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TG/DTA/MS OF POLY(METHYL METHACRYLATE)
The role of the oxidative environment

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Abstract

Degradation of relatively large particle size, 0.5 mm of Type-G PMMA (Rohm and Haas) were conducted with thermogravimetric analysis and evolved gas measurements using quadrupole mass spectrometer under conditions of mass transport limitation. In addition, differential thermal analysis was performed in order to furnish information with regards to exothermic or endothermic reactions associated with the degradation. The tests were conducted in an inert environment of pure N_2 and oxygenated environment. The results indicated one step degradation process in pure N_2 and the degradation process is endothermic. As the O_2 fraction increases the degradation process is transformed to exothermic.

Keywords: DTA/TG/MS, evolved gas analysis, PMMA

Introduction

Fire safety considerations have gained significant importance with advent of long term facilities in space such as the international space station. Minor incidents had occurred on board of the space shuttle mission mainly caused by electrical overload heating with polymeric insulation [1]. These events have motivated the research of such polymeric materials, in order to rank their tendency to ignite when they are exposed to an incident heat flux and source of ignition (piloted ignition).

An event of fire can be described as a sequence of events [2], at first the polymer is at initial temperature at T_∞. Once an incident heat flux is applied the temperature of the material began to rise until fuel vapor evolve from the sample surface, at this point the temperature is denoted by the pyrolysis temperature and the time required to attain this temperature is the pyrolysis time. Following this period, fuel vapor mix with the environment, the boundary layer, until the attainment of lean flammability limit, this period is denoted by the mixing time. Finally the final period is the induction time where the temperature of the gases rises until the attainment of self-sustain flame. Thus an event that leads to a fire consists of three stages, the inert preheating, the mixing time and the induction time. Following this methodology the ignition delay time is a summation of the pyrolysis time, the mixing time and the induction time. In the presence of strong pilot the induction

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time is small compared to the pyrolysis time, hence can be neglected. In addition for relatively high incident heat fluxes the mixing time can be neglected and as approximation the ignition delay time can be considered as equal to the pyrolysis time [3]. However, this is not the case when the incident heat fluxes reaches critical value typical to environments in space [4], beyond that even with the presence of a strong pilot the material will not ignite. For this case the mixing time should be retained and the ignition delay time is equal to the pyrolysis time plus the mixing time.

Following this methodology, the ignition delay time can be approximated as the pyrolysis time, or the ignition temperature of the surface sample exposed to an incident heat flux is equal to pyrolysis temperature. Thus, analytical solution for the one dimensional energy equation based on linearization of the surface re-radiation exists and the ignition delay time is determined by modeling the inert heating process of the polymer until the attainment of certain pyrolysis or ignition temperature [5]. This simplification approach works well for relatively high incident heat fluxes but as the incident heat fluxes reaches critical values the approximation deteriorate. Other modeling approaches are available among them models that include the degradation chemistry [6], these models in order to be implemented require three parameters, the activation energy, the pre-exponential factor of the solid decomposition and the heat of combustion. Thus these parameters motivated the application of TG/MS/DTA.

The main objective of this paper is to obtain information on whether the reaction is endothermic or exothermic and determine the heat of reaction under mass transport limitation based on DTA curves. The information in the literature is scarce on the heat of combustion of PMMA and there are no data in an oxidative environment on the endothermicity or exothermicity of the degradation process. Hopkins *et al.*[7] investigated the ignition and burning rate of various combustible samples, their main objective was to determine the material properties from cone calorimeter, they have reported value of 2.8 kJ g^{-1} for black PMMA, while this value was higher than the value reported by Tewarson [8] 1.6 kJ g^{-1}, they attributed and illustrated [9] such differences to commercial product variation, though both methods were not based on DTA.

