Pyrolysis of Melamine–Formaldehyde and Urea–Formaldehyde Resins

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SYNOPSIS

Pyrolysis of melamine–formaldehyde and urea–formaldehyde resins in helium and air was investigated by means of TG and gravimetry with isothermal heating, as well as elemental and HCN analyses. Weight loss curves suggest three kinds of reactions involved in the pyrolysis, namely, initiation reactions, reactions splitting off volatile fragments, and reactions forming stabilized structures. In TG, in both helium and air atmospheres, the active weight loss of the melamine resin was completed in two steps, and that of the urea resin was completed in one step, which, however, consisted of a few small successive steps. The isothermal heating weight losses progressed through a few stages of first- and zeroth-order reactions. Arrhenius parameters were obtained for the weight losses in TG and with isothermal heating. The residue from the melamine resin is rich in carbon and nitrogen, and poor in oxygen and hydrogen, while that from the urea resin is rich in carbon, and poor in nitrogen, oxygen, and hydrogen. The effects of temperature on HCN yield changed, depending on the amount of air fed. The melamine resin evolved much more HCN than the urea resin because of the more stable C—N linkages in the resin.

INTRODUCTION

Large amounts of resins of melamine–formaldehyde and urea–formaldehyde are used as adhesives for wood materials and also in many kinds of moldings and coatings. The combustion of these amino resins produces an acute toxicant, hydrogen cyanide in gas phase, because they contain nitrogen in a fairly high concentration. In addition to the combustion toxicity, there is another side of the resins which has to be taken into consideration for fire safety: Combustion of wood-based materials could be significantly affected by high temperature change of the strength of the resins applied to the wood. Pyrolysis of the adhesives would cause disintegration of wood-based materials such as plywood, particle board, and so forth, into their structural units such as veneer and chips, and then the materials would become easy to burn because of increases in surface area heated and in passages for pyrolysis products. In fact, however, only a very limited number of studies on their pyrolysis has been published.

In general, linear polymers like vinyl polymers have much simpler chemical structures and properties compared to polymers with networks found in these resins. Thermal decomposition of the majority of linear polymers has been explained by a chain mechanism with several elementary reactions. On the other hand, that of the resin of macromolecules is very complicated and has not clearly been explained, because network linkages with different bond energies appear to be irregularly severed and recombined on heating. The twofold purpose of the present paper is to cast some light on this obscure situation about the pyrolysis and to measure production of hydrogen cyanide.

EXPERIMENTAL

Samples

A sample of melamine–formaldehyde resin was prepared by hardening pure oligomer soak MA-50

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(provided by Honen Oil Co.) at a temperature of about 120°C for approximately 2 h. Urea–formaldehyde resin was prepared from 1 mol urea and 1.8 mol formaldehyde in a solution of hexamethylenetetramine and sodium hydroxide with ammonium chloride a hardener at temperature 105°C.

The melamine resin consisted of two major structures of rings of triazine and chains of methylene ether linkages, which were joined to each other through iminos or nitrogen to form network. The urea resin also has a network which mainly consists of groups of iminos, carbonyls, and methylenes. Although the complete structures are not exactly specified, parts of typical structures of melamine and urea resins are shown in Figures 1 and 2, respectively.

Both the resins were pulverized into fine particles smaller than 0.1 mm in diameter by a ball mill, and dried at 60°C longer than 48 h prior to pyrolysis.

Weight Loss Measurement and Elemental Analysis

Two kinds of weight loss data were obtained. One, by using a thermal balance with an imaging furnace (Sinku-Riko TGD-5000), was from thermogravimetry (TG) at heating rates of 0.5, 1.0, 2.0, and 5.0°C/min. The other was obtained with isothermal heating, where the sample temperature was elevated from room temperature to the desired constant value within one minute. The approximately 10 mg samples were contained in a platinic cell for isothermal heating or a quartz cell for TG. The samples were heated in air or helium (He) gas which was introduced at a rate ranging from 70 to 80 mL/min. For the He atmosphere, after evacuation to 0.1–0.2 Torr, the thermal balance system was rapidly filled and then supplied with He at the above rate.

Residue after isothermal heatings was dried over phosphorus petoxide at 60°C under reduced pressure. A Perkin-Elmer 240 elemental analyzer was used for the elemental analysis of the dried residue.

Analysis of Hydrogen Cyanide (HCN)

Production of HCN during TG was determined under conditions of a heating rate of 5°C/min, a flow rate of 100 mL/min of air or He, and about 50 mg initial sample weight. The pyrolysis gas was trapped in a gas washing bottle, as shown in Figure 3, which contained 20 mL of 0.1*N* sodium hydroxide solution and was replaced by a new one after a given lapse of heating time. The solution was analyzed for HCN using a Yokogawa IC-500 ion chromatoanalyzer with an ED-11 electrochemical detector.

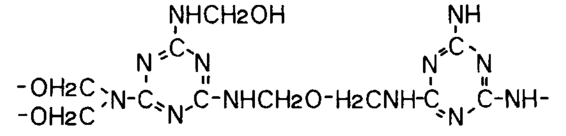

Figure 1 Typical linkages in melamine–formaldehyde resin.

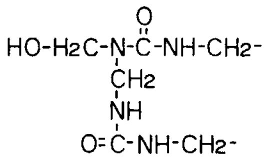

Figure 2 Typical linkages in urea–formaldehyde resin.

HCN production was also determined from isothermal heating by using an apparatus, as shown in Figure 4. An approximately 300 mg sample was heated in an air atmosphere flowing at rates of 30, 100, 300, and 600 mL/min. The imaging furnace used enabled the sample temperature (room temperature) to reach 600, 800, and 1000°C within 1 min. Pyrolysis products were collected by a series of two spiral traps through a glass tube heated at 300°C, until the sample monitored by a balance was exhausted. The traps were chilled by dry ice–methyl alcohol in Dewar flasks, but the inlet portion of the first one was heated by a flexible mantle heater to 300°C. Therefore, it condensed products in a wide temperature range. The products in the traps were resolved in 0.1*N* sodium hydroxide solution, which was analyzed for HCN by the above ion chromatoanalyzer.

RESULTS

TG

The melamine resin showed two steps of active weight loss with elevated temperature, as seen from

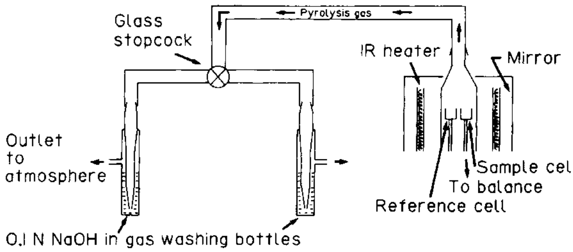

Figure 3 Traps for hydrogen cyanide (HCN) from thermogravimetry (TG).

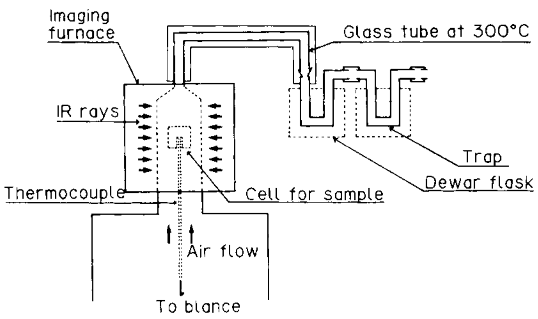

Figure 4 Furnace and traps for HCN from isothermal heating.

the examples of TG curves at a heating rate 1°C/min in Figure 5. On the other hand, the urea resin lost the majority of its weight in an active step over a temperature range of about 220–280°C, which, however, seemed to consist of a few small steps in weight loss. The threshold temperature for the active weight loss agrees with the one for fully cured urea–formaldehyde resin obtained by Sekine.[1] The weight loss in the air atmosphere was accelerated and the residue yields were smaller compared with those in the He atmosphere. The larger weight loss in air was probably caused by oxidation in addition to pyrolysis reaction. It is noted in He that the residue of the urea resin seems to be more stable than that of the melamine sample, as revealed by the lowest rate of weight loss, though at low temperature the weight loss of the urea resin was not only larger but also less stable than for the melamine resin.

The derivative thermogravimetric (DTG) curves, shown in Figure 6, were derived from the measured TG curves numerically. Here, also, the two steps of active weight loss of the melamine resin are clearly visible. Furthermore, small DTG peaks were observed at high temperatures, though that in air was not given in the figure because it exceeded 500°C. For the urea resin, different numbers of DTG peaks among heating rates were observed and the number of peaks common to all runs was four in air and two in He, as shown in Figure 6.

