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Lin, Han Chien
Department of Forest Products Science, College of Agriculture, Naationa Chiayi University

Ohuchi, Takeshi
Laboratory of Wood Material Technology, Division of Biomaterial Science, Department of Forest and Forest Products Sciences, Faculty of Agriculture, Kyushu University

Murase, Yasuhide
Laboratory of Wood Material Technology, Division of Biomaterial Science, Department of Forest and Forest Products Sciences, Faculty of Agriculture, Kyushu University

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Estimating Thermal Behavior and Analyzing Evolved Species of Adhesives through Thermogravimetric Analysis combined with Spectrometric Techniques

Han Chien LIN[1], Takeshi OHUCHI and Yasuhide MURASE*

Laboratory of Wood Material Technology, Division of Biomaterial Science,
Department of Forest and Forest Products Sciences, Faculty of
Agriculture, Kyushu University, Fukuoka 812–8581, Japan

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Four types of commercial adhesives, urea formaldehyde resin adhesives (UF), melamine–urea formaldehyde copolymer resin adhesives (MUF), phenol formaldehyde resin adhesives (PF) and diphenylmethane diisocyanate adhesives (MDI) were studied, by first using thermogravimetric analysis (TGA) alone, and then by using thermogravimetric analysis with infrared spectrometry (TGA–IR). Results obtained from the TGA tests found that MDI exhibited the highest initial decomposition at a temperature of 297°C and better overall thermo–stability than the other types of adhesives. PF and MDI provided a better yield of char at about 24.88 and 20.61 wt%, respectively, at 850°C. This showed that their thermal behavior was better than that of UF (5.40 wt%) or MUF (6.99 wt%). The IR response of all adhesives in the TGA–IR tests showed that the absorbance of UF, MUF and MDI was higher than that of PF; this indicated that the concentration of evolved species of PF was less than that of MDI, and less than that of the urea copolymer series adhesives, UF and MUF. It has been suggested that PF is the most environmentally friendly adhesive, because it has the least environmental impact when used in many industrial and domestic applications, such as for structural members in furniture or architecture. These results, when compared to the molecular structures of the adhesives, enabled us to point out the kinds of evolved species (functional bases or the change in molecular structures) for referencing the thermo–degradation processes of the adhesives. Using TGA–IR, to analyze the thermal behavior of 4 types of adhesives, in combination with TGA analysis, has led to useful results, involving the identification of pyrolysis products.

INTRODUCTION

In the event of a fire, smoke inhalation usually presents the gravest danger for survivors. This is because, those who find themselves in a burning building, may experience post–exposure pulmonary (lung) complications, which can lead to subsequent injury or death from the inhalation of emitted gases and complications from thermal burns (Baker, 1991). Combustion toxicology embraces the nature, severity and the time course of adverse effects produced from exposure to fire–generated toxic species (Hartzell, 1996).

The thermal behavior (pyrolysis, thermal decomposition or combustion) of every combustible material or product produces a toxic smoke atmosphere. This toxic smoke atmosphere, in sufficiently high concentrations, presents a hazard to exposed animals and humans. These hazards include impaired vision, due to eye irritants; narcosis from

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[1] Department of Forest Products Science, College of Agriculture, National Chiayi University, Chiayi, Taiwan, ROC.

* Corresponding author (E-mail: ymurase@agr.kyushu–u.ac.jp)

inhalation of asphyxiates; and irritation to the upper or lower respiratory tracts. These effects often occur simultaneously, and contribute to physical incapacitation, loss of motor coordination, faulty judgment, disorientation, restricted vision and panic (Hartzell, 1996).

