

Study on the Suppression Mechanism of Water Mist on Poly(methyl methacrylate) and Poly(vinyl chloride) Flames

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ABSTRACT: In this study, the action of water mists on poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) in a confined space under different external radiant heat fluxes was studied. Water mist was generated by a downward-directed single pressure nozzle. Physical characteristics of the water mist were measured by laser doppler velocimetry and the adaptive phase doppler velocimetry system. The heat release rate, oxygen, carbon dioxide, and carbon monoxide concentrations, and other important parameters of the interaction under various experimental conditions were measured with cone calorimeter. To explain experimental results, the chemical suppression mechanisms

of water mist extinguishing PMMA and PVC flames are investigated from literatures, and the corresponding proposed chemical reactions with water mist are presented. The investigation shows that aromatic compounds are formed by light hydrocarbon products with water mist for PMMA flame. Otherwise, for PVC flame, the decrease of temperature with water mist prevents aromatic compounds from oxidation and degradation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1130–1139, 2006

Key words: suppression mechanism; water mist; PMMA; PVC; aromatic compounds

INTRODUCTION

The increasing usage of plastics inevitably involves plastics of different kinds in fires. Therefore, the behavior of decomposing or smoldering plastics and their flames in fires must be known to have a measure for the environment effects and extinguishing methods of burning plastics. There are concerns on the possible fire hazard of the extensive use of polymers in buildings, especially when the number of fires appears to be increasing all over the world. In spite of the importance of extinguishing polymer fires, there are few literatures related to it.¹ Two typical polymer materials that have been widely used in buildings are poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC). PMMA is a combustible material which would be softened or melted upon heating. The limiting oxygen index is only about 17.3.² Burning PVC would give dioxins and other compounds containing chlorine which are harmful. Therefore, a better

understanding of extinguishing PMMA and PVC fires is important.

Water mist is now commonly used in fire extinguishing systems as an alternative to gas protection with halogenated agents. There is another advantage of using smaller amount of water to give less water damage. However, the performance of water mist system depends on the fire scenario due to different physical suppression mechanisms which basically can be grouped into: (1) mist droplet evaporation for removing heat from the surface of combustibles or within the gaseous flames; (2) fine droplets evaporate in the hot environment even before reaching the flame. This will generate stream to dilute oxygen in air approaching the flame. Therefore, the extinction is similar to those by inert gas such as carbon dioxide; and (3) mist blocks the radiative heat transfer between the fire and combustibles. Note that blockage of radiation is only effective in reducing the intensity or fire spreading rate. It is rarely sufficient to extinguish a fire by this mechanism. The water mist fire suppression systems have been reviewed.^{3–6}

However, there might be chemical reactions with the possibilities of having both inhabitation and combustion enhancement. Therefore, studying the chemical effects of water mist on different fires is necessary. Despite this, there are few literatures related to it.⁷ Homogeneous interaction of water with gas fuel in the combustion and heterogeneous oxidation of carbon in

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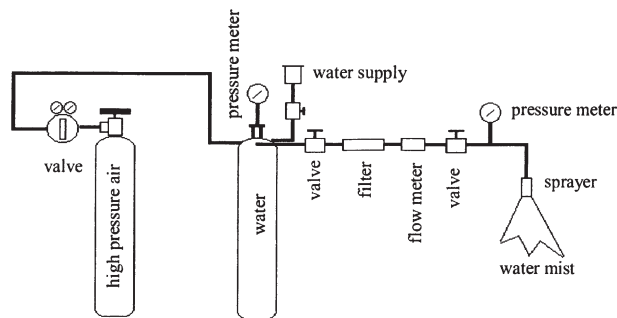


Figure 1 Generation of water mist.

the presence of water have been discussed. Those are considered key combustion reactions of polymers which also suggest the importance of chemical effects of some chemically inert agents. The results are useful for studying the suppression chemistry of water mist on polymers. In this study, the action of water mists on PMMA and PVC in a confined space under different external radiant heat fluxes is studied. To explain experimental results, the chemical suppression mechanisms of water mists extinguishing PMMA and PVC flames are investigated from literatures, and the corresponding proposed chemical reactions with water mist are presented. The experimental details, results and discussions, the proposed chemical reaction mechanisms of PMMA and PVC flames with water mists are discussed, followed by conclusions and future work.

EXPERIMENTAL

Generation of water mist

Water mist was generated by a single pressure atomizer as shown in Figure 1. A commercial full-cone nozzle with an effective angle of about 90° was used to generate the water mist. Water should be filtered before delivering into the nozzle. The particle size, velocity distribution, and mist volume flux of the discharged water mist flow were measured experimentally by laser doppler velocimetry and the adaptive phase doppler velocimetry system (LDV/APV). The measuring techniques and the system configuration have been described in detail.^{8,9} This system is based on the light scattering theory of nonconductive spherical particles and the characteristics of water mist. Major components include laser, light beam optics, a transmitting system, a collecting system, photodetectors, splitting signal processing electronics, an external data input device, and a computer with software.

Using LDV/APV, the radial distribution of the water mist characteristic values at operating pressure of 0.4 MPa is shown in Figure 2. From Figure 2, the volume mean diameter of the water mist is about $65 \mu\text{m}$, which accords well with the definition of water mist.