Other studies have investigated the decomposition of PMMA utilizing thermogravimetry and differential scanning calorimetry, one study concentrated on polymer layered silicate nanocomposites [10], the study compared the degradation based on TG/DSC/FTIR and MS/GC of PMMA filled nanocomposites to that of pure PMMA. The results indicated based on TG and DSC of enhanced thermal stability and higher glass transition of filled PMMA nanocomposites with respect to that of pure PMMA. It is worth noting that in both cases the decomposition can be described as two-step reaction. The compatibility of polymer blends were investigated by DSC-FTIR [11], in order to furnish information with regards to mixing of PVDF with amorphous polymers, PMMA and PiPMA, thus impacting the crystallization and growth rate based on the blend content and crystallization temperature. The results indicated major differences, PVDF/PMMA blend in terms of crystallization and growth rate is invariant regardless of the blend content and crystallization temperature. In contrast to PVDF/PiPMA blend results which indicated that the growth rate and crystallization are variant, thus less impacted by the blend content and scale differently with respect to temperature. Similar study [12] concentrated on the crystallization dynamics analysis utilizing DSC-FTIR for PVDF/PMMA and PVDF/PEMA blends. Information with regards to miscibility was extracted. While the above studies mainly concentrated on blending two polymers, a study addressed the uncertainty of extracting the kinetic parameters [13] solely from thermogram curves, thus modification of the Ozawa method was introduced to tackle complex TG curve, since the traditional approach of the integral method has major limitations in extracting reliable kinetic parameters. The method implemented in extracting the multiple decomposition kinetics is based on subtraction of the mass of specific event from the total mass loss, and then addressing the following event on the TG curve. For PMMA the results demonstrated that the decomposition could be described in terms of both depolymerization and vaporization while for PTHF it can be described in terms of vaporization only. A TG/MS/DTA in conjunction with FTIR [14] was used to study the discoloration of patching material that was used for historic stone preservation. The change of color to black was attributed to using PMMA as patching material, though black discoloration has not been able to be determined with confidence.

It can be seen that neither of these studies has investigated the role of the oxidative environment, thus the TG/DTA/MS results that will be presented possess great significance.

Experimental

Apparatus and sample handling

The industrial grade PMMA particles of 0.5 mm were obtained by shaving from a large board of PMMA. The thermal curves were measured by Cahn instruments (model 2131). The evolved gas analysis was performed by quadrupole mass spectrometer (MS) VG-GAS (Gaslab300). The TG was coupled to the MS through a capillary tube packed with fused silica. The transfer line was heated to 150°C to prevent water condensation. The flow through the TG was maintained at 90 ml min^{-1}. The PMMA mass of the sample was 90 mg, this mass was chosen in order to improve the signal to noise ratio for the MS transient measurements. A 4 mm diameter bucket was used in the sampling.

DTA calibration

The calibration coefficient is determined by using compounds having a known heat of transition. The metals used included indium, lead and zinc. These metals were chosen in order to cover the range of the PMMA degradation. Two different tests were performed, one with emphasis on the dependence of the calibration factor on temperature and the other, on the effect of the mass of the sample on the calibration factor. The area under the DTA curve was calculated by $\Delta H\mathrm{m}=KA$, where ΔH is the heat of the reaction, m is the mass of the sample, K is the calibration factor and A is the area under the DTA curve. The results indicated that for heating rate of 4°C min^{-1} the calibration factor can be equal approximately to 0.45 J $^{\circ}\mathrm{C}^{-1}$ s^{-1}.

Results and discussion

Differential thermal analysis was implemented in pure nitrogen and 5%, 7.5%, 10%, 15% and 21% O_2 in N_2. The temperature of the sample and an inert reference sample was recorded as a function of time. A run without the sample at the same heating rate was conducted and the temperature difference between the empty pan and the reference sample was recorded. The recorded temperature with sample was subtracted from the dry run, thus obtaining the final DTA curves.

DTA curves at inert environment and oxidative environments

Figure 1 shows the recorded DTA curve and the mass loss rate for industrial-grade PMMA as a function of temperature. The DTA curve suggests and corroborates that the degradation process in nitrogen can be described as one step reaction. The maximum mass loss rate temperature coincides with that of the minimum of DTA signal. The DTA signal indicates that the decomposition process is endothermic. Determination of the heat of reaction was obtained by calculating the area under the DTA curve. The heat of reaction was obtained with the aid of the calibration factor, it was found that it was –2.8 kJ g^{-1}, this value is comparable to that determined by Hopkins and Quintiere [7] who implemented different methodology, the cone calorimeter to extract the heat of combustion.