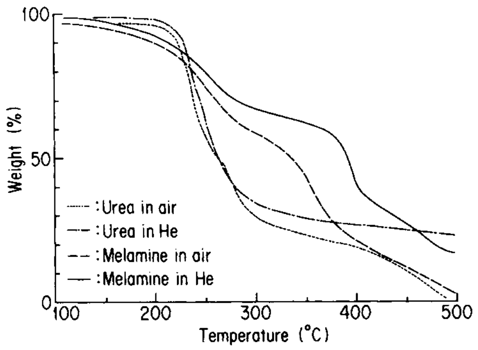

Figure 5 TG curves of melamine and urea resins in helium and air. Gas flow rate 70–80 mL/min; heating rate 1°C/min.

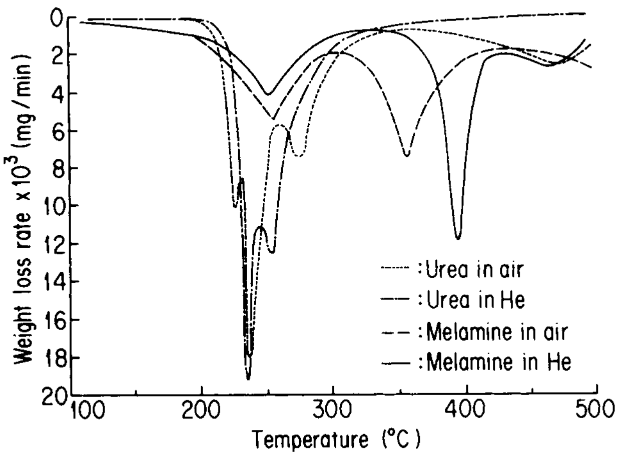

Figure 6 DTG curves of melamine and urea resins. Gas flow rate 70–80 mL/min; heating rate 1°C/min.

The weight loss rate for the present samples may be expressed as

$$\frac{dW}{dt} = A \exp\left(-\frac{E}{RT}\right)(W_0 - W)^n \qquad (1)$$

where W is the weight loss by time t, W_0 is the initial decomposable weight of reactant, E and A are the activation energy and the pre-exponential factor of the Arrhenius equation, respectively, T is the sample temperature, R is the gas constant, and n is the order of reaction. From eq. (1) Akita and Kase[2] have derived

$$\frac{\phi}{T_m^2} = \frac{nR}{E} A (W_0 - W)^{n-1} \exp\left(-\frac{E}{RT_m}\right) \qquad (2)$$

where ϕ is the constant rate of temperature rise and the subscript m denotes the state of maximum rate of weight loss. The activation energy can be determined from plots of logarithms of the left-hand side versus $1/T_m$ in eq. (2), according to the method originally presented by Kissinger.[3] Thus, plots according to eq. (2) were made using the given heating rates and temperatures at maximum rates of weight loss. These plots formed straight lines with good agreement, though the number of points plotted was small, as shown in Figures 7 and 8. Obtained activation energies are listed together with pre-expo-

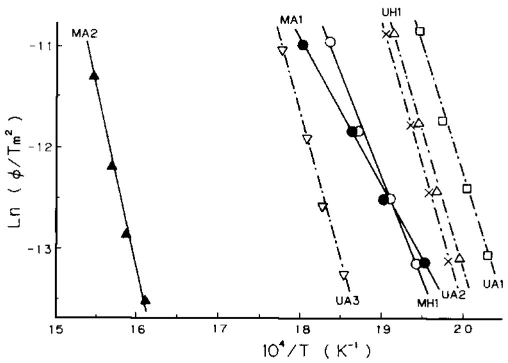

Figure 7 Plots of $\ln(\phi/T_m^2)$ versus $1/T_m$ in temperature range 210–380°C. Samples of melamine and urea resins, atmospheres of helium and air, and stages of weight loss first to third are designated by M and U, H and A, and numbers, respectively. The plots for the second stage of weight loss of the urea resin in helium (UH2) are omitted for simplification.

nential factors derived from the intercepts by assuming first-order reactions in Table I.

The second stage of weight loss of the urea resin in air (Table I) seems to correspond to the first stage of weight loss in He, because both these weight losses formed the deepest main DTG valley. In He, a small shoulder peak such as the first peak in air was not substantiated on the low temperature side of the main peak. Therefore, the third weight loss in air probably corresponded to the second stage in He. The fourth weight loss in air seems to have been caused by oxidation.

Weight Loss with Isothermal Heating

Melamine Resin

Weight loss of the melamine resin in the air atmosphere increased with increase in heating temperature in a low temperature range from 175 to 312°C, as shown in Figure 9. Also weight loss during preheating for temperature rise to a programmed value is seen to increase with increasing temperature. In a high temperature range from 312 to 363°C, however, behavior of the weight loss is different from that in the low temperature range, as shown in Figure 10, where weight loss curves cross at four points. Although the initial weight loss in a first few minutes of the heating time increased with an increase in temperature, the residue yield after prolonged heating is the largest at the highest temperature 363°C. Furthermore, the residue yield at 347°C is larger than that at 332°C.

In He, the weight loss increased and then the residue yield decreased with increase in temperature from 211 to 262°C, but at 285°C the ultimate residue seems larger than those at 245, 257, and 262°C, as shown in Figure 11. Weight loss curves in a high temperature range from 301 to 391°C show more complicated behavior, as shown in Figure 12. In the temperature range from 301 to 341°C the weight loss increased and the residue decreased in a similar manner. The residue yields at 301 and 313°C are larger than that at 285°C, though the initial weight losses were more rapid than at 285°C. Despite the slower initial rate, the weight loss at 361°C was faster than that at 341°C in the later stage and the curve seems similar to that at 371°C. It is interesting that the initial weight loss at 391°C is largest but that the ultimate residue amount is larger than those at 371 and 382°C.

In the kinetic analysis, the rate of weight loss in air was plotted against the residual weight. The rate decreased with the reduction in residual weight and did not give linear plots over a wide range of the residual weight. Linear plots over limited ranges, however, were found, as shown in Figures 13–15. In the low temperature range from 175 to 296°C (Figs. 13 and 14) the plots suggest two stages of weight loss. From the slopes of linear plots two rate constants of weight loss for each temperature from 221 to 282°C and one for each of others were determined by assuming first-order reaction. Satisfactory linear plots were not found in the high temperature range from 296 to 363°C (Fig. 15), but rate constants were obtained from straight parts at higher weight percentage, though a few data were plotted for each temperature.

Arrhenius plots of the obtained rate constants each formed straight lines for the weight loss in the high temperature range (designated the first stage in Table II) and for the second stage of the weight loss in the low temperature range (the third stage in Table II), but the two lines crossed at 251°C for

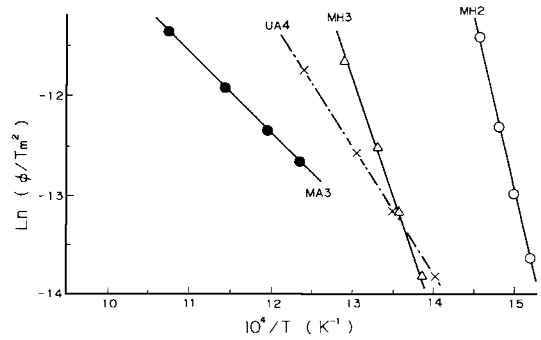

Figure 8 Plots of $\ln(\phi/T_m^2)$ versus $1/T_m$ in temperature range 380–660°C. The symbols such as UA3 and MH2 work in the same way as in Figure 7.

Table I Arrhenius Parameters of Weight Loss in Thermogravimetry

Samples	Atmosphere	Weight Loss Stage	Activation Energy (kJ/mol)	Pre-exponential Factor (s^{-1})
Melamine resin	Helium	First	169	8.5×10^{13}
		Second	281	1.4×10^{19}
		Third	200	1.2×10^{11}
	Air	First	136	4.0×10^{10}
		Second	291	2.3×10^{21}
		Third	68	10.9
Urea resin	Helium	First	223	1.5×10^{20}
		Second	213	2.1×10^{18}
	Air	First	205	4.6×10^{18}
		Second	233	1.2×10^{21}
		Third	238	9.4×10^{19}
		Fourth	108	1.7×10^{4}

the first stage in the low temperature range (the second stage in Table II), as shown in Figure 16. Pseudo-Arrhenius parameters calculated from the plots are listed in Table II. The values of pre-exponential factors and activation energy are considerably smaller than those for the first and second stages of weight loss of the same sample in Table I. Especially, those for the weight loss in the high temperature range and for the first stage on the lower temperature side in the low temperature range are too small to be directly accepted.

