Physical and Chemical Effects of Diethyl *N,N'*-Diethanolaminomethylphosphate on Flame Retardancy of Rigid Polyurethane Foam

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ABSTRACT: Diethyl *N,N*-diethanolaminomethylphosphate could react with isocyanate because it contained hydroxy group. This was confirmed by FTIR spectrum. It did not produce any effect on the foam structure of rigid polyurethane foam (RPUF). SEM, IR spectrum, and thermal analysis were used for investigation of the physical and chemical changes during the combustion of flame-retardant RPUF. It was shown that the flame retardancy changed the thermal decomposition behavior of RPUF, widened the decomposition temperature region of RPUF, reduced the amounts of decomposition products at high temperatures, and increased the decomposition residuals arisen from charring of flame-retardant RPUF. Those changes improved the flame retardancy of RPUF. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 276–282, 2001

Key words: rigid polyurethane foam; reactive flame retardant; physical and chemical changes

INTRODUCTION

Rigid polyurethane foam (RPUF) is recognized as an outstanding material for insulation and building applications. It exhibits many desirable properties, such as a low thermal conductivity, an excellent dimensional stability, resistance to compression, a low moisture permeability, and a reduced water absorption.[1] The flammability of RPUF and the smoke that evolved when burning may be drawbacks in building applications, which are governed by ever-increasingly stringent fire regulations. This has prompted active efforts in achieving better flame retardancy. In the past, a large number of articles dealing with the improvement of fire performance of polyurethane foams were published.[2–15]

The traditional technique of preparing flame-retardant RPUF is to blend flame-retardant additives with the foam-forming mixture and physically disperse into the final material. Although this method is convenient for RPUF to achieve flame retardancy, bonding flame-retardant groups to polyurethane backbone (i.e., using a reactive flame retardant) has attracted much attention recently.[2–11] Commonly, this procedure was performed by reacting phosphorus-containing diols with diisocyanate.[2–10] Novel diisocyanate that contains a flame-retardant element can also be used.[11] However, usually this method is too expensive to be put into use in production. The use of a reactive flame retardant has the advantage of permanent attachment of the flame retardancy. This will lead to the acquirement that a much smaller amount of flame retardant is required to reach a certain degree of flame retardancy. Consequently, a much smaller influence is brought upon the physical and mechanical properties of RPUF.

Table I Formulations of Flame-Retardant RPUF

Foam Ingredient	Parts by Weight (pbw)
Polyether polyol (N303) (OH NO.492)	50
Silicon oil	0.2
Triethanolamine	0.9
Distilled water	1
Reactive flame retardant	0–20
PAPI ($R = 1.05$)	90

Halogenated reactive flame retardant has been studied frequently, but there has been a debate about the evolution of dichloroethane (carcinogen).[12] Therefore, the trend is toward using nonhalogenated flame retardant. Consequently, phosphorus and nitrogen compounds are the materials of choice for the flame retardation of RPUF. The burning of the phosphorus-containing flame retardant is mainly through a condensed-phase mechanism.[13,14] This mechanism leads to the production of a relatively incombustible carbonaceous char. At the same time, fewer toxic gases are released into the atmosphere.

Diethyl N,N'-diethanolaminomethylphosphate (DDMP) is just this kind of flame retardant. It can participate in polymerization as a monomer to make flame-retardant polyurethane foam. In this study, SEM, IR spectra, and thermal analysis were used to investigate the physical and chemical changes during the combustion of RPUF that contained DDMP. To provide a theoretical base for controlling the flame retardancy and physical properties of RPUF, the flame-retardant mechanism of RPUF in which the flame-retardant group was bonded was verified.

EXPERIMENTAL

Materials

DDMP was made according to the literature.[15] Industrial-grade polyether polyol (N303) and polymethylene–polyphenylpolyisocyanate (PAPI) were supplied by the Chinese Academy of Engineering Physics (Mianyang). Triethanolamine was provided by the First Shanghai Chemical Reagent Factory. Silicone oil was received from the First Tianjin Reagent Factory.

Preparation of Flame-Retardant RPUF

One-step expanding foam technology was used to prepare the flame-retardant RPUF. First, the raw materials were maintained at 20–21°C; subsequently, the various materials (except for isocyanate), called white materials, were weighed in a plastic cup according to formulations and were blended evenly by a high-speed electric stirrer. In another plastic cup, a fixed proportion of isocyanate was weighed and poured into the mold for foaming. After curing, the mold was unloaded. Formulations and technical parameters of flame-retardant RPUF were shown in Tables I and II.

