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A study of the combustion and fire-retardance behaviour of unsaturated polyester/phenolic resin blends

H.-T. Chiu *, S.-H. Chiu, R.-E. Jeng, J.-S. Chung

Graduate School of Textile and Polymer Engineering, National Taiwan University of Science and Technology, 43 Keelung Road, Section 4, Taipei 10672, Taiwan

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Abstract

The thermal degradation and combustion behaviour of an interpenetrating network (IPN) structure of unsaturated polyester UP resin and a resole type of phenolic resin was studied. Thermal gravimetric analysis (TGA) was used to monitor the degree of thermal decomposition for the UP/phenol IPN structure and the change of the oxygen index (OI) was used to describe the variation of the combustion behaviour. The smoke density was measured via a non-flaming process to detect the amount of smoke generated during the combustion. A homemade cone calorimetric dynamic flammability evaluation system was assembled to analyse the gas evolved and to measure the heat release rate (HRR) during the combustion. Under simulated conditions of a burning field at the temperature of 757°C, the variation of the concentration of carbon monoxide (CO) and the HRR of the UP/phenol IPN structure were studied. The results show that modification of the essentially flammable UP resin by the phenol structure to form an IPN system cannot only remarkably improve the heat resistance but also help to suppress the smoke, toxic gas and heat release during the combustion. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Flammability; Fire retardant; Interpenetration network (IPN); Phenol; Unsaturated polyester

1. Introduction

In recent years, fire and burning are taking place almost everywhere due to the tremendous amount of flammable interior decoration and construction materials which are used. The main reason for serious damage to life and property is that these kinds of material can catch fire very easily and can keep burning to propagate the flame, so that a large amount of toxic gas and heavy smoke are generated. Therefore, the development of polymer flame retardant technology regains a focus in the Western countries, Japan and Taiwan for the past few years. Such technology seeks the development of a flame retardant, low toxic, low corrosive, minimal smoke generating and good heat resistant material. Generally speaking, various flame retardant additives are currently used in engineering plastic materials to achieve the objectives. However, polymer blends and grafting techniques are believed to be the key studies to overcome the problems in the near future.

Unsaturated polyester resin (UP), is an economical thermoset material that is widely used, due to its excellent processability and good cross-linking tendency as well as the fairly good oil, moisture and acid resistances and mechanical properties when cured [1]. However, the major drawback of UP resin is quite high flammability and a large amount of heavy smoke generated when burning. Two common ways to make UP become flame retardant are: (1) introducing halogens into the polyester structure; (2) blending flame retardant materials with the UP resin. Typical flame retardant additives can be categorized into two systems: inorganic series and halogen series. In the inorganic system, ATH ($Al(OH)_3$), is used most, but quite a large amount of ATH is needed to obtain the required flame retardant effectiveness, and the consequent difficulties during processing are its limitation. Although flame retardant additives of the halogen type are widely used in many applications, harmful (toxic) gases and smoke and high concentration of the smoke are generated when burning and may interfere with the vision during escape.

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* Corresponding author. Tel.: +886-273-76520; fax: +886-223-789028.
E-mail address: ch5793@ms31.hinet.net (H.-T. Chiu).

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One of the main characteristics of the phenolic resins is excellent flame retardance and heat resistance. Compared to other organic materials, phenol resin is more difficult to burn. Even after burning, phenol resin has the least smokes and toxic gases generated [2] and the highest amount of carbon residues.

In this study, phenol resin featuring low toxic smoke evolution and good flame retardance was selected to blend with UP resin to improve its poor properties on burning. To measure the effects of the IPN structure on the improvement of flame resistance and combustion behaviour, thermal gravimetric analysis (TGA) was used to monitor the degree of thermal decomposition for the UP/phenol IPN structure and the change of the oxygen index (OI) was to describe the variation of the combustion behaviour. Also the density of smoke, the amount of smoke or gas evolved and the heat release rate (HRR) during the experiments of flammability were analysed and studied.

2. Experimental

2.1. Materials

Resin — UP from Yong-Shun Chemicals (157BQD), phenol (Resole type) from Showa (SHONOL BLS-794Z which contains 10% of PVB fibre reinforced modifier). Hardener — BPO (benzoyl peroxide); TBPB (*tert*-butyl perbenzoate).

2.2. Preparation of the specimens

2.2.1. UP specimens

In a typical preparation, 100 parts of UP resin were mixed with 1 part of hardener BPO and 1 part of TBPB. Mixing was carried out under vacuum to avoid voids and bubbles at a stirring speed of 100 rpm for 30 min. The mixture was poured into a mould then cured at a temperature of 100°C for 2 h in a vacuum oven. After cooling to room temperature, the mould was detached and the cured resin cut into small specimens.

2.2.2. Phenol and UP/phenol IPN blends specimens

In a typical preparation, UP resin was mixed with 1 phr of hardener BPO and 1 phr of TBPB. Phenol resin was added at the required ratio. Mixing was carried out with 30 phr of acetone, under vacuum to avoid voids and bubbles at a stirring speed of 100 rpm for 30 min (the stirring speed was set to 200 rpm in the first 5 min). The materials are mixed under vacuum to avoid voids and bubbles at the stirring speed of 100 rpm for 30 min. The mixture was cast into a mould then placed in a vacuum oven to go through the curing process as follows. 40°C/15 h, 50°C/12 h, 60°C/24 h, 80°C/6 h, 100°C/4 h, 120°C/3 h, 150°C/12 h. After cooling to room temperature, the mould was detached and the cured resin cut into small specimens.

2.3. Analysis

2.3.1. Thermal gravimetric analysis (TGA)

A thermal gravimetric analyser, ULVAC TGC 700RH, was used to carry out the TGA experiments on the weight loss and thermal decomposition behaviour for UP/phenol IPN composites in this study. The heating rate was 20°C/min, from 30 to 1000°C, under nitrogen.