Also rates of weight loss in He were plotted against weight. At first the rates steeply decreased with the advanced weight loss, as shown in Figure 17. But, the rates at 361, 371, and 382°C became constant and then again those at 371 and 382°C linearly decreased as the weight decreased. Also, a stage of constant rate of weight loss was found at temperatures of 341 and 329°C. Other heatings at temperatures lower than 329°C gave neither a constant nor linearly decreasing rate over any distinct duration of weight loss. Two kinds of rate constants were obtained from the constant rates and the linearly decreasing rates of weight loss, by assuming zeroth- and first-orders of reactions, respectively. Also an apparent rate constant for first-order reaction was obtained from the linear plots in a weight range 36–41% at 391°C in Figure 17. Arrhenius plots were made for the rate constants obtained, as shown in Figure 18, and Arrhenius parameters, as given in Table II, were obtained from the plots.

In order to obtain kinetic parameters for the weight loss in the low temperature range, an equation

$$\int_{W_0}^{W_0-W} \frac{dW}{(W_0 - W)^n} = A \exp\left(-\frac{E}{RT}\right) t \qquad (3)$$

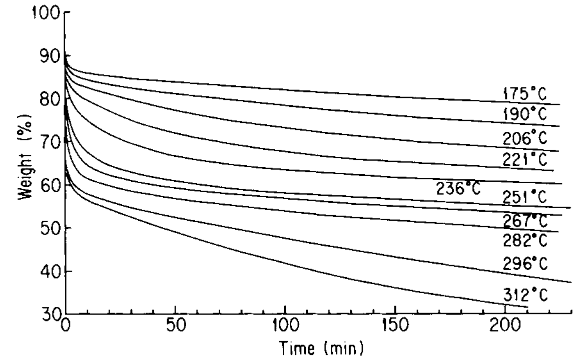

Figure 9 Weight loss curves of melamine resin with isothermal heating in temperature range 175–312°C in air.

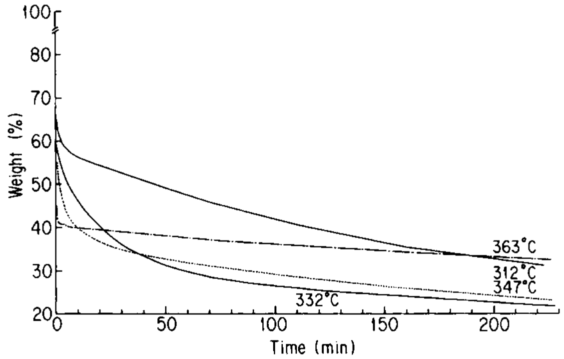

Figure 10 Weight loss curves of melamine resin with isothermal heating in temperature range 312–363°C in air.

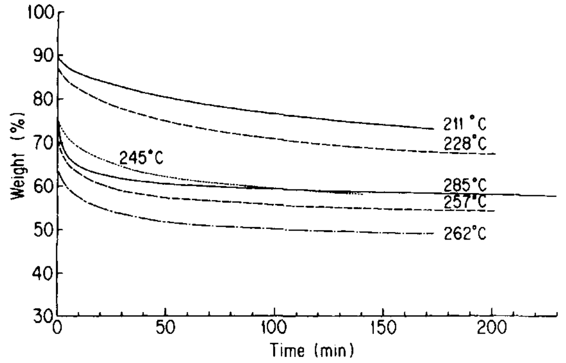

Figure 11 Weight loss curves of melamine resin with isothermal heating in temperature range 211–285°C in helium.

was derived from eq. (1) under the condition of constant temperature, where W is zero at $t = 0$. Since the left-hand side of eq. (3) yields an identical value with a specific weight irrespective of temperature and time, plots of $\ln(1/t)$ versus $1/T$ at the specific weight should enable us to calculate the activation energy. In fact, however, the number of different temperatures for which an equal weight remained is very limited due to loss by preheating, as seen in Figure 11. Therefore, the weight loss curves were reformed on the basis of the weights at $t = 0$, as shown in Figure 19. Thus, the plots for 90, 85, 80, and 75% of the weight were made to statistically construct straight lines, as shown in Figure 20, but a line is not drawn for the 75% weight due to excessive dispersion of the points. Activation energies from the slopes are listed in Table II. These decreased with the progress of the pyrolysis and are much smaller than those in the high temperature range.

Urea Resin

Initially the weight in the air atmosphere was rapidly reduced and then the rate of weight loss gradually decreased with time, as shown in Figure 21. The weight lost for preheating plus the first 1 minute at constant temperature, which was 13% even at the lowest temperature 224°C, increased with increasing temperature and amounted to 45% at the highest temperature 287°C. It is noted that, despite the larger initial weight loss, the residual weight at 276°C became larger than that at 266°C after 2 min had lapsed. Also at 246°C a residual weight larger than that at 235°C is found for a duration between 50 and 145 min.

Behavior of the weight loss in the He atmosphere is simpler compared with that in air, as shown in Figure 22. As a function of time, the weight was more smoothly reduced than that in air, and the residue yield after prolonged heating seems to decrease with increasing temperature.

Plots of rates of weight loss against residual weights in air were made, as shown in Figures 23 and 24. From the plots the course of weight loss is found to be divided into three stages, as shown by a typical example for heating at 266°C, where the rate at first steeply, then slowly, and again steeply decreased with the decrease in weight. In the experimental range the steepest weight loss of the third stage is not observed for the two temperatures higher than 266°C. At temperatures lower than 266°C the second stage is short and in some cases gave rates which increased even with the decrease in weight, as shown in Figure 24. Assuming first-order reaction, rate constants for the first, second, and third stages were obtained from the linear plots at all the temperatures used, at three temperatures from 266 to 287°C, and at six temperatures from 224 to 266°C, respectively. Arrhenius plots for the rate constants formed straight lines except for those at the lowest temperature, as shown in Figure 25, and the Arrhenius parameters thus determined are listed in Table III. It is noted that temperature dependence is much greater for the second stage than for the others, the former of which was more definitely substantiated with the increase in temperature, as shown in Figure 23.

Also plots of the weight loss rates versus the weights in He suggest the presence of three steps in the pyrolysis at temperatures 255, 265, and 273°C, as shown in Figure 26. Those in the temperature range from 284 to 306°C, however, indicate two steps, as shown in Figure 27. This is probably because the first step occurred when the weight which

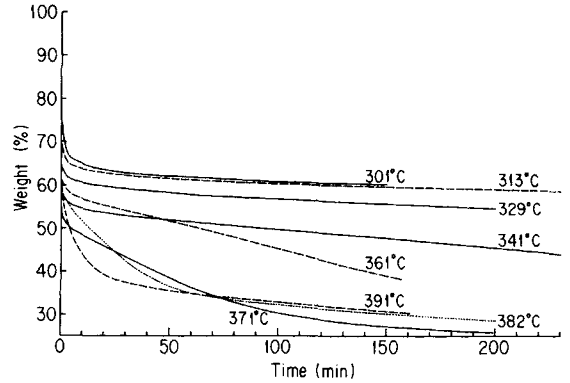

Figure 12 Weight loss curves of melamine resin with isothermal heating in temperature range 301–391°C in helium.

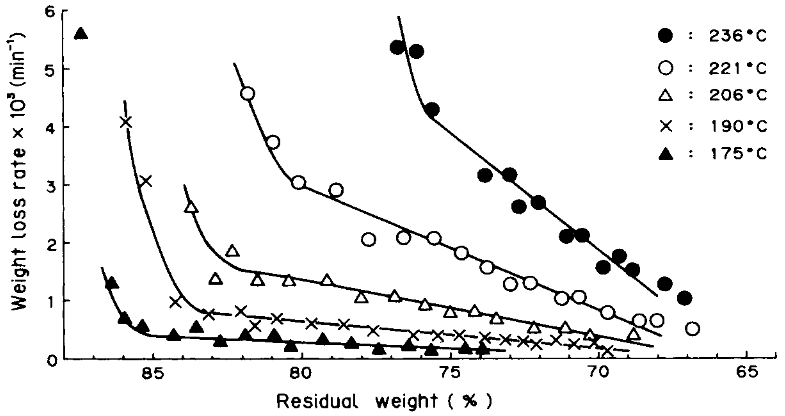

Figure 13 Plots of weight loss rate vs. weight for melamine resin in temperature range 175–236°C in air.

was lost during preheating was greater than 80%. The first step was ignored because the number of rate constants obtained was too small for the kinetic analysis. Therefore, the second and third ones were named the first and second stages, respectively. Arrhenius plots for the rate constants, which were obtained under the assumption of first-order reaction, were made, as shown in Figure 28. The derived parameters are listed in Table III. Activation energy is a little higher for the second stage than for the first stage.

