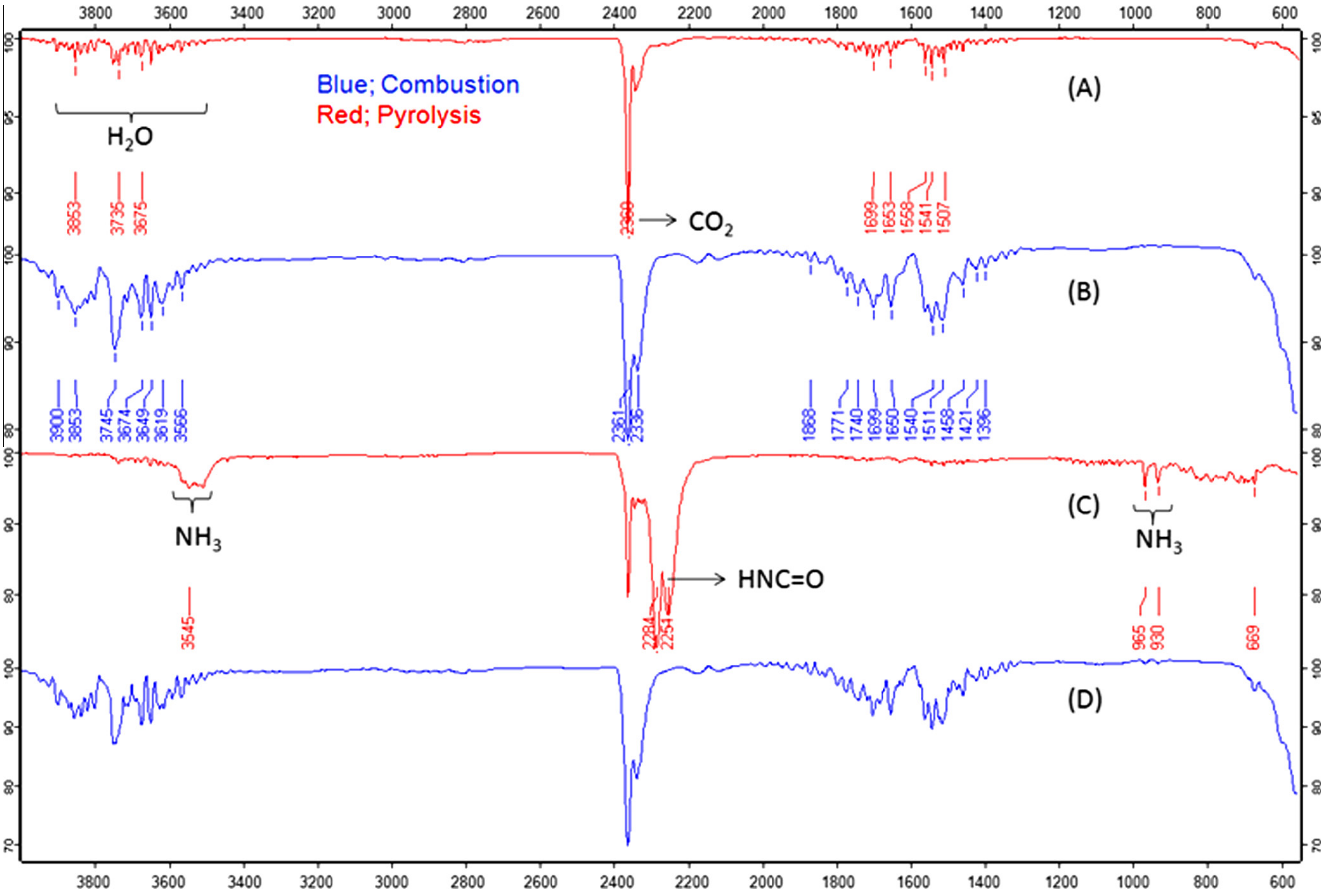


Figure 4 Spectrograms during pyrolysis and combustion of UFE (A) pyrolysis at 200 °C (B) combustion at 200 °C (C) pyrolysis at 300 °C (D) combustion at 300 °C.