Instrumental Analysis

IR spectra were recorded with KBr powder using a Nicolet FTIR 170SX infrared spectrophotometer. Thermogravimetric analysis (TGA) was performed by a DuPont 1090B thermogravimetric analyzer at heating rate of 10°C/min under air atmosphere with a flowing rate of 80 mL/min. Differential scanning calorimetry (DSC) thermograms were recorded with a DuPont 1090 thermogravimetric analyzer at a heating rate of 10°C/min in air atmosphere. Scanning electron micrographs were obtained on a S-450 scanning electron microscope (samples were gold coated by an IB-3 Ionic sputtermeter). Limited oxygen index (LOI) values were measured on a JF-3 oxygen index meter according to GB2406-93.

RESULTS AND DISCUSSION

The flame retardant contained active hydroxy, so it could react with isocyanate. To demonstrate whether they react or not, the FTIR spectra of flame-retardant RPUF containing DDMP (20 pbw) and plain RPUF were studied and shown in Figure 1, in which I denotes the plain RPUF and II denotes the flame-retardant RPUF containing DDMP.

Table II Technical Parameters of Flame-Retardant RPUF

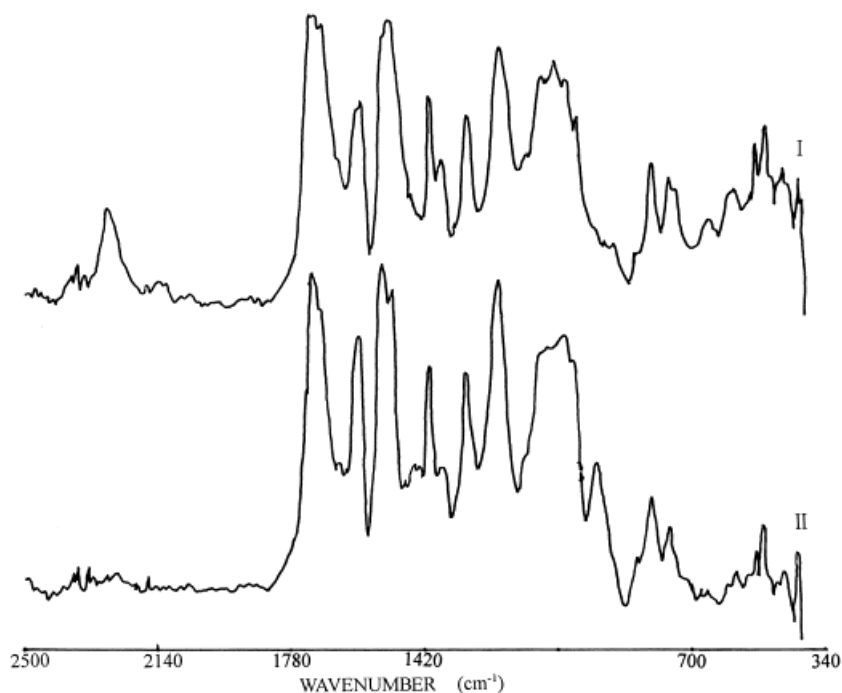| Item	Technical Parameters
Stirring time	1 min
Temperature of raw material	20–21°C
Temperature of mould	41–43°C
Curing	100, 4 h

Figure 1 FTIR spectrum of plain RPUF (I) and flame-retardant RPUF (II).

Contrasting the spectrum of I and II, we can see that the band of II at 1560 cm^{-1}, which associated with —C=O, is obviously stronger than that of I and that the band at 980 cm^{-1} is a new peak of II which is very characteristic of —P—O—C, due to the stretching vibration. From above we conclude that because the flame retardant could react with isocyanate, the phosphonate ester that contained nitrogen was bonded to poly-

urethane molecule. At the same time, we used SEM to observe the foam structure of RPUF, in which one is flame-retardant and the other is plain (shown in Figs. 2 and 3). From the photograph, we can see that the flame retardant does not produce any effects on the foam structure of RPUF.