Currently, studies concerned with so called "eco–materials" and the environment, are increasingly focused on the effective or functional use of natural resources, the recycling of industrial wastes and the development of new environmentally friendly materials (Okuma, 1998). Methods, to recycle discarded materials, are encouraged (renewable resources), including the development of new wood–based materials in accordance with the principle of cascade utilization (Akiyama, 1998; Kuwahara, 1996). However, the structural members of furniture or buildings are generally manufactured using extra–strength adhesives, which are widely utilized in many industrial and domestic applications. Such discarded materials are extremely difficult to recycle and use as a raw material, because they do not possess a critical bonding quality, as do virgin wood chips or particles (Kobayashi *et al.*, 2000; Shibuwaza, 2000). In many cases the final treatment, for this type of waste, is to remove it from service and burn it (Jang, 1997). Therefore, it is necessary to determine the thermal behavior of these organic adhesives during combustion, including such things as, pyrolysis temperature, compounds emitted, total amount of volatiles evolved and the amount of char formed (Kercher *et al.*, 2001).

In order to provide an understanding of the fundamental thermal behavior of these adhesives, this study comprised two categories of examination. The first was connected to the study of thermal decomposition, by examining the effectiveness of the pyrolysis of adhesives, using thermogravimetric analysis (TGA). The second applied thermogravimetric analysis with infrared spectrometry (TGA–IR), to monitor the effectiveness, on an analytical scale, of the four adhesives and also to examine the emissions of certain compounds in each particular analysis. The commercial adhesives tested included urea formaldehyde resin adhesives (UF), melamine–urea formaldehyde copolymer resin adhesives (MUF), phenol formaldehyde resin adhesives (PF) and diphenylmethane diisocyanate adhesives (MDI). Our goal in this research was to acquire fundamental knowledge of the thermal behavior of adhesives, while at the same time obtaining an air pollution reference for gas emissions.

MATERIALS AND METHODS

Adhesives

The commercial adhesives used in this study are summarized as follows:

a. Urea formaldehyde resin adhesives (UF Resin–180, UF);
b. Melamine–urea formaldehyde copolymer resin adhesives (MUF PB–1230, MUF);
c. Phenol formaldehyde resin adhesives (PF PB–1310, PF);
d. Diphenylmethane diisocyanate adhesives (MDI PB–1605, MDI).

These adhesives were provided by Oshika Shinko Co. Ltd., Fukuoka. The percentage of resin solids obtained from the adhesives was 61.2 (UF), 60.3 (MUF), 45.5 (PF) and 96.3 (MDI), after they had been placed into convection ovens at 105°C for over 3 h. These air–dried UF, MUF, PF and MDI specimens were individually tested, using thermogravimetric analysis, to determine the thermal behavior of adhesives; thermogravimetric analysis, with infrared spectrometry, was used to examine the emissions of certain compounds (evolved species) during the pyrolysis of the adhesives.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a common technique for measuring the weight change of a material as a function of temperature. Throughout this research project, TGA was carried out using a Perkin–Elmer TGA 1, fully supported by computer–controlled software options, from Perkin–Elmer Thermal Analysis Systems, for control and data handling. The samples, approximately 5.0–10.0 mg in weight, were placed into an open experimental sample pan, and suspended from a sensitive microbalance. A furnace surrounded the sample to provide accurate heating from 50 to 850 °C, while the measurement was taking place. In order to isolate the pyrolysis step, considered the most important step in the burning process for materials or products, a nitrogen atmosphere was selected for TGA analysis (Hsu *et al.*, 2000). All runs were purged in nitrogen atmosphere, at a flow rate of 50 ml/min, with a heating rate of 20 °C/min. The thermal behavior for the four types of adhesives was then tested.