2.3.2. Oxygen index (OI)

The OI was measured by a Limiting Oxygen Index Tester, Polymer Laboratories Ltd. HFTA II, 20 s after the ignition. According to the ASTM D2863 standard, the specimens were cut into sizes of 140×6.5 mm, 2 mm thick.

The definition of OI is “The minimum concentration of oxygen to maintain a candle-like burning for a testing material under an environment with slowly rising gas of nitrogen/oxygen mixture”. The thermal equilibrium is established between the heat released during the specimen is burning and the heat loss from the testing environment. The OI of a test material therefore can be identified either by a specific burning time period (3 min) or by a specific burned length of the specimen (50 mm, 75 mm). The OI then is defined as:

$$[\mathrm{OI}]\% = \frac{[\mathrm{O_2}]}{[\mathrm{O_2}] + [\mathrm{N_2}]} \times 100\%$$

$[\mathrm{O_2}]$ = volumetric flow rate of $\mathrm{O_2}$, $\mathrm{cm^3/s}$;
$[\mathrm{N_2}]$ = volumetric flow rate of $\mathrm{N_2}$, $\mathrm{cm^3/s}$.

2.3.3. Specific optical density of smoke (D_s)

A Smoke Density Tester, Polymer Laboratories Ltd., NBS was used to measure the specific optical density of smoke (D_s) of the UP/phenol IPN composites under a non-flaming process. According to the ASTM E662 standard, the specimens were cut into sizes of 76×76 mm, 2 mm thick.

The smoke properties are defined as follows;

I — specific optical smoke density, D_s :

$$D_s = \frac{V}{A \cdot L} \log \frac{100}{T}$$

where

V: volume of the smoke box, $\mathrm{m^3}$;
A: exposure area of the specimen, $\mathrm{m^2}$;
L: length for the light travelled, m;
T: penetration rate of light (%)

II — $D_{s,4}$: the smoke density at the fourth minute, representing the smoke density at the initial state;

III — tD_{16}: the time when D_s is reaching 16, representing the smoke rate at the initial state;
IV — the relationship between the smoke density and smoke concentration:

$D_s = 50$: normal for smoke density;
$D_s = 100$–300: dense for smoke density;
$D_s \geqslant 400$: very dense for smoke density.

V — the rate of increase in smoke density, R

$$R = \frac{1}{4}\left[\frac{0.9D_m - 0.7D_m}{t_{0.9} - t_{0.7}} + \frac{0.7D_m - 0.5D_m}{t_{0.7} - t_{0.5}} + \frac{0.5D_m - 0.3D_m}{t_{0.5} - t_{0.3}} + \frac{0.3D_m - 0.1D_m}{t_{0.3} - t_{0.1}}\right]$$

where

D_m: maximum density of smoke;
$t_{0.9}$: the time to reach 0.9 D_m;
$t_{0.7}$: the time to reach 0.7 D_m;
$t_{0.5}$: the time to reach 0.5 D_m;
$t_{0.3}$: the time to reach 0.3 D_m;
$t_{0.1}$: the time to reach 0.1 D_m.

VI — the smoke obscuration index, SOI:

$$\mathrm{SOI} = \frac{D_m \cdot R}{100 \cdot tD_{16}}$$

where

SOI = 5–10: little danger to decrease the visibility;
SOI = 10–30: dangerous for decrease in visibility;
SOI > 30: very dangerous for decrease in visibility.

2.3.4. Measure of the carbon monoxide and HRR

A homemade dynamic flammability evaluation system [3], according to the ISO 5660 and ASTM 1354 standards, was assembled to measure various flammability and thermal properties of the UP/phenol IPN composites. This system can record mass loss rate, HRR, toxic gases, and other combustion properties in real time. Experiments are carried out to measure the