When the plain and flame-retardant RPUF were burning, it was observed that thick black smoke was released from both of them. This
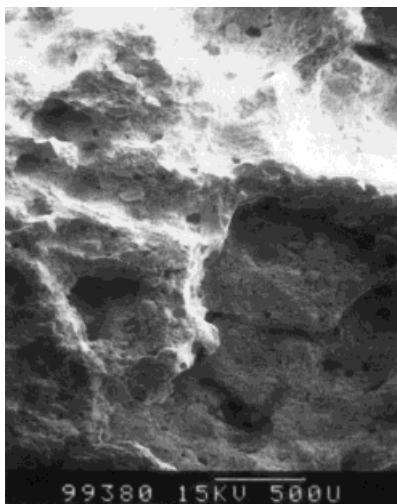

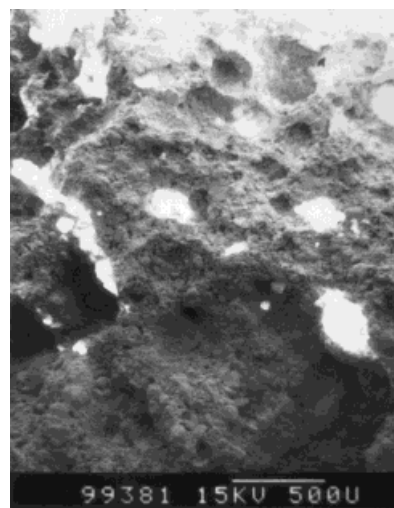**Figure 2** SEM photograph of flame-retardant RPUF containing DDMP (20 pbw).
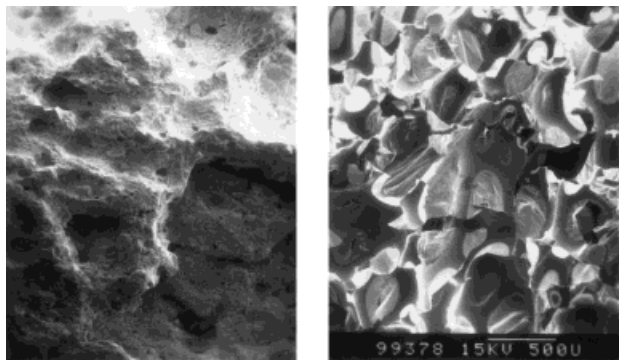

Figure 3 SEM photograph of plain RPUF.

Figure 4 SEM photograph of flame-retardant RPUF before (L) and after (R) combustion test (×40).

smoke is caused by the RPUF that was made by aromatic isocyanate. The char was produced when the flame-retardant RPUF was burning. By using SEM, we could see that (in Fig. 4) the foam structure of flame-retardant RPUF was destroyed and was coated by black solid when it burned, which indicated the creation of char.

Figures 5 and 6 display DSC thermograms of flame-retardant RPUF and plain RPUF, respectively. These figures reveal an endothermic baseline shift which corresponds to the glass transition temperature (T_g). Polyurethane containing DDMP displays higher T_g than that of plain polyurethane. The exothermic peak of DSC thermograms of plain RPUF should be associated with the melting temperature of polyurethane. The

melting process of flame-retardant RPUF is changed because of the decomposition of DDMP. The DSC thermogram of flame-retardant RPUF shows a new exothermic peak which should be attributed to the thermal decomposition of polyurethane because the peak occurred at the temperature at which the corresponding TGA trace of flame-retardant RPUF exhibited rapid weight loss (Fig. 7). This behavior would possibly be due to the formation of protective coating at the condensation phase during polyurethane decomposition, which also can be demonstrated by the SEM photograph shown in Figure 4 (right).