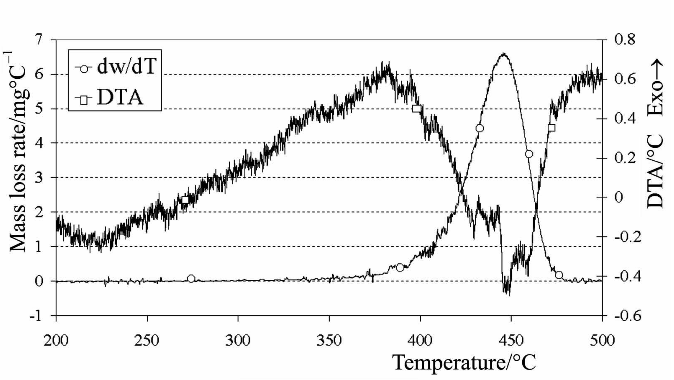

Fig. 1 DTA and DTG curves of industrial-grade PMMA *vs.T*

Figure 2 illustrates the degradation of industrial-grade PMMA in diluted nitrogen, 5% O_2 in N_2 at heating rate of 4°C min^{-1}. Observation of the mass loss rate curve indicates that the curve is somewhat skewed due to impact of the oxidative environment. Thus this might suggest that the degradation is one step reaction. However, the recorded DTA signal indicates that the process is far more complicated than that observed by the mass loss rate. The decomposition process can be described as three steps rather than one. The first step is an exothermic reaction, the degradation initiates around 230°C, the second step is endothermic reaction, the process began around 420°C, and the final step is a very narrow peak with very minor loss in mass com-

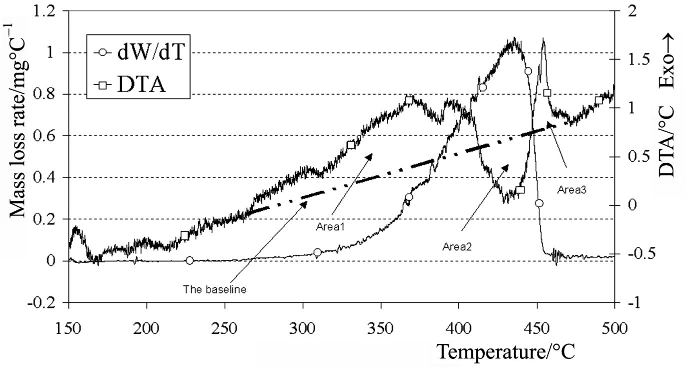

Fig. 2 Degradation of industrial-grade PMMA in diluted nitrogen by 5% O_2

mencing at around 440°C attributed to char oxidation. Char is carbon residue left behind once the PMMA degradation is completed. It appears that the mass transport effects impacted by oxidative processes, which includes surface and sub-surface oxidation, transformed the decomposition from endothermic in an inert environment to exothermic in an oxidative environment. Further more, the impact of the oxidative environment is dramatic causing the degradation to be less stable. The initiation of the decomposition is around 260°C, while in an inert environment it was initiated at approximately 350°C.

It is worth noting, that the rise in the base line of the DTA curve is attributed to relatively fast heating rate, which introduced small temperature gradients inside the sample, though not compromising the ability to extract information on the heat of reaction. The higher heating rate was selected in order to achieve much closest condition to that associated with ignition temperature when approaching critical heat fluxes for PMMA, these critical heat fluxes are around 11°C min^{-1}. The heats of reaction are 3.75 kJ g^{-1} and -1.14 kJ g^{-1} for the first and second steps.