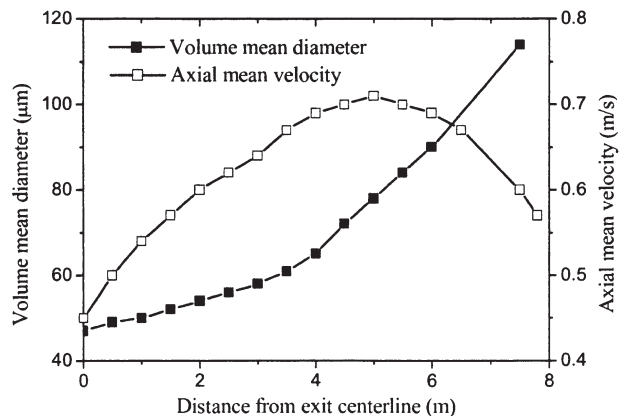


Figure 2 Radial distribution of the water mist characteristic values including volume mean diameter and axial mean velocity at operating pressure of 0.4 MPa.

Experimental methods

A standard cone calorimeter following ASTM E1354 with a small water mist system was used,¹⁰ a schematic diagram of which is shown in Figure 3. The cone calorimeter was developed to measure the heat release rate from a burning surface and analyze the combus-

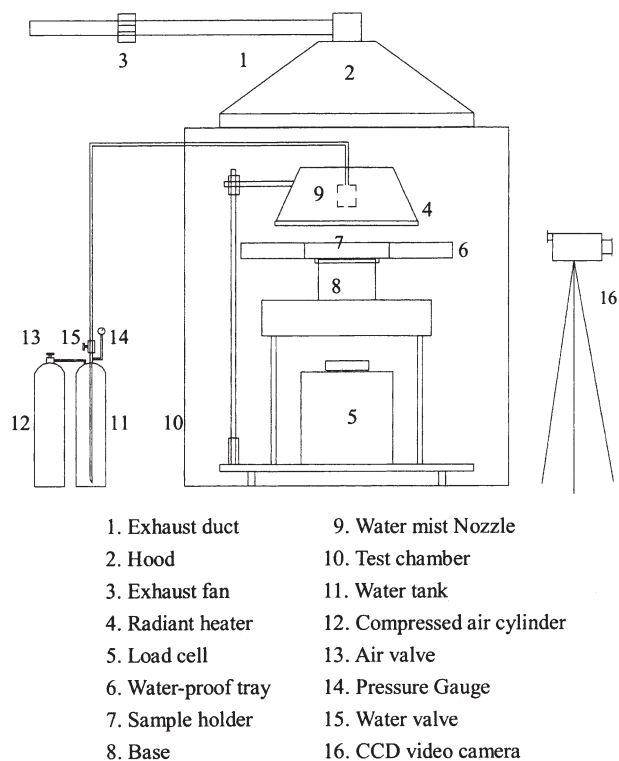


Figure 3 Experimental set-up: (1) exhaust duct, (2) hood, (3) exhaust fan, (4) radiant heater, (5) load cell, (6) water-proof tray, (7) sample holder, (8) base, (9) water mist nozzle, (10) test chamber, (11) water tank, (12) compressed air cylinder, (13) air valve, (14) pressure gauge, (15) water valve, and (16) CCD video camera.

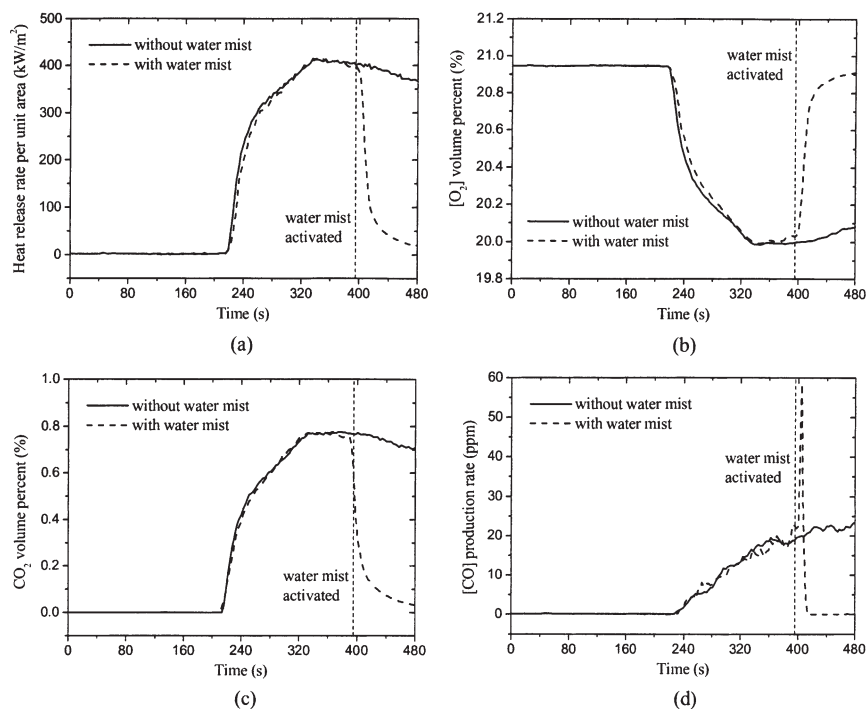


Figure 4 Experimental results including (a) heat release rate per unit area, (b) [O₂] volume percent, (c) [CO₂] volume percent, and (d) [CO] production rate of PMMA flames without and with water mist (operating pressure of 0.4 MPa) under radiant heat flux of 20 kW/m².

