Thermal decomposition of BAMO/AMMO with and without TiO$_2$

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Abstract

An experimental study of 3,3′-bis(azidomethyl) oxetane/3-azidomethyl-3-methyloxetane (BAMO/AMMO) and BAMO/AMMO/TiO$_2$ was performed to investigate thermal decomposition of the copolymer and the effect of TiO$_2$ on its decomposition. Experiments were conducted at 0.1 MPa with heat fluxes of 100 and 400 W/cm^2, delivered by a CO$_2$ laser. Gaseous samples were extracted by quartz microprobes and analyzed in a triple quadrupole mass spectrometer (TQMS). Gas-phase temperature profiles and surface temperatures were measured using the micro-thermocouple technique to investigate gas-phase reaction zones identified by the species measurement. Species measurements revealed that decomposition products of BAMO/AMMO were quite similar to those reported for BAMO and that the addition of TiO$_2$ caused no significant changes in mole fractions of the products, except for an increase in NH$_3$. Product species were indicative of simultaneous decomposition of the backbone structure and side chains. No evidence of gas-phase reaction was found in gas-phase species or temperature profiles, indicating that the reactions are occurring in the condensed-phase or in a near-surface reaction zone. The regression rate was substantially reduced by the addition of TiO$_2$ at a heat flux of 400 W/cm^2. Based upon the species and temperature measurements, it is argued that this reduction is primarily a result of physical, rather than chemical, effects of the TiO$_2$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Thermal decomposition; Triple quadrupole mass spectrometer; BAMO/AMMO copolymer

1. Introduction

In the search for new energetic binder materials, a great deal of interest has centered on azido compounds, such as 3,3′-bis(azidomethyl) oxetane (BAMO), 3-azidomethyl-3-methyloxetane (AMMO), glycidyl azide polymer (GAP) and their copolymers. These polymers draw considerable interest, since they have potential as energetic binders and plasticizers in gun and rocket propellants, where relatively low flame temperature, high mass impetus and stable combustion are desirable.

Despite considerable interest, only a limited number of research results have been published on the thermal decomposition of BAMO, AMMO and their copolymers [1–7]. In fact, only one previous study of the decomposition of BAMO/AMMO copolymer appears in the literature from Kimura and Oyumi [7]. In their study, thermal decomposition of BAMO/AMMO under isothermal and slow heating (80 K/min) conditions were reported along with results for other copolymers, including BAMO/3-nitratomethyl-3-methyloxetane (NMMO) and BAMO/tetrahydrofuran (THF). The results for BAMO/AMMO indicated that the decomposition of AMMO did not affect that of BAMO. Therefore, it was concluded that the thermochemical characteristics of copolymer were the same as those of

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BAMO. However, no reaction pathways or chemical structure of products were reported for the decomposition of the copolymer.

For some propellants, especially those containing ammonium perchlorate (AP), TiO_2 has been investigated as an additive for burning rate suppression [8] and plateau-burning [9]. While, the mechanism by which TiO_2 achieves these effects is not agreed upon, it has been reported that thermogravimetric studies of AP/hydroxyl-terminated poly-butadiene (HTPB) propellants indicate faster weight loss with TiO_2 [10]. Addition of TiO_2 to propellants with azide binders is worthy of investigation because they have shown intrinsic instabilities during laboratory studies [1,11,12]. Also, plateau-burning is of interest for certain applications using propellants formulated with energetic binders. Therefore, it is important to obtain experimental data for the effect of TiO_2 on the thermal decomposition of BAMO/AMMO.

Given the current level of understanding of BAMO/AMMO decomposition processes and the lack of data for the effect of TiO_2 on energetic binders, this work was undertaken to investigate physical and chemical processes during thermal decomposition of BAMO/AMMO with and without TiO_2. Primary efforts focused on BAMO/AMMO thermal decomposition and interaction of the two components of the copolymer. The results for BAMO/AMMO, along with previous data for BAMO [1] at the same experimental conditions, allow the effect of AMMO to be examined. Also, studies of BAMO/AMMO with and without TiO_2 were performed to identify its effects on decomposition.

2. Experimental approach

The experimental apparatus is basically composed of a high-power CO_2 laser used as the heat source for ignition and sustaining combustion, visual diagnostics for the examination of flame behavior and species sampling height, a triple quadrupole mass spectrometer (TQMS) for gaseous product analysis and a data acquisition and analysis system. Since, detailed features of the experimental setup have been described elsewhere [1,13,14], only a brief explanation directly relevant to this study will be given here.

Experiments were conducted at 0.1 MPa (1 atm) in an argon environment, with heat fluxes of 100 and 400 W/cm^2. Gaseous products evolved from the propellant surface were extracted by quartz microprobes and analyzed in the TQMS. Using parent and daughter modes of the TQMS and careful calibration, it was generally possible to differentiate and quantify species at the same mass-to-charge (m/z) value. For each m/z value selected, the parent mass was fragmented using the process of collision-induced dissociation (CID) in daughter mode operation. Then, the most probable chemical structures for the parent mass were deduced from the observed daughter ion masses, a library of mass spectra and available results in the literature. Temperature profiles were measured using the micro-thermocouple technique to investigate gas-phase reaction zones identified by the species measurements and to determine the surface temperatures. Both tungsten/rhenium (W/Re) and platinum/rhodium (Pt/Rh) type thermocouples of 25 μm diameter were used for the measurements. Flame structure and surface behavior were observed using a high-magnification video system.

The BAMO/AMMO copolymer used in this study was a yellow-white, highly viscous liquid with the molar ratio of 3/2, which corresponds to a mass ratio of approximately 2/1. Fig. 1 illustrates the structures of AMMO and BAMO. The BAMO/AMMO/TiO_2 mixtures were prepared by physical mixing of small amounts of the copolymer and TiO_2 powder, both of which were provided by Thiokol. The mixtures were
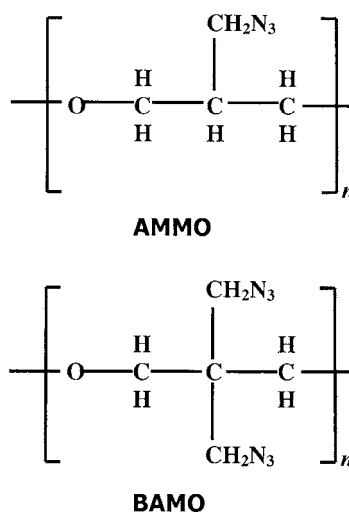

Fig. 1. Structures of AMMO and BAMO.

not cured. To examine the effect of TiO_2, two different mixtures were prepared with 1 and 5% TiO_2 by mass; in the rest of the paper these will be referred to as B/A/T1 and B/A/T5. For testing, a sample was shaped by placing it into a segment of quartz tube to form a cylindrical shape with a diameter and height of 6.35 mm (1/4 in.). The cylindrical sample was removed from the quartz tube and glued to a small sample holder angled at $45°$ to the incident laser beam so that the sampling microprobe could approach the sample perpendicular to the sample surface along its centerline. This sample holder was attached on a linear positioner, which permitted precise vertical positioning and movement of the test sample with respect to the position of the sampling probe orifice. During a test, the sample was pushed toward the sampling probe by the linear positioner to obtain species mole fractions versus height from the sample surface.

