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Disclaimer

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ABSTRACT

A combination of thermogravimetric analysis (TGA) and temperature programmed decomposition (TPD) was employed to identify the outgassing species, the total amount of outgassing, and the outgassing kinetics of high density polyethylene (HDPE) in a vacuum environment. The isoconversional kinetic analysis was then used to analyze the outgassing kinetics and to predict the long-term outgassing of HDPE in vacuum applications at ambient temperature. H_2O and C_nH_x with n as high as 9 and x centering around 2n are the major outgassing species from solid HDPE, but the quantities evolved can be significantly reduced by vacuum baking at 368 K for a few hours prior to device assembly.

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INTRODUCTION

HDPE, $[-CH_2-CH_2-]_n$, is resistant to many solvents, has a higher tensile strength than many polymers, and can withstand operating temperatures as high as 100 ^{0}C without damage. HDPE finds use in a variety of applications, including containers, furniture, pipes, insulation for heavy-duty electrical power cables, and vacuum devices. Outgassing from HDPE in vacuum devices may lead to compatibility issues and even undesirable effects on electronic components.[1-2] In this article, the investigation on the outgassing species, the total amount of outgassing, and the outgassing kinetics of HDPE in a vacuum environment at moderately elevated temperatures are reported. The long-term vacuum outgassing of HDPE at room temperature is, then, predicted based on the measured outgassing kinetics and the isoconversional thermal analysis method.[3-6] Effective techniques to mitigate the outgassing will also be presented.

EXPERIMENTS

The HDPE used in this investigation was manufactured by Simona America Inc. For a typical TPD experiment, a thin slice of sub-millimeter thick HDPE was enclosed in a 1cm^2 platinum foil envelope to assure uniform heating. The side of the envelope facing the mass spectrometer was thoroughly perforated. The loaded foil was then attached to a sample holder by way of mechanical clamps and transferred into an ultrahigh vacuum (UHV) sample chamber with a base pressure of 10^{-6} Pa through a differentially pumped load lock. In the sample chamber, the sample holder sat on a rotatable XYZ manipulator. The sample temperature was measured using a type K thermocouple inserted between the Pt envelope front surface and one of the clamps holding the envelope. Heating of the sample was done by passing a current through a flat

spiral tungsten coil located 2 mm behind the sample. The sample chamber was connected through a 6 mm diameter orifice with a separately pumped detector chamber equipped with a quadrupole mass spectrometer. The base pressure in the detector chamber was usually a decade better than that in the sample chamber. During the TPD experiment, the sample was positioned 2 mm away from the orifice, facing the detector chamber. This arrangement guaranteed that only gases originating from the portion of the sample facing the 6 mm orifice contributed to the signals detected by the quadrupole mass spectrometer. To compliment the TPD experiments, a Cahn Versatherm vacuum microbalance with a base pressure in the range of 100 mPa - 200 mPa was employed to obtain the weight loss of HDPE samples as a function of heating time and temperature.

RESULTS & DISCUSSION

Mass spectra obtained from an empty platinum foil envelope and one containing a 0.7 mm thick HDPE sample, shortly after they reached a temperature of 340 K, are presented in Fig. 1(a) and (b), respectively. The signal intensities in these plots are not corrected for instrument response due to the lack of proper calibration gases. From Fig. 1(a), H_2, H_2O, N_2, O_2, and CO_2 were the main background gases. The peak at ~73 atomic mass units (amu) was due to an organic contaminant left in the mass spectrometer from previous experiments with silicones. The fact that this 73 amu peak is seen in both the background spectrum and the HDPE spectrum with similar intensities confirms that it did not originate from the HDPE sample. C_nH_x species with n as large as 9 and x centering around 2n were clearly associated with the outgassing of the HDPE sample [Fig. 1(b)]. The mass spectrometer signal strengths of the C_nH_x species strongly decreased with increasing n. C_nH_x species with low values of n have been reported to originate

from weak link sites inherent to the polymer (due to oxidation during the polymerization process).[7-11] The H_2 and O_2 signal intensities in the mass spectrum of the HDPE sample [Fig. 1(b)] are about the same as those of the background [Fig. 1(a)], suggesting that the HDPE sample did not outgas H_2 or O_2 after 30 minutes in UHV prior to the start of the heating and mass spectrum acquisition. Similar to the case of hydrogen and oxygen, N_2 and CO_2, being nonpolar gases, are expected to be easily removed from the HDPE after 30 minutes of vacuum pump. In Fig. 1(b), a hydrocarbon peak is seen to coincide with the N_2 background peak. This makes this peak appear to double its intensity in comparison with the N_2 signal in the background spectrum [Fig. 1(a)]. The H_2O signal intensity from the HDPE sample is much stronger than that in the background spectrum, indicating that the polar H_2O molecules, hydrogen-bonded to each other and/or to oxygen-containing defects in HDPE [e.g. $-CH_2-CO-CH_2-$, $-CH_2-COH-CH_2-$, or $-CH_2-O-CH_2-$], were not as readily pumped out of the HDPE network as nonpolar gases.[12,13] The hydrocarbon peaks identified in Fig. 1(b) are consistent with the desorption of various alkanes and alkenes as reported in the decomposition of polyethylene at higher temperatures.[14-16] Unfortunately, the large number of overlapping peaks in the mass spectrum of these compounds makes it extremely difficult to quantitatively identify the C_nH_x species without proper calibration gases.

