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TG/MS OF POLY(METHYL METHACRYLATE)
The effect of heating rate on the rate of production of evolved gases

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Abstract

Thermogravimetric analysis coupled with quadrupole mass spectrometry was performed to study the effects of heating rate on the rate of gasification of gases evolving from 0.5 mm particles size industrial-grade PMMA. The controlled mass loss measurements and the evolved gases were conducted in pure nitrogen and various oxidative environments under heating rates of 2 to 5°C min^{-1}. The results indicated major differences, in pure nitrogen, the rate of production of gases is steeper compared to those associated with oxidative environment. Furthermore as the heating rate is lowered, it appears that the gases emanating from the surface are more volatile in the sense that they burst more abruptly from the surface.

Keywords: mass transport effects, MS, PMMA, rate of gasification, TG

Introduction

Modeling of fire growth over polymeric solid is extremely complex due to the coupling of the heat generated by the flame, hence raising the solid surface temperature and the rate of gasification of the combustion products emanating from the surface. While several studies had been conducted to study the effect of the environment, pure nitrogen or oxidative, on the rate of gasification of the combustion products under variety of external radiant heat fluxes or heating rates, the outcome of these studies remain to be controversial. For steady state burning, some studies indicated no apparent effects of oxygen on the gasification rate [1, 2], while others indicated that oxygen have a major role [3, 4]. Furthermore it appears that mass transport effects has major influence on the rate of production of gases evolving from PMMA. Since the boiling point of MMA is M101°C [5], this temperature is far lower than the degradation products, as a consequence of the lower boiling points the superheated, nucleate to form bubbles in depth of the polymer. Due to high viscosity of the surface of the polymer [6], only bubbles in the close vicinity of the surface will burst out. The sub-

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surface bubbles also find their way out through very small holes, these bursts tend to be like free layer jets containing the degradation product gases to the surface. It was found [6] that by increasing the oxygen concentration of the external gas flow, the melt viscosity of the heated surface of the polymer tends to be much lower than that in nitrogen and higher temperature. Thus tending to enhance the early appearance of the bubbles with higher frequency that will alleviate the sudden appearance of the jets. On the other hand under oxidative environment the burst create much larger holes, thus permitting oxygen to find its way to the subsurface, hence subsurface oxidation will occur in addition to diffusion. An interesting point that linking the transient gasification rate to the surface temperature was not successfully established and gasification rate increases even though the surface temperature is constant. To that end, subsurface degradation is playing the major role on enhancing the gasification rate. Furthermore the competition between oxygen diffusion and convective flow due to rate gasification has an impact on the mass flux and depend on the degree of gas phase oxygen. It appears that at lower external incident radiation the mass flux increases due to lower counter flow of decomposed gases from the surface, and at higher incident radiation the mass flux decreases [6].

The subject of this paper is to elucidate some aspects of the gasification rate with respect to pure nitrogen or oxidative environment, furthermore also to get some insight on the decomposition process and the effect of the heating rate on the rate of gasification. Recently the heat of reaction of various oxidative environments and pure nitrogen was evaluated and the exo-thermicity or endo-thermicity of the decomposition process was determined [7] for pure nitrogen and oxidative environment, furthermore the oxidative environment caused the degradation to be less stable. In addition the effect of the particle size on the nature of the reaction in pure and oxidative environment was investigated [8], and the result demonstrated major differences that are attributed to the particle size impacting on the degradation. One of the important conclusions of these studies [7, 8] that the decomposition of relatively small particle size 0.1 mm PMMA, can be modeled by the Arrhenius type formula while for relatively large particle size of 0.5 mm the degradation cannot be modeled by the Arrhenius dependence formula. Since mass transport effects are not well understood phenomena, the rate of gasification associated with the heating rate will provide information with regards to some aspects of the problem.

Experimental setup

The TG device is Cahn Instruments coupled to a quadrupole mass spectrometer (GasLab) [7] through a capillary pipe 0.25 inch diameter. The capillary pipe was heated to 150°C in order to prevent water condensation. The mass spectrometer was tuned to detect major species with various mass to charge ratio. The mass spectrometer-sampling probe was located 1 cm above the industrial-grade PMMA sampling crucible.