Thermogravimetric analysis with Infrared spectrometry (TGA–IR)

TGA, described in the previous section, is a quantitative technique, which does not identify evolved compounds. To understand the evolved species produced by the pyrolysis of the four types of adhesives, analysis was carried out using a TGA (Perkin–Elmer Pyris 7 TGA model), linked to a secondary method of analysis, Fourier–Transform Infrared Spectroscopy (using a Perkin–Elmer FTIR), which was able to identify the evolved species during the TGA measurements (Statheropoulos, 2000). The TGA and FTIR (TGA–IR) were connected using a transfer line with a continuous scanner in a gaseous cell. The Infrared spectrometric (IR) response data was recorded by a personal computer. The time–based software obtained and analyzed the evolved species as they occurred. The samples, weighing about 5.0 mg., were placed in an open pan and suspended from a sensitive microbalance in the Pyris 7 TGA model. The conditions were set the same as for the Perkin–Elmer TGA 1, described above, for heating and nitrogen flow rates. The evolved species analysis was performed on the TGA–IR. However, the IR response obtained for various evolved species using the TGA–IR appeared about 10 sec later, when compared to the TGA traces. In order to discuss the criteria and limitations of both TGA–IR and TGA for each particular analysis, and to ensure accurate results, it was necessary to carefully study and compare the results obtained between the pyrolysis temperature (obtained from TGA) and the decomposition time of the evolved species from the IR response (obtained from TGA–IR).

RESULTS AND DISCUSSION

Thermal decomposition of adhesives

TGA is an established technique, used in the quantification of weight changes within a material, as a function of temperature or time. To comprehend the thermal behavior (pyrolysis, thermal decomposition) of the four types of adhesives, the adhesive specimens were measured by TGA, after being air–dried at ambient temperatures. Decomposition profiles were obtained while heating at a rate of 20 °C/min in nitrogen, between 50 °C (initial temperature) and 850 °C (end temperature). The relationships of TGA and DTG curves between temperature and weight loss, and the derivative weight for each adhesive specimen, UF, MUF, PF and MDI, are shown in Fig. 1.

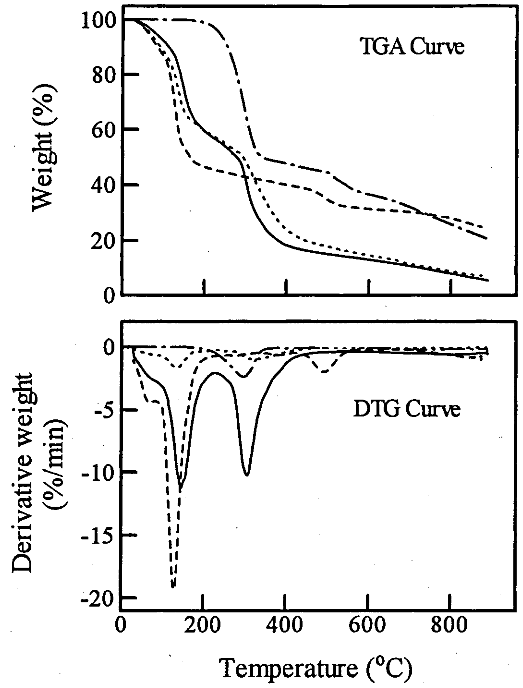


Fig. 1. TGA and DTG curves for 4 types of adhesives (UF, MUF, PF and MDI) in nitrogen at 20 °C/min.
Symbols: —— : UF, ·······: MUF, - - -: PF, -·-: MDI.
Notes: Urea formaldehyde resin adhesives (UF), Melamine-urea formaldehyde copolymer resin adhesives (MUF), Phenol formaldehyde resin adhesives (PF), Diphenylmethane diisocyanate adhesives (MDI).

As expected, the four types of adhesives typically showed gradual weight loss. The thermogram, resulting from the analysis of UF (solid line) and MUF (dotted line), showed that there were two subtle changes (shoulders) at temperatures of 50 to 390 °C, suggesting that both had almost identical initial (the first sharp step) and secondary decomposition temperatures, because UF and MUF are copolymers. The onset of weight loss under nitrogen was observed at temperatures of 127 and 285 °C for UF and at temperatures of 109 and 290 °C for MUF. This is supported by the derivative (DTG) curve, which showed two peaks at temperatures of 145 and 306 °C for UF and at temperatures of 132 and 321 °C for MUF (the bottom of Fig. 1). Considering the amount of char for both UF and MUF, at a temperature of 850 °C, UF was 5.40 wt% and MUF was 6.99 wt%; these were lower than the other two (PF and MDI).