In Fig. 2 (a) and (b), the TPD spectra, at a heating rate of 0.03 K/s, of H_2O and C_2H_x where n = 4, 6, 7 and x = 2n are plotted as a function of temperature. At a heating rate of 0.3 K/s, the thermal desorption of the hydrogen-bonded H_2O molecules from HDPE appeared to be completed at 370 K while C_nH_x species still strongly desorbed. So, the outgassing of C_nH_x species from the HDPE structure has a much higher activation energy barrier than that corresponding to the thermal desorption of hydrogen-bonded H_2O molecules. The

experimentally measured thermal desorption activation energy for hydrogen-bonded water from polymeric materials is on the order of 36.4 kJ/mol with a first-order pre-exponential factor of 1.3×10^3 s^{-1}.[17, 18] This translates to a complete vacuum desorption of hydrogen-bonded water molecules from within solid polymers in less than a day even at room temperature.[17, 18]

From the TPD spectra in Fig. 2(b), the hydrocarbon signals are seen to have the same temperature dependence, reaching a maximum at ~ 370 K, then declining, but not disappearing. A possible cause for the similarity in the TPD spectra of the different C_nH_x species may be the desorption of only one or two large species (e.g. 1-octene, C_8H_{16}, and 1-nonene, C_9H_{18}) from HDPE with increasing temperature.[19] The series of hydrocarbon signals observed in Figs. 1 and 2 would then be a result of the cracking of 1-octene and 1-nonene in the ionizer of the quadrupole mass spectrometer. But it might also be that the structural changes in the HDPE near its melting point promote the release of multiple C_nH_x species with $n < 9$ from weak link sites.[7-11, 15]

From Fig. 2(b), the evolution of C_nH_x species with increasing temperature seems to be in unison with one another, albeit with different intensities. So the outgassing kinetics for the C_nH_x species can be approximated by analyzing just the strong C_4H_8 signal [see Fig.1(b) and Fig. 2(b)]. Note that since the focus of this work was on the outgassing of solid HDPE in vacuum applications at or a little above ambient temperature, behavior above the melting point (~ 405 K) was not considered. The rate equation for a solid-state reaction can be approximated by:[3]

$$\frac{d\alpha}{dt} = k.f(\alpha) = \upsilon.e^{-\frac{E}{RT}}.f(\alpha) \qquad (1)$$

where t is time; α is the reacted, desorption, outgassing, or decomposition fraction (0 to 1); k is the rate constant; υ is the pre-exponential factor which includes many constants describing the initial state of the sample such as three dimensional shape factors of initial particles, molecular mass, density, stoichiometry, active surface factors, number of lattice imperfections, and so

forth; E is the activation energy for the rate controlling process; R is the gas molar constant, T is temperature in Kelvin; and $f(\alpha)$ is an analytical function determined by the rate-limiting reaction mechanism.

With a heating rate of $\beta = dT / dt$:

$$\frac{d\alpha}{dT} = \left[\frac{\upsilon}{\beta} \cdot f(\alpha)\right] \cdot e^{-\frac{E}{RT}} \tag{2}$$

At maximum conversion rate or peak position T_p:

$$\frac{d}{dT}\left(\frac{d\alpha}{dT}\right)_{T_p} = 0 \tag{3}$$

Sorting through the algebra:

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{RT_p} + \ln\left[\left(\frac{R\upsilon}{E}\right)\left(-\frac{d}{d\alpha}\{f(\alpha)\}\right)_{\alpha_{\max}}\right] \tag{4}$$

The term $\left(-\frac{d}{d\alpha}\{f(\alpha)\}\right)_{\alpha_{\max}}$ implies the derivative of $f(\alpha)$ with respect to α and evaluated at α_{max}, which is the fractional extent of conversion value corresponding to the maximum rate temperature T_p. Equation (4) is known as the generalized Kissinger equation.[20-22] A plot of $\ln\left(\frac{\beta}{T_p^2}\right)$ vs. T_p^{-1} yields the activation energy barrier E. From equation (4) and the TPD spectra of C_4H_8 (56 amu) at three different heating rates [Fig. 3(a)], an activation energy barrier of ~ 142.5 kJ/mol is obtained and presented in Fig. 3(b). However, unless one already knows what is the rate limiting step or equivalently which form of $f(\alpha)$ to use in equation (4), kinetic prediction will be cumbersome.

In contrast to the generalized Kissinger analysis, which only deals with the peak of $d\alpha/dT$, the Friedman isoconversional analysis evaluates the whole $d\alpha/dT$ vs. T curve.[3] Upon

taking the natural logarithm on both sides of equation (1), the Friedman isoconversional analysis yields:

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + \ln\{\upsilon f(\alpha)\} \tag{5}$$

A plot of $ln(\mathrm{d}\alpha/dt)$ vs. T^{-1} at some α value for a set of β values has the slope $-E/R$.[3] A plot of E vs. α is thus obtained by repeating the above procedure at other chosen α values between 0 and 1. In Fig. 4, a plot of the variation of E with respect to α for the outgassing of C_nH_x from HDPE is presented. The isoconversional analysis shows that the activation energy barrier for the outgassing from HDPE varies somewhat from 150 kJ/mol down to 115 kJ/mol over the course of the outgassing process, in general agreement with the value obtained from the Kissinger analysis.

Note that both E and $\{vf(\alpha)\}$ can be obtained from the Friedman method based on the slopes and the intercepts of equation (5) at each value of α. The time prediction t_α for a specific conversion α to be reached at the isothermal temperature T_o can be obtained, without any knowledge of the exact form of $f(\alpha)$, from the rate equation (1) as following:

$$t_\alpha = \int_0^{t_\alpha} dt = \int_0^{\alpha} \frac{d\alpha}{\{vf(\alpha)\}e^{-\frac{E}{RT_o}}} \tag{6}$$

The isoconversional kinetic predictions for the outgassing of C_nH_x species from HDPE, based on equation (6), at 323 K and at 333 K are shown in Fig. 5. Vacuum baking at 323 K and 333 K for 48 hours should remove fractions of 0.47 and of 0.76 of the total outgassing potential, respectively.