tion products when a constant flow of air is provided into the confined space. The combustion characteristics such as heat release rate, combustion efficiency, burning delay time, and gas concentration can be determined. This apparatus was modified in this article to study the interaction of water mists with PMMA and PVC flames in a confined space. Combustion characteristics can be measured without and with water mist. The experiments were performed in a glass-walled enclosure of size 0.6 × 0.6 × 0.7 m³ in a cone calorimeter. The fuel sample was placed on an electronic balance under different radiant heat fluxes. In this study, radiant heat flux of 20 kW/m² (the corresponding temperature is 584°C) was used for PMMA flames, and 50 and 70 kW/m² (the corresponding temperatures are 800 and 892°C) were used for PVC flames. The reason for the higher radiant heat fluxes used for PVC is that PVC is not easy to combust because 56.8% of the base polymer weight of PVC is chlorine. The combustion products were all collected by the hood and transferred for measurement and analysis. The rate of fresh air flow into the confined space was adjusted by varying the speed of the fan installed. In this study, 24 L/s flow rate of air was chosen.

A water-proof shield was necessary to protect the load cell from water spray. This shield was made out of 1 mm mild steel galvanized sheet. Also a tray was placed underneath the radiant heater to accumulate the excess and run-off water.

Samples of PMMA and PVC slab of 100 × 100 mm² were studied. The slab thicknesses of PMMA and PVC are 10 × 3 mm², and their weights are about 116 and 41 g, respectively. The distance between the nozzle tip and the sample was kept at 80 mm to obtain full coverage of the sample surface.

Before carrying out the test, all specimens were put on the kaowool mat in a 25 mm deep stainless-steel tray. The surface of the specimen was kept at the same level as that of the top edge of the tray. Specimens were wrapped in aluminum foil to minimize the edge effects and maintain only one-dimensional heat conduction in the thickness direction. The radiant heater was set to the desired value. The sample was exposed to external radiation by placing the sample holder under the radiant heater, and at the same time, the electric spark of the cone calorimeter was operated. Once steady burning with a relatively stable flame appeared on the surface of the specimen, the electric spark was turned off. And then, PMMA and PVC samples were allowed to burn under the preset conditions until their heat release rates were stable. Water mist was then discharged for some time, and was stopped when the flame was extinguished.

RESULTS AND DISCUSSIONS

The heat release rate per unit area, [O₂] volume percent, [CO₂] volume percent, and [CO] production rate of PMMA flames without and with water mist (oper-

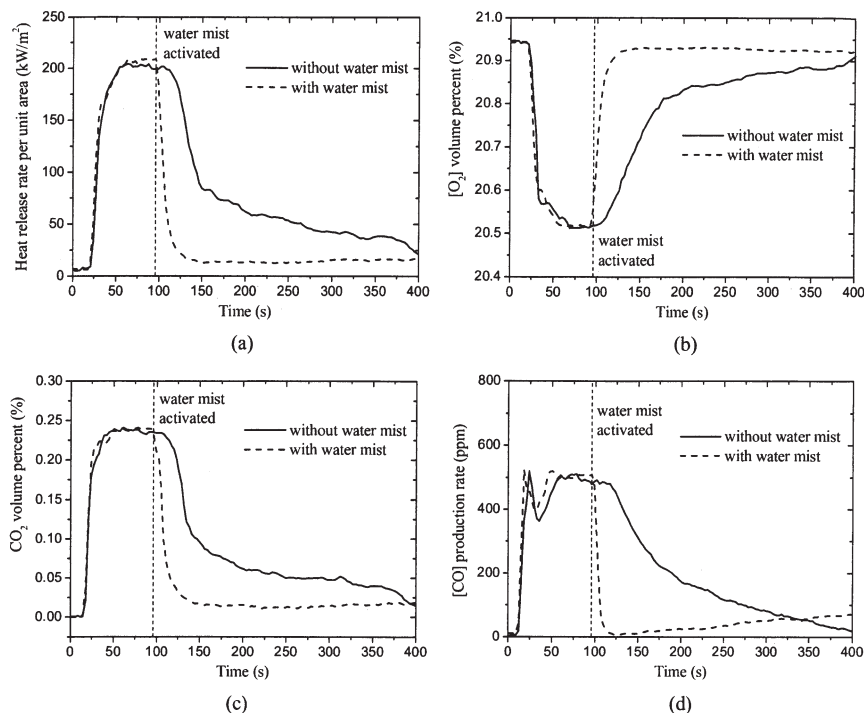


Figure 5 Experimental results including (a) heat release rate per unit area, (b) $[O_2]$ volume percent, (c) $[CO_2]$ volume percent, and (d) $[CO]$ production rate of PVC flames without and with water mist (operating pressure of 0.4 MPa) under radiant heat flux of 50 kW/m².