Results and discussion

Pure nitrogen

Figures 1–3 show the mass loss rate and the mass to charge ratio curves for pure nitrogen for heating rates 5, 4, 3°C min^{-1}, respectively. While the mass loss rate does not show any change in the nature of the curve, the mass spectrometer indicate that the mass to charge curves are truncated, thus the reaction limitation is controlled by mass transport effects. The question that rises immediately is the mass transport limitation controlled from the inside to the outside or the opposite. Since the surrounding environment is pure nitrogen it is more likely that the rate limiting process is that of transport of decomposition products from the inside to the outside. This transport is more likely through the mechanism of bubble burst, thus the feeding mechanism of the bubbles prior migration outside is through the diffusion instead of the sentence of part of the volatile by adding energy to the polymer. As the heating rate is lowered, Fig. 2, the mass to charge curves is getting narrower. Further lowering the heating rate to 3°C min^{-1} in pure nitrogen as indicated in Fig. 3, will cause the mass to charge

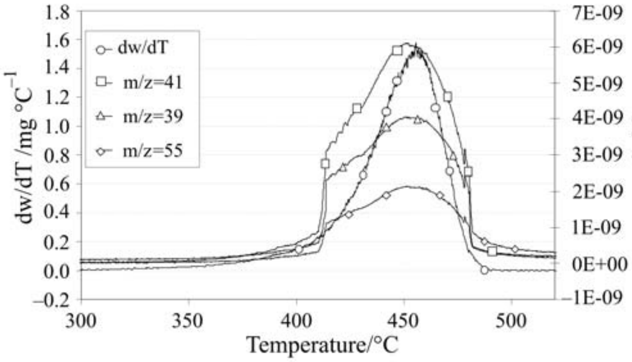

Fig. 1 Mass loss rate and mass to charge ratio for PMMA degradation in pure nitrogen at 5°C min^{-1}

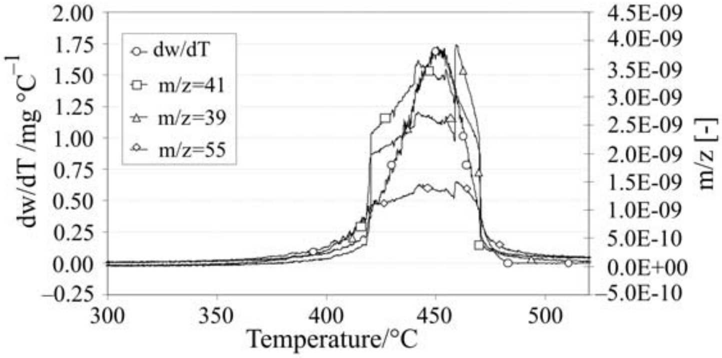

Fig. 2 Mass loss rate and mass to charge ratio *vs*. temperature for PMMA degradation in pure nitrogen at 4°C min^{-1}

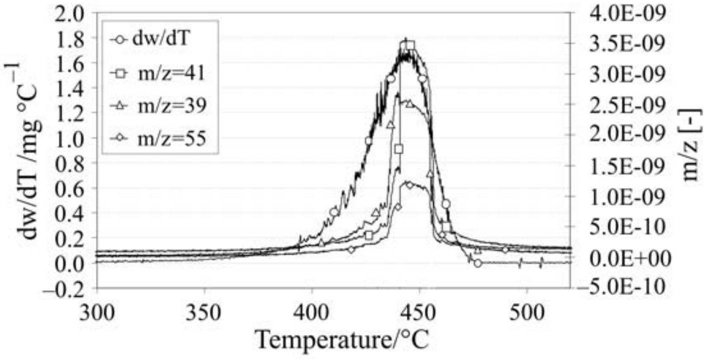

Fig. 3 Mass loss rate and mass to charge ratio *vs*. temperature for PMMA degradation in pure nitrogen at 3°C min^{-1}

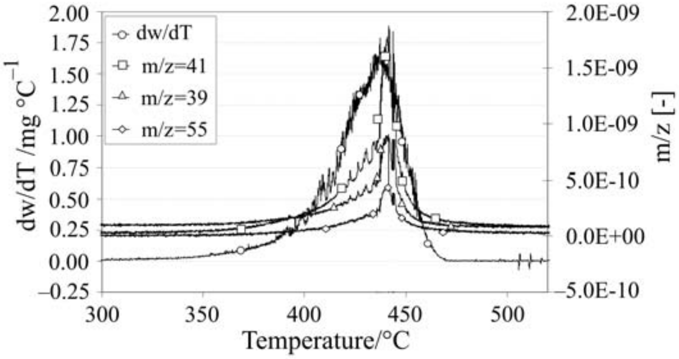

Fig. 4 Mass loss rate and mass to charge ratio *vs*. temperature for PMMA degradation in pure nitrogen at 2°C min^{-1}

ratio curves to get narrower and less truncated. In comparison, Fig. 4, for heating rates of 2°C min^{-1} shows no truncation and smooth curves for the evolved gases. To that end, mass transport effects play the major role in truncation of the curves for heating rates greater or equal than 3°C min^{-1}. For heating rates lower than 3°C min^{-1} the mass transport limitation vanishes or almost negligible. Thus no change in the slope is identified, hence the volatile escape from the polymer with almost no effects of the bubble forming. It also interesting to point out that as is evident from the mentioned figures, as the heating rate is reduced the amount of volatile production decreases, thus less volatile escape from the surface.