3. Results

3.1. Decomposition behavior and regression rate

The decomposition behavior was examined primarily using the video recordings. For BAMO/AMMO, weak blue flames were usually observed in the gasphase throughout the experiments, similar to those observed in BAMO [1]. The contour of the surface of the copolymer during regression was very sensitive to the distribution of the applied laser flux so that the surface became uneven due to even slight non-uniformity in the distribution of the flux. Regression rates were 2.2 ± 0.3 and 5.0 ± 0.6 mm/s at 100 and 400 W/cm^2, respectively, lower than those of obtained for BAMO, which were 3.4 ± 0.6 and 10.7 ± 2.0 mm/s at 100 and 400 W/cm^2, respectively [1]. The lower regression rate would seem to be an effect of the AMMO, which is a less energetic molecule than BAMO.

With the addition of TiO_2, no changes in the visible flames were observed. However, compared with the neat copolymer, the mixtures showed more uniform burning surfaces, with less sensitivity to the applied heat flux. Within the limit of measurement errors, the regression rates of B/A/T1 and B/A/T5 were same at the same heat flux and were estimated to be 2.0 ± 0.4 and 3.0 ± 0.7 mm/s at 100 and 400 W/cm^2, respectively.

Thus, at the lower heat flux, the regression rate was reduced by approximately 10% relative to that for BAMO/AMMO, while at the higher heat flux, the regression rate was reduced by approximately 40%. Possible explanations for the effect of TiO_2 on the regression rate are discussed after the presentation of species and temperature profiles.

3.2. Identification of product species

The results of identification and differentiation of species for each major parent mass in this study are shown in Table 1. The identity of the major species was same for the neat copolymer and the mixtures. The major signals were found at m/z value of 28, 27, 30, 29, 41, 17, 42, 39, 43 and 18, in the order of descending intensity. Minor signals were measured at m/z value of 46, 45, 44, 31, 26 and 16. Based upon the daughter masses measured in the daughter mode experiments using high collision energy, possible species for each of the parent masses and their chemical structures were determined (Table 1). The major species are the same as those measured for BAMO under similar test conditions [1].

Three species are found at mass 28: N_2, CO and C_2H_4, with N_2 being the dominant species, followed by CO and then C_2H_4. In a previous study of BAMO [1], the amount of C_2H_4 was below the limit of detection of 0.001 mole fraction, so the presence of measurable amounts for the copolymer would appear to be attributable to the AMMO. Mass 27 is totally composed of HCN, without C_2H_3, due to the small amount of C_2H_4 at mass 28. H_2CO is the dominant species at mass 30. In the present study, mass 29 was found to be composed primarily of CHO with a small amount of H_2CNH. However, no previous studies of azido polymers reported the existence of H_2CNH. H_2O is believed to account entirely for mass 18, therefore, no daughter mode analysis was performed for mass 18. Mass 17 is mainly composed of NH_3 with a limited amount of OH, a fragment from the measured H_2O signal.

At mass 42, the daughter mass spectrum in Table 1 is significantly different from that found previously for BAMO [1]. No chemical structure can be suggested from the measured spectra of mass 42 at this time. Mass 41 also has daughter masses that are significantly different from that of BAMO [1]. In the copolymer,

Table 1
Daughter mass ions (in the order of descending intensity) for each major parent mass of the BAMO/AMMO copolymer at 100 W/cm^2

Parent mass	Daughter mass ions in the high-energy mode	Most probable chemical structure
28	14 > 12 > 15	N_2, CO > C_2H_4
27	13, 14, 12 (all small)	HCN
30	14 ≫ 15, 16 (very small)	H_2CO ≫ C_2H_6, NO
29	14, 12, 13	CHO (fragment from H_2CO) > H_2CNH
41	15, 27, 14, 16	CH_2CNH ≫ CH_3CN
17	N/A	NH_3 ≫ OH (fragment from H_2O)
42	15, 29, 28, 27	No explicit species was found.
39	13, 14, 18, 15, 26	No matching stable species was found
43	15, 27, 28, 29, 26	CH_3CHNH and CH_3CO (fragment from CH_3CHO)
18	N/A	H_2O
44	28, 29 ≫ 30 (very small)	CO_2 and CH_3CHO, almost no N_2O
45	15, 29, 17, 28, 27	$C_2H_5NH_2$ or $(CH_3)_2NH$
31	14, 15 (all small)	No matching stable species was found
26	13, 14, 12, 15	C_2H_2

CH_2CNH comprises most of mass 41, with a very limited amount of CH_3CN, while the opposite was true for BAMO. Daughter mass spectra measured at mass 39 were similar to those found in BAMO [1], but no stable species could be found for this mass. The products at 43 through 39 might be attributed to propylene (C_3H_6) [15], however, calibration results for C_3H_6 are not consistent with the daughter mass patterns observed in the present experiments.

At mass 43, the daughter species indicate that the atomic composition of the larger species at this mass is C_2H_5N, with a small amount of CH_3CO present. The most likely structure for the C_2H_5N is CH_3CHNH, as was found in the earlier study of BAMO. Previous results for BAMO, however, did not show evidence of CH_3CO in the measured daughter ion pattern [1]. No stable species with a molecular formula C_2H_5N were commercially available, therefore, no direct calibration evidence of the daughter mass distribution could be obtained for comparison with the measured daughter masses of mass 43. Mass 43 was previously reported in a low temperature effusion cell–MS study [2] as a product from AMMO, resulting from backbone scission and C_2H_3O was assigned to this mass. Thus, it would appear that the small amount of CH_3CO detected in the present study is formed from the AMMO or from the interaction of AMMO and BAMO.

For BAMO, higher molecular masses such as 54, 55, 56 and 69 were measured as major species [1]. However, none of these molecular weights were measured in BAMO/AMMO, even as minor products. This is the most significant chemical difference between the copolymer and the neat BAMO. The presence of the AMMO may be the source of this difference. However, since the BAMO and the BAMO/AMMO were from two different suppliers, it is also possible that some difference in samples, such as the molecular weight distribution, may account for the lack of higher molecular weight species.

Minor masses were also investigated to identify possible chemical species. Mass 44 is composed of CO_2 and CH_3CHO. In the study of BAMO decomposition [1], mass 44 was too small in intensity to be considered as even a minor product. Therefore, CO_2 and CH_3CHO appear to result from the presence of the AMMO. Mass 45 seems to include two species, $C_2H_5NH_2$ and $(CH_3)_2NH$, based upon its daughter mass spectra; the relative amount of these species is not certain at this time. No stable species could be suggested for mass 31, since the levels of daughter mass signals were relatively low. Mass 26 is probably C_2H_2; no fragments from higher mass signals were found that might contribute to this mass signal.