ating pressure of 0.4 MPa) under radiant heat flux of 20 kW/m² are shown in Figure 4(a–d). When PMMA is ignited, the heat release rate of PMMA flame increases, and consumes oxygen in environment ($[O_2]$ volume percent decreases in Fig. 4(b)) and results in the products of CO_2 and a small quantity of CO ($[CO_2]$ volume percent and $[CO]$ production rate increase in Fig. 4(c,d)). After the heat release rate reaches the maximum value, it begins to drop slowly, and $[O_2]$, $[CO_2]$ volume percents and $[CO]$ production rate have this trend. Once water mist is injected, PMMA flame is extinguished rapidly, and the heat release rate also quickly decreases to almost zero. Thereby, $[O_2]$ volume percent increases and $[CO_2]$ volume percent decreases rapidly. But $[CO]$ production rate jumps almost three times, and then falls down rapidly. Such phenomenon can be also found in the literature.¹¹ It is obvious that some different reactions are produced due to water mist action, which would be described in detail in the next section.

The experimental results including the heat release rate per unit area, $[O_2]$ volume percent, $[CO_2]$ volume percent, and $[CO]$ production rate of PVC flames without and with water mist (operating pressure of 0.4 MPa) under radiant heat flux of 50 kW/m² are shown in Figure 5. And Figure 6 gives the experimental results of PVC flames without and with water mist (operating pressure of 0.4 MPa) under radiant heat flux of 70 kW/m². As PMMA flame, when PVC is ignited, the heat release rate, $[CO_2]$ volume percent,

and $[CO]$ production rate increase, and $[O_2]$ volume percent decreases. After the heat release rate reaches the maximum value, it begins to drop slowly, and $[O_2]$, $[CO_2]$ volume percents, and $[CO]$ production rate have this trend. Once water mist is injected, PVC flame is extinguished rapidly, and the heat release rate also quickly decreases to almost zero. $[O_2]$ volume percent increases and $[CO_2]$ volume percent decreases rapidly. Unlike PMMA flame, $[CO]$ production rate of PVC flame decreases rapidly, and then slowly ascends. It means that the chemical suppression mechanism of PVC flame extinguished by water mist differs from that of PMMA flame.

Through comparison of Figures 5 and 6, higher radiant heat flux does not enhance PVC combustion in spite of the increases of heat release rate of about 6.5% and $[CO_2]$ volume percent of about 10%, and the decrease of $[O_2]$ volume percent of 8% at 70 kW/m² compared to 50 kW/m². But $[CO]$ production rate increases 40% at 70 kW/m² comparing to 50 kW/m². Comparing Figures 5 and 4, PMMA flame takes on higher heat release rate, consumes more oxygen, and produces more carbon dioxide though it is under 20 kW/m² radiant heat flux compared to PVC flame under 50 kW/m² radiant heat flux. But $[CO]$ production rate in Figure 5 is 25 times more than that in Figure 4. The data of $[CO]$ production rate from the literature¹² show that $[CO]$ production rate of PVC flame is 10 times more than that of PMMA flame at the same of radiant heat flux.

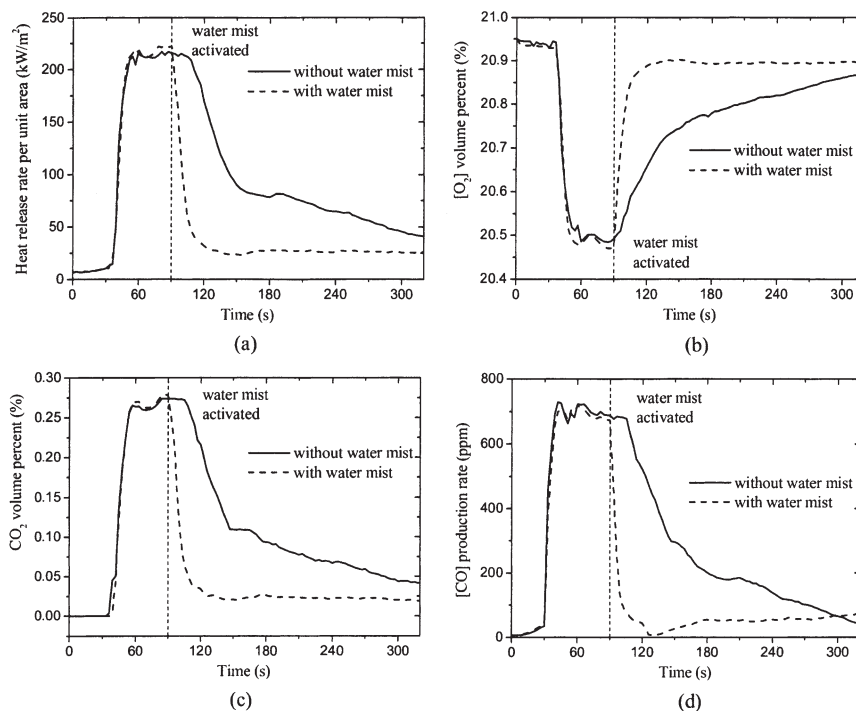


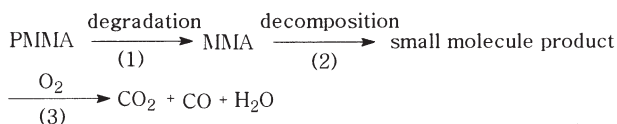
Figure 6 Experimental results including (a) heat release rate per unit area, (b) $[O_2]$ volume percent, (c) $[CO_2]$ volume percent, and (d) $[CO]$ production rate of PVC flames without and with water mist (operating pressure of 0.4 MPa) under radiant heat flux of 70 kW/m^2 .