Oxygenated environment

As the oxygen concentration is elevated to 5%, the mass loss rate is affected, it appears that diffusion of oxygen causes the curve to be somewhat asymmetric about its peak [7]. This was clearly seen at heating rate 4°C min^{-1}. For 15% O_2 in N_2 at lower heating rate a sharp peak towards the end of the degradation can be identified and much clearly seen at heating rate 2°C min^{-1} (Fig. 5). This suggests that mass transport effects are much pronounced at higher end temperature of the degradation and or the particles are smaller or more porous and thus cause sharper transitions for heating rates less than 3°C min^{-1}. At lower degradation temperature the effect of diffusion is less than that at higher end degradation temperature. Furthermore, this can be explained by the fact that at lower heating rate, the unzipping of the polymer to monomer, and the transport of the monomer to the surface by the mechanism of bubbles is small, making the process of oxygen penetration to the subsurface relatively small. In order to corroborate this hypothesis, the MS data clearly support this scenario. The rate of production of several evolved gases is seen clearly in addition a change in the slope of the rate of production indicates a change or a competing of two or more kinetic mechanisms. As the heating rate decreases (Figs 5–7), the sharp change in the slope of the rate of mass loss shiftes to higher temperatures, which indicates that the lower heating rates allow sufficient time at higher temperatures to avoid mass transport limitations. The mass transport effects enhance the production of the evolved gases. It can be noticed, at the higher heating rate, that the MS curves follow the mass

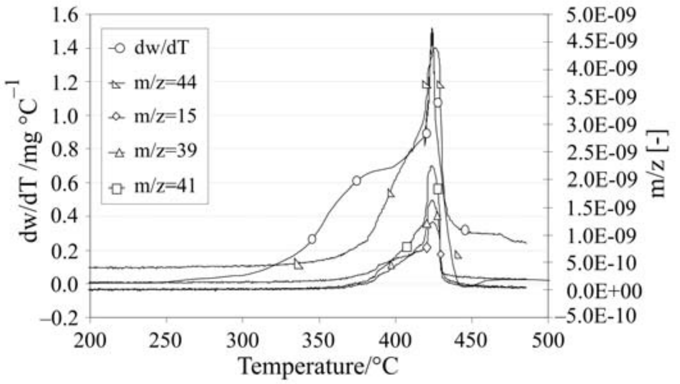

Fig. 5 Mass loss rate and evolved gases as a function of temperature for PMMA degradation (15% O_2 in N_2) at 2°C min^{-1}

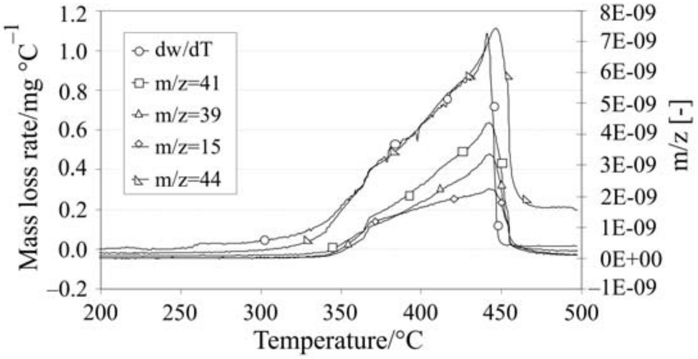

Fig. 6 Mass loss rate and evolved gases as a function of temperature for PMMA degradation (15% O_2 in N_2) at 5°C min^{-1}

loss rate. On the other hand the significance of evolved gases is relatively small at the lower heating rates where mass transport effects are negligible.

Figures 5–8 show the mass loss rate and the evolved gases for 15% O_2 in N_2 for heating rates 2, 5, 4 and 3°C min^{-1}, respectively. At heating rate 5°C min^{-1}, the main mechanism is the diffusion of oxygen from the surroundings to the surface of the PMMA. This is illustrated by the change of the slope of the mass loss rate and by the MS curves of the evolved gases. The diffusion mechanism is enhanced as the temperature of the sample increased. At a certain point a small char peak is identified and the evolved gases curve decays sharply. It is likely that diffusion of oxygen into the sample is the main mechanism of the production of gases. The process is initiated at around 350°C. As the heating rate is lowered the mass to charge ratio exhibits sharp change in the slope of the rate of mass loss and appears to be shifted to a higher temperature, thus, the diffusion process is shifted to higher temperature. At lower heating rates the effects of mass transport are more profound, thus, due to adding energy to the sample the mass transport initiates deeper in the sample, hence the main mechanism is the transport of fuel volatile from the inside to the outside.