3.3. Gas species and temperature measurements: BAMO/AMMO

The results of gas-phase species measurements for BAMO/AMMO at 100 and 400 W/cm^2 are shown in Figs. 2 and 3, respectively. Because no species measurements for the BAMO/AMMO are available in the
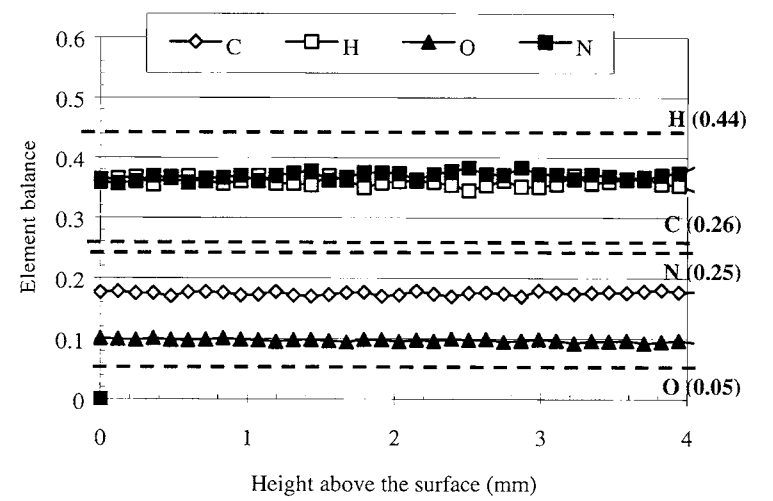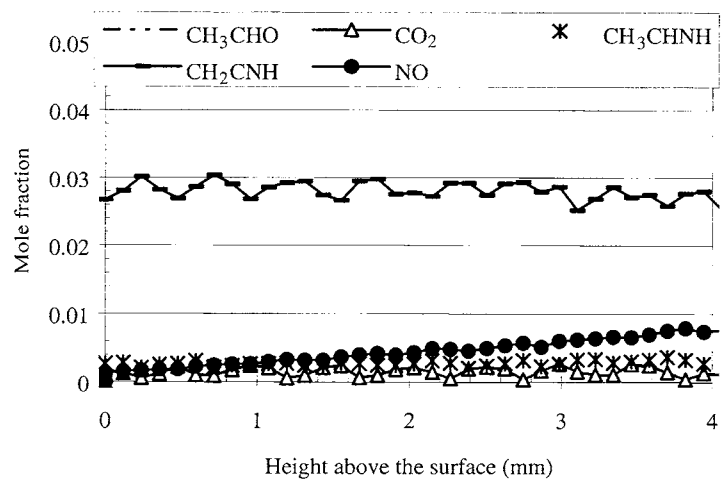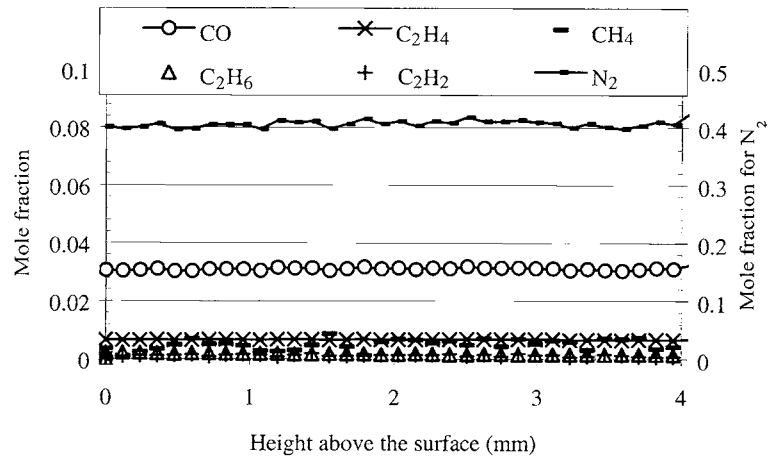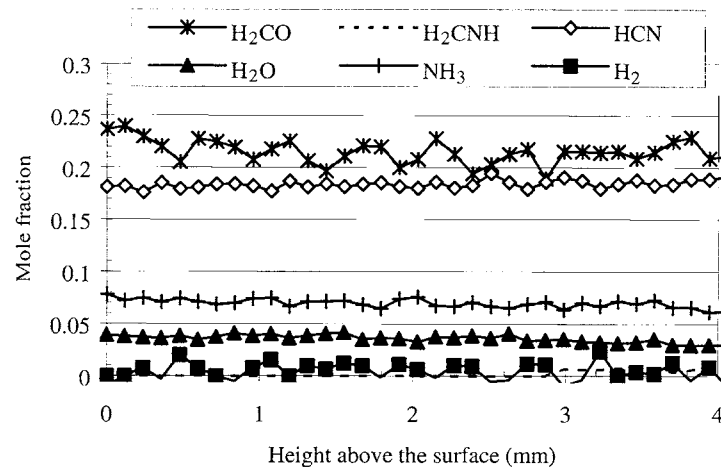
Fig. 2. Species profiles and element balance for BAMO/AMMO at 100 W/cm^2.

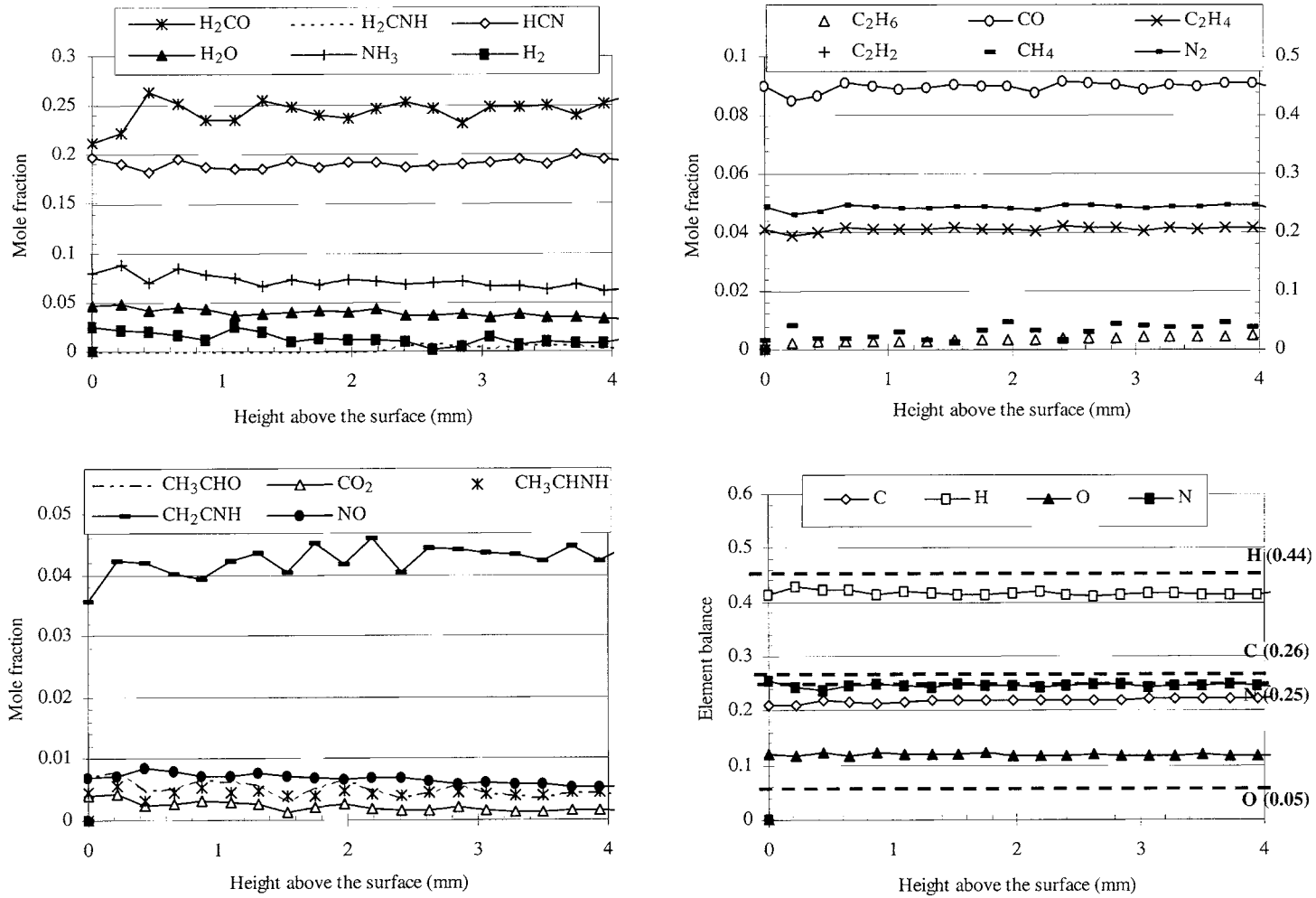Fig. 3. Species profiles and element balance for BAMO/AMMO at 400 W/cm^2.