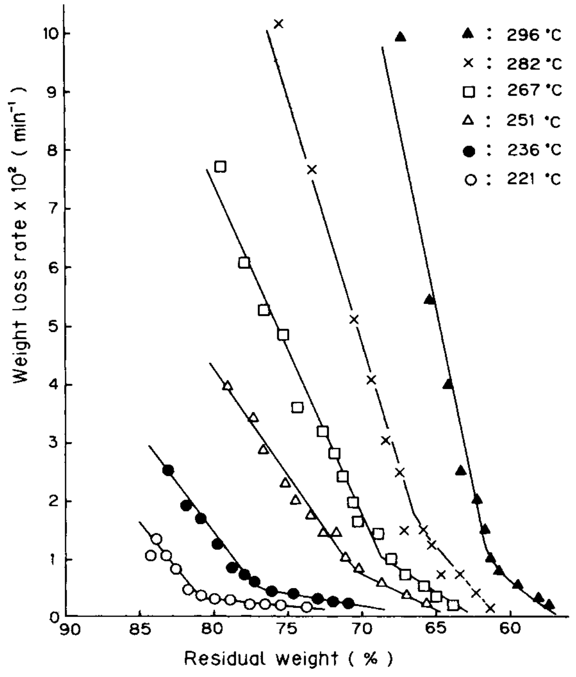

Figure 14 Plots of weight loss rate vs. weight for melamine resin in temperature range 221–296°C in air.

Elemental Analysis

Initially carbon and nitrogen contents of the melamine resin in He steeply increased with the time of heating at 330, 370, and 390°C, but seemed to become constant after prolonged heating, as shown in Figures 29 and 30. Though the dots plotted on the figures are somewhat scattered, the constant values appear to be about 41% for carbon and 47% for nitrogen, respectively. In contrast, the hydrogen content decreased with time and the decrease rate became larger with increasing temperature, as shown in Figure 31. In addition, the initial increase rates for the carbon content at 370 and 390°C are larger than for 330°C. Also in air at 300°C, carbon and

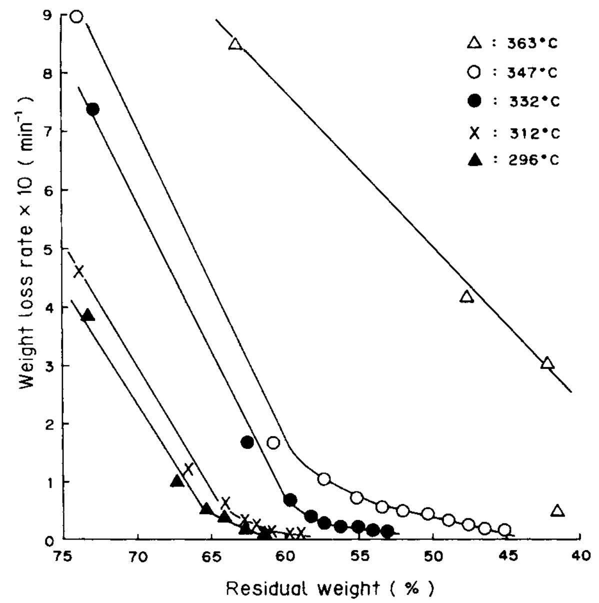

Figure 15 Plots of weight loss rate vs. weight for melamine resin in temperature range 296–363°C in air.

Table II Arrhenius Parameters of Weight Loss of Melamine Resin with Isothermal Heating

Atmosphere	Weight Loss Stage (Temperature Range, °C)	Reaction Order	Activation Energy (kJ/mol)	Pre-exponential Factor (s^{-1})
Air	First (296–347)	First	23	8.9
	Second (251–296)	First	72	9.5×10^4
	(221–251)		16	0.2
	Third (175–282)	First	83	1.7×10^5
Helium	First (329–371)	Zeroth	195	2.5×10^{11}
	Second (371–391)	First	221	3.0×10^{14}
	(211–262)			
	Weight loss,			
	10%	—	94	—
	15%	—	87	—
	20%	—	74	—

nitrogen contents rapidly increased with time at first and then seemed to reach constant values of about 40 and 42%, respectively, after prolonged heating, as shown in Figure 32. The hydrogen content slightly decreased with time.

Assuming the oxygen content is the difference between 100% and the total of carbon, nitrogen, and hydrogen contents, the elemental compositions of the original and heated samples were calculated. The values are given in chemical formulae in Table IV.

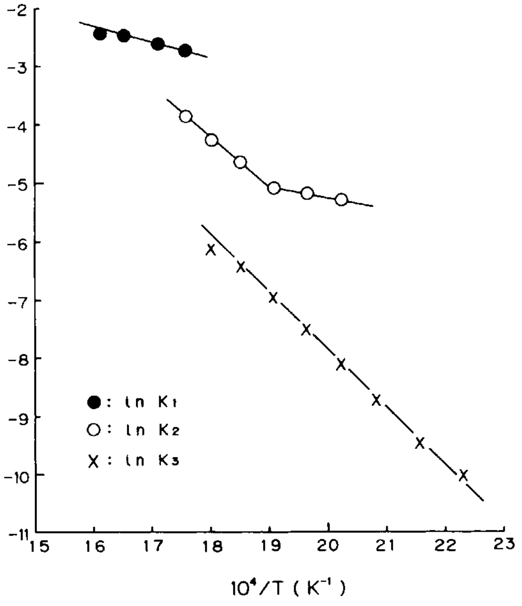

Figure 16 Arrhenius plots for weight loss of melamine resin in air. K_1 = rate constants in high temperature range, K_2 and K_3 = rate constants for first and second stages in low temperature range, respectively.

The oxygen and hydrogen contents, especially of the initial sample at heating time 0, might be partially due to moisture absorbed by the sample during preparation for the elemental analysis runs, coinciding with weight loss at low temperature around 100°C in Figure 5, which suggested moisture absorption. Also the calculated residual elemental weights are shown as percentages of the initial quantity in the table. The element loss is seen to be the largest for oxygen, the second largest for hydrogen, and the smallest for nitrogen in both atmospheres.

On the other hand, nitrogen and hydrogen contents of the urea resin decreased and that of carbon increased with both heatings at 235°C in air and 255°C in He, as shown in Figure 33. Initially these changes were large but became smaller with increasing time. Chemical formulae and residual weights of elements, calculated according to the manner stated above, are listed in Table IV. It shows that the element loss with heating was the largest for hydrogen, the second largest for oxygen, and the smallest for carbon.

HCN Production

With isothermal heating, production of HCN from the melamine resin increased with increasing temperature in flow rates of air from 30 to 300 mL/min. For a flow rate of 600 mL/min, however, it was the largest, not at the highest temperature, but at 800°C, as shown in Figure 34. The HCN production from the urea resin seems to linearly increase with increasing temperature at a flow rate of air 30 mL/min but for the other flow rates it was the largest

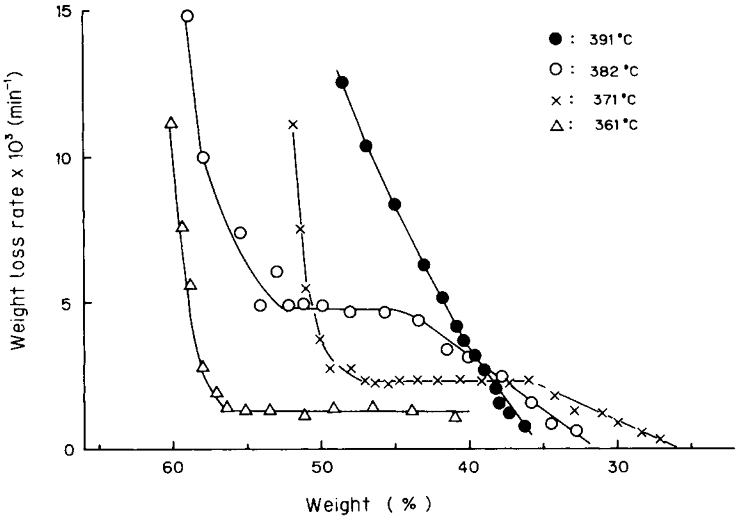

Figure 17 Plots of weight loss rate vs. weight for melamine resin in helium.

at 800°C. It also decreased with increasing air supply.

However, the effect of air on the HCN production from the melamine resin is not simple compared with the urea resin. Only at the temperature of 1000°C did the production decrease with increasing air supply. The largest productions at temperatures 600 and 800°C were observed for flow rates of 30, and 30 and 600 mL/min, respectively.