In order to make a correlation between the outgassed C_nH_x species and the percentage of HDPE weight loss due to this outgassing, a vacuum microbalance was employed to obtain the weight loss as a function of heating time at 323 K and 333 K (Fig. 6). In order to completely

remove all trapped gases like H_2, N_2, O_2, CO_2, and H_2O, HDPE samples for the isothermal vacuum weight loss experiments were pumped for 24 hours at room temperature prior to the start of the measurements. The temperature spike at around 31 hours into the isothermal weight loss experiment at 323 K was due to a glitch in the feedback loop for the computer controlled heating program. The relatively sharp weight drop in Fig. 6(a) at 31 hours is a result of this temperature spike. The correlation between the outgassed C_nH_x species and the percentage of HDPE weight loss due to this outgassing was accomplished by determining the multiplicative factor that would allow good overlaps of the α vs. t curves from the isoconversional kinetic predictions (Fig. 5) and the *weight loss percentage* vs. t curves from the vacuum microbalance experiments (fig. 6). The fits are presented in Fig. 7. The correlation obtained from this matching is:

Percentage wt. loss = $\alpha/(4.8 \pm 0.6)$.

Now that a correlation has been made between α and the percentage of weight loss from HDPE due to vacuum heating, predictions for the outgassing kinetics of HDPE in terms of weight loss can be made. Weight loss predictions for HDPE at 298 K and 368 K after 24 hours of vacuum pumping at room temperature (to remove all trapped gases like H_2, N_2, O_2, CO_2, and H_2O) are presented in Fig. 8. It is seen that vacuum baking HDPE at 368 K for 16 hours would remove most of the potential outgassing that would otherwise slowly evolve over many years at 298 K in vacuum applications. Even mild vacuum baking at 343 K for 16 hours was reported to be enough to cut down the total outgassing and outgassing rate significantly.[2] The maximum outgassing weight loss from solid HDPE due to the release of C_nH_x species is ~ 0.21 ± 0.02 wt% (corresponding to $\alpha = 1$) over 12 years at room temperature.

CONCLUSION

A combination of vacuum microbalance and mass spectrometry based techniques has been employed to identify the outgassing species as well as the total amount of outgassing from HDPE under vacuum. After 30 minutes of vacuum pumping, the HDPE samples under investigation were free of inert nonpolar gases like H_2, N_2, O_2, and CO_2, which were present in the storage atmosphere. Even H_2O molecules hydrogen-bonded to each other and/or to oxygen-containing defects in HDPE could be removed from HDPE in less than a day of vacuum pump at room temperature. Thereafter, the majority of the outgassing species were C_nH_x with n = 2 to 9. The total hydrocarbon outgassing at room temperature was ~ 0.21 ± 0.02 wt.% of HDPE, and had an activation energy barrier of about 150 kJ/mol near the beginning of the outgassing process but reduced to 115 kJ/mol near the process completion. Isoconversional kinetic predictions suggest that much of the outgassing takes place slowly over many years at room temperature. However, if HDPE parts are vacuum baked at 368K for 16 hours, most of the potential outgassing can be eliminated.

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FIGURE CAPTIONS

Fig. 1: The mass spectra obtained by heating a platinum foil envelope (a) and a 0.7 mm thick HDPE sample inside a platinum foil (b) at 340 K.

Fig. 2: The evolution of H_2O (a) and C_nH_x where n = 4, 6, and 7 (b) as a function of temperature at a heating rate of 0.03 K/s.

Fig. 3: TPD spectra of C_4H_8 at three different heating rates (a) and the activation energy barrier determination for the release of C_nH_x according to the generalized Kissinger equation (b).

Fig. 4: The variation of E with respect to α for the outgassing of C_nH_x from HDPE.

Fig. 5: The isoconversional kinetic prediction for the outgassing of C_nH_x species from HDPE, based on equation (6), at 323 K and at 333 K.

Fig. 6: The weight loss of HDPE due to the outgassing of C_nH_x species as measured by a vacuum microbalance at 323 K (a) and 333 K (b). The HDPE samples had been vacuum pumped for 24 hours at room temperature to remove all trapped gases like H_2, N_2, O_2, CO_2, and H_2O.

Fig. 7: Matching the α vs. t curves from the isoconversional kinetic predictions and the *weight loss percentage* vs. t curves from the vacuum microbalance experiments at 323 K (a) and 333 K (b). The correlation obtained from this matching is: Percentage wt. loss = $\alpha/(4.8 \pm 0.6)$

Fig. 8: Predictions for the outgassing kinetics of HDPE in term of weight loss at 298 K (a) and 368 K (b) after 24 hours of vacuum pump to remove all trapped gases like H_2, N_2, O_2, CO_2, and H_2O. The weight loss presented here is completely due to the outgassing of hydrocarbons.