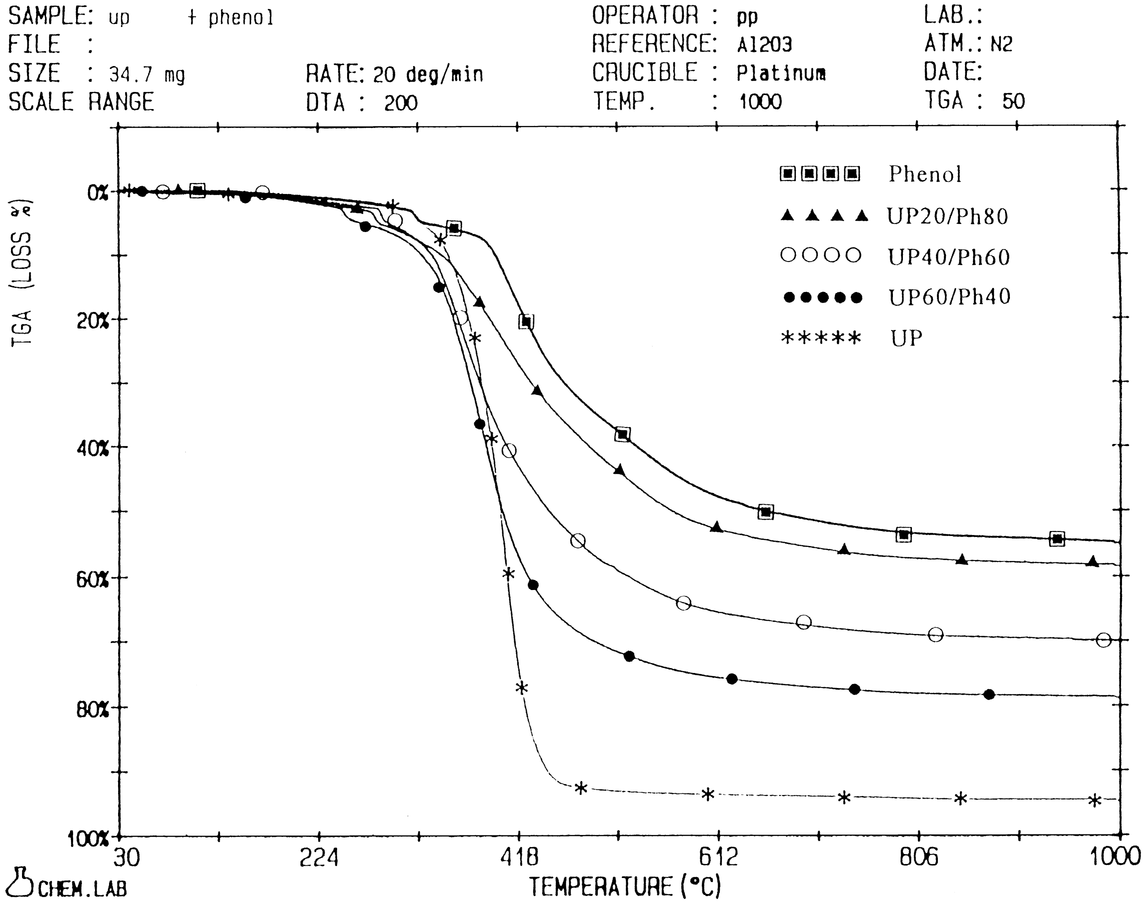

Fig. 1. Thermogravimetric analysis of UP/phenol resin blends.

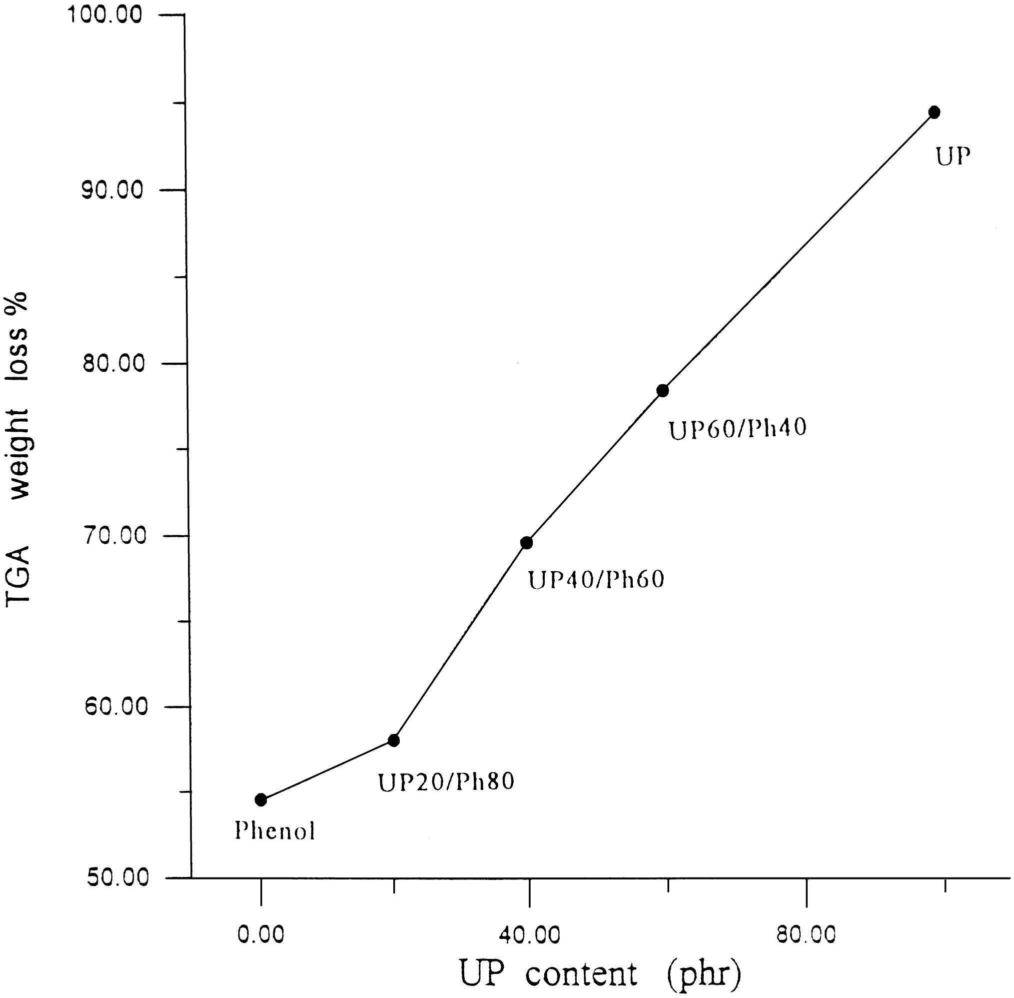

Fig. 2. Weight loss % in TGA of UP/phenol resin blends.

real time variation of CO gas and HRR in a simulated fire field which is under a condition of a heat flux = 50 kW/m^2, and its temperature is controlled as $T = 757$°C. The size of the specimen is 100×100 mm^2, 2 mm thick.

Detection of CO concentration [3] — CO concentration is detected by CO sensor (TROLEX company, model no. TX3241.01). Detection range is 0–300 ppm. Output voltage signal is 0.4–2 V. The CO concentration is calculated by following method,

$$[\mathrm{CO}] = 89.5522 \times V_0 - 35.8209$$

[CO] : CO concentration (ppm);

V_0 : output voltage signal(V).