The melamine resin produced much more HCN than the urea resin. Rates of increase in HCN production with increasing temperature were obtained from the straight lines drawn for the 30 mL/min flow rate of air shown in Figure 34. The values of CN^- ion production per unit weight of the original samples are 24.1 mg/g/°C for the melamine resin and 21.5 mg/g/°C for the urea resin, respectively.

HCN, accumulated in a trap for each of five or six successive periods of TG temperature ranges, was converted into production per unit weight lost for the period. The HCN production from the melamine and urea resins increased at higher temperatures, as shown in Figures 35 and 36. The increase became prominent after the temperature exceeded 300°C. It is noted from comparison between the TG curves and the histograms of HCN production in the figure that more HCN was produced by slow pyrolysis of the residues than by active pyrolysis. Also in this case, much more HCN was produced from the melamine resin than from the urea resin.

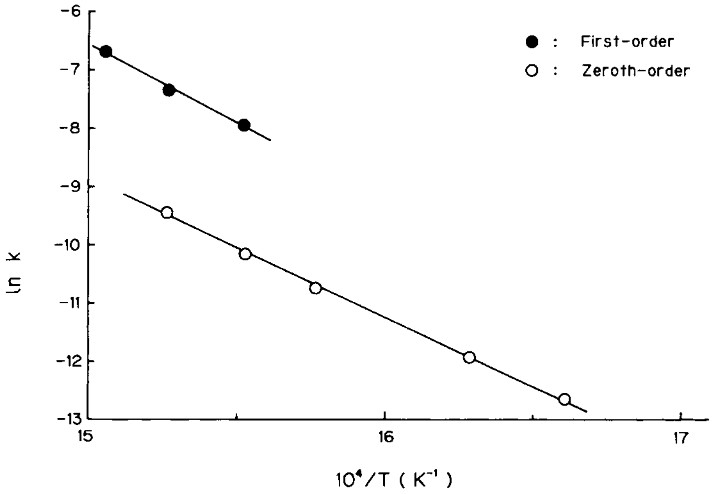

Figure 18 Arrhenius plots for weight loss of melamine resin in helium.

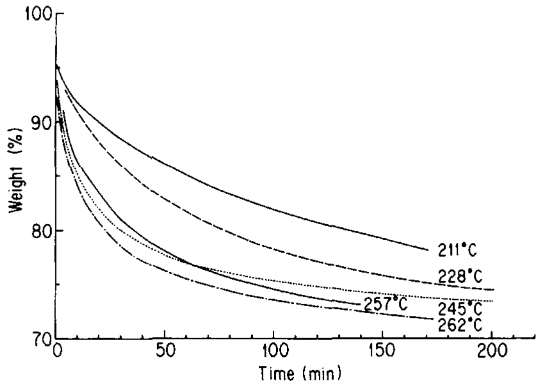

Figure 19 Reformed curves of weight loss of melamine resin in low temperature range in helium.

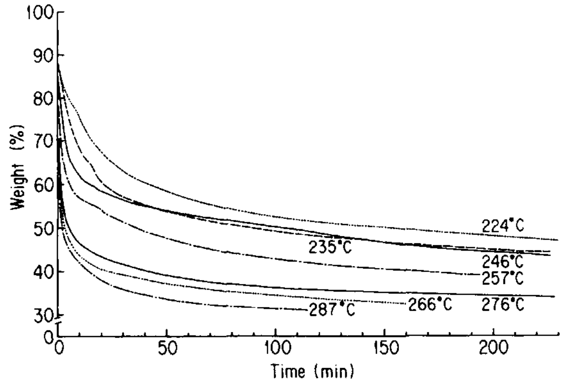

Figure 21 Weight loss curves of urea resin with isothermal heating in air.

The amount of residue from the melamine resin at 500°C is greater in air than in He. Furthermore, these residue amounts are greater than those of the urea resin in either atmospheres, which is inconsistent with the TG findings above. The apparent disagreement is probably a result of the different initial sample weights in the two experiments. It is inferred from results of pyrolysis of cellulose[4] that oxygen not only decreased the char by oxidation but also accelerated the char formation from the melamine resin. The oxidation would be affected much more by the surface area of the sample exposed to air than the charring or carbonization would. Since, despite the constant area exposed to air, the initial weight of the sample in the cylindrical cell (8 mm diameter) was five times larger in the HCN runs than in the TG runs above, the char yield in the former run was larger than in the latter probably due to accelerated char formation. Furthermore, the sample amount might affect pyrolysis reactions through diffusion of pyrolysis products thus possibly affecting the residue yield.

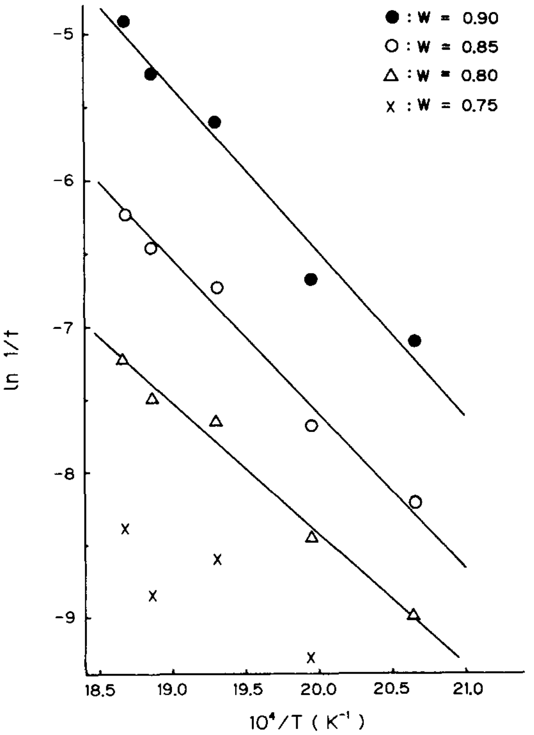

Figure 20 Plots of $\ln(1/t)$ vs. $1/T$ for melamine resin in helium.

DISCUSSION

Weight Loss

Melamine Resin

It is inferred, from results for butylated melamine–formaldehyde resin heated in air by Lady et al.[5] and

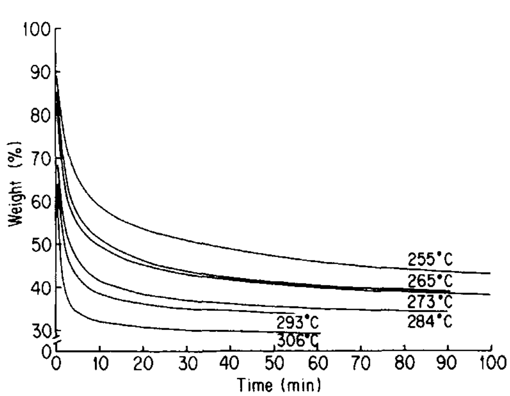

Figure 22 Weight loss curves of urea resin with isothermal heating in helium.

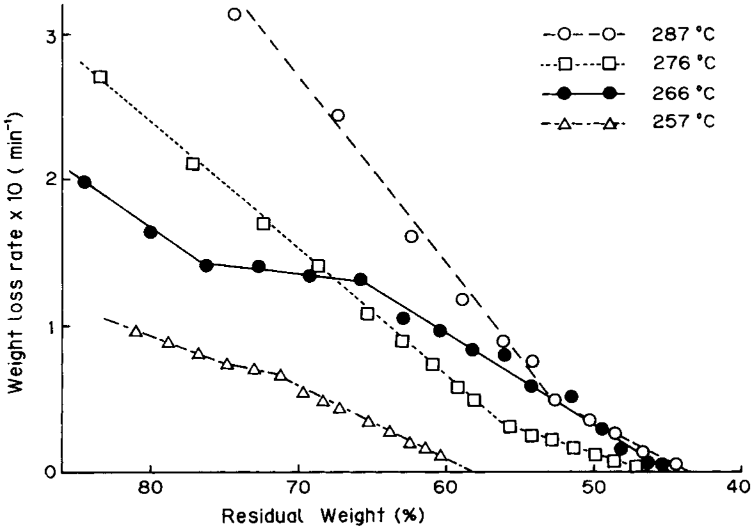

Figure 23 Plots of weight loss rate vs. weight for urea resin in temperature range 257–287°C in air.

Conley,[6] that the first significant pyrolysis of the present melamine resin is scission of a C—N linkage between a free end group of hydroxymethyl and NH on a triazine ring followed by cleavage of other C—N linkages bonding methylene ether, via formation of hydroperoxide intermediate if in air. This is supported by the lower bond energy of the C—N linkage compared to that of other linkages. These reactions produce aminos on triazine rings and volatiles such as carbon dioxide, formaldehyde, water, formic acid, and so forth.