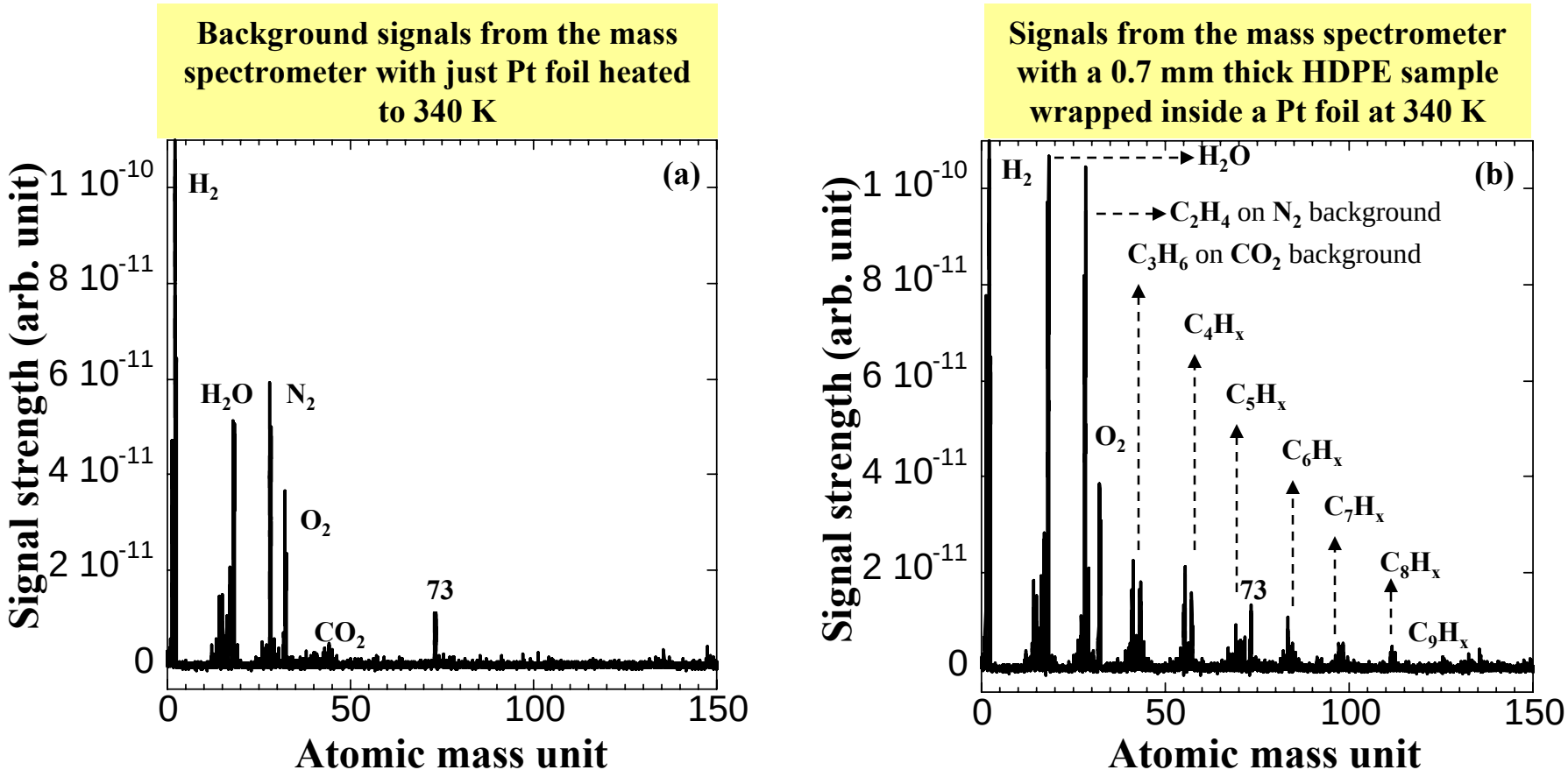

Background signals from the mass spectrometer with just Pt foil heated to 340 K
Signals from the mass spectrometer with a 0.7 mm thick HDPE sample wrapped inside a Pt foil at 340 K
Signal strength (arb. unit)
Atomic mass unit
(a)
(b)
H2
H2O
N2
O2
CO2
73
C2H4 on N2 background
C3H6 on CO2 background
C4Hx
C5Hx
C6Hx
C7Hx
C8Hx
C9Hx
1 10-10
8 10-11
6 10-11
4 10-11
2 10-11
0
0
50
100
150