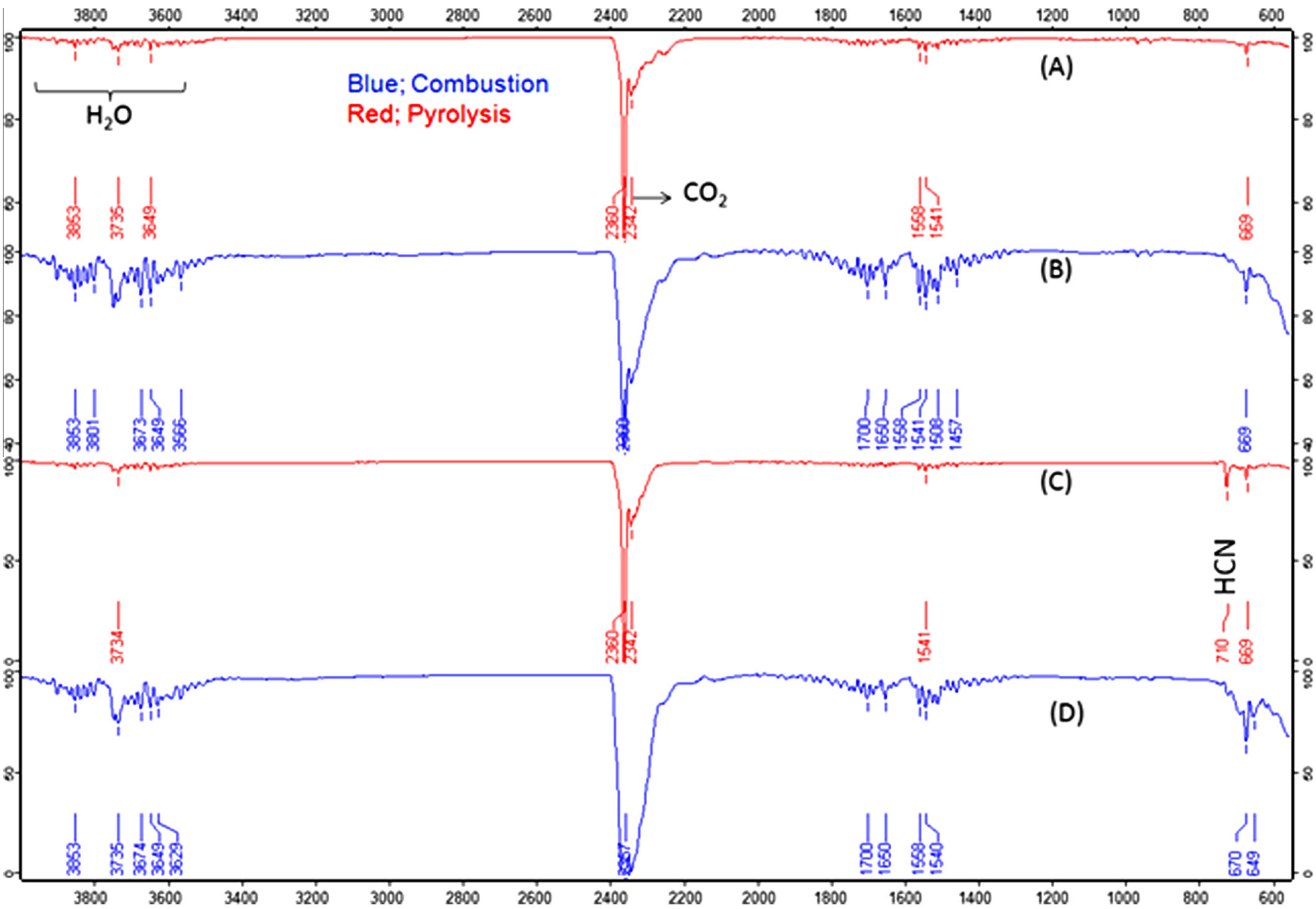


Figure 5 Spectrograms during pyrolysis and combustion of UFE (A) pyrolysis at 400 °C (B) combustion at 400 °C (C) pyrolysis at 700 °C (D) combustion at 700 °C.

recorded during the TG experiments performed under different controlled conditions. It should be noted that the peaks in the Gram–Schmidt plot are shifted to higher temperature than the corresponding DTG curve; this is due to the delay time between the gas generation and its detection in the FTIR equipment. A single peak during the combustion of UFE observed in the Gram–Schmidt is big, suggesting that the amount of the evolved gases is large in all the three stages and with high infrared extinction coefficients. While the Gram–Schmidt plot during the pyrolysis shows three peaks, the first peak in small intensity suggests that the amount of evolved gas in this stage is very low and with low infrared extinction coefficients.