Table 2
Species mole fractions at the surface for 400 W/cm^2

	C_2H_3N	H_2CO	C_2H_4	N_2	CO	HCN	H_2O	NH_3	CH_4
BAMO [1]	0	0.15	0	0.42	0.02	0.22	0.05	0.10	0
BAMO/AMMO	0.04	0.23	0.04	0.25	0.09	0.19	0.05	0.08	0.01
B/A/T1	0.03	0.21	0.05	0.24	0.07	0.19	0.05	0.11	0.01
B/A/T5	0.04	0.21	0.05	0.24	0.07	0.19	0.05	0.12	0.01

literature, a direct comparison of the species results in the present study with others was not possible. At both heat fluxes, the major decomposition products maintain uniform concentration up to 4 mm above the surface. Due to the very fuel rich nature of the copolymers, essentially no oxidizing species are present in the gas-phase, so fuel species, such as H_2CO and HCN have nothing with which to react, leading to the constant mole fractions observed. The lack of variation in the mole fractions of gas-phase species suggests that the reaction is occurring primarily in the condensed-phase or in a near surface reaction zone that cannot be resolved at the spatial resolution of the sampling system, which is estimated to be 0.10 mm.

The quantified species were used to calculate element balances, which are shown in Figs. 2 and 3. At 100 W/cm^2, the element fractions deviate significantly from the expected values, indicated by the dashed lines, for all atomic species, while the element fractions for the 400 W/cm^2 results are much closer to the expected values. The primary difference between the two sets of data is the relative amount of N_2 and CO, which is determined by the daughter masses. This difference suggested that the calibration of the daughter masses at mass 28 might be incorrect. However, a re-check of the calibration did not show any problems with the data. Also, the results for the BAMO/AMMO/ TiO_2 mixtures, which were wholly independent tests, show similar trends. Thus, the result appears to be repeatable and not related to calibration. Another possible source of the difference in the quality of the element balances at the two heat fluxes are species that could not be quantified. The sum of the signal intensity of each species quantified in Figs. 2 and 3 represents only 80% of the total signal from the parent mode experiments, leaving 20% of the total signal unquantified. Also, in all tests, a white aerosol was observed which could not be quantified and included in the element balances.

Table 2 presents a comparison of surface species mole fractions for all the fuels tested, along with results for BAMO from a previous study, at 400 W/ cm^2 [1]. The results are tabulated only for the higher heat flux because the element balances were much better at this test condition. The results indicate that the H_2CO at the surface increased from 0.15 for BAMO to ∼0.25 for BAMO/AMMO and that the HCN decreased from 0.22 to 0.19. These trends are consistent with the results of a previous study of BAMO and AMMO polymers, in which products were determined at a heating rate of 150 °C/s and 0.10 MPa [4]. For AMMO the major species detected by FTIR were H_2CO, HCN, NH_3 and CO, while for BAMO the major species were HCN, CO, H_2CO and NH_3 (in descending order of mole fraction). These results suggest that a copolymer of BAMO and AMMO would have higher H_2CO and lower HCN than neat BAMO, just as was observed in the present study.

Typical gas-phase temperature profiles at 100 and 400 W/cm^2 for BAMO/AMMO are shown in Figs. 4 and 5 for a distance of 2 mm above the sample surface. Both profiles show large fluctuations about a relatively constant temperature, with the average temperature being slightly higher at the higher heat flux. The constant mean gas-phase temperatures are consistent with the species measurements in which no reaction appears to occur in the gas-phase. The high frequency fluctuations in the temperature appear to be the result of oscillation of the thermocouple induced by the high velocity gas-flow from the surface, nearly all of the video recordings show the fine-wire thermocouple vibrating significantly. There may also be some inherent unsteadiness in the decomposition process at these test conditions.

Separate tests were performed with the thermocouple held on the sample surface to determine the surface temperatures. They were measured to be 950 ± 50 and 1050 ± 50 K at 100 and 400 W/cm^2, respectively. The
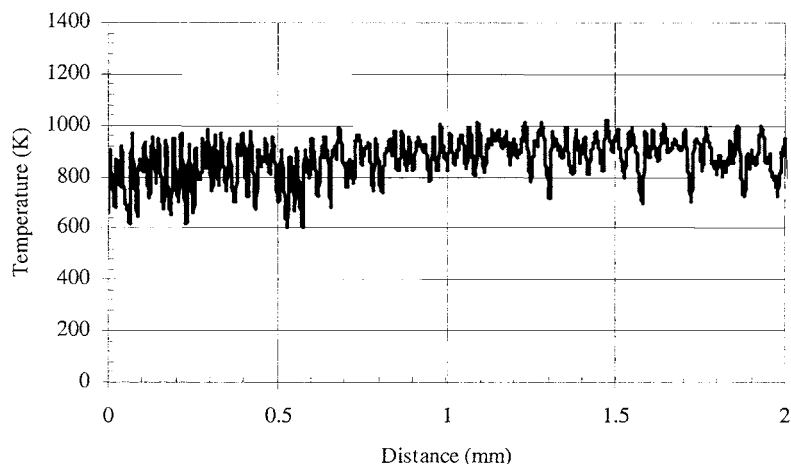
Fig. 4. Temperature profiles for BAMO/AMMO at 100 W/cm^2.

higher surface temperature at the higher heat flux is consistent with the higher burning rate observed there as well. Previous work with BAMO at 100 W/cm^2 showed its surface temperature was approximately 1000 ± 50 K, somewhat higher than the copolymer. A lower surface temperature for the BAMO/AMMO is consistent with the less energetic nature of the copolymer compared to neat BAMO. Other researchers reported that AMMO did not affect the thermal decomposition of BAMO [7]. However, the result may be related to the lower heating rate (80 K/min)

used in that study. Heating rate has been shown to affect product composition in the study of other energetic materials [16].