PROPOSED CHEMICAL REACTIONS MECHANISM

Discharging water mist might enhance the combustion through evaporation expansion to give better mixing of the fuel vapor and air. Water vapor interacts with the chain reactions to suppress soot formation, and hence reducing the radiant heat loss.¹³ On the other hand, water mist suppresses the gas phase combustion through cooling, oxygen displacement, and attenuation of thermal radiation. The two opposing mechanisms would be competing with each other while applying water mist. The enhancing effect of combustion becomes insignificant when the water mist system is operating with the proper characteristics such as adequate volume flux. The next will describe the proposed chemical reactions mechanisms of PMMA and PVC flames with water mist from literatures.

PMMA flame with water mist

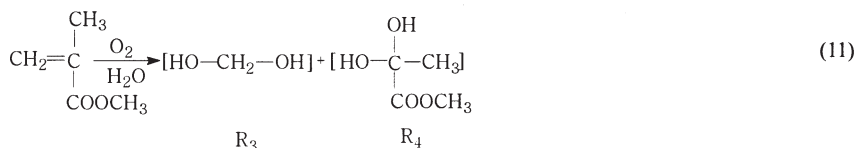
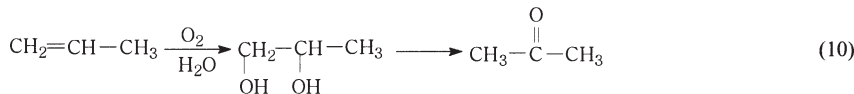
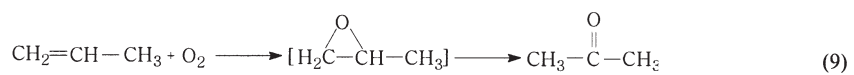
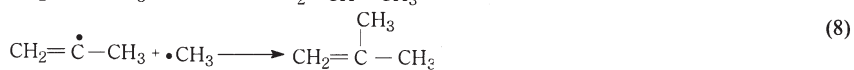
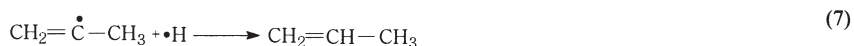
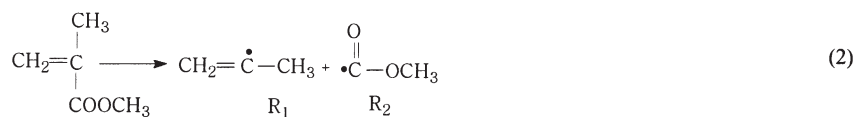
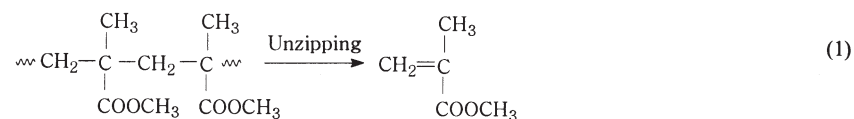
It was reported by Zeng et al.¹⁴ that PMMA combustion at 500°C includes three board stages (Scheme 1).



Scheme 1

Firstly, PMMA is heated by a heat source and degraded to form MMA; secondly, MMA is decomposed into small molecule products; and thirdly, the generated small molecule gaseous products are burned to produce the final combustion products.

The detail chemical reactions are listed in Scheme 2. PMMA firstly is unzipped (degraded) into MMA (1). And then MMA would decompose to generate free radicals R_1 and R_2 (2). R_2 continues to break down to form CO_2 and CO (3,4) and the methoxyl and methyl group produced combine with the free radical H to form CH_3OH and CH_4 (5,6). R_1 will react with the free radical H to produce propylene (7) or combine with methyl to generate 2-methyl propylene (8). Acetone will be produced by the reaction between propylene and oxygen and then further reaction of rearrangement of 2-methylepoxy ethane, (9) or 1,2-propanediol (10) in the presence of H_2O . Methyl pyruvate and formaldehyde will be generated by the following reactions. Firstly, MMA reacts with oxygen to produce active intermediates R_3 and R_4 (11), then R_3 and R_4 dehydrate to produce formaldehyde (12) and methyl pyruvate, respectively (13). At high temperature, methyl pyruvate decomposes to generate acetone by the stripping down of the ester group (14). But it was stated that the direct reaction between MMA and oxygen is minor in the process of PMMA combustion by Zeng et al.¹⁴ Finally, small molecule products undergo combustion and this leads to the formation of the final products and the release of heat (15). Where X repre-



Scheme 2

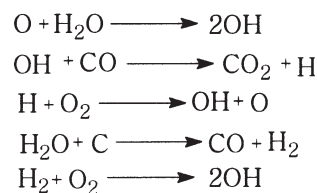
sents methanol, methane, formaldehyde, propylene, 2-methyl propylene, acetone, etc.