Definition of HRR and its measuring principle — there are many methods to measure HRR. In this study, instantaneous HRR is calculated using the oxygen consumption principle. Based upon ASTM 1354 and ISO 5660 Part-I, heat release can be calculated from the consumption of oxygen during the combustion process. Its maximum tolerance is only ±5%, which is more accurate than thermopile method (ASTM E906-83). Huggett's [4] study showed that for most organic materials, total heat released per unit oxygen consumed in a combustion process is almost a constant, 13.1 MJ/kg. The HRR is calculated by:

$$\dot{q}(t) = \left(\frac{\Delta h_c}{r_0}\right)(110)C\sqrt{\frac{\Delta P}{Te}}\frac{x^0_{O_2} - x_{O_2}}{1.105 - 1.5x_{O_2}}$$

where

$\dot{q}(t)$ = HRR;

$\Delta h_c/r_0 = 13.1\times10^3$ kJ/kg;

Δh_c = net combustion heat;

r_0 = oxygen burning ratio based on mass flow rate;

C = analytical constant of oxygen consumed;

ΔP = pressure drop;
Te = absolute temperature;
$x^0_{O_2}$ = initial oxygen mole ratio;
x_{O_2} = final oxygen mole ratio.

3. Results and discussion

3.1. Thermal decomposition of UP/phenol IPN blends

Though it is known that the UP resin is not quite compatible with phenol resin [5], the network of UP and phenol resin might form an integral interpenetrated structure rather than forming delaminated independent networks by a simultaneous IPN curing operation via a dispersive mechanical stirring and mixing process. Various parameters that may affect degree of the network interpenetration like: viscosity of the IPN components, dispersivity, compatibility, and the curing rate. Basically, chain breaking will take place at the weakest chemical bonds on UP and phenol structure when the IPN structure is attacked by heat or other energy source. The TGA curve of UP in Fig. 1 shows minor weight loss before 340°C, mainly due to the escape of unreacted styrene monomer and non-fully cross linked oligomers [6]. In the temperature range of 340–460°C, the major decomposition area occurs on the ester chain (-CO–C-) and the unsaturated chain (-C=C-) which are the weakest chemical bonding points in the main chain. In this area, large amounts of decomposition are observed. Finally, when the temperature reaches 1000°C, about 5% of carbide is formed, that means total weight loss is around 95%.

On the other hand, from the studies of Conley [7,12], and Yamashita [8] on the thermal decomposition of the phenol resin, there are three stages of decomposition for the resole type phenol. Before 400°C, there is about 8% of weight loss showed on TGA experiments, mainly due

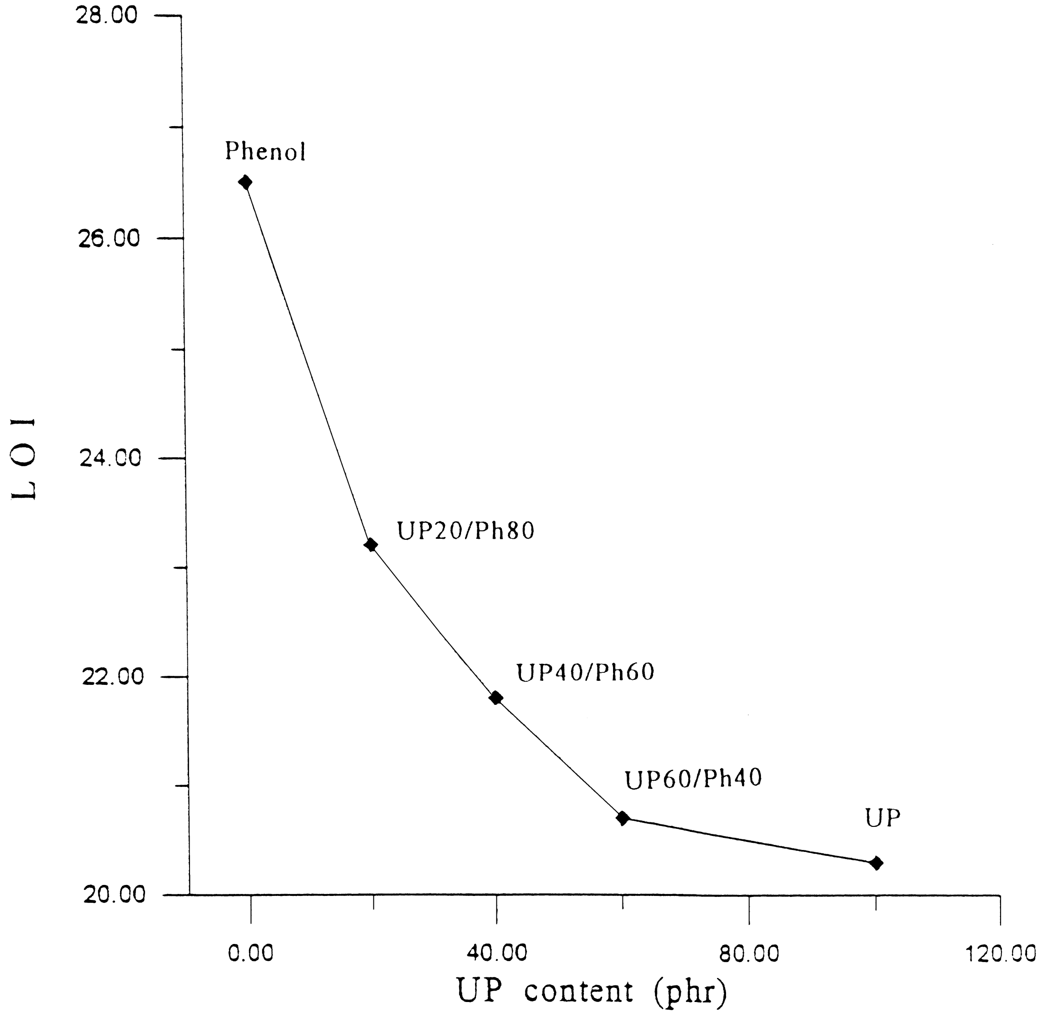

Fig. 3. LOI value of UP/phenol resin blends.