3.4. Species and temperature measurements: BAMO/AMMO/TiO$_2$

Results of gas-phase species measurements for B/A/T1 and B/A/T5 at 100 and 400 W/cm^2 are shown in Figs. 6–9. All four sets of data show the same relatively constant gas-phase profiles observed for the
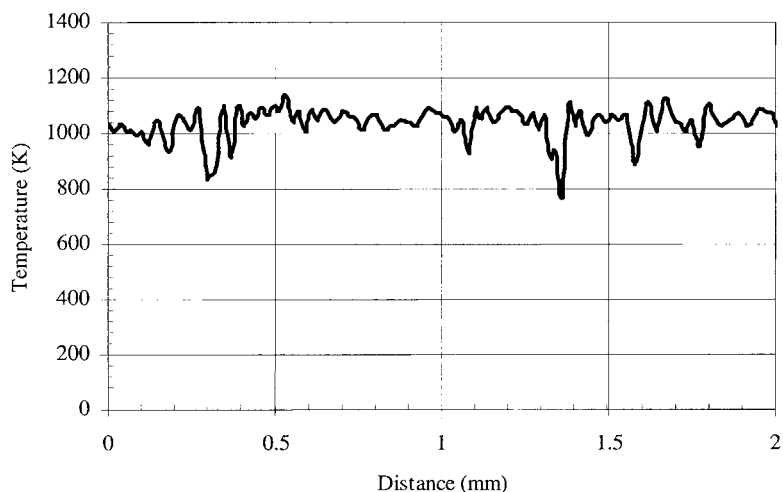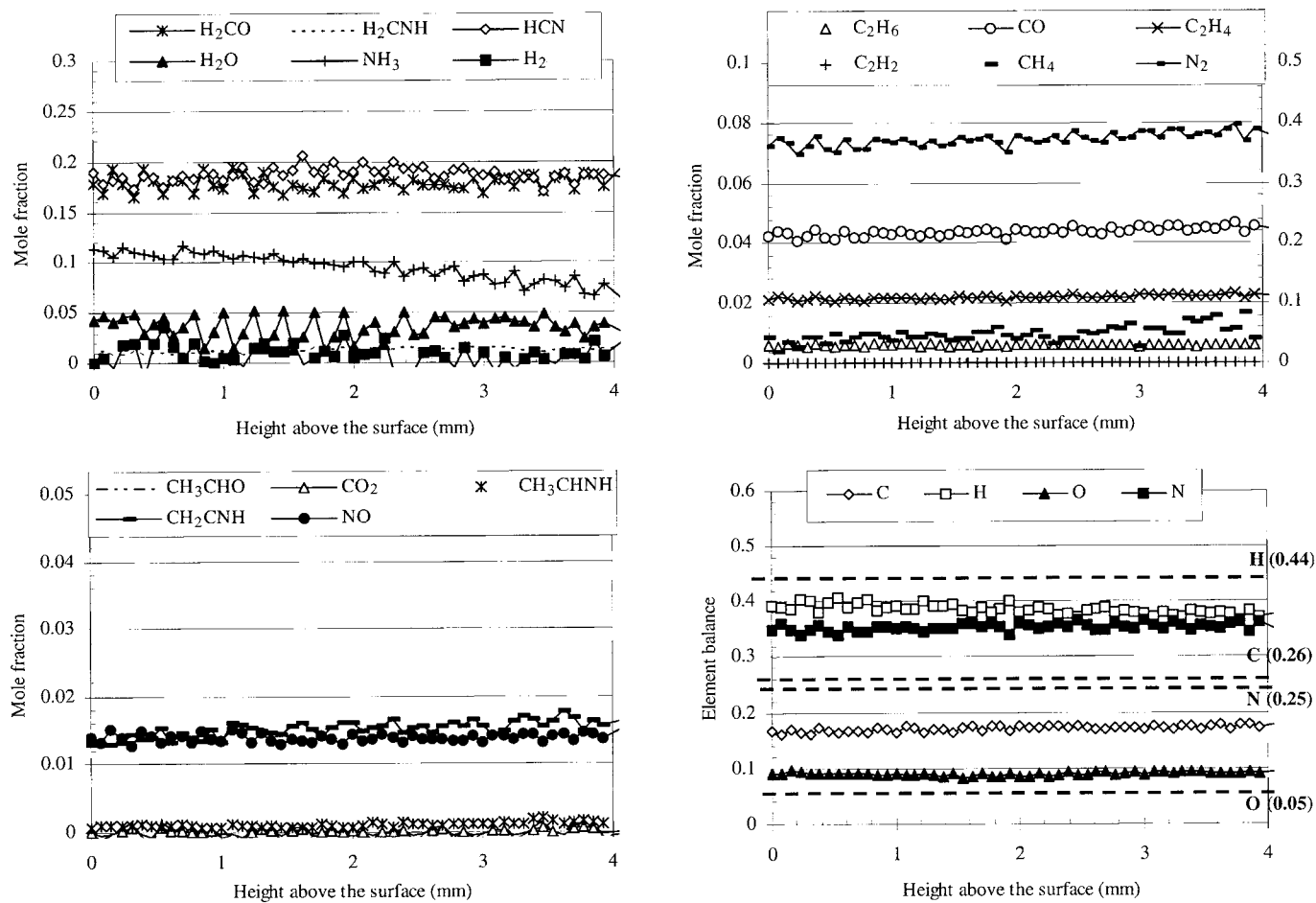

Fig. 5. Temperature profiles for BAMO/AMMO at 400 W/cm^2.