Figure 3, further illustrates the impact of the oxidative environment, 10% O_2 in N_2 on the degradation, enriching the environment with oxygen caused the endotherm to vanish, thus the decomposition process can be described as two-step reaction, the second step

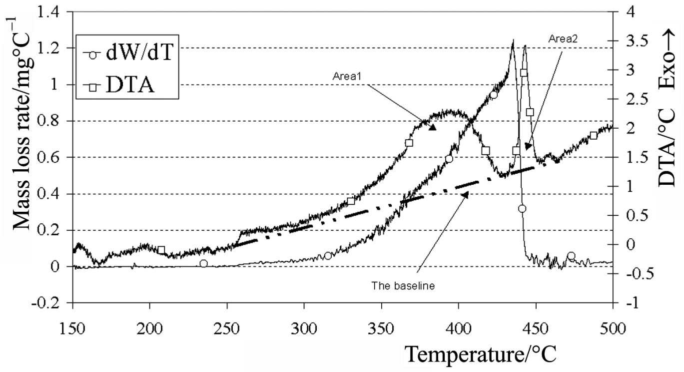

Fig. 3 Degradation of industrial-grade PMMA in diluted nitrogen by 10% O_2

is due to char oxidation. By inspecting both the mass loss rate and the recorded DTA curve, an interesting scenario is elucidated, though the masking effects of the mass loss rate due to surface and/or subsurface diffusion, thus preventing to identify the reactions steps from the mass loss rate. The DTA curve was capable to provide not only information on the reaction steps but also to reveal that the maximum mass loss temperature around 390°C, hence applying DTA in oxidative environment demonstrated to be a powerful tool in the analysis of oxidative degradation. The mismatch in peak decomposition temperatures for the char oxidation step is attributed to a wee-bit slower response of the DTA sampling, although the initial decomposition temperature rise coincide for both curves. The heat of reaction is 6.49 kJ g^{-1} for the first step reaction.

Figure 4 display the DTA curves in both pure nitrogen and in various oxidative environments. This plot enhances our understanding of the effect of oxidative environment on the decomposition process of industrial-grade PMMA. It is clearly seen that in pure nitrogen the reaction is one step and endothermic. By increasing the oxygen content to 5% O_2 in N_2, the decomposition process can be described as three steps, the first is exothermic due to the impact of oxygen which include both surface and sub-surface oxidation, the second step is endothermic, and the third step is char oxidation. The same description holds for oxidation content of 7.5% O_2 in N_2, though the endotherm value is much smaller than that in lower oxidative environment. This situation is terminated at 10% oxygen content, thus the decomposition consists of two-step reactions. Further enriching the environment with oxygen to 15 and 21%, thus discerning the reaction steps prior to that of char oxidation is no longer feasible, hence indicating, that the heating rate of 4°C min^{-1} is too fast to resolve the oxidative pyrolysis process at lower degradation temperatures. Albeit, the degradation are exothermic in both environments. Other distinctions that can be identified, for higher oxygen content the degradation is less stable, the decomposition initiation temperature is reduced to 240°C in 21% O_2 in N_2 compared to 260°C in 5% O_2 in N_2 and 360°C in an inert environment. The char DTA signal is shifted to lower temperature with increasing oxygen concentration, this is due to mechanisms associated with formation of carbon residue. It is important to note that the maximum DTA signal appears to be fixed at around 390°C, furthermore, increasing the oxygen content cause the char oxidation step initiation to be accelerated relatively compared

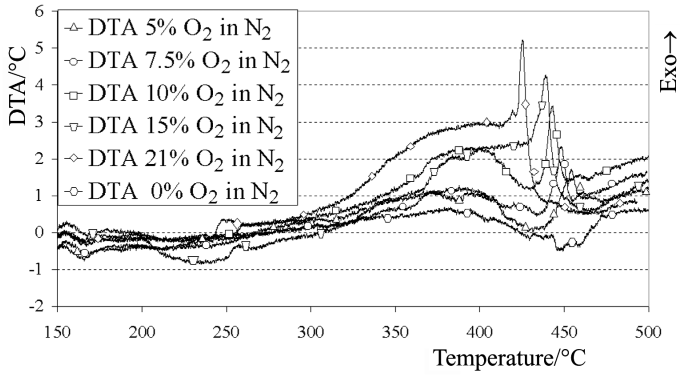

Fig. 4 DTA curves of PMMA in various oxidative environments

to an environment with lower oxygen content. This is due to the fact that more oxygen molecules are available to react with carbon, thus facilitating the decomposition to lower temperature, hence abundance of oxygen will react, to that end the DTA peaks magnitudes have higher values.