Jiang et al.'s¹¹ experiments showed that aromatic compounds, conjugated rings, and long carbon chain aliphatic hydrocarbon compounds were detected in the combustion products of PMMA/water vapor, especially for aromatic compounds with relatively high intensity. But there were no macromolecules in the combustion products of PMMA. The experimental re-

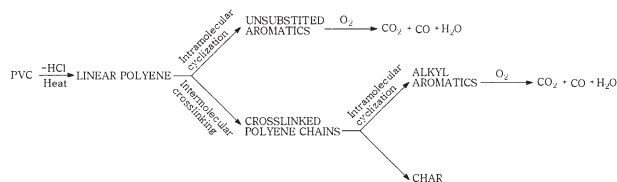
sults indicate that in the existence of water, the chemical reactions of PMMA combustion may be changed. Scheme 3 can be proposed to explain this. One of the most important features of methylene chemistry is its role in addition reaction (1) with acetylene which leads to the formation of higher hydrocarbon fragments (2,3) where the singlet methylene is mainly formed by



Scheme 3



Scheme 4



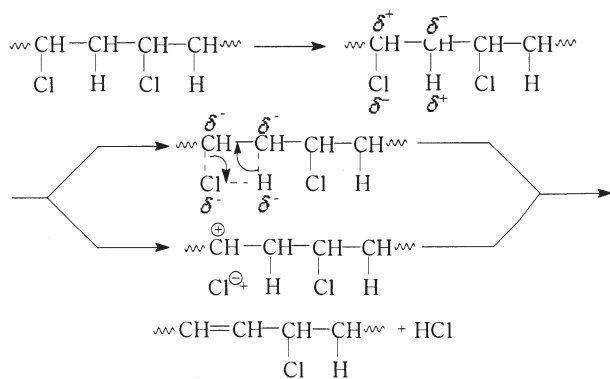
Scheme 5

H and OH radical attack on CH_4 (4,5). H and OH radicals are partly provided with the injection of water mist (Scheme 4).

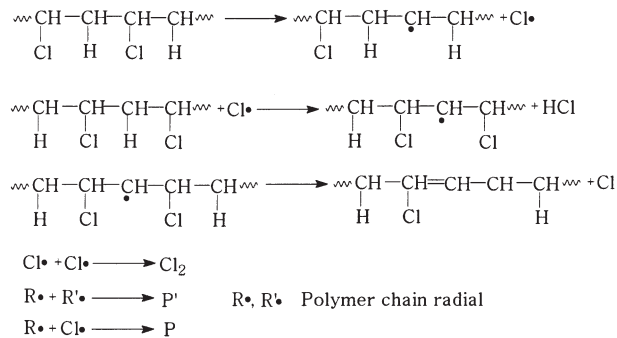
With water mist, the products of PMMA combustion have aromatic compounds such as benzene, etc. It is clear that the oxidation of aromatic compounds at high temperature, such as benzene, always has incomplete combustion, which forms CO. That is reason that once water mist is injected, [CO] production rate jumps almost three times. At the same time, water mist removes heat and the oxidation of aromatic compounds stops, which let [CO] production rate fall down rapidly.

PVC flame with water mist

PVC decomposes in two decomposition steps.^{15,16} The first decomposition step is the dehydrochlorination at about 320°C, the second step at about 450°C is the formation of a mixture of hydrocarbons containing mostly aromatic compounds. The dehydrochlorination of PVC is accompanied by mainly benzene formation. Scheme 5 is designed to accommodate two distinct processes that may cause the evolution of aromatic compounds.¹⁷ In fact, linear polyenes are predicted to disappear through two competing processes: (1) an intramolecular cyclization reaction which produces only unsubstituted aromatics such as benzene, naphthalene, anthracene, etc., and (2) intermolecular crosslinking leading to the formation of crosslinked polyene structures. Crosslinked polyene



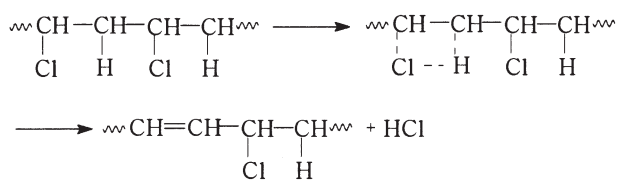
Scheme 6



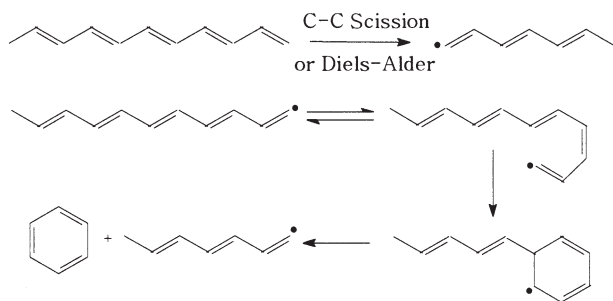
Scheme 7

chains are predicted to undergo further reaction through two competing processes: (1) further thermal decomposition to produce char residue, (2) intramolecular cyclization reactions to produce alkyl-aromatics such as toluene, methylnaphthalene, etc. The evolution of the alkyl-aromatics would occur at higher temperatures than the unsubstituted aromatics. Finally, the aromatics are burned to produce the final combustion products.