The adhesive specimen weight for PF (dash line) was significantly less at temperatures between 50 °C and 500 °C in the TGA tests; the weight loss for MDI (dash–dot–dash line) was significant at temperatures from 200 to 400 °C. This indicates that the chemical structure, in the molecular chain, or chemical composition, of PF and MDI is different. For the onset of weight loss, the temperature was at 61, 116 and 481 °C for PF, and at 247, 501 and 541 °C for MDI. The DTG curve was specified in three peaks at temperatures of 65, 129 and 493 °C for PF, and 297, 514 and 547 °C for MDI (the bottom of Fig. 1). The amount of char for PF and MDI left 24.88 wt% and 20.61 wt%, respectively, of stable residue, at a temperature of 850 °C.

The above results, obtained from the TGA tests, showed that MDI had the highest initial decomposition temperature (297 °C), and better overall thermal stability, than the others. Moreover, when comparing the char of the four types of adhesives, PF and MDI provided better yield of char at 850 °C. This showed that the thermal behavior of PF and MDI is better than that of UF and MUF, as the proposed action mechanism is based on the charred layer acting as a physical barrier, which slows down heat, and results in mass transfers between the gas and condensation phases (Camino, 1993; Hornsby, 1996; Zhu, 2001).

Infrared spectrometric response of adhesives

Figure 2 shows the Infrared spectrometric (IR) response of the four types of adhe-

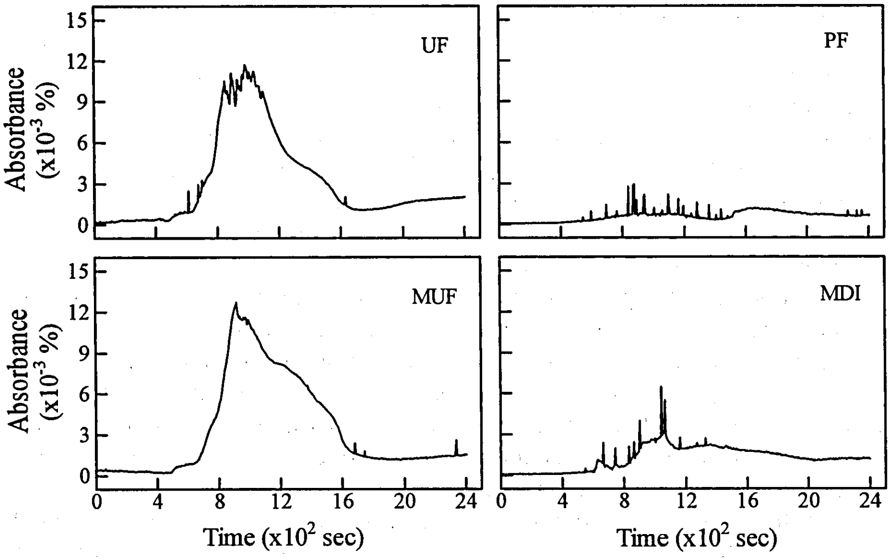


Fig. 2. IR response of 4 types of adhesives (UF, MUF, PF and MDI) from TGA–IR analysis. Note: Abbreviations of UF, MUF, PF and MDI are the same as Figure 1.

sives in the TGA–IR measurements. The change in absorbance (concentration of evolved species %) corresponded to the increase in decomposition time for the four adhesives. The concentration of evolved species for the IR response of UF and MUF increased slowly, to about 620 sec, from the start of decomposition. Subsequently, this increasing tendency rose linearly to about 900 sec. The high point of absorbance was shown as 981.3 sec for UF and 906.6 sec for MUF. After that, the change in concentrations of evolved species tended to decrease, until the end of decomposition. Furthermore, the IR response of UF, between 840 and 1080 sec, showed a greater mountain peak. This suggested that the concentration of evolved species for UF is higher than for MUF.

