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TG/DTA/MS OF POLY(METHYL METHACRYLATE)
The effect of particle size

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Abstract

Thermogravimetric analysis in conjunction with evolved gas analysis are discussed for powder PMMA, particle diameter of 0.1 mm. Furthermore, differential thermal analysis measurements were performed in both pure nitrogen and oxidative environment. These measurements are conducted to assess major differences associated with particle size. The results indicated for powder PMMA, in pure nitrogen the degradation can be described as three-step reactions, while in oxidative environment it is two-step reactions. Furthermore the reaction in both environments are mainly endothermic. This in contrast to results reported for industrial-grade PMMA with relatively larger particle size of 0.5 mm.

Keywords: differential thermal analysis, mass spectrometry, powder PMMA, thermogravimetry

Introduction

A recent event of fire on board of MIR space station [1] have raised many issues with regards to fire safety, such as fire detection, fire suppression, fire restoration and material flammability for future space exploration in general and for the planned international space station in particular. Thus for material flammability studies, mainly two-test materials have been widely used, PMMA and a mixture of polypropylene and glass fibers [2]. These reference materials, were used for both studies of ignition and flame spread.

The idea behind these tests is to determine the flammability of materials, thus selecting the material that best retard fire in the event of ignition source for space stations cabins. The current protocol used by NASA for ranking the material flammability to be used in space is 'Flammability, Odor, Off gassing and Compatibility Requirements Test Procedure for Materials in Environment that Support Combustion' [3]. Based on this protocol, a material is adequate to be used in space subject to two tests, the upward propagation flame test and the heat and visible smoke release rate test. A selected material can pass the first test if the flame spread in vertical upward direction is extinguished less than 0.15 m from the point of ignition in terrestrial environment. The second test is some kind of assessment of the potential damage of a fire. While these tests are conducted in normal gravity environment, the material ranking obtained by this protocol is questionable in mi-

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cro-gravity environment. Furthermore, due to lack of buoyancy in micro-gravity environment, typical forced flow caused by heating systems is on the order 0.1 m s^{-1}. Thus simulating experiments in terrestrial environment were the typical forced flow are of order 1 m s^{-1} is impossible, hence rendering numerical simulation of piloted ignition and flame spread of forced flow over a polymer surface exposed to an incident heat flux is very attractive and cost effective. Since experimentation in space are accessible for few affluent countries, numerical simulation of piloted ignition and flame spread under space conditions can achieve more than adequate results with a fraction of the cost required to conduct these experiments on board the space shuttle or the international space station.

Although numerical simulation based on degradation chemistry [4] has some advantages, the major drawback of this technique is that, it is time consuming and required relatively fast computers and a large amount of memory space unless smartly implemented. In addition, implementation of this technique requires information associated with the decomposition endothermic or exothermic reactions, which is the subject of this paper. In a previous paper [5], I have reported results for industrial-grade PMMA with relatively large particle diameter of 0.5 mm. The DTA results for industrial-grade PMMA indicated that for nitrogen the reaction is endothermic and can be modeled as one step reaction and in oxidative environment, the reaction is exothermic and the degradation can be modeled mainly as two steps.

Furthermore there have been numerous [6–8] publications during the recent years discussing mainly the effect of polymer blends on the degradation utilizing DSC-FTIR and TG/DSC/FTIR. These studies investigated the crystallization and growth rate with respect to blend of various amorphous polymer contents including PMMA, in addition information with regards to miscibility of different blends were extracted.

The current paper will discuss DTA of powder PMMA of particle diameter of 0.1 mm. This is essential in order to compare results associated with the particle size effects on PMMA degradation.

Experimental apparatus and sample handling

The experimental apparatus is described elsewhere [5], the only thing that is worth emphasizing is the coupling between the TG and the quadrupole mass spectrometer. The pure powder PMMA samples were obtained from Aldrich Company. The samples consist of a chain of 130.0000 molecules, this specific number of molecules in a chain was chosen, in order to better compare the results of the pure powder PMMA with that of industrial-grade PMMA [5], which has the same number of molecules per chain. The controlled mass loss measurements and differential thermal analysis were conducted with sample mass of 20 mg. The DTA curves were subtracted from a dry run thus obtaining the final DTA curves. The flow rate of the pure nitrogen and oxidative environment gas was maintained at 90 mL min^{-1}.

Results and discussion

DTA was conducted for pure powder PMMA in conjunction with controlled measurements mass loss rate and evolved gas analysis in an inert environment of pure nitrogen and in an oxidative environment of 5%, 10% and 21% O_2 in N_2. The main goal is to compare differences attributed to the impact of particle diameter size on the degradation and heat of reactions of pure powder PMMA and industrial-grade PMMA.