Despite numerous investigations, there is no secure knowledge about the reaction course of the dehydrochlorination. It is supposed that the dehydrochlorination occurs in ionic (Scheme 6), radical (Scheme 7) and unimolecular (Scheme 8) reactions.¹⁵ The reaction order of 1.5 found in this investigation supports a radical mechanism suggested by Stromberg et al.¹⁸ ionic and unimolecular reactions should occur with a reaction with order of one. According to Montaudo and Puglisi,¹⁹ the formation of benzene can occur by the mechanism indicated in Scheme 9, involving the intramolecular cyclization of the polyene radicals formed both by C—C scission and/or by a Diels–Alder process of the type in Scheme 10. The overall process is therefore seen as a chain depolymerization reaction producing benzene. And then unsubstituted aromatics may be produced equally well by intramolecular cyclization of the polyene radicals, starting from opportunely folded chains, as shown in Scheme 11.¹⁹ It can be seen that the mechanism proposed is quite homogeneous and accounts for the simultaneous evolution of unsubstituted aromatics in the decomposition of PVC. Scheme 12 presents a sequence of reactions that would lead to the formation of toluene starting from a



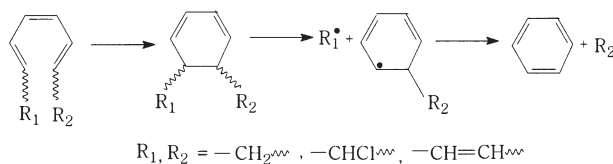
Scheme 8



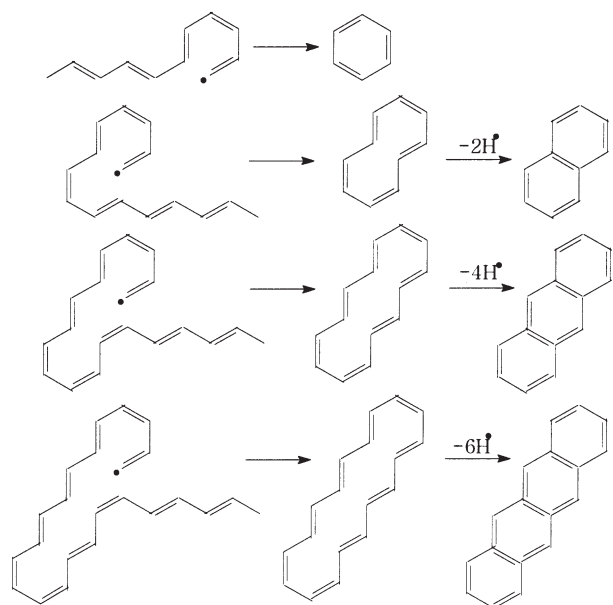
Scheme 9

crosslinked structure. According to Scheme 12, the formation of a polyene radical close to a crosslink point may lead to an intramolecular cyclization reaction, which may ultimately produce toluene through a number of hydrogen elimination/abstraction reactions and some C—C bond cleavages. And then, aromatics are oxidized with oxygen in high temperature. Benzene is burned or decomposed to form small molecule products, as shown in Scheme 13. Scheme 14 shows that toluene is burned or decomposed to form small molecule products. Finally, these small molecule products are burned to produce the final combustion products.

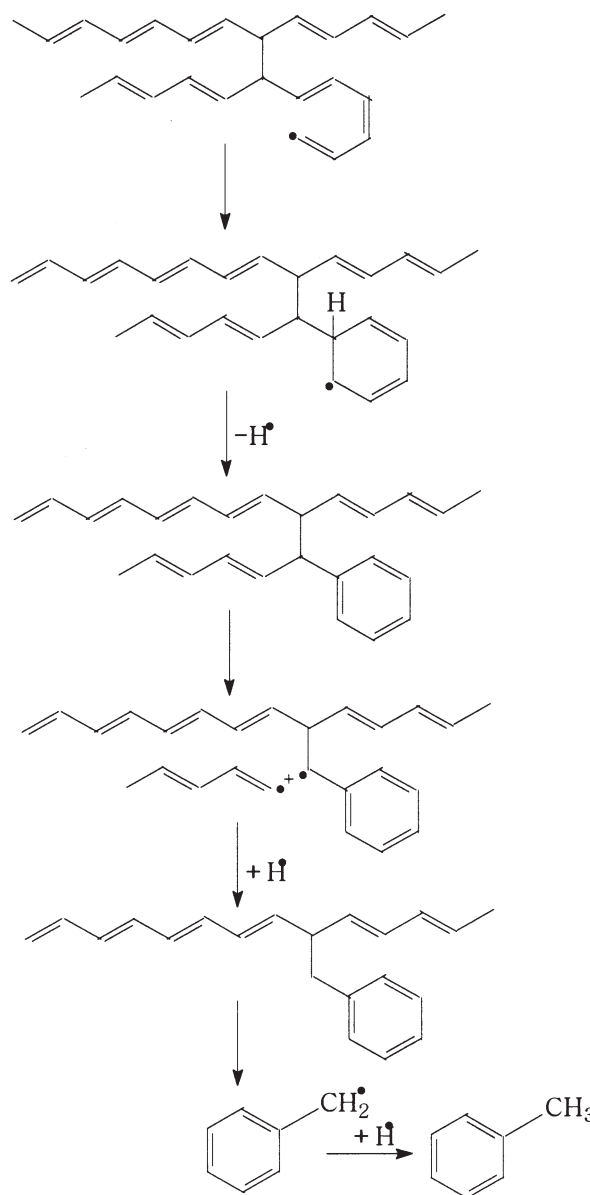
With water, the chemical reactions of PVC combustion might be changed in the processes of aromatics