Thermogravimetric (TG) curves of flame-retardant and plain RPUF provide information regarding their thermal stability and thermal degradation behavior. Figure 7 displays the TG curve for flame-retardant (A) and plain (B) RPUF evaluated in air. The plain RPUF is stable up to 282°C, whereas the flame-retardant RPUF exhibits an initial weight loss at around 225°C. The plain RPUF shows a rapid weight loss around 282–311°C and it has almost no decomposition residuals at 700°C. The flame-retardant RPUF sample that contained DDMP (20 pbw) has two decomposition stages: one is around 225–294°C; the other is about 483–649°C. The char residuals of flame-retardant RPUF are about 19% at 700°C. The initial weight loss temperature of flame-retardant RPUF was lower than that of plain RPUF, indicating that the stability of the former is less than
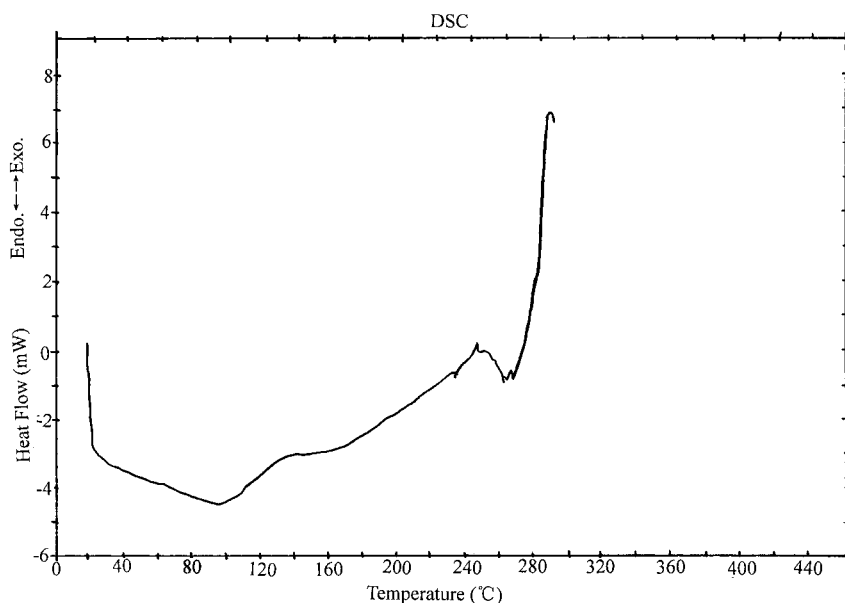

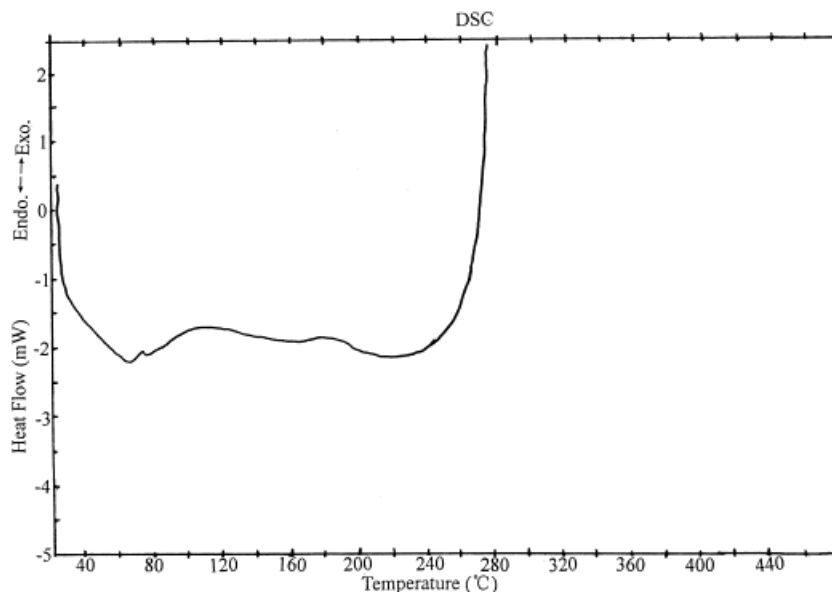**Figure 5** DSC thermogram of flame-retardant RPUF containing DDMP (20 pbw).

Figure 6   DSC thermogram of plain RPUF.

that of the latter. It is also noticed that the char residuals of flame-retardant RPUF decrease with the decrease of DDMP content (see Table III). The less thermal stability of DDMP containing RPUF has also been reported in other works.[2,9,10] Such behavior characterizes most phosphorylated polymers and is attributed to the relatively easy thermal degradation of phosphorus segments.[10,11,14] When in flame, the phosphorus-containing groups

of polyurethane decompose more rapidly than the polymer matrix, resulting in high yields of char residuals and the decrease of the pyrolysis products of the high-temperature zone of 550–700°C. This phenomenon produces a flame-resistant effect toward polyurethanes.