The concentration of evolved species from the IR response of PF was similar to a hillock with several independent plants, ranging from 380 sec to the end of decomposition. The high point of absorbance occurred at 864.8 sec. The concentration of evolved species in the IR response of MDI increased slowly to about 600 sec from the beginning of decomposition. Subsequently, the time change in the concentration of evolved species became the ridge of a house. The high point of absorbance occurred at 1055.2 sec.

Comparing the IR response of all adhesives, the absorbance levels for UF, MUF and MDI were higher than for PF. This indicated that the concentration of evolved species of PF was less than those of MDI or the urea copolymer series adhesives, UF and MUF. Of them all, PF was considered to be the best adhesive with the least environmental impact. A similar conclusion was reached in previous research (Lin *et al.*, 2001), which indicated that PF was the most environmentally friendly adhesive for manufacturing particleboard, because the emission contents (such as carbon monoxide, nitrogen monoxide and sulfur dioxide) of PF were less than UF, MUF and MDI, when the used particleboard was destroyed by combustion.

TGA–IR spectra and typical structure of adhesives

In recent years, there has been much attention paid to the use of adhesives (formaldehyde copolymer compounds), because, during combustion, they emit toxic gases and corrosive smoke; exposure to these toxic and acidic fumes can cause great harm to people and can also damage costly equipment (Ladomersky, 2000). With the use of TGA–IR, it is possible to simultaneously monitor evolved species, pyrolysis temperature and concentrations formed (absorbance), as well as the evolution profile of certain compounds. Moreover, IR spectrometry is a common means of evaluating a functional base when a material undergoes degradation.

The evolution of decomposition time (or pyrolysis temperature) on absorbance and wavenumbers (basically, IR spectra) for the various types of adhesive specimens (UF, MUF, PF and MDI) is shown in Fig. 3. The distribution of wavenumbers at the end of each 120 sec, during decomposition time, was analyzed. The results obtained, summarized below, analyze the data between the TGA curve (pyrolysis temperature) in the TGA tests and TGA–IR response (decomposition time along with wavenumbers and absorbance) in the TGA–IR measurement.

For TGA–IR spectra of UF (the top left of Fig. 3), the CO_2 peak, located at 2300 and 2400 cm^{-1} is shown beginning from about 240 sec (at a temperature of about 127 °C in the TGA tests) to the end. CO_2 increased linearly to the top point of absorbance at about 960 sec (367 °C), then decreased at about 1680 sec (607 °C) and kept the same concentration