Scheme 10

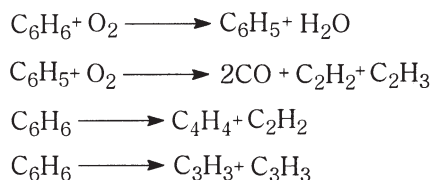


Scheme 11

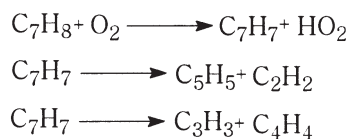


Scheme 12

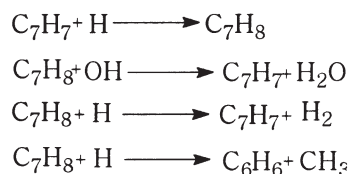
oxidation. That temperature decreases because of the injection of water mist let aromatics not continue to oxidize and decompose, i.e., Scheme 13 and 14 do not occur. Conversely, Scheme 15 for benzene and Scheme 16 for toluene might occur. H and OH radicals are partly provided with the injection of water mist, as shown in Scheme 4.



Scheme 13



Scheme 14



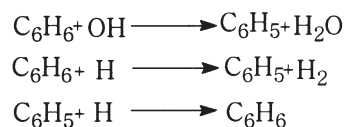
Scheme 16

From the above analysis, with the injection of water mist, aromatics can not be burned or decomposed to form small molecule products. It is also the reason that [CO] production rate of PVC flame decreases rapidly with the injection of water mist. It should be stated that unlike PMMA combustion, in the process of PVC combustion, PVC slab expanded almost five times in the thickness direction and cracked. When water mist was turned off, some water remained in the inner PVC slab, though the water in the surface of slab was vaporized under the radiant heat flux.

And so the reason that [CO] production rate slowly ascends after the water mist was turned off is the reaction products of C and H₂O. PVC contains 56.8% chlorine, and PVC combustion needs dehydrochlorination, which makes the heat release rate of PVC flame is far less than that of PMMA flame. After dehydrochlorination, the most of hydrocarbon products of PVC flame are aromatic compounds. That is why [CO] production rate of PVC flame is far more than that of PMMA flame. The efficiency of aromatics oxidation and decomposition depends on temperature, which is the reason that [CO] production rate of PVC flame increases 40% at 70 kW/m² compared to 50 kW/m², otherwise, [CO₂] volume percent only increases about 10% and [O₂] volume percent only decreases about 8%.

CONCLUSIONS AND FUTURE WORK

This article presents the study on the interaction of water mist with PMMA and PVC flames in a confined space under different external radiant heat fluxes. The experimental data show that the chemical suppression mechanism of PMMA flame extinguished by water mist differs from that of PVC flame. And so, to explain experimental results, the chemical suppression mechanisms of water mist extinguishing PMMA and PVC flames are investigated from literatures, and the corresponding proposed chemical reactions with water



Scheme 15

mist are presented. The main conclusions are listed below:

1. Aromatic compounds formed by light hydrocarbon products with water mist for PMMA flame. Otherwise, for PVC flame, the decrease of temperature with water mist prevents aromatic compounds from oxidation and degradation. These make PMMA and PVC flames be extinguished and their heat release rates decrease.
2. Once water mist is injected to PMMA flame, [CO] production rate jumps almost three times. The reason is that the products of PMMA combustion with water have aromatic compounds. At the same time, water mist removes heat and the oxidation of aromatic compounds weakens, which let [CO] production rate fall down rapidly.
3. For PVC flame, with the injection of water mist, aromatics can not be burned or decomposed to form small molecule products, which is the reason that [CO] production rate of PVC flame decreases rapidly with the injection of water mist. After water mist was turned off, water in the inner of PVC slab reacted with C to form CO, and results in the [CO] production rate slowly ascends.

Future work should be concentrated on measuring the detail reaction products of PMMA and PVC flames with water mist by some apparatuses, for example, gas chromatography (GC) and mass spectrometry (MS), etc. And then the dominating mechanisms of the production of such products are also further studied.

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