In TG the present sample showed two active stages of weight loss, and also a very slow stage was distinguished at high temperature. The first active weight loss may be attributable to cleavage of weak linkages of C—N of the chain structures. The second one is inferred to involve triazine rings in addition to the chains, since melamine, a triazine ring, is believed to vaporize and probably decompose at around 350°C and the triazine rings stabilized in the resin network would cause such changes at higher temperature, agreeing with the TG curves in Figure 5. This inference seems consistent with observations using infrared spectrometry by Lady et al.[5] that triazine rings start to be broken at temperatures between 200 and 300°C. The third slow stage may be

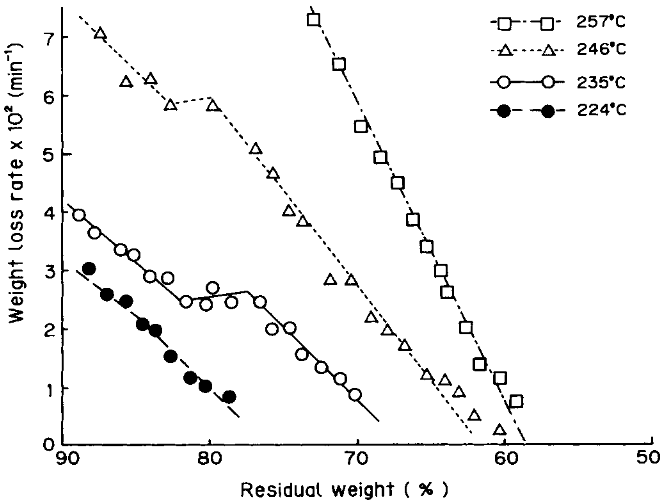

Figure 24 Plots of weight loss rate vs. weight for urea resin in temperature range 224–257°C in air.

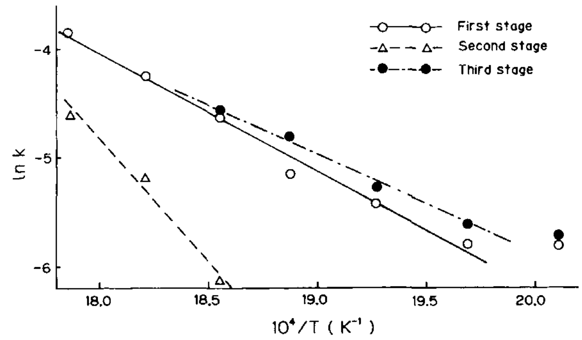

Figure 25 Arrhenius plots for weight loss of urea resin in air.

decomposition of condensates formed through the second stage. Activation energy in Table I shows that the two stages of the first weight loss, and especially of the third weight loss, were accelerated in air, but that the second one was not much affected by air.

With respect to pyrolysis during isothermal heating, three groups of reactions may be mentioned according to the weight loss behavior. The first one consists of initiation reactions, the second group of reactions directly cause weight loss or produce small fragments, and the third group forms stabilized structures. After a short initial time reactions of all three kinds may occur simultaneously according to their probability which depends on temperature. The second reactions compete with the third ones. In a low temperature range the second reactions seem to occur following the initiation and to overcome the third ones, as proven by weight loss which accelerates with increasing temperature. In a high temperature range, however, the third ones could become faster than the second ones in some cases, as shown by larger yields of residue given at higher temperatures than at lower temperatures in Figures 10 and 12.

The first weight loss of zeroth order of two stages, found in a high temperature range in He, may be established under a stationary state. Assuming that radicals which are produced from an initiation reaction are consumed by the above two reactions of production of volatile fragments to cause weight loss and of stabilization of the structure, the weight loss rate may be expressed by an equation

$$\frac{dW}{dt} = k_{dp} m_0 N_r \tag{4}$$

where k_{dp} is the rate constant of the production of volatiles, m_0 the average molecular weight of the volatiles, and N_r the radical number. If, in the zeroth order state, not the concentration but the number of radicals is assumed constant, though the mechanism cannot be given here, then the Arrhenius parameters in Table II correspond to the production reaction. In the first-order state N_r may be assumed a function of two rate constants of the initiation and stabilization reactions, and the weight or linkage number. Therefore, the three rate constants of the above reactions may be involved in the Arrhenius parameters for this stage.

Activation energies of weight losses in air and in the low temperature range in He are lower by more than one half compared to those in the high temperature range in He. The former two weight losses with low activation energies occurred when the residual weight was more than 60%. On the other hand, the latter occurred when the residual weight was less than 55%. Furthermore, the former activation energies are much lower than those for the first stage in TG, though these weight losses occurred in the almost same weight range. The reason for this inconsistency may be given as follows:

Pyrolysis with isothermal heating would proceed through a different mechanism from that in TG. In isothermal heating at a given temperature, for example, 250°C, intact structures of the original sample begin pyrolysis. In other words, various structures simultaneously undergo pyrolysis reactions followed by recombination to form stabilized struc-

Table III Arrhenius Parameters of Weight Loss of First Order of Urea Resin with Isothermal Heating

Atmosphere	Weight Loss Stage	Activation Energy (kJ/mol)	Pre-exponential Factor (s^{-1})
Air	First	90	5.3×10^{6}
	Second	186	2.6×10^{15}
	Third	75	1.9×10^{5}
Helium	First	77	2.7×10^{5}
	Second	91	2.2×10^{6}

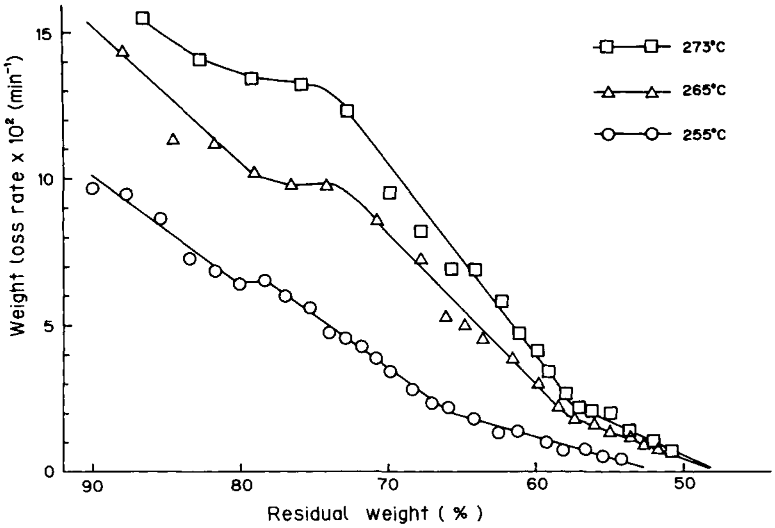

Figure 26 Plots of weight loss rate vs. weight for urea resin in temperature range 255–273°C in helium.

tures. Therefore, initial weight loss occurs with low activation energy due to the presence of weak structures. On the other hand, in TG the weakest linkage first breaks to produce volatiles and form some stabilized structures, and similar processes repeat to form more stabilized structures as the temperature increases. Thus, at high temperatures such as 250°C and so forth, much modified resin undergoes pyrolysis reactions with high activation energy. Also the high activation energies for the pyrolysis advanced with the isothermal heating in He can be satisfied with this explanation.

In the weight loss observations with isothermal heating, more oxygen and hydrogen was lost than carbon and nitrogen, and the number of nitrogen atoms in the residues approached to that of carbon atoms, as shown in Table IV. This suggests that the weight loss came more from the chain structure than the triazine ring structure and that nitrogen is bonded in a stable network probably with triazine rings.

Urea Resin

Sekine[1] has suggested a pyrolysis mechanism of a urea resin where an end group of hydroxymethyl is first split to form formaldehyde and then is followed by cleavage of C—N linkages to produce volatiles

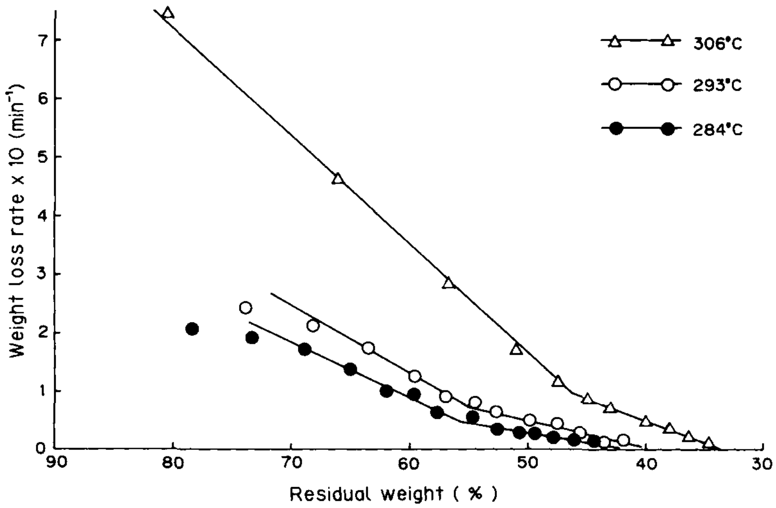

Figure 27 Plots of weight loss rate vs. weight for urea resin in temperature range 284–306°C in helium.