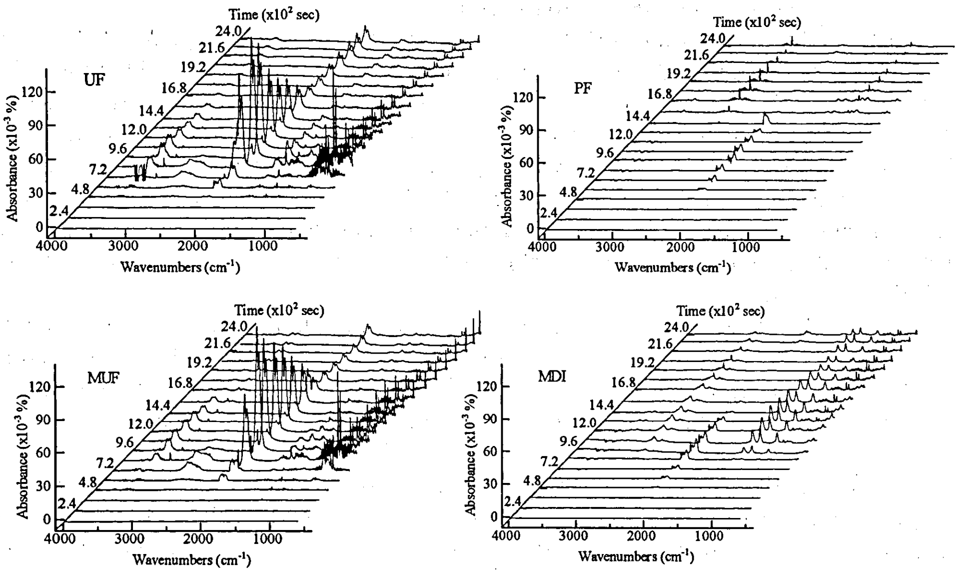


Fig. 3. TGA-IR spectra of 4 types of adhesives (UF, MUF, PF and MDI).
Note: Abbreviations of UF, MUF, PF and MDI are the same as Figure 1.

of CO_2 till the end of the tests. 3545 and 3509 cm^{-1} was assigned to the N-H stretching of NH_2 moieties (Zhu, 2001) from about 360 sec (167 °C) to the end. A higher concentration of N-H stretching was seen between 840 and 1440 sec (327 to 527 °C). The range from 480 to 1180 sec (207 to 440 °C) showed a weak peak at 2921 and 2851 cm^{-1}, respectively, which was attributed to the C-H stretching of CH_2 moieties. Another weak peak, at 1447 cm^{-1}, was attributed to C-H stretching of CH_2 moieties, from 480 sec. The weak peaks at 1701 and 1625 cm^{-1} were assigned to the C=O (carbonyl group), stretching from 480 sec to the end. Moreover, several weak peaks at 972 or 962 cm^{-1} also emerged due to C=O stretching, during the period from 480 sec to the end. The top point of absorbance for C=O stretching at 972 or 962 cm^{-1} was found at 960 sec, which was the same as the top point of absorbance for CO_2.

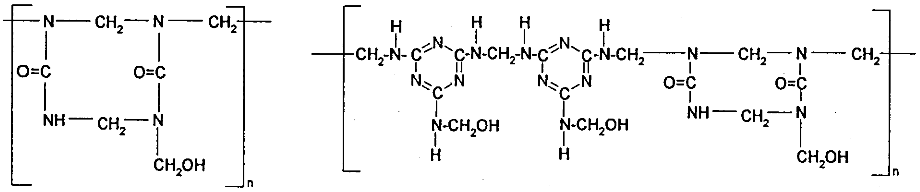
TGA-IR spectra of MUF are shown in the bottom left of Fig. 3. The results indicated that UF and MUF present the same tendency in TGA-IR spectra (the left side of Fig. 3), as both belong to the same copolymer urea formaldehyde series. The results for the absorbance peak and the time location (including the decomposition temperature) of CO_2, N-H stretching, C-H stretching and C=O stretching for MUF were the same as for the TGA-IR spectra of UF; the N-H deformation vibration of NH_2 moieties was found at 1605 and 1649 cm^{-1}, from about 360 sec (167 °C) to the end. The weak peak at 1449 cm^{-1} was attributed to C-H deformation vibration of CH_2 moieties, while at 1414 cm^{-1}, it was assigned to C-N stretching. Both of these began close to 480 sec (207 °C) to the end. A weak peak of C=O stretching, located at 1736 cm^{-1}, was also found from 600 sec to the end (247 to 850 °C). In addition, two weak peaks of triazine, located at 1365 and

1565 cm^{-1}, began from about 480 sec to the end.

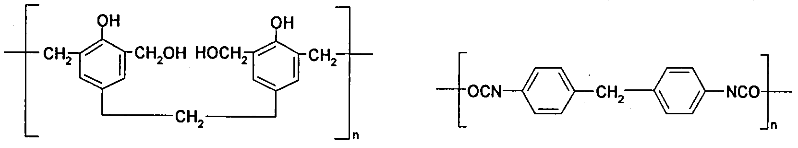
For the TGA–IR spectra of PF (the top right of Fig. 3), the weak peaks of CO_2 were also located at 2300 and 2400 cm^{-1} and began from about 600 to 1440 sec (247 to 527 °C), almost disappearing towards the end of the tests. Some of weak board absorbance at 3300 to 3600 cm^{-1} was assigned to OH groups from about 720 sec (287 °C) to 2160 sec (767 °C). A weak peak at 2980 cm^{-1} was assigned to out–of–plane bending of C–H on the benzene (aromatic) ring, from 1440 sec (527 °C) to the end. The spectrum results in this study are similar to those reported by Reghunadhan Nair (2001). Another weak peak at 1100 cm^{-1} was attributed to the stretching vibration of benzene C–C, from 1560 sec (567 °C) to the end.