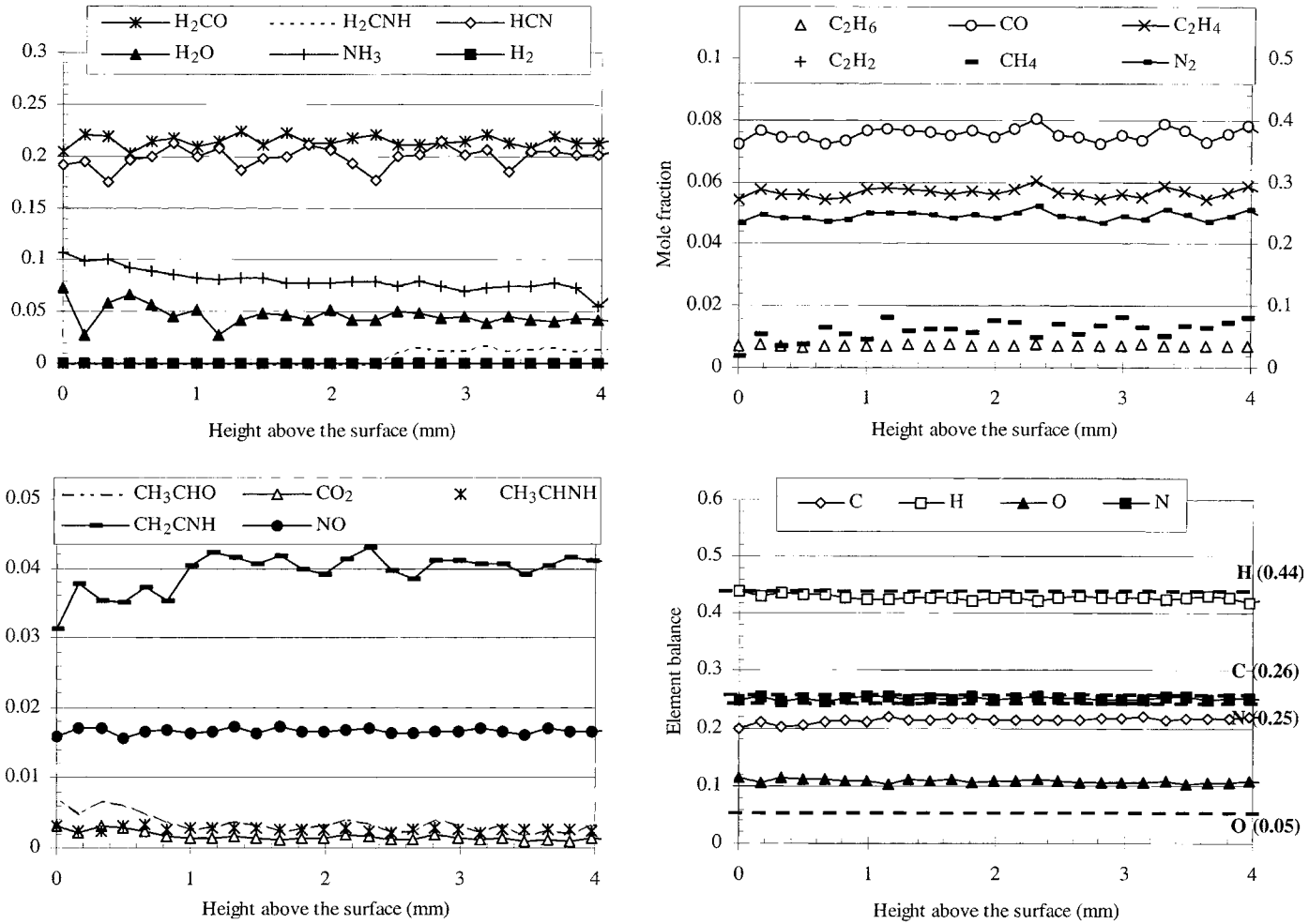Fig. 6. Species profiles and element balance for B/A/T1 at 100 W/cm^2.

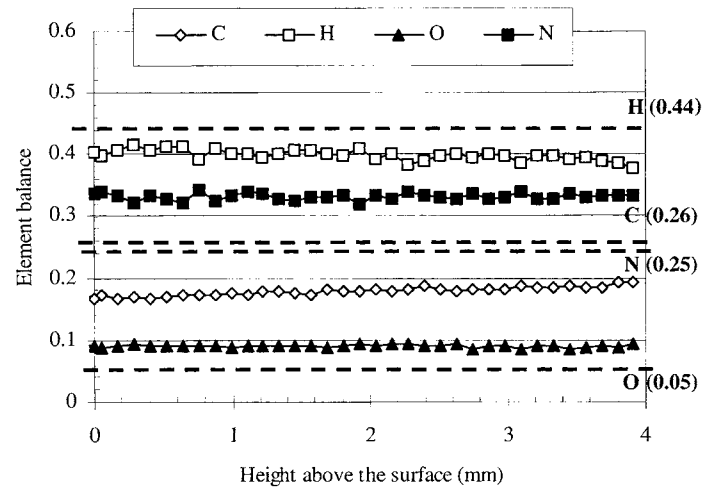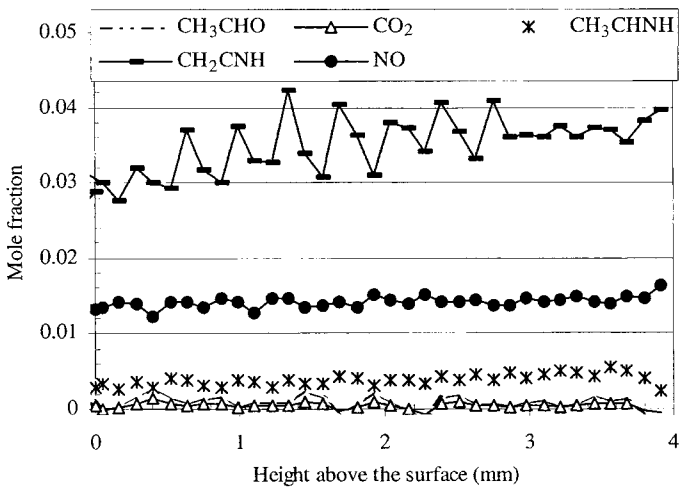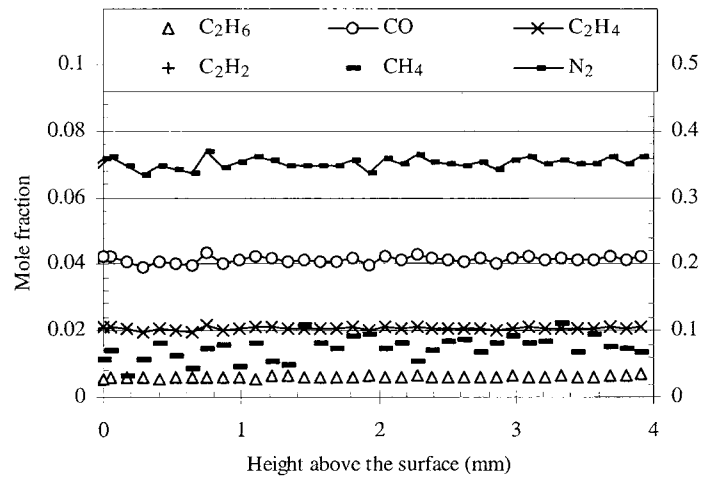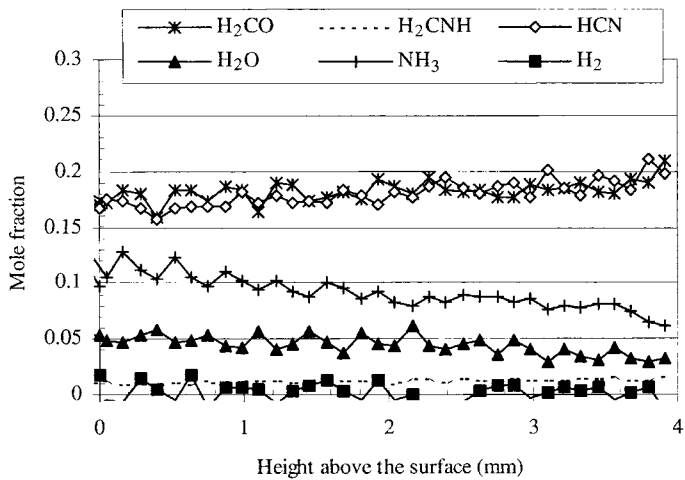Fig. 7. Species profiles and element balance for B/A/T1 at 400 W/cm^2.