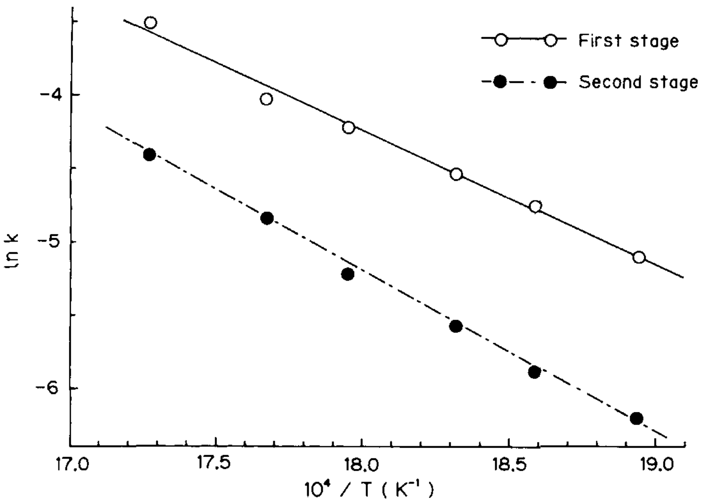

Figure 28 Arrhenius plots for weight loss of urea resin in helium.

containing nitrogen. In the present study formaldehyde was actually detected by a photoelectric colorimetry test for ammonium acetate–acetylacetone solution of pyrolysis products from an isothermal heating run at 235°C in air. The formaldehyde production accumulated for the first 5 min and after it was 1.9 and 0.8 mg/g of weight loss, respectively. Furthermore, this mechanism seems to be supported by the results of elemental analysis, indicating faster losses in hydrogen, oxygen, and nitrogen than carbon. Lady et al.[5] have shown from infrared spectral changes on heating a butylated urea–formaldehyde resin in air that the initial changes are the fast loss in the end butoxyl groups and the slow decreases in amino, hydroxyl, and carbonyl species to form oxidation products or cyclic amides and that all bands are rapidly lost above 250°C. Conley[6] has calculated an activation energy 90 kJ/mol for the splitting of the end groups in their study.

In spite of this information, however, it is difficult to correlate the specific groups or linkages of the resin shown in Figure 2 with two steps in He or three steps in air, found in the stage of active weight loss in TG. Activation energies for these steps are over 200 kJ/mol, while an activation energy for the weight loss from oxidation of the residue (fourth stage) is almost one half of these, but is 40 kJ/mol higher than that for the oxidation of the melamine resin, as shown in Table I. The residue from this resin in He seems more stable than that from the melamine resin, as shown in Figure 5. Therefore, the activation energy for the residue oxidation of this resin is higher than that for the melamine resin.

In the isothermal heating the weight losses except the second stage in air occurred with activation energies lower than one half of those for TG, as seen by comparison between Tables I and III. The lower activation energies may be explained by difference in the pyrolysis course between the two heatings, as

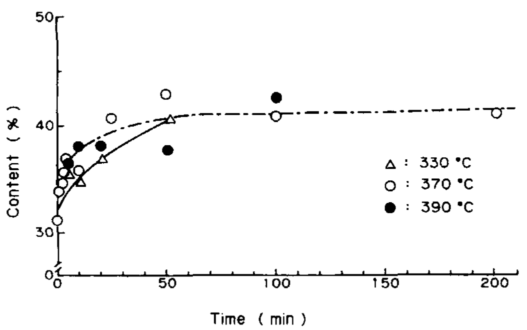

Figure 29 Changes in carbon contents of melamine resin with heating in helium.

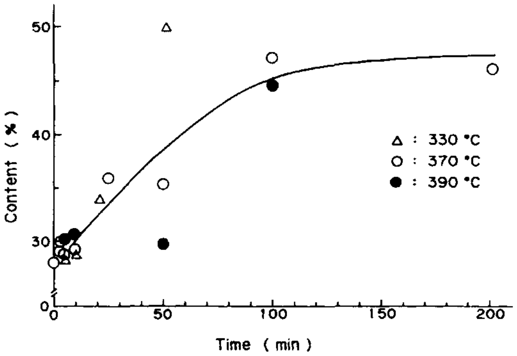

Figure 30 Changes in nitrogen contents of melamine resin with heating in helium.

Table IV Composition and Residual Weight of Elements

Samples	Heating Time, Temperature, and Atmosphere	Chemical Formulae	Residual Weight (%)			
			C	N	O	H
Melamine resin	0 min	$C_8N_6O_{5.5}H_{13}$	100	100	100	100
	100 min, 390°C, helium	$C_8N_8O_{1.4}H_{5.9}$	42	57	10	18
	50 min, 300°C, air	$C_8N_{7.2}O_{2.1}H_{9.6}$	62	77	23	47
Urea resin	0 min	$C_3N_2O_{1.4}H_{5.1}$	100	100	100	100
	100 min, 255°C, helium	$C_3N_{1.7}O_{1.1}H_{3.1}$	50	42	37	30
	100 min, 235°C, air	$C_3N_{1.5}OH_{2.9}$	59	44	42	34

was stated above about the melamine resin. The second stage of weight loss with the high activation energy in air may be attributable to pyrolysis of structures stabilized by oxygen through the first stage. It is interesting that the activation energy for the first stage in air exactly agrees with the above one by Conley.[6]

HCN Production

The HCN yields increased with temperature up to 500°C, shown in Figures 35 and 36, and agree with results by Jellinek et al.,[7-13] who have measured HCN yields from pyrolyses of polymers in oxidative and inert atmospheres and developed the kinetics. At low temperature HCN was produced more in air than in He, as shown in the figures. Similar observations can be derived from comparison between results in air and nitrogen by Jellinek and Dunkle.[11-13] According to them, HCN production accelerates in air due to oxidation through hydrogen abstraction from the resins by oxygen molecules followed by formation of hydroperoxides on carbon and nitrogen atoms which split off HCN.

Effects of temperature higher than 600°C on the HCN yields changed depending on the air flow, as shown in Figure 34. Jellinek and Dunkle[9,12,13] have reported that dependencies of HCN yields on oxygen concentration differed with temperature, that in air the maximum HCN yield from aliphatic polyurethane was given at 515°C and those from aromatic and secondary polyurethane were given at 600°C, and that a peak and a minimum were generated at 575 and 750°C on a temperature–HCN yield curve for poly(diphenyl methane pyromellitimide) in air,

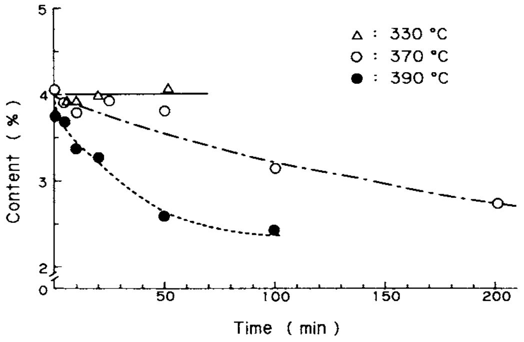

Figure 31 Changes in hydrogen contents of melamine resin with heating in helium.