The TGA–IR spectra of MDI are shown in the bottom right of Fig. 3. The results indicated that the two weak peaks of CO_2 were the same for UF, MUF and MDI, located at 2300 and 2400 cm^{-1} and which began from about 480 to 1560 sec (207 to 567 °C), almost disappearing towards the end of the tests. Some weak board absorbance located at 3700 cm^{-1}, was assigned to N–H stretching from about 600 sec (247 °C) to 1440 sec (527 °C). In addition, some weak board absorbance, found at 3100 cm^{-1}, was assigned to OH group, from about 960 sec (367 °C) to the end. Other weak peaks at 1624 cm^{-1} were assigned to C=O (carbonyl group) stretching from 840 sec (327 °C) to the end. Two weak peaks at 972 or 927 cm^{-1} also emerged as C=O stretching, from 1200 sec (447 °C). Results obtained also showed several weak peaks at 1114 and 1206 cm^{-1}, which were assigned to the C–NH group and N=C group (Levchik, 1995) from 840 sec (327 °C) to the end, respectively.

To clarify the effectiveness of the analytical scale towards the four adhesives, and to identify the evolved compounds of each particular analysis, the most probable structures for the different polymers found in these adhesives (Chen, 1996), are included in Fig. 4., showed their typical molecular structures. UF analysis of the TGA–IR response showed that the thermal decomposition of the NH groups at a temperature of about 167 °C was initially determined as a possible degradation species. The same results were previously reported in literature (Zhu, 2001). The CH_2 and C=O groups were then degraded at about 207 °C; the final contents of the char, therefore, were practically negligible (5.40 wt%). Some of the MUF evolved species are the same as the UF evolved species, because they belong to the same series of copolymers. The TGA–IR results showed that the N–H groups were degraded at a temperature of 167 °C, while the CH_2 and triazine groups were degraded at 207 °C. In the case of PF, the thermal decomposition of the OH groups was found to be significant at 287 °C, although it could be degraded earlier, at temperatures of 65 and 129 °C; this information was obtained from the results of the TGA tests. In addition, the CH_2 groups were degraded at 527 °C and the benzene C–C at 567 °C. For MDI, the C=O and N=C groups were degraded at about 327 °C, which was analogous to the thermal decomposition of the OCN group during MDI pyrolysis, because of the resultant chemical reactions. Also, the char left at 850 °C in the TGA tests for PF and MDI was 24.88 and 20.61 wt%, respectively. The benzene (aromatic groups) structures for PF and MDI are of note in Fig. 4. That is, the thermal performance was enabled when the chemical compounds included aromatic groups. From these results, it may be concluded that still higher temperatures are needed for analysis of the char. Future study will continue in this direction.



Urea formaldehyde resin adhesives (UF) Melamine-urea formaldehyde copolymer resin adhesives (MUF)



Phenol formaldehyde resin adhesives (PF) Diphenylmethane diisocyanate adhesives (MDI)

Fig. 4. Typical polymer molecular structure for 4 types of adhesives.