Fig. 1

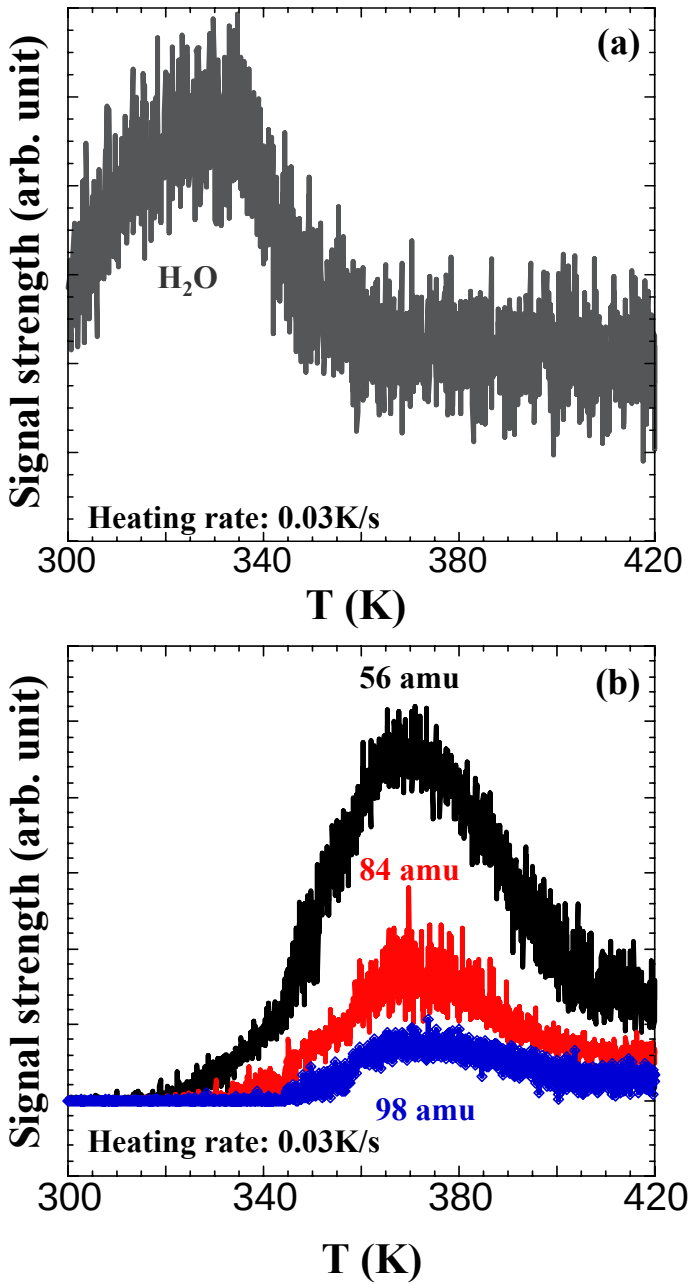
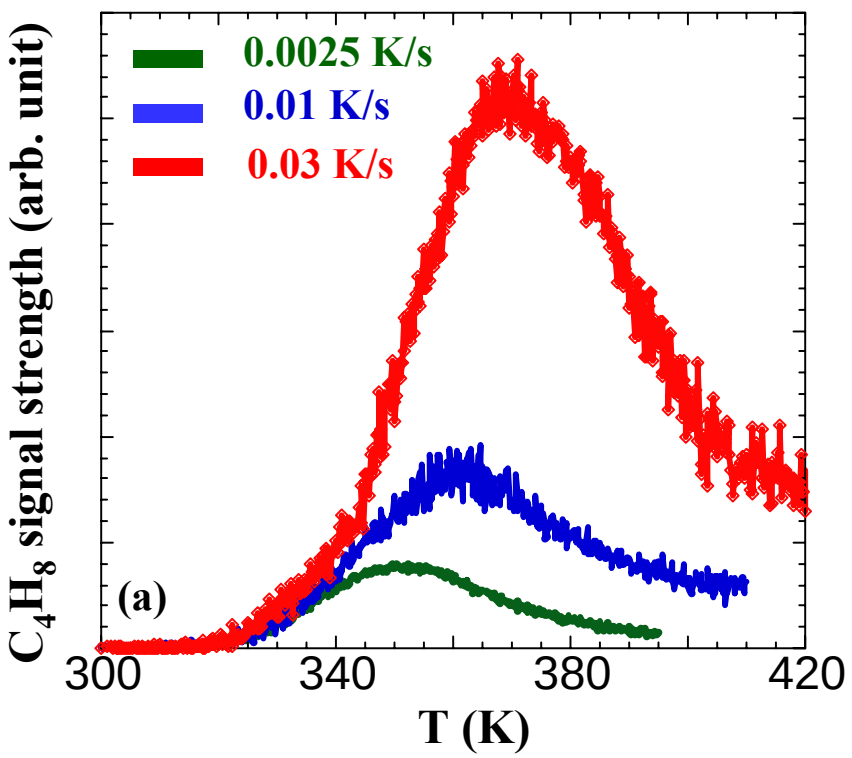

(a)
Signal strength (arb. unit)
H2O
Heating rate: 0.03K/s
300
340
380
420
T (K)
(b)
56 amu
84 amu
98 amu
Signal strength (arb. unit)
Heating rate: 0.03K/s
300
340
380
420
T (K)