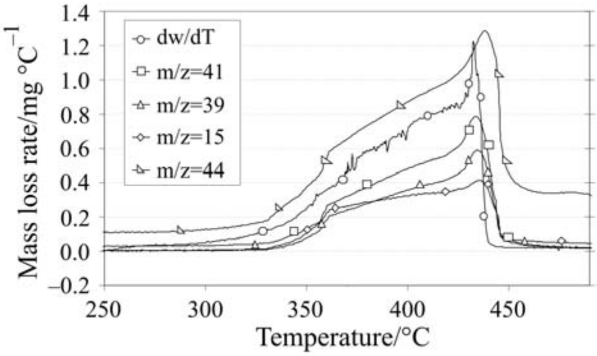

Fig. 7 Mass loss rate and evolved gases *vs.* temperature for PMMA degradation (15% O_2 in N_2) at 4°C min^{-1}

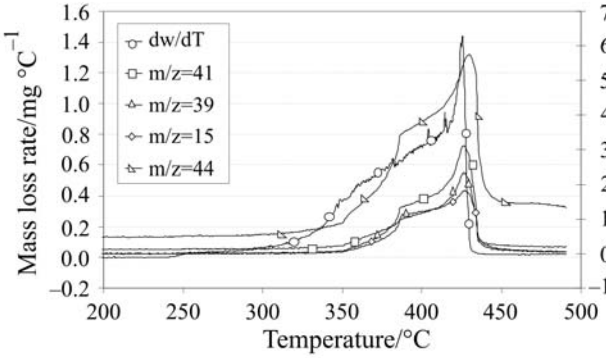

Fig. 8 Mass loss rate and evolved gases *vs.* temperature for PMMA degradation (15% O_2 in N_2) at 3°C min^{-1}

Conclusions

The above figures indicate the high complexity of the mass transport effects of industrial-grade PMMA in both inert and oxidative environments. It appears that the mass transport effects are manifested at lower temperatures in an oxygenated environment as compared to an inert environment, this is clear by inspecting the inflection points in both environments. To that end the effect of oxygen is to enhance the occurrence of mass transport phenomena at lower temperature. In an inert environment and higher heating rate, the point of inflection indicates the initiation of mass transport via bubble forming. It appears that at lower heating rate the mass transport is shifted to higher temperatures. This might be attributed to much more deeper bubble forming is accumulating before it bursts out, thus, the bursting of the volatile are much more volatile, to that end we see very sharp rise in the evolved gases. For the higher heating rate less in-depth bubbles forms, thus burst is less violent, hence the rate of production is lower.

By introducing the oxygen it is clearly seen that the process is controlled by diffusion. The effects of diffusion are more distinct at lower temperature with a higher heating rate (above 3°C min^{-1}). For higher heating rate since the bubbles are much closer to the surface and fuel volatile emanating from the surface are less violent, oxygen can reach the surface and surface and in-depth diffusion are the controlling mechanisms. On the other hand at lower heating rate, although the bubbles can be formed much deeper in the sample, but since they tend to burst more abruptly, the convective forces appears to reduce the effect of counter flow diffusion.

It appears that the industrial-grade PMMA was treated with chemical additives. This treatment will increase the polymer to char, thus inhibiting the combustion of gases, hence acting as a thermal barrier around the unburned material. The second peak at the end degradation temperature is believed to be due to char oxidation, this is attributed to the sharp decay of the production of gases. Char is carbonized polymer residue, which is left behind once the PMMA degradation is almost completed. The carbonized residue after the completion of the PMMA degradation is attacked by oxygen molecules and facilitated by the higher temperature. The outcome of the process is char layer that inhibits the production of gases. At lower heating rate due to more overall simmering of the sample, the amount of carbon residue is higher, hence the magnitude of the char peak is higher for lower heating rate as it is illustrated by the figures.

The decomposition of PMMA in an oxygenated environment can be considered as primarily controlled by a two-step reaction. For heating rates above 2°C min^{-1}. The first step is diffusion limited, where the slope is almost linear and the second step is a very sharp peak toward the end of the decomposition that is attributed to char oxidation. It is noteworthy that the char oxidation involves almost no change in mass. At high heating rates it is difficult to discern the peak but as the heating rate is lowered the peak began to be seen clearly.

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