Fig. 3 shows 3D FTIR spectra for the gases produced from thermal degradation and Figs. 4 and 5 show the spectrograms at different temperatures during pyrolysis and combustion of UFE. The main evolved products in the first degradation stage at 200 °C are identified as water (H_2O) and carbon dioxide (CO_2) during combustion and pyrolysis. The absorption bands between 2331 and 2361 cm^{-1} are attributed to CO_2 (Mocanu et al., 2010). Other substances such as water between 3550 and 3800 cm^{-1} are also detected in the first stage during pyrolysis and combustion. In the pyrolysis process during the second stage between 225 and 400 °C, a very broad absorption band between 2251 and 2284 cm^{-1} is due to the main nitrogen-containing product (HCNO) emission. While during combustion HCNO is not emitted out, other two sharp bands with low intensity at 930 and 935 cm^{-1} are attributed to N–H stretching vibration of ammonia during pyrolysis with these bands also absent in the thermal degradation of UFE during combustion between 225 and 400 °C (Ahamad and Alshehri, 2011).The maximum emission of NH_3 and HNCO is found around 400 °C during pyrolysis and decreases slowly after 550 °C. The emission of CO during combustion was confirmed by the appearance of very small bands at 2185 cm^{-1} during the thermal degradation at 400 °C, while during pyrolysis the concentration of CO is very low. In the second stage during combustion, the intensity of bands between 14,001,700 cm^{-1} and 3450–3800 cm^{-1} is increased suddenly due to O–H bonds that are caused by water release, but in this region also attributed to O–H bonds of the alcoholic group. In the last stage during the pyrolysis of UFE, HCN is found as a nitrogen containing product at high temperature between 500 and 775 °C and was confirmed by the appearance of sharp bands at 710 cm^{-1}. Taking into account the above mentioned results, it is possible to postulate that the main volatile products obtained are CO_2, CO HCN, NH_3, HNCO, H_2O during thermal degradation of UFE.

3.4. MS measurement

The exact composition of the UFE degradation products was determined by thermogravimetry coupled to a Mass Spectrom-