Fig. 2


0.0025 K/s
0.01 K/s
0.03 K/s
(a)
C4H8 signal strength (arb. unit)
300
340
380
420
T (K)

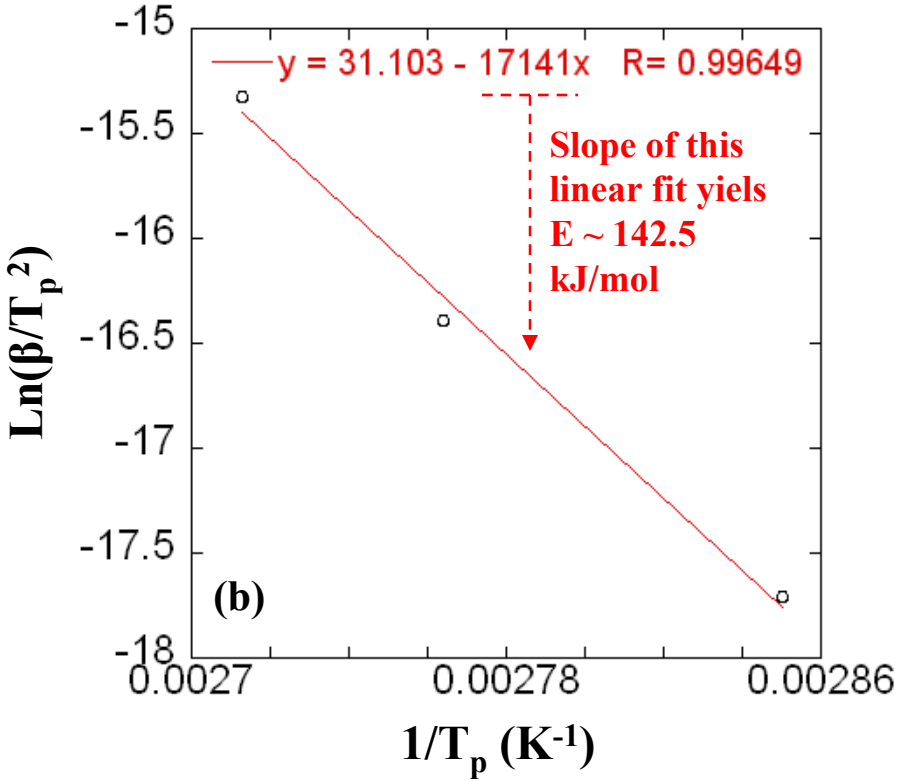

y = 31.103 - 17141x R= 0.99649
Slope of this linear fit yiels E ~ 142.5 kJ/mol
(b)
Ln(β/Tp2)
-15
-15.5
-16
-16.5
-17
-17.5
-18
0.0027
0.00278
0.00286
1/Tp (K-1)

Fig. 3

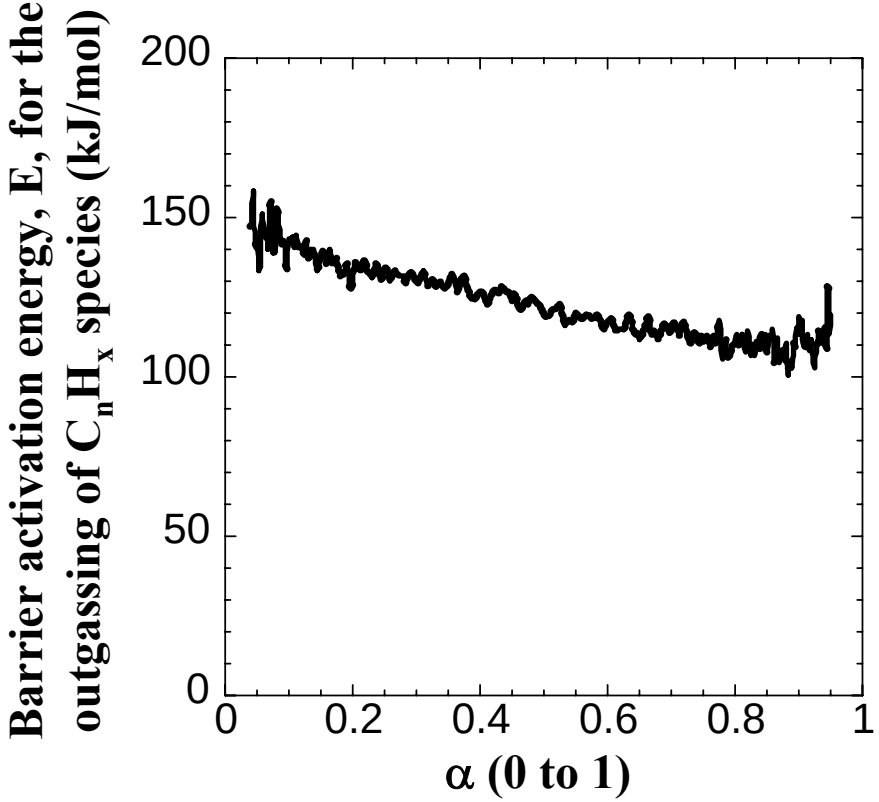

Barrier activation energy, E, for the outgassing of C_nH_x species (kJ/mol)
200
150
100
50
0
0
0.2
0.4
0.6
0.8
1
α (0 to 1)

Fig. 4

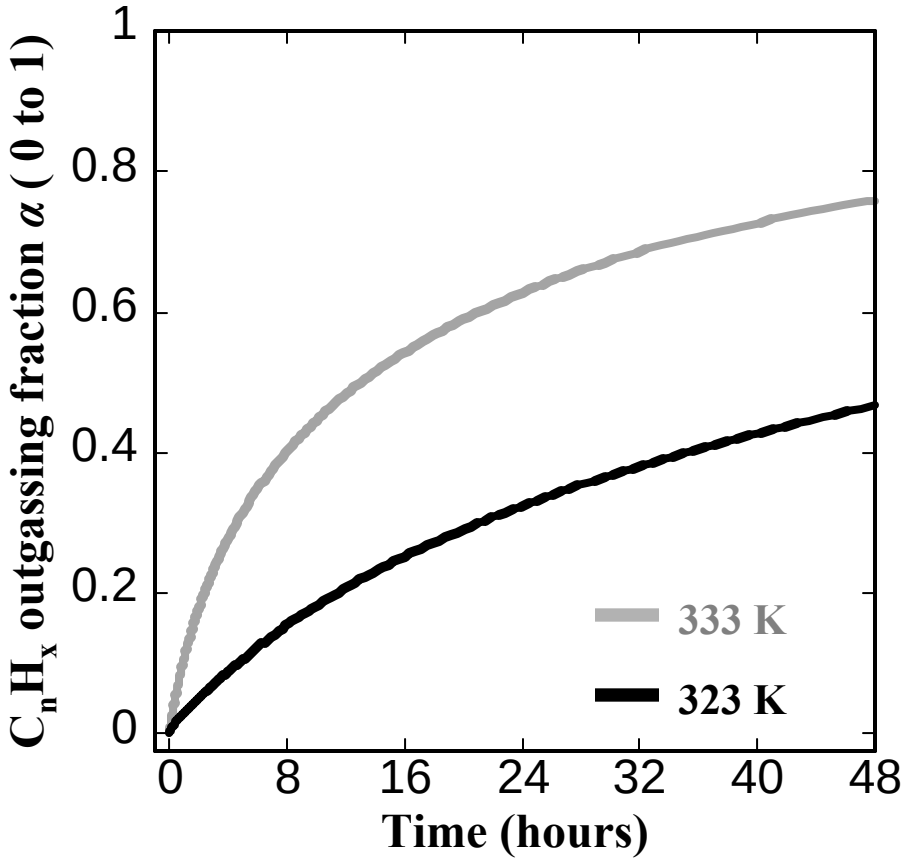

C_nH_x outgassing fraction α (0 to 1)
1
0.8
0.6
0.4
0.2
0
0
8
16
24
32
40
48
Time (hours)
333 K
323 K