The flame resistance of flame-retardant RPUF was evaluated by determining its LOI value. Table III lists LOI values of flame-retar-
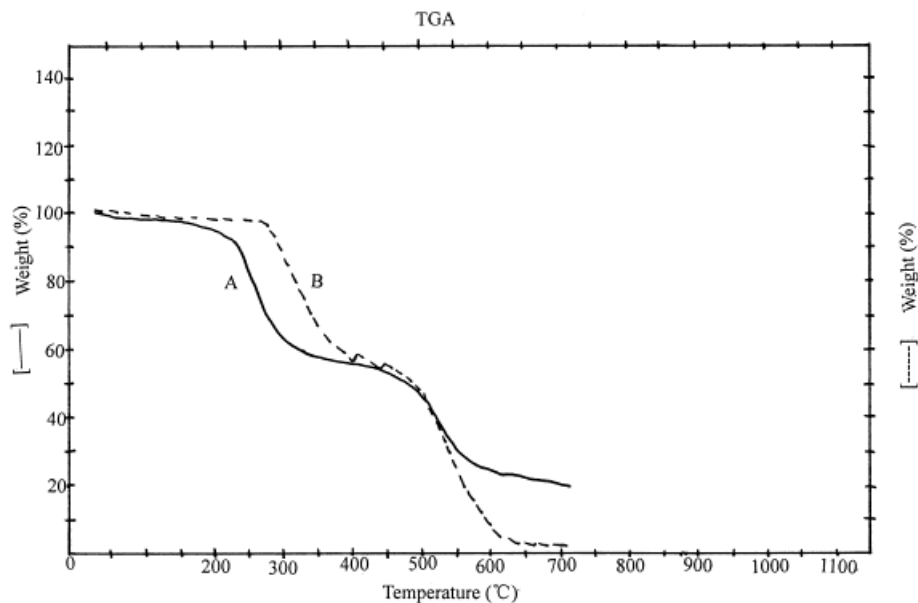

Figure 7   TG curves for flame-retardant RPUF containing DDMP (20 pbw) and plain RPUF.

Table III   TGA and LOI Analysis of Data of Pure and Flame-Retardant RPUF

pbw of DDMP	TGA Data in Air				LOI (%)
	2% Weight Loss Temperature (°C)	PDI$_{max}$[a] (°C)		Char Yield[b] (%)	
0 (Plain RPUF)	70	282	538	0	23
5	—		—	—	24
10	—		—	—	26
15	64	308	528	12	27
20	42	257	528	19	29

[a] Rapid decomposition temperatures of polyurethane.
[b] Char yields at 700°C.

dant RPUF and plain RPUF. Because certain LOI values of RPUF were around 23,[2] the flame retardancy of polyurethane was enhanced by incorporating DDMP into polymers, and the LOI values increased with the increase of DDMP content.

When RPUF contained DDMP, its infrared spectrum was still similar to the infrared characteristic absorption of polyurethane. By contrasting infrared spectra of retardant RPUF in various temperatures (shown in Fig. 8), we can see that the absorption at 1230 cm^{-1} (—P=O) has gradually weakened with the rise of temperature, and the band at 1080 cm^{-1}, which is associated with —P—O—C (aliphatic), is also weakened. This phenomenon happened at a temperature of 250°C, which is basically consistent with the results of TGA.

From the results above, we can deduce the mechanism of flame-retardant RPUF: because flame retardant contained hydroxy group, it could react with PAPI directly and produce such a group in the molecular structure of polyurethane (Scheme 1).

The addition of flame retardant could obviously change the thermal decomposition behavior of RPUF, widen the decomposition temperature region of RPUF, and reduce the amount of decomposition product in the combustible temperature region. The flame retardant had some promotional effects on the degradation of the polyurethane molecule under the igniting temperature of polyurethane, whereas above the flame temperature, it could promote the charring residue of RPUF. Therefore, we could say that the flame retardant at least acted in the site of condensed phase.