DTA curves in an inert and oxidative environment

DTA curve as a function of temperature, as well as the mass loss rate in pure nitrogen environment is illustrated in Fig. 1. By inspecting both curves it is evident that the degradation can be described as three-step reaction. Two minor steps with maximum mass loss rate and minimum DTA curves around 235 and 275°C, and a major step reaction at approximately 355°C. It is clearly seen that all the steps are endothermic. By comparing these results with results reported for industrial-grade PMMA [5], the degradation for both types of polymers in an inert environment are endothermic, although for the industrial-grade PMMA the decomposition can be described as only one step.

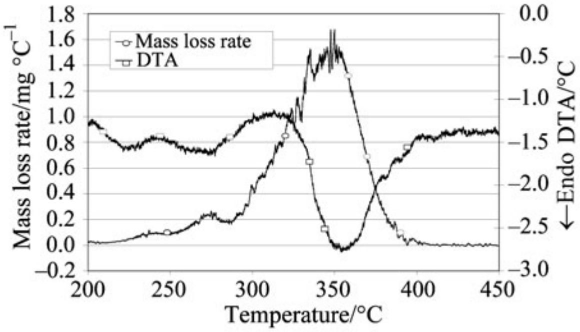

Fig. 1 Mass loss rate and DTA curve as a function of temperature for pure powder PMMA in pure nitrogen, heating rate of 4°C min^{-1}

By diluting the nitrogen with 5% oxygen as shown in Fig. 2, the minor step reactions constituting the early decomposition are vanished according to the mass loss rate curve and the degradation might suggest that it is one step reaction. Further inspection of the DTA curve reveals a complex degradation scenario that can be described as three-step reaction. The first step is at 255°C, the second step at 310°C and a third step at around 360°C. It appears that the effect of dilution shifted the minor reactions observed in pure nitrogen to higher temperatures, contrarily, the major step reaction impacted by the oxidative environment accelerated the decomposition, thus shifting the reaction to lower temperature. All three reactions are clearly endothermic.

By further diluting the environment to 10% O_2 in N_2, as seen from Fig. 3. Based on the DTA curve, the first step reaction observed appears to remain fixed at temperature around 255°C and corresponds to the same step at 5% O_2 in N_2, thus indicating that for the first step reaction introducing the oxidative environment has dramatic impact. Further enriching the environment with oxygen has no impact in terms of accelerating the decomposition since the peak is fixed with respect to temperature. For the major step or the second step reaction, the effect of oxygen is to cause the decomposi-

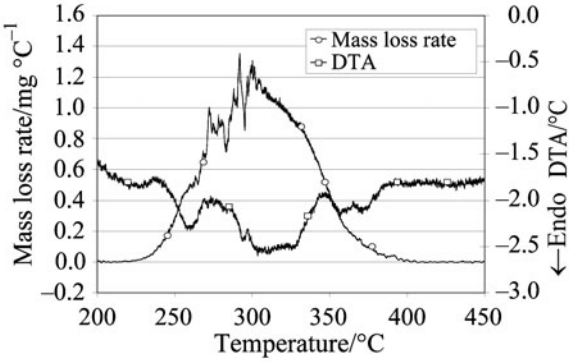

Fig. 2 Mass loss rate and DTA curve as a function of temperature for pure powder PMMA at 5% O_2 in N_2, heating rate of 4°C min^{-1}

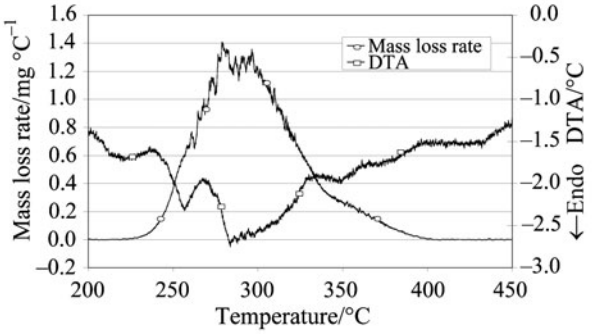

Fig. 3 Mass loss rate and DTA curve as a function of temperature for pure powder PMMA at 10% O_2 in N_2, heating rate of 4°C min^{-1}

tion to be less stable. As for the third step it appears that toward the end of degradation the effect of oxygen is to diminish this step. All three steps are endothermic.