Fig. 5

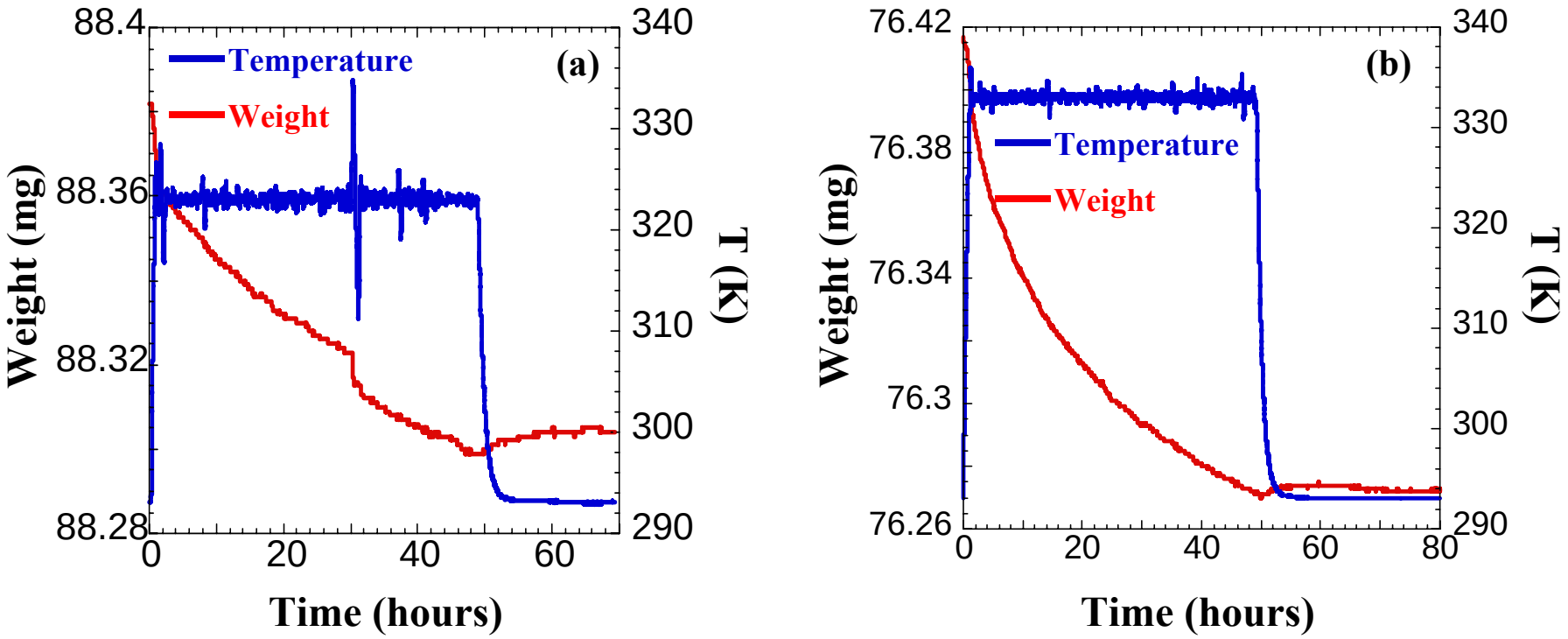
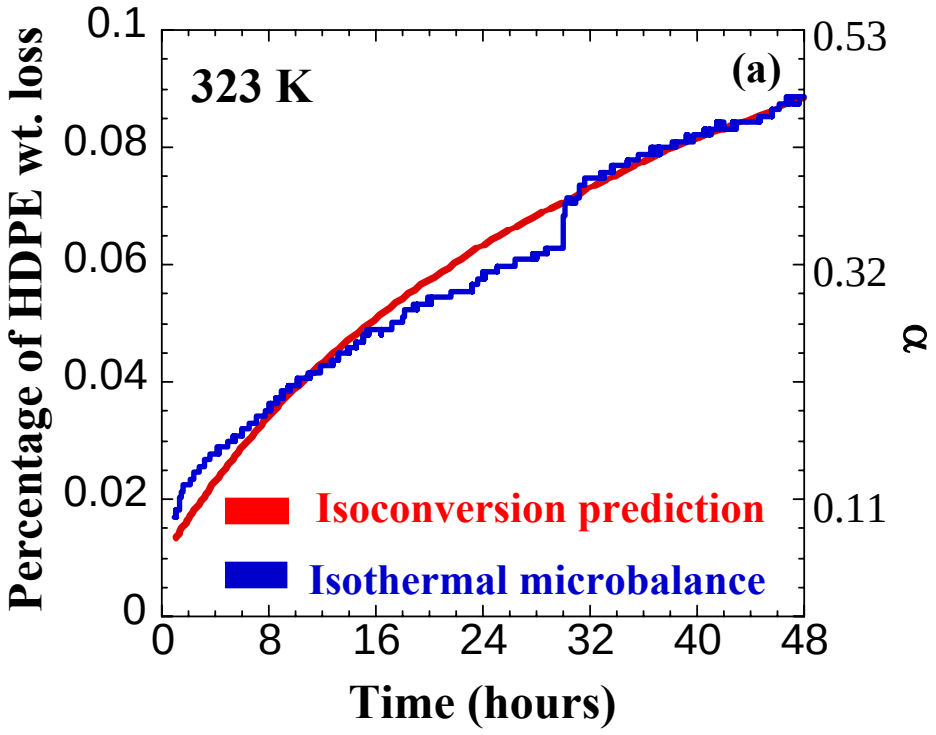