CONCLUSION

DDMP was a reactive flame retardant which could react with isocyanate. This was confirmed by IR spectra. It had no effect on the foam structure of RPUF, which was demonstrated by SEM photographs. The flame-retardant RPUF containing DDMP was less thermally stable and decomposed at relatively low temperatures, around 225°C, indi-
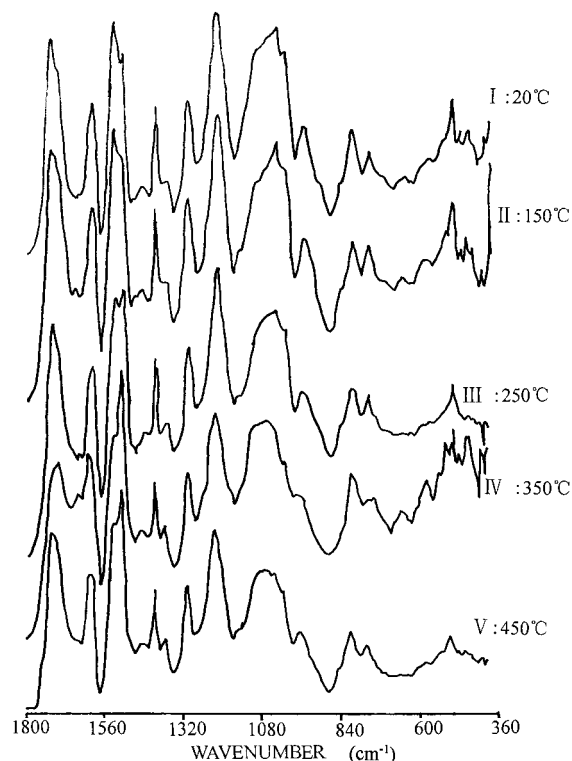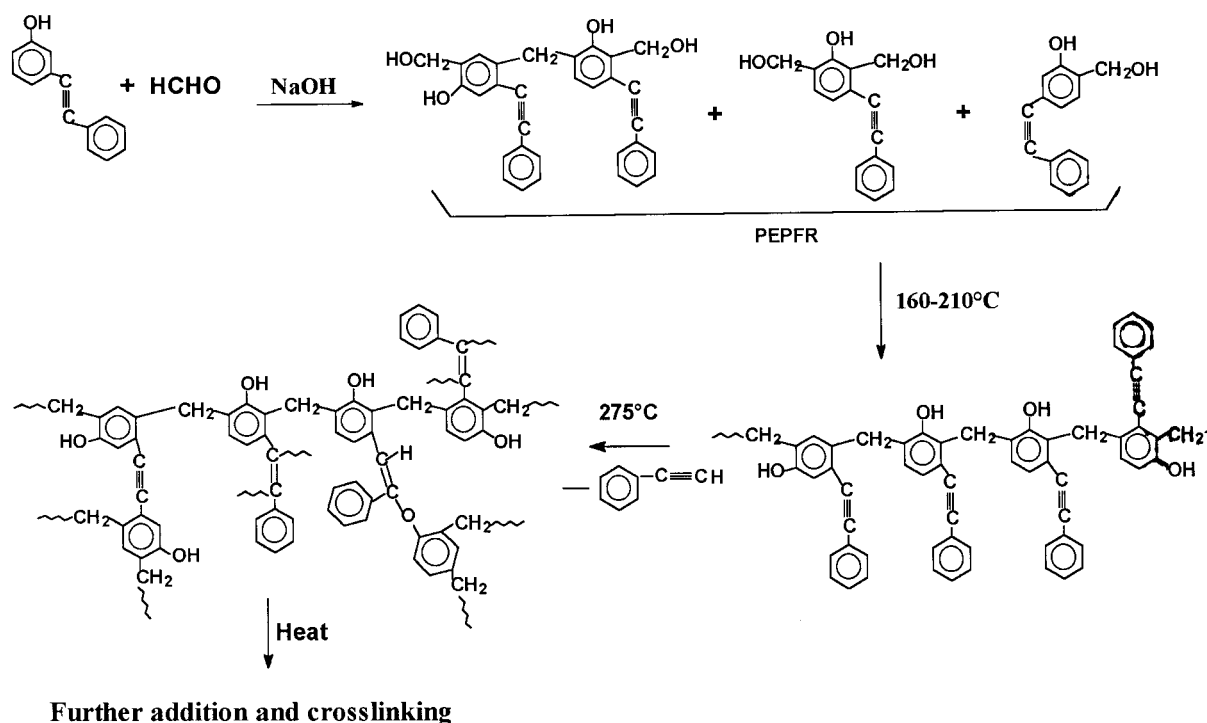

Figure 8   FTIR spectra of flame-retardant RPUF containing DDMP (20 pbw) in various temperatures.

Scheme 1   Synthesis of PEPFR resin and probable mechanism of crosslinking.

cating that DDMP widens the temperature range of RPUF decomposition and reduces the amount of combustible volatile products within the range of combustible temperatures of RPUF. On the other hand, at high temperatures (say above 550°C), some degraded products of RPUF containing DDMP are charred, which can result in protective char formation that is to form a barrier between the flame zone and the condensed zone. This will prevent further decomposition of polymer. In addition, high char yields were associated with the flame retardancy of prepared RPUF, a property that was further demonstrated by high LOI values of RPUF measured as 29.

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