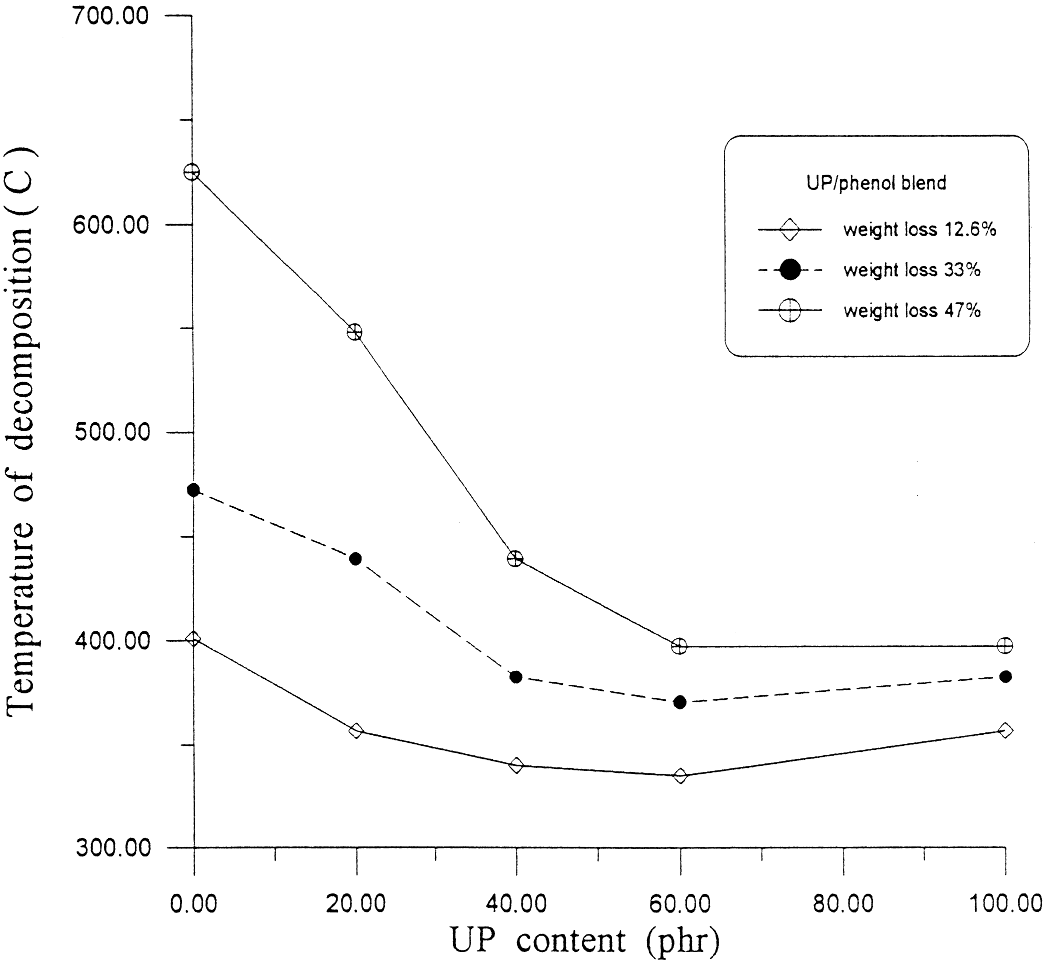

Fig. 4. Thermal decomposition temperature of UP/phenol resin blends at loss of 12.6, 33, 47wt.% respectively.

to excess phenol, aldehyde, oligomer, and water. For the thermal decomposition within the range of 400°C–600°C, decomposition products are CO, CO_2, benzaldehyde, phenol and its polymer, H_2O, CH_4 and H_2, as reported by Shulman and Lochte [9]. In Fig. 1, the TGA curve of phenol also shows consistency with the above results, which is considered as the main temperature range of decomposition takes place, thermal weight loss is about 32%. For the case of temperature above 600°C, Conley [7,10], Yamashita [8] and Lausevic[11] showed the evidence that dehydration occurs and a carbon-like structure is gradually formed then is accumulating as char alone with a carbon monoxide as by-product. A small amount of weight loss showing on the TGA curve of phenol resin above 600°C in Fig. 1 demonstrates this phenomenon. Beyond this temperature, the curve is flat. Total thermal weight loss for phenol resin is accumulated as 54% when temperature reaches 1000°C.

Compared to the TGA curve of phenol resin in Fig. 1, the first stage of thermal decomposition shifts to lower temperature for the UP/phenol IPN structure and the range of temperature also becomes narrower. It is believed that when both UP and phenol resin network are cross linked with each other to form the IPN structure, the structure also interferes or blocks some molecules which should be reacted to the resin itself away from linking. Thus more monomers and un-cross linked

Table 1
Thermal decomposition temperature of UP/phenol resin blends at given weight losses

	Thermal decomposition temperature (°C) at different weight loss (wt.%)		
Component (phr/phr)	12.6%	33%	47%
Phenol	401.0	472.0	625.0
Ph80/up20	356.5	439.0	548.0
Ph60/up40	340.0	382.0	439.0
Ph40/up60	335.0	370.0	397.0
Up	356.5	382.0	397.0