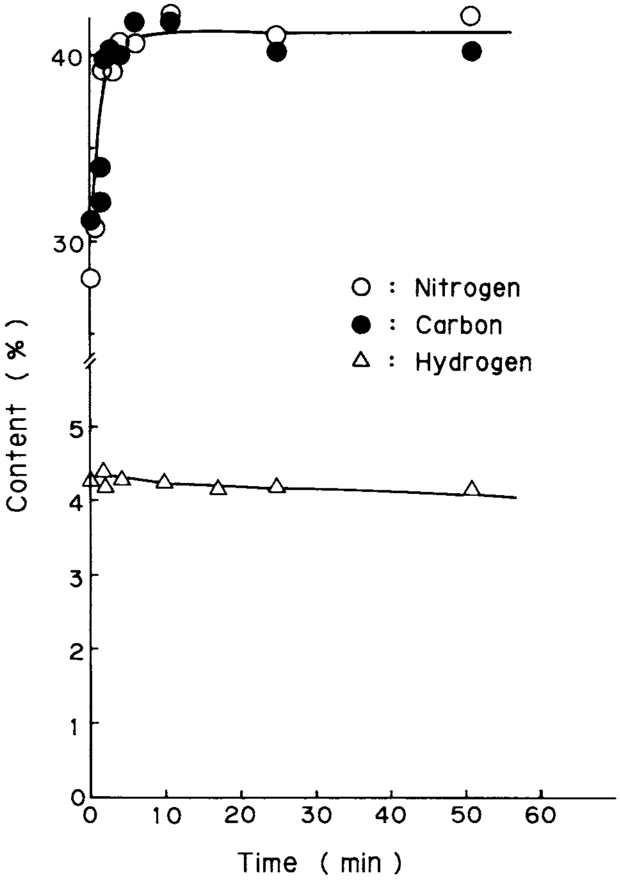

Figure 32 Changes in element contents of melamine resin with heating at 300°C in air.

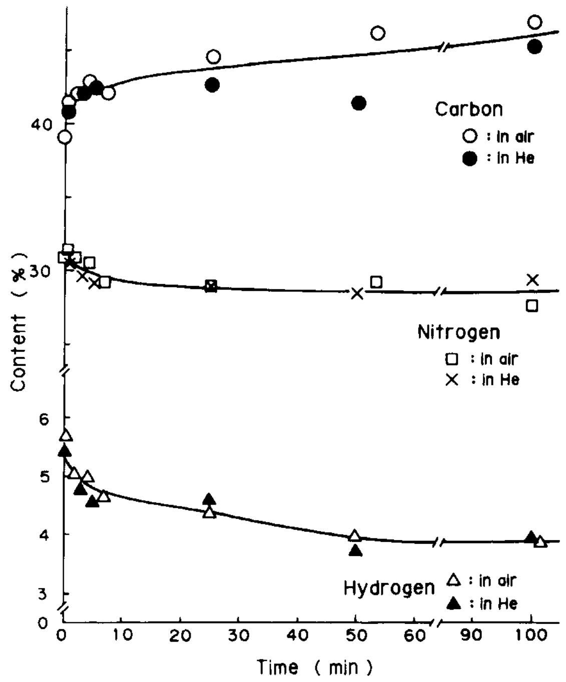

Figure 33 Changes in element contents of urea resin with heating at 235°C in air and 255°C in helium.

respectively. Also Figure 34 suggests the presence of some peaks or maxima of the HCN yield in the neighborhood of 800°C at high rates of air flow. Two reactions, acceleration of HCN production by oxygen and oxidation of HCN, might be involved in the peak formation. In a high temperature range from 900 to 1000°C, HCN yield has been reported to decrease due to thermal decomposition,[11,13] but this is not clear from the present study.

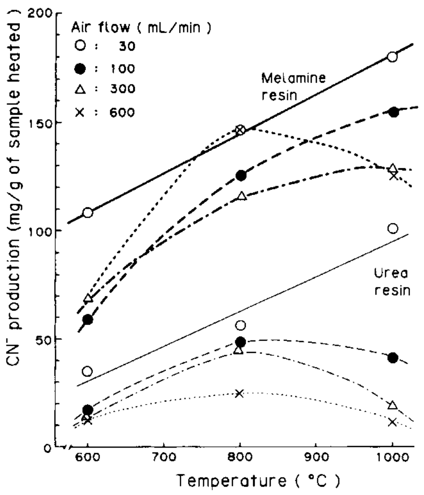

Figure 34 Effects of temperature on HCN yield from melamine and urea resins.

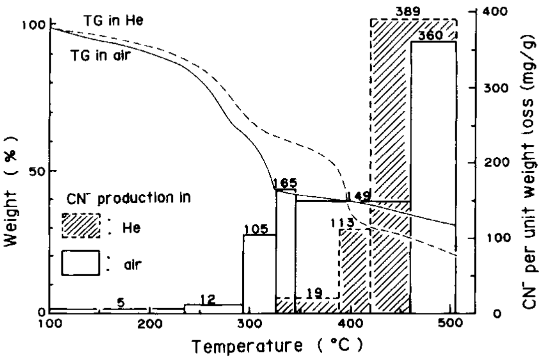

Figure 35 HCN yield from melamine resin during TG. Heating rate: 5°C/min.

In spite of the almost equal nitrogen content the urea resin evolved much less HCN than the melamine resin. This seems to have come from weaker C—N linkages in the urea resin than in triazine rings of the melamine resin, which is proven by the results of elemental analysis in Figures 32 and 33.

CONCLUSIONS

1. Three kinds of reactions: initiation reactions, reactions splitting off volatile fragments, and reactions producing stabilized structures are inferred to be involved in the pyrolyses of both melamine–formaldehyde and urea–formaldehyde resins from the weight loss behavior with isothermal heating.
2. In TG the weight loss of the melamine resin progressed through two active steps and one slow step, all of which occurred at lower temperatures in air than He. For the weight loss of this resin with the isothermal heating two stages of reactions of zeroth and first orders

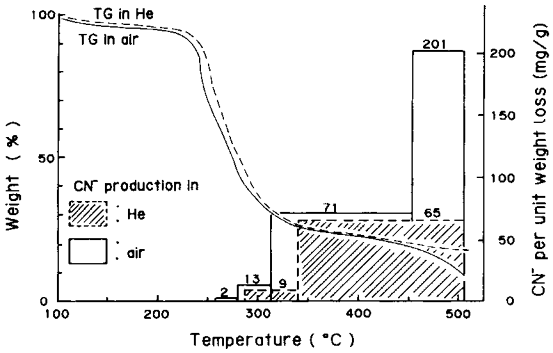

Figure 36 HCN yield from urea resin during TG. Heating rate: 5°C/min.

in He, and three stages of first-order reaction in air were found from plots of the weight loss rates against the weights. Activation energies for the weight losses in TG (except for the slow step in air) and with isothermal heating in the high temperature range in He are much higher than those for the isothermal heating in the whole range of temperatures used in air and in the low temperature range in He. The higher activation energies may be attributable to structures stabilized with the progress of pyrolysis.

3. The weight loss of the urea resin in TG was substantially completed through one active step to leave the residue. The step, however, consisted of a few small steps, as found by DTG. Two stages in He and three stages in air of first-order reaction were found for the weight loss of this resin with the isothermal heating. Activation energies for the weight losses (except for the oxidation of residue in TG) are divided into two groups of values larger than 200 kJ/mol and less than 100 kJ/mol, respectively. The reason can be given as being due to the stabilization of structures stated above for the melamine resin.
4. Results of elemental analysis of the residues indicate that the melamine resin lost hydrogen and oxygen more than carbon and nitrogen with the heating, and that the urea resin lost carbon less than nitrogen, hydrogen, and oxygen.
5. HCN from the two resins increased with temperature up to 500°C and at low temperature was produced more in air than in He. However, effects of temperature higher than 600°C on the HCN yield changed depending on the rate of air flow. The melamine resin evolved much more HCN than the urea resin, probably because of more stable C—N linkages in the former resin than in the latter resin.
6. Future investigation on the pyrolysis of these resins will focus on the chemical mechanisms associated with the kinetics.

REFERENCES

1. Y. Sekine, *J. Chem. Soc. Jpn. Ind. Chem. Sect.*, **63**, 1657 (1960).
2. K. Akita and M. Kase, *J. Polym. Sci. A-1*, **5**, 833 (1967).
3. H. H. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).
4. T. Hirata and K. E. Werner, *J. Appl. Polym. Sci.*, **33**, 1533 (1987).
5. J. H. Lady, R. E. Adams, and I. Kesse, *J. Appl. Polym. Sci.*, **3**, 65 (1960).
6. R. T. Conley, *Thermal Stability of Polymers*, R. T. Conley, Ed., Dekker, New York, 1970, Vol. 1, pp. 501–506.
7. H. H. G. Jellinek and K. Takada, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 2709 (1975).
8. H. H. G. Jellinek and A. Das, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 2715 (1978).
9. H. H. G. Jellinek and S. R. Dunkle, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 1471 (1980).
10. H. H. G. Jellinek and S. R. Dunkle, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 85 (1982).
11. H. H. G. Jellinek and S. R. Dunkle, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 2313 (1982).
12. H. H. G. Jellinek and S. R. Dunkle, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 487 (1983).
13. H. H. Jellinek and S. R. Dunkle, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2111 (1983).

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