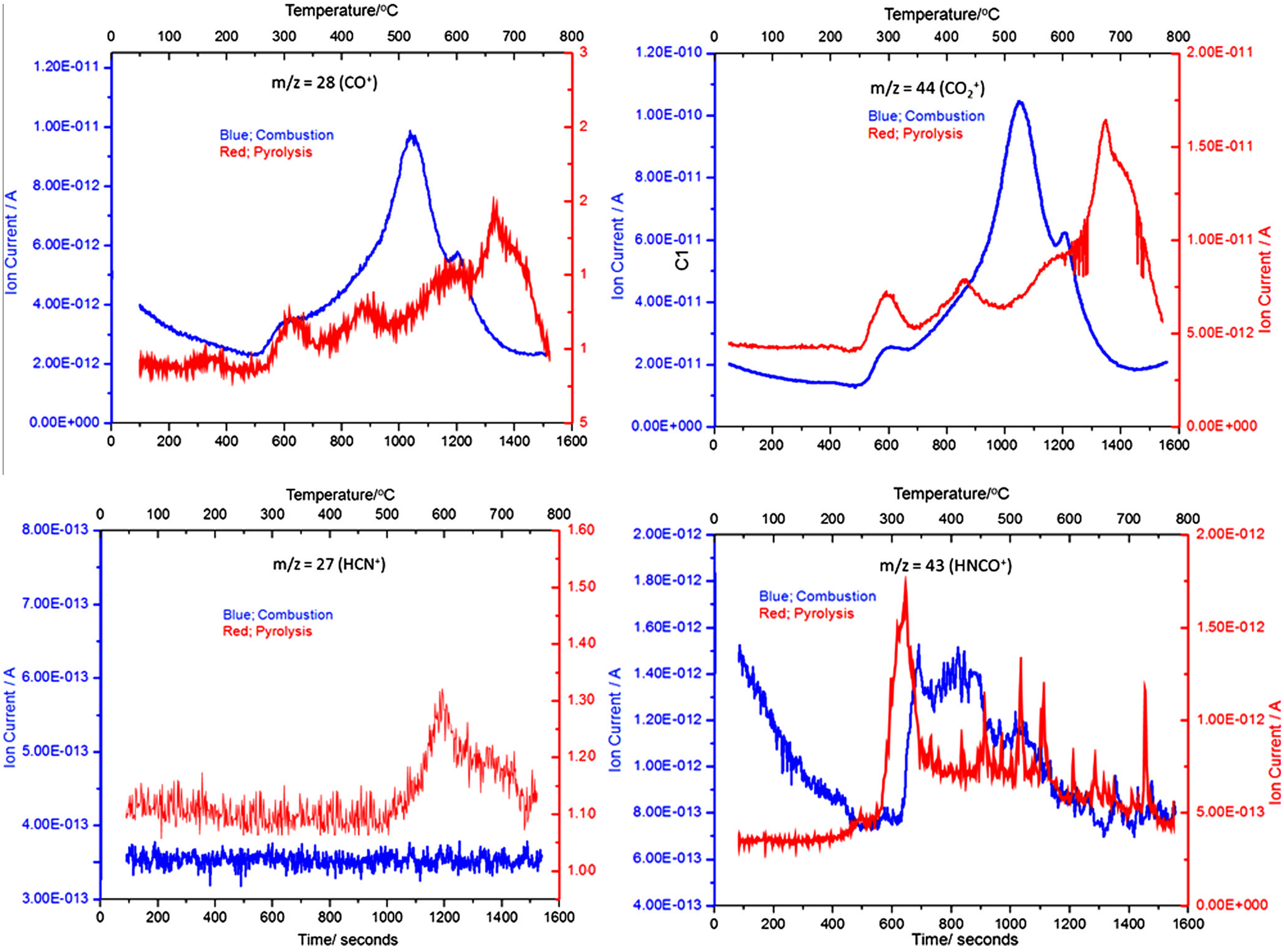


Figure 6 Single ion current curves during combustion and pyrolysis.

eter. The release of carbon dioxide during pyrolysis and combustion was confirmed by a fragment at *m*/*z* 44 (CO_2^+). The maximum amount of CO_2 occurs at 550 °C and 700 °C during combustion and pyrolysis, respectively as shown in Fig. 6a. It is also supported by FTIR data where carbon dioxide has been observed in all the three stages, but it is much more pronounced in the last step of the degradation during pyrolysis. The CO_2^+ ion current is very low during pyrolysis than combustion suggesting that the amount of evolved CO_2 is very low and with low ion current.

The Single Ion Current at *m*/*z* 28 CO is shown in Fig. 6b. The intensity of CO is very low during thermal degradation of UFE. The peaks at *m*/*z* 27 which appear with strong intensity in the last degradation step can be assigned to HCN (Xuguang et al., 2007). These fragments start to appear in the second degradation step (from 400 °C) with low intensity, and continue to appear with high intensity in the last degradation step during pyrolysis. HNCO can be indentified ($m/z = 43$) in the second degradation step during pyrolysis (Xuebin et al., 2010), while during combustion HCN and HNCO can be oxidized into other volatile gases such as CO_2 and H_2O as shown in below equations:

$HCN + O_2 \rightarrow CO_2 + H_2O + NO_n$

$HNCO + O_2 \rightarrow CO_2 + H_2O + NO_n$

The comparison between the results obtained with the TG–FTIR and the TG–MS shows some differences. For all profiles, fewer fluctuations appear on the curves of FTIR than on TG–MS ones. This is probably due to the optical cell of FTIR, which tends to average the signals because of its volume. In addition, a shift of curves appears between the two techniques. It can be explained by the different residence time induced by the experimental devices. Although some interesting results have been provided by the FTIR analysis, this technique has two main drawbacks. First, as observed on 3D plot of the FTIR spectra, a strong IR signal caused by absorption of H_2O appears during the pyrolysis, which can hide the detection of some gases. Secondly, there were gases released during the thermal decomposition, which were undetectable with FTIR such as H_2 and Cl_2. Considering the details each gaseous compound, we can note that for H_2O and CO_2, the two profiles show the same tendencies. Thus, the FTIR analysis and the mass spectrometry have advantages and disadvantages. However, using the information provided by each of them, it is possible to have an identification of the gases emitted by degradation of UF and epoxy blend during pyrolysis and combustion.

4. Conclusion

The aim of this work was to compare the thermal degradation of UF and epoxy blend (UFE) during pyrolysis and combustion. The result of TG–FTIR–MS revealed that the main volatile products obtained were CO_2, CO, HCN, NH_3, HNCO, H_2O during pyrolysis and during combustion. These two techniques are therefore complementary since they can refine the identification of gases. A major drawback of UF resin is the continuous emission of formaldehyde during production or by the heat and moisture. In this study, we found that there is no emission of formaldehyde found during the thermal treatment of UFE polymeric blend. The results revealed that the properties of formaldehyde can be improved using other polymeric materials and can be used for indoor or outdoor application in wood industries.

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