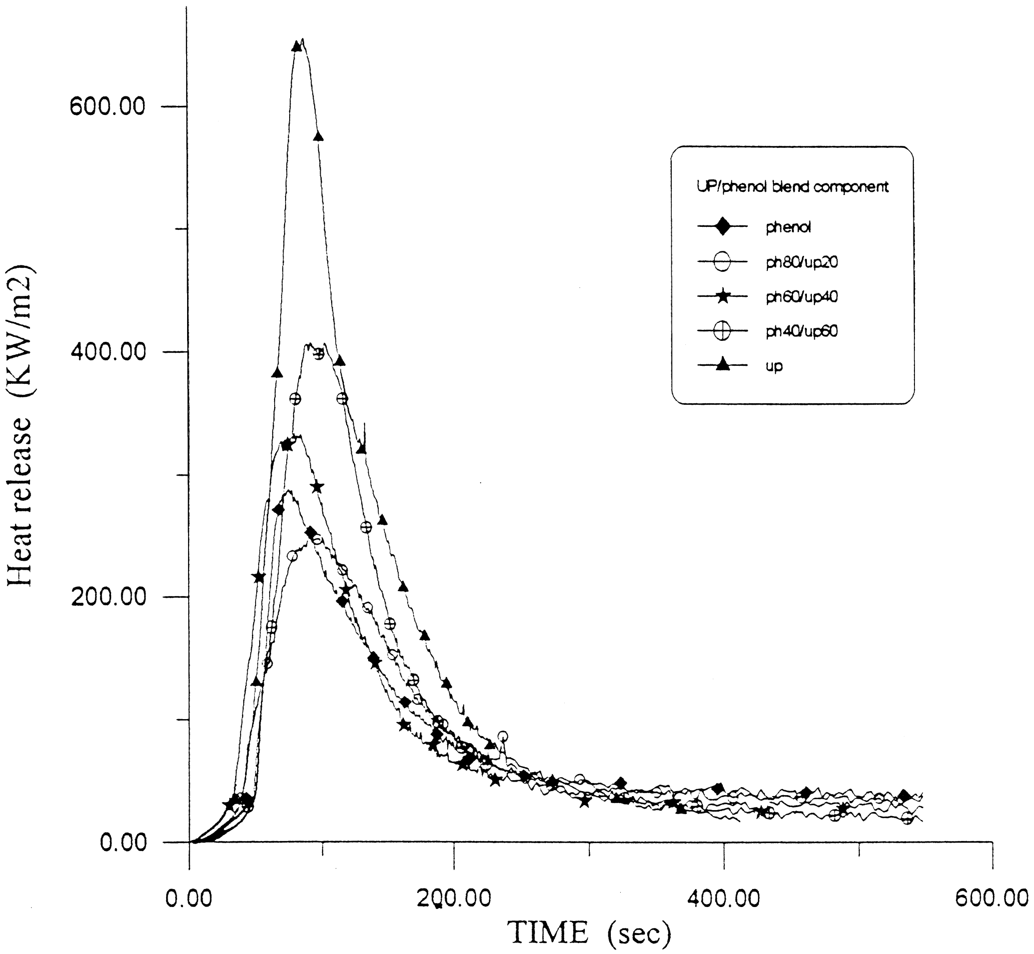

Fig. 5. HRR curve of UP/phenol resin blends.

oligomers are left in for the IPN structure after the curing process, compared to the pure UP or phenol cured system. Fig. 2 shows the relationship between thermal weight loss and the UP content in UP/phenol resin blends. The percentage of weight loss is remarkably reduced as the content of phenol resin increases.

3.2. Flame retardation of UP/phenol IPN blends

For evaluation of the flame retardation of a material, temperature of thermal decomposition (T_d) is usually a reference index that can be determined from the inflection point of the TGA curve. However, for the realistic applications, limiting oxygen index (LOI) is used. The larger value of LOI, the harder it is for the material to catch fire and to burn. Generally speaking, for the case of OI below 21, the material is considered as "flammable"; for OI = 22–125, the material is "self extinguishable"; and for the case of OI is above 26, the material is "hard to burn."

Fig. 3 demonstrates the relationship between UP content in UP/phenol resin blends and LOI. The value of LOI increases as the content of phenol resin increases. By reviewing data from the thermal decomposition temperature of UP/phenol resin blends at given weight losses (see Fig. 4 and Table 1), when the thermal weight loss reaches 47%, T_d for phenol resin is about 625°C and T_d for UP resin is 397°C. Intrinsically, larger LOI value for phenol resin than that of UP resin is due to more functional benzene rings in the phenol chemical structure, therefore the better flame retardation for the phenol resin.

However, from the study of variation of T_d or LOI with the resin-blending ratio, it is found that the blending UP with phenol resin shows a non-linear downward curve relationship for either T_d or LOI. The interaction within the UP/phenol resin blends is very weak, in that the IPN structure is basically randomly entangled by a mechanical mixing effect. Such interpenetrated network structure may cause some interference or phase separation due to the difference between resin density, viscosity and curing rate during the blending process. The flame retardation of the IPN resin blends therefore is non-additive.