Figure 4 shows the DTA curve and mass loss rate curve in 21% O_2 in N_2 at a heating rate of 4°C min^{-1}. The figure illustrates the two-step reaction, the first step is maintained at peak DTA temperature of 255°C, and the second step was shifted to lower maximum mass loss rate temperature, due to impact of the enrichment of the oxidative environment. Furthermore, evolved gas analysis and mass loss rate as manifested in Fig. 5 illustrates and corroborates the rate of production of gases does not exhibit any change of slope as encountered for large particle diameter size for industrial-grade PMMA [5]. The smooth curves of mass to charge ratio of 44, 41, 39 and 15, thus suggesting that the degradation limiting process are kinetically controlled rather than diffusion controlled, to that end, the smaller particle diameter in an inert and oxidative environment might have dramatic impact on the decomposition process. It is clearly observed that the decomposition initiation temperature for pure powder PMMA is far lower than those of industrial-grade PMMA, 225 *vs*. 245°C, respectively. The rate of production detected by the quadrupole mass spectrometer revealed peculiar picture, manifested by separation of the rate evolving gases emanat-

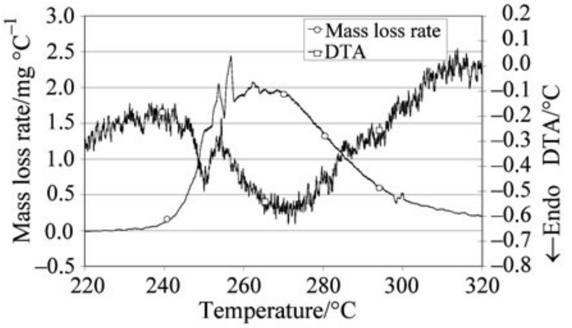

Fig. 4 Mass loss rate and DTA curve as a function of temperature for pure powder PMMA at 21% O_2 in N_2, heating rate of 4°C min^{-1}

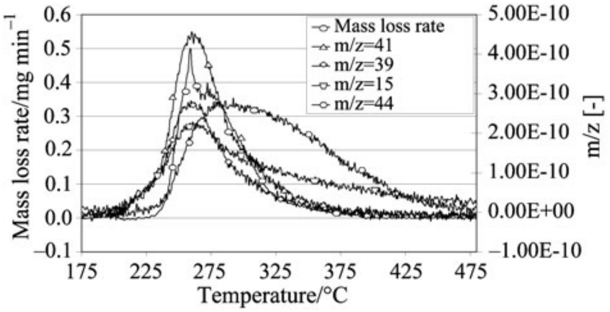

Fig. 5 Mass loss rate and evolved gases as a function of temperature for powder PMMA at 21% O_2 in N_2, heating rate of 4°C min^{-1}

ing from the sample, thus the rate of production of gases with mass to charge ratio 41, 39 and 15 exhibits sharp rise and sharp decay. The maximum rate production coincide with the maximum mass loss rate for the first step, hence indicating that the first step reaction in an oxidative environment seems to be associated with the gas products with mass to charge ratio 41, 39 and 15. On the other hand, the rate of production of carbon dioxide, mass to charge ratio 44, has tamer rise and slow decay. The maximum production rate coincides with the maximum mass loss rate of the second step, therefore indicating that the second step is linked mainly to the production of carbon dioxide. The slow decay might be attributed to residence time of formation of the carbon with oxygen.

Conclusions

Degradation of chemically pure powder PMMA in nitrogen and oxygenated environments was studied with thermogravimetric analysis, differential thermal analysis and evolved gas measurements using quadrupole mass spectrometer. It can be concluded that mass loss rate measurements in pure nitrogen can be modeled as three-step reaction, the first and second step are minor steps and the third is a major one. As oxygen fraction increased to 5% O_2 in N_2, the degradation can be described as three steps, though the presence of oxygen shifted the first step to higher temperature, while causing the major second step to be less stable. A third step is observed toward the decomposition end of the mass loss rate. Further increasing the presence of oxygen, to 10 and 21% O_2 in N_2, impacting the degradation dramatically, the first step appears to be fixed at 255°C, therefore, there is no any effect of oxygen in terms of stability of the degradation. For the second step the presence of oxygen caused the degradation to be less stable for both 10 and 21% dilution.

By comparing the results of the chemically pure powder PMMA with results for industrial-grade PMMA. The absence of mass transport limitation due to small particle diameter size has dramatic impact on the degradation. The reaction steps are all endothermic in both pure nitrogen and oxidative atmospheres, while in industrial-grade PMMA, due to relatively large particle diameter, the reaction is endothermic in pure nitrogen but exothermic in the presence of oxygen. Coupling the MS to the TG proved to be essential to detect such mass transport limitation based on the change of slope of the rate of production of gases. For powder PMMA this effect of change of slope of MS curve was not observed, therefore due to small particle size mass transport limitation was not the controlling mechanism in the degradation of pure powder PMMA.

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