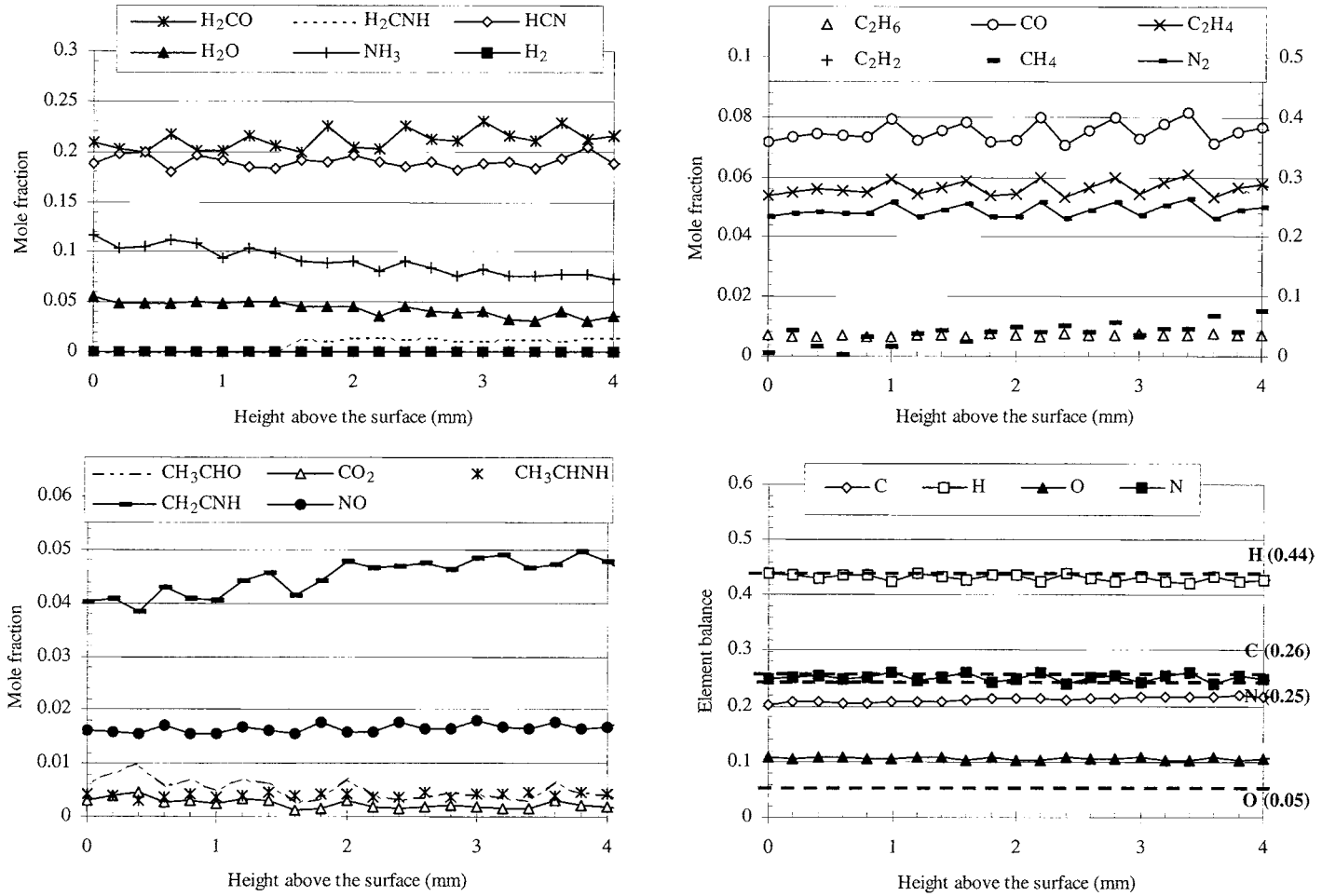Fig. 8. Species profiles and element balance for B/A/T5 at 100 W/cm^2.

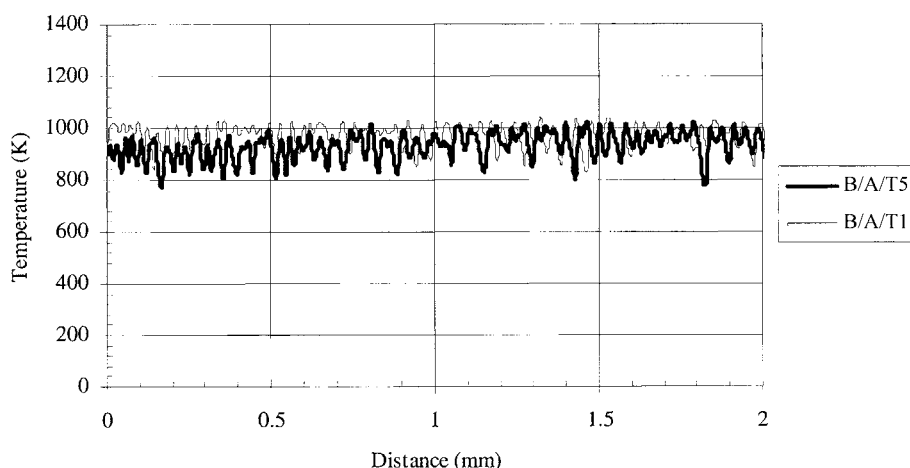Fig. 9. Species profiles and element balance for B/A/T5 at 400 W/cm^2.

Fig. 10. Temperature profiles for B/A/T1 and B/A/T5 at 100 W/cm^2.

neat copolymer, indicating the absence of any significant gas-phase reactions. Comparison of these results for TiO$_2$ with those for the neat copolymer shows that the addition of TiO$_2$ did not lead to any new species. Estimated uncertainties in the mole fractions are ±20%. Only the change in the NH$_3$ mole fraction exceeds this level; it increased to ∼0.12 from 0.08 for the neat copolymer. Further, the species mole fractions at the sample surface, presented in Table 2, are essentially the same regardless of the amount of TiO$_2$ added, indicating that increasing the amount of TiO$_2$ does not result in any substantial changes in the decomposition species.