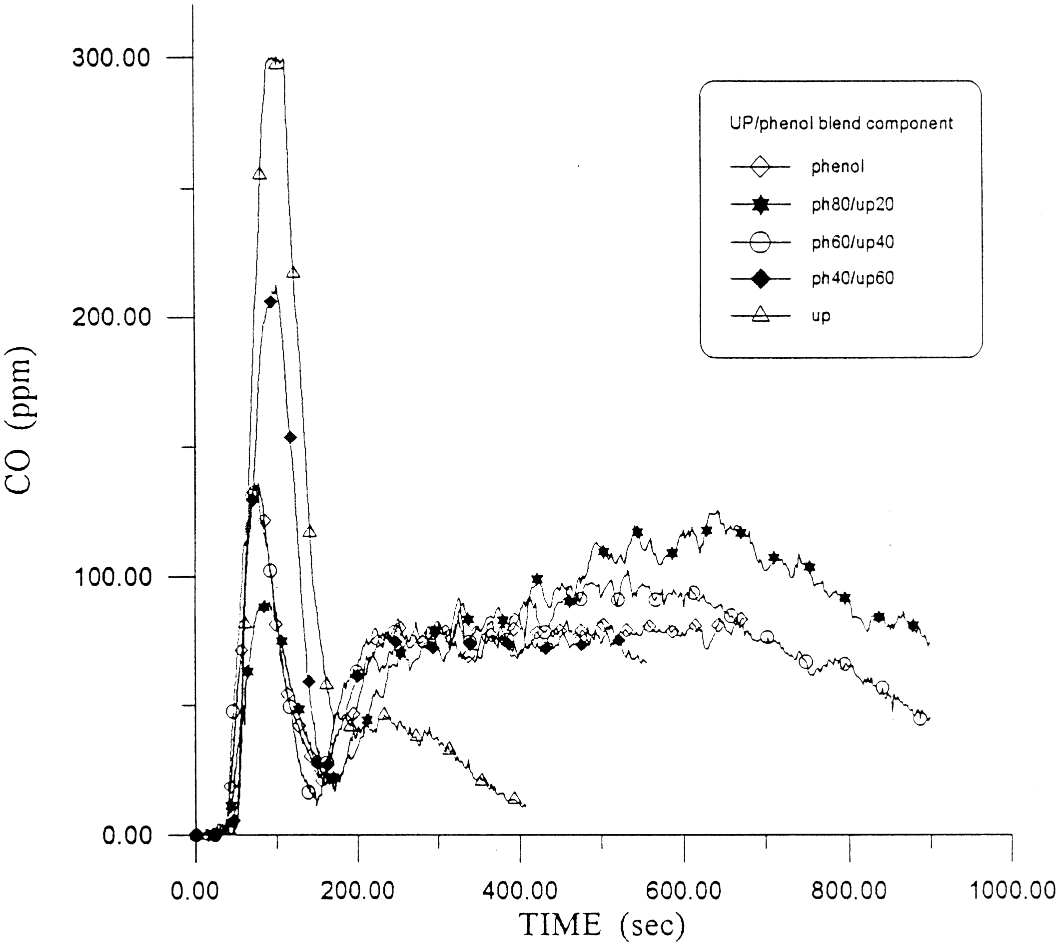

Fig. 6. CO evolution curve of UP/phenol resin blends.

3.3. Combustion behaviour of UP/phenol IPN blends

Besides the concentration of O_2 in the combustion process, material intrinsic property like heat of decomposition, HRR and produced gas after decomposition are all the elements to study the behaviour of combustion.

In order to analyse and study the combustion behaviour of UP/phenol resin blends in a real fire field (757°C), HRR is adopted to describe the heat generation during the combustion process [13–15]. Fig. 5 shows the HRR curve for UP/phenol resin blends. It is found that the slope of HRR curve is dramatically increased at a time of 30 s during the test. The rate of combustion is very fast and it can also be confirmed from the TGA curve for UP resin. The specimen is burned in a very short time and a large amount of combustion heat is released simultaneously. In the real world, such heat will radiate to all the surrounding items and make these things start burning very quickly. Furthermore, hot air is also moving upward very fast, which speeds up the convection to the surrounding atmosphere. The fire then quickly propagates! At the highest point of the HRR curve, most of the UP resin is about to burn out; therefore the HRR drops dramatically thus making the curve like a sharp peak. On the other hand, HRR_{max} of phenol resin and UP/phenol resin blends are much lower than that of UP resin (see Fig. 5). This is because a layer of char [7,8,10,11] is formed on the surface of the resin blend, which inhibits the flammable gases and oxygen to go through further mixing and burning. The heat release during the combustion is reduced and the heat radiated to the surroundings is retarded as well. The peaks of HRR curve for the phenol resin and UP/phenol resin blends are lower than that of UP resin; the rate of combustion is also slower thus making the curve more bell-like. It is also found that the HRR for the phenol resin and UP/phenol resin blends keep a lower and stable value even the curve has passed the maximum point. Such results are consistent with the study of Mathys et al. [2]. This is due to the fact that chemical structure of phenol resin is deformed, and a layer of char is found on the surface of the blends. Flame-less (or non-flaming) combustion takes place and keeps heat

Table 2
The dynamic flammability parameters of UP/phenol resin blends

Component (phr/phr)	Max. HR (kW/m^2)	Time to reach max. HR(s)	Total HR (MJ/m^2)	Max. <CO> (ppm)
Phenol	288.3	75	32.25	136
Ph80/up20	250.9	90	33.49	125
Ph60/up40	333.3	79	36.07	136
Ph40/up60	407.0	91	41.34	212
Up	653.8	87	56.38	Above 300

release at a constant rate under a high temperature of 757°C.

Fig. 6 shows the gas evolution detected by the dynamic cone calorimetric meter during the combustion. For UP resin, combustion occurs vigorously at the time of 30 s, a great degree of the polymer decomposition is also taking place at this point. Since the supply of oxygen is insufficient, decomposed molecules are not fully burned, thus a very high concentration of monoxide is evolved. In Fig. 6, the concentration of CO sharply increases and exceeds the upper limits (300 ppm) of the detector; consequently the specimen is gradually burned out, then the CO concentration quickly drops. After 170 s, CO concentration slightly increases. This may be due to the following reason: the area of specimen carrier cover exposed under the radiant heat is 94×94 mm. Specimen dimension is 100×100 mm. The outside circle area of specimen exposed under radiant heat is not directly that which made burning delayed.

In UP/phenol blends, due to the existing of phenol, the concentration of CO in the first step is decreased. After 165 s, concentration of CO increases slightly to become a stable plateau. The major reason is proved by Lochte et al. [7,10] that phenol decompose into small molecules and release water when burning. Then after 600°C, coal tar accumulates and CO is generated. This is why at the end of the test, the CO concentration increases and becomes a stable plateau. The dynamic flammability parameters are listed in Table 2. In general, lower maximum HR, total HR, maximum CO concentration indicate less fire hazard.