Relationship of thermal decomposition and IR response of adhesives

Because of these relationships between the TGA–IR spectra and the molecular structures of the adhesives, the authors of this study suggest that this experimental data can be used to reference the thermo-degradation processes of adhesives. Considering the sharp (decomposition) weight loss in the TGA tests and the IR response from the TGA–IR analysis, the relationships between the adhesives can be seen in Fig. 5. The maximum value (dotted line) of the four types of adhesives from the IR response in the TGA–IR tests, and the decomposition step (solid line) in accordance with the decomposition time in the TGA tests, found that the adhesives did not present the evolved species during the initial decomposition steps: UF at 448.6 sec, MUF at 410.1 sec, and PF at either 204.7 or 399.9 sec; nevertheless, they showed a significantly higher amount (concentration) of CO_2 emitted during absorbance between 2300 and 2400 cm^{-1}.

In combustion toxicology, CO_2 is normally considered to be a significant toxicant and is also the best–known greenhouse gas, as it is capable of increasing the average global temperature, depending on the sensitivity of the atmosphere (such as the concentration of CO_2) to greenhouse forcing. On the other hand, Goto (1969) reported that the shear–test strength of an adhesive bond by compression loading, for a structural laminated and glued wooden beam, under fire tests with several temperature points, obtained higher values for urea series resins (UF and MUF) than for others (PF and MDI). It can be concluded, therefore, that the fire resistance of UF and MUF is higher, because they both produce CO_2 gas, which acts as a natural barrier, and slows down heat, during fire tests.

Results (Fig. 5) obtained also showed that both UF and MUF produced more kinds/higher concentrations of evolved species than PF and MDI; this was especially true for PF, in which only a small quantity of CO_2 was present at the maximum value of the IR spectra during PF pyrolysis. This infers that the ignition point and/or heat decomposition

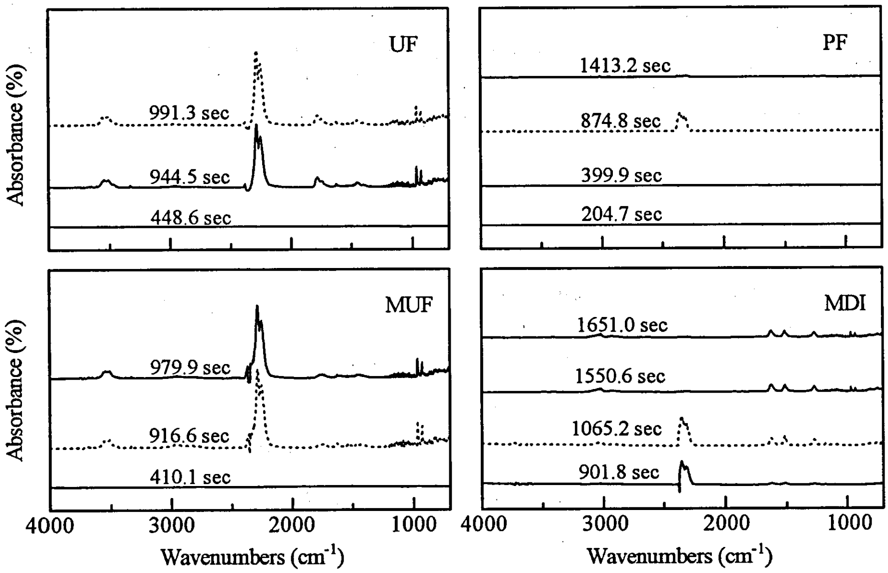


Fig. 5. IR spectra of 4 types of adhesives (UF, MUF, PF and MDI) at the maximum value of absorbance from IR response and at the decomposition steps of each adhesives.
Symbols: ········ : Maximum value, ——: decomposition step.
Note: Abbreviations of UF, MUF, PF and MDI are the same as Figure 1.

of the adhesives may influence their thermal behavior in relation to the extent and chemical nature of the smoke released during the burning process (Lin *et al.*, 2001). Therefore, further identification of pyrolysis products may lead to useful results concerning the discard process of chemical synthesis compounds or principal component analysis, using combined methods, such as TGA–IR, with the basic molecular (influencing factors or composed elements) structure of materials or products, in addition to the adhesives, themselves.

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