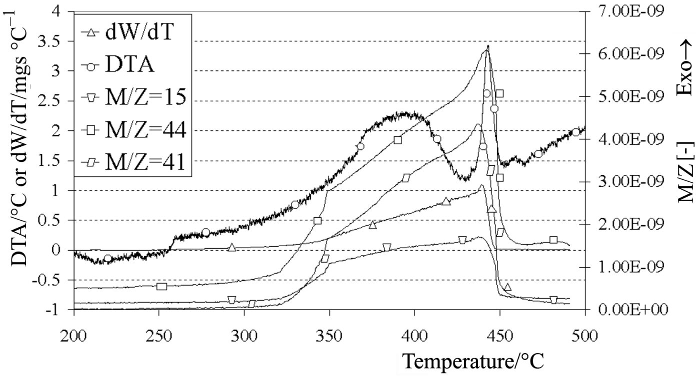

Fig. 5 DTA and DTG as well as quadrupole MS curves of PMMA at 10% O_2 in N_2

Figure 5 shows DTA curve, mass loss rate and the rate of production of gases evolving from the sample detected by the quadrupole mass spectrometer at 10% O_2 in N_2. It is evident that the maximum DTA char oxidation curve matches the maximum rate of production of the carbon dioxide, mass to charge ratio equal to 44. Char oxidation proceeds to perform carbon residue, thus liberating carbon molecules, hence facilitating the carbon dioxide production. As the oxygen concentration increases the magnitude of this effect increases due to the abundant of oxygen that attack carbon molecules. From this figure one can clearly observe that the DTA curve is less sensitive to diffusion process. This is evident by comparing the curves of the MS rate production where the change in the slope becomes linear, then a sharp rise in slope towards the char oxidation. The rate of production of gases detected is mass to charge ratio of 15 and mass to charge ratio of 41.

Figure 6 shows the DTA curves as a function of temperature for 10%, 15% and 21% O_2 in N_2, at heating rate of 1.5°C min^{-1}, lowering the heating rate was essential in order to identify major and minor step reaction. Furthermore at heating rate less or equal to 2°C min^{-1} the base line of the DTA curve is horizontal, thus the temperature gradients can be considered negligible. A minor step reaction occurred at DTA maximum curve at temperatures 248, 244 and 238°C respectively. A major step reaction occurred at 388°C for all cases. The curves illustrate the effects of the oxidative environment on the degradation. The more abundant oxygen, the easier to identify the reaction steps such as the one occurs at around 330°C. The char oxidation peaks are shifted to lower temperature, the same trend occurred in the case of higher heating rate as described earlier. It appears that DTA maximum char temperature shifts have linear relation with oxygen concentration, as is manifested in Fig. 6.

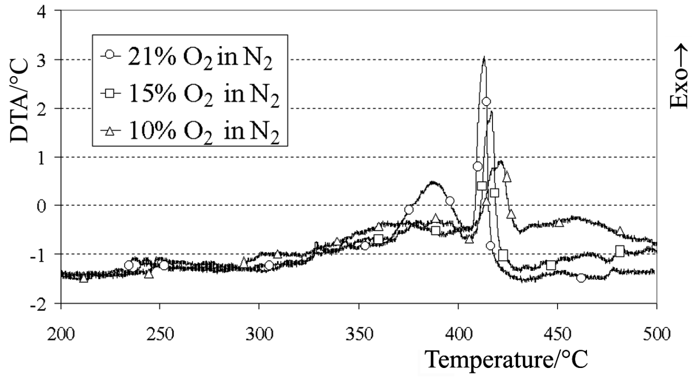

Fig. 6 DTA curves of PMMA in various oxidative environments at heating rate 1.5°C min^{-1}

Conclusions

The importance of coupling the TG with MS was demonstrated, it appears that MS data are more sensitive to diffusion effects, this was manifested by the rate change of the slope production of gases. DTA applied in conjunction with TG revealed that in an inert environment the reaction is endothermic, while in an oxidative environment the reactions are exothermic for 10% O_2 in N_2. The heat of combustion was calculated under certain oxidative environments. The role of oxygen was to lower the decomposition initiation temperature, hence causing the degradation to be less stable. Clarification of these parameters and the endothermic or exothermic reactions are essential for developing and applying new models for ignition delay time and flame spread growth.

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