Typical gas-phase temperature profiles for B/A/T1 and B/A/T5 at 100 and 400 W/cm^2 are shown in Figs. 10 and 11. Consistent with the species profiles, the temperature profiles are relatively constant. Separate measurements to determine the surface temperatures indicate, however, that they are affected by the addition of TiO$_2$. At 100 W/cm^2, the surface temperature for the B/A/T1 and B/A/T5 is 900 ± 50 K, while at 400 W/cm^2, the surface temperatures are 1000 ± 50 and 950 ± 50 K for B/A/T1 and B/A/T5, respectively. Thus, the data indicate that the addition of TiO$_2$ tends to decrease the surface temperatures relative to the neat copolymer.
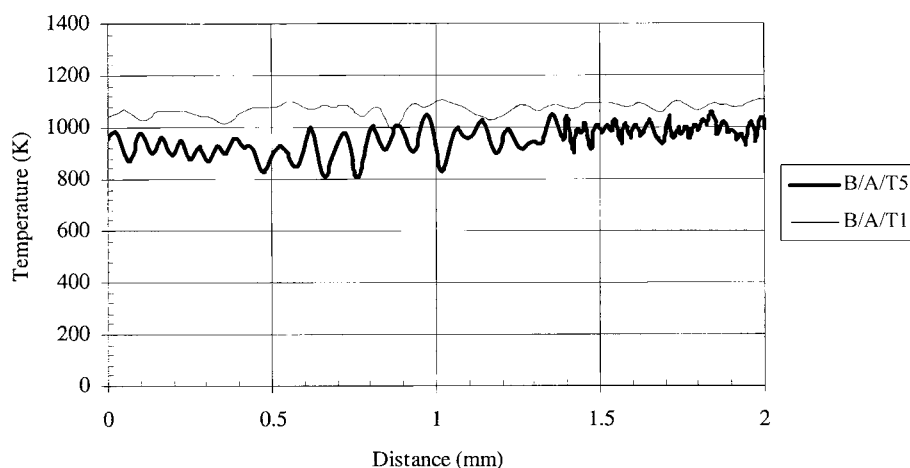

Fig. 11. Temperature profiles for B/A/T1 and B/A/T5 at 400 W/cm^2.

4. Discussion

4.1. Chemical pathways

In their study of GAP, Arisawa and Brill [17] discussed the various chemical pathways that are involved in its decomposition during flash pyrolysis; the pathways for BAMO/AMMO decomposition in the present study would appear to be quite similar. The initial decomposition reaction is the elimination of nitrogen from the azide group to form a nitrene. The nitrene can then undergo competing reactions to form HCN or NH_3. Arisawa and Brill noted that NH_3 is expected to form more slowly than HCN, since multiple steps are required to form NH_3. In the present study, the HCN mole fraction is more than twice that of NH_3 for neat BAMO/AMMO, at a heat flux of 400 W/cm^2, consistent with the fact that HCN can form more easily than NH_3. Addition of TiO_2 to the copolymer resulted in a significant increase in the amount of NH_3 indicating that the TiO_2 is promoting the reactions that form NH_3 (a corresponding decrease in the amount of HCN is not observed, which may be due to the experimental uncertainty in the HCN measurements or changes in nitrogen containing species that could not be quantified in the present study). The other major nitrogen containing species found in this study is at mass 41, with the atomic composition of C_2H_3N. This product apparently forms from the decomposition of the backbone with the nitrene group attached as only the decomposition of the backbone can yield a species with a C–C–N structure.

The major oxygen containing products are CO and H_2CO. These products are expected because breaking of one of the C–O bonds in the backbone will result in the formation of a C=O bond, which is very strong. The hydrocarbon formed at the largest mole fraction in this case is C_2H_4, which is expected to form during the breakdown of the backbone. CH_4 is also observed at approximately 0.01 mole fraction. It likely forms from the CH_3 group that is part of AMMO.

In all tests, an aerosol was formed that was white to yellow-white in color. No aerosol was visible above the burning surface, so it is believed that the aerosol results from the condensation of higher molecular weight products that are not detected in the mass spectrometer.

Arisawa and Brill also noted the presence of GAP oligomers in the gas-phase during their GAP studies [17].

4.2. Possible mechanism for TiO_2 effects

The experimental observations of the effects of TiO_2 addition to the neat BAMO/AMMO with an incident laser flux can be summarized as follows:

1. No new reaction products are observed.
2. Changes in surface mole fractions of the decomposition products are within experimental uncertainty, except for that of NH_3 and they are not affected by increasing the amount of TiO_2 from 1 to 5%.
3. Surface temperatures are slightly decreased, relative to the neat BAMO/AMMO; within experimental uncertainty, this decrease is the same for 1 and 5% TiO_2.
4. Regression rate is slightly reduced at 100 W/cm^2 and substantially reduced at 400 W/cm^2.
5. The reduction in regression rate is independent of the amount of TiO_2 for 1 and 5% TiO_2 by mass.

The addition of TiO_2 does appear to enhance the reactions which lead to the production of NH_3, but this is the only direct evidence of a chemical effect of the TiO_2. The fact that the increase of NH_3 is nearly independent of the amount of TiO_2 added is consistent with the TiO_2 acting as a catalyst for these reactions. Surface temperatures are reduced slightly with the addition of TiO_2, consistent with results of other researchers who report that the addition of TiO_2 is not expected to strongly affect surface temperature [18]. The addition of TiO_2 does have a substantial effect on the burning rate, but only at the higher heat flux. The absence of any significant changes in the decomposition products or their mole fractions would seem to indicate that the effect leading to the reduction of the regression rate is not chemical in nature. Thus, the explanation seems to lie with physical effects of the addition of TiO_2 that can reduce the regression rate.

The TiO_2 could simply act as an inert species consuming energy and lowering the surface temperature or it could affect the thermal conductivity of the sample in such a way that the surface temperature is lowered.

These effects should become more significant as the amount of TiO_2 is increased. However, the present results indicate that the effect on regression rate is independent of the amount of TiO_2, which appears to eliminate these two effects as the cause of the reduced regression rate. The final possibility is that the effect on regression rate is an artifact of the nature of the experiments arising from the fact that the addition of the TiO_2 increases the reflectivity of the surface.

Increasing the reflectivity would lower the amount of laser energy absorbed by the sample and lower the regression rate and probably the surface temperature as well. The overall regression rate will be driven by the energy release from the copolymer decomposition plus the energy absorbed from the laser flux. If increased reflectivity is the reason for the decreased regression rate observed, the effect should be more substantial when the amount of incident laser flux is increased, which is precisely what is observed in the measurements. Further, the addition of greater amounts of TiO_2 may not affect surface reflectivity judging from the "whiteness" of the samples which is the same for 1 and 5% TiO_2. This line of reasoning leads to the conclusion that the effect of TiO_2 in the present study is primarily physical and related to the use of a laser heat source.

5. Conclusions

Comparison of the results of the present study of the decomposition of BAMO/AMMO to those of an earlier study of BAMO indicate that the AMMO reduces regression rates and surface temperatures and modifies the mole fractions of some of the major decomposition products. The results for BAMO/AMMO with TiO_2 show that the decomposition products and their mole fractions are largely unchanged by the TiO_2. Only the mole fraction of NH_3 was changed by an amount larger than the experimental uncertainty. Thus, direct chemical effects of TiO_2 are small in the present study. The most substantial effect of the addition of TiO_2 is on the regression rate at the higher heat flux of 400 W/ cm^2, which is consistent with an effect of TiO_2 on the reflectivity of the sample surface. Such an effect may occur for actual propellants at rocket motor pressures where radiative feedback from the flame to the propellant would be reduced. However, the importance of the effect in actual motors cannot be assessed based upon the present results.

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