Various gases evolved during the combustion process obviously affect the flame retardation and optical smoke density of a material. Fig. 7 is the test results for smoke density under non-flaming process by NBS. It shows that the smoke density (D_s) for UP resin is higher than that of UP/phenol resin blends; the maximum density of

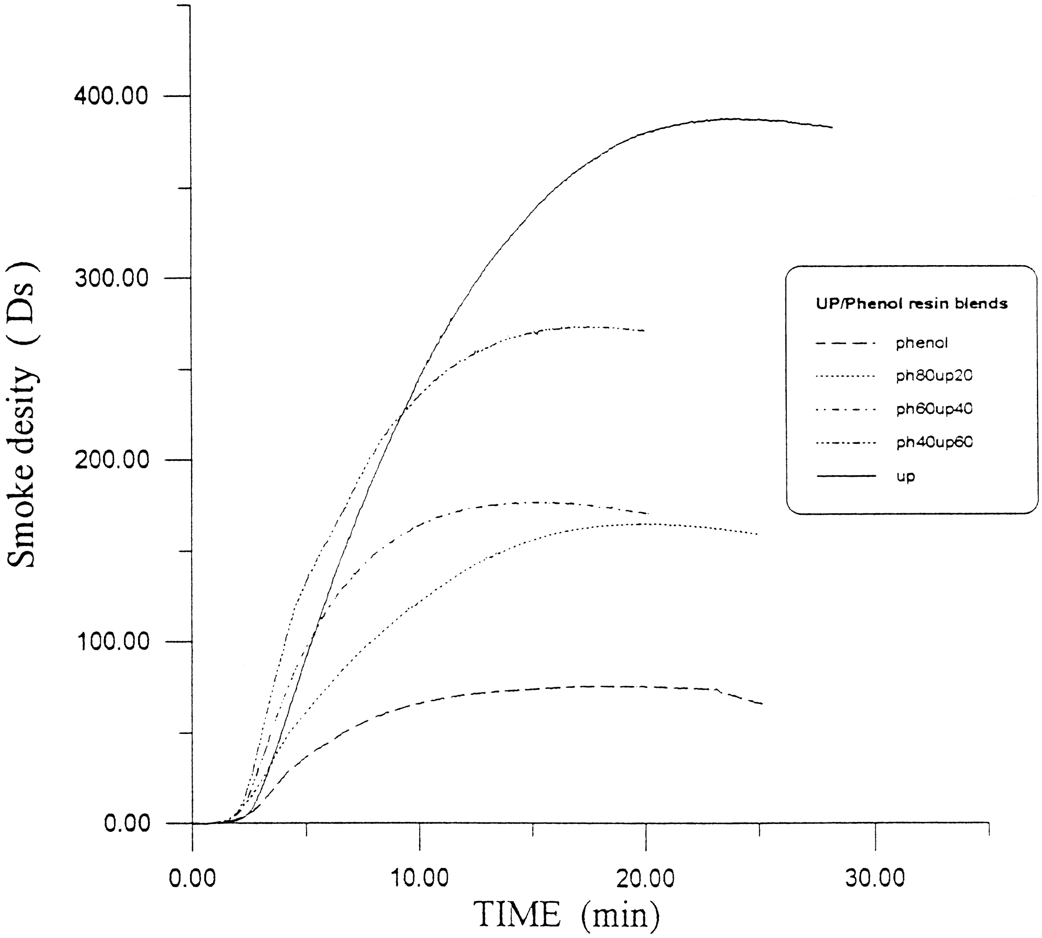

Fig. 7. Smoke density of UP/phenol resin blends for non-flaming process.

Table 3
The smoke properties of UP/phenol resin blends

Component (phr/phr)	$D_{s,4}$	tD_{16} (min)	R (min^{-1})	SOI	D_m
Phenol	25.78	3.35	9.24	2.08	75.3
Ph80/up20	45.08	2.62	13.76	8.65	164.7
Ph60/up40	68.46	2.48	24.77	17.64	176.7
Ph40/up60	96.00	2.34	32.06	37.36	272.7
Up	53.00	2.91	27.33	36.31	386.6

smoke (D_m) is 386.6. This is because the combustion for the UP resin is quite vigorous with little amount of carbon left. Insufficient oxygen supply makes the combustion incomplete, therefore, heavy smoke is generated when the nonflammable gas, flammable gas and micro solid particles are cooled.

From the D_s curve of phenol resin, it is found that the combustion rate is quite slow, consequently less gas is evolved and more carbon is left. The maximum density of smoke is quite low ($D_m = 75.3$) which is obviously much lower than that of UP resin. However, in the first three minutes of the initial stage of combustion, the smoke density of UP/phenol resin blends is actually higher, this might be due to the interference or blocking caused by the IPN structure that is mentioned previously. Table 3 shows the variation of smoke property for UP/phenol resin blends under a non-flaming process. UP resin has a highest D_s value because of its intrinsic chemical composition and molecular structure.

4. Conclusions

Summarizing the analytical results from the TGA, LOI, D_s and dynamic flammability evaluation system, the capability of flame retardance for pure UP resin is very poor. Within a narrow range of temperature, 340–460°C, thermal decomposition speedily occurs, weight loss of thermal decomposition is around 82% and the total weight loss is 94.4% in the entire combustion process. Furthermore, the combustion behaviour with respect to LOI, density of smoke, carbon monoxide and HRR are so poor that little capability shows on the fire or flame retardant applications. Therefore, there is a need to be able to flame retard UP.

In this study, we introduce phenolic resin into UP to form an IPN structure to improve its combustion behaviour. The result in thermal decomposition study of UP/phenol IPN blends shows that the percentage weight loss is remarkably reduced as the content of phenolic resin increases.

From evaluation of flame retardation of UP/phenol IPN blends, it shows LOI value increases as content of phenolic resin increases which means material from “flammable” becomes “hard to burn”. Thermal decomposition temperature (T_d) of each material has the same trend as LOI value shows.

From the combustion behaviour study, the maximum heat releases of UP/phenol IPN blends are much lower than that of UP resin. Due to the phenol, the concentration of CO in the first step of combustion is decreased. After 165 s, the concentration of CO increases slightly to become a stable plateau. Smoke density studies also sho that the smoke density (D_s) for UP/phenol IPN blends is much lower than that of UP resin.

According to the above results, the UP/phenol IPN structure cannot only remarkably improve the heat resistance but also help to suppress the smoke, toxic gas and heat release during the combustion process.

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