(a)
Temperature
Weight
Weight (mg)
T (K)
Time (hours)
88.4
88.36
88.32
88.28
340
330
320
310
300
290
0
20
40
60
(b)
Temperature
Weight
Weight (mg)
T (K)
Time (hours)
76.42
76.38
76.34
76.3
76.26
340
330
320
310
300
290
0
20
40
60
80

Fig. 6


323 K
(a)
Percentage of HDPE wt. loss
Time (hours)
α
Isoconversion prediction
Isothermal microbalance
0.1
0.08
0.06
0.04
0.02
0
0
8
16
24
32
40
48
0.53
0.32
0.11

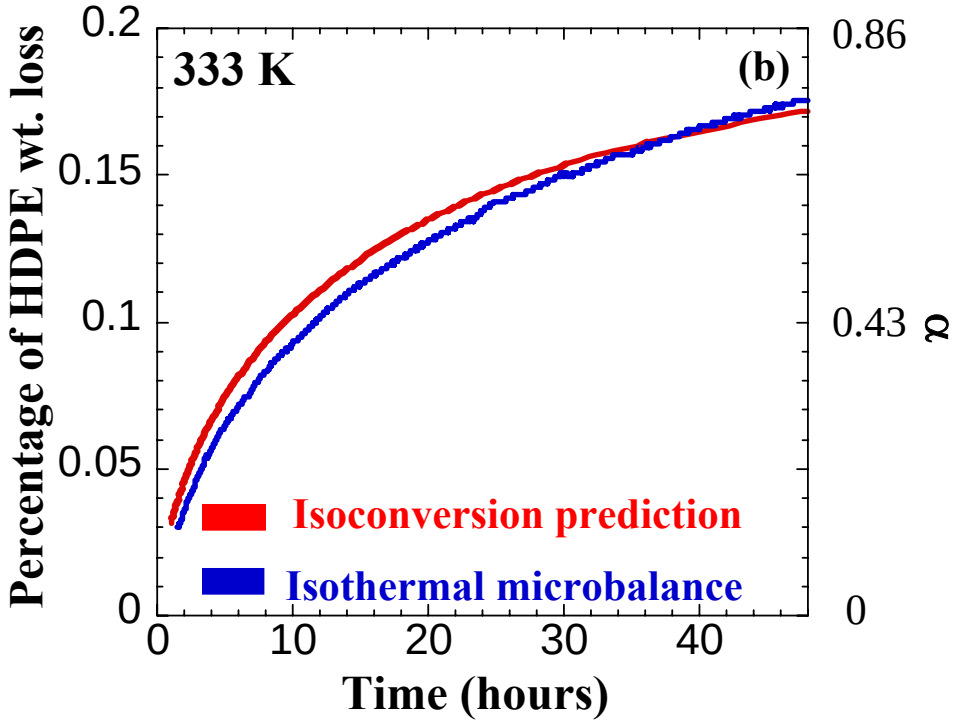
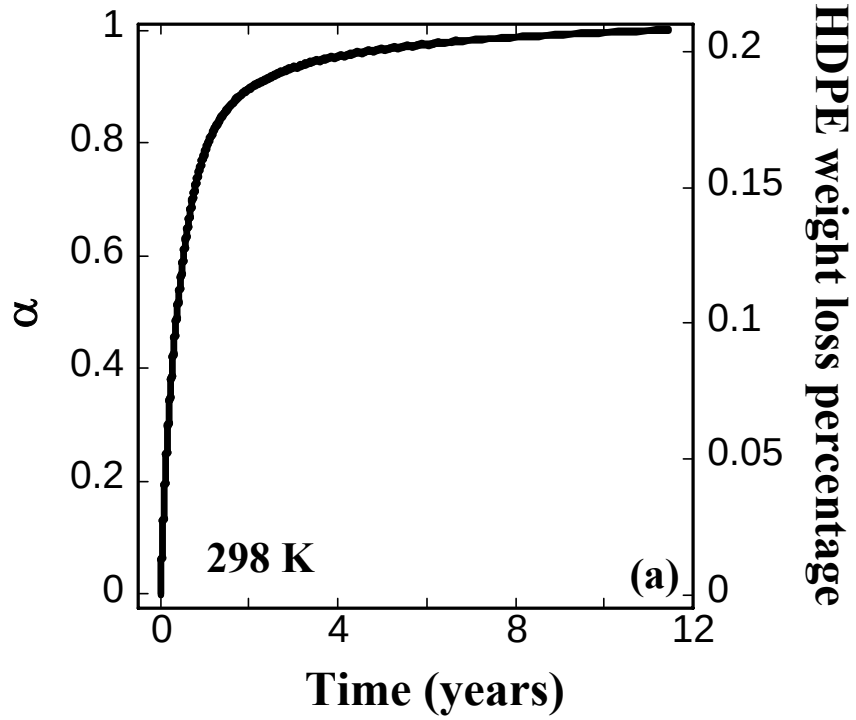

333 K
(b)
Percentage of HDPE wt. loss
Time (hours)
α
Isoconversion prediction
Isothermal microbalance
0.2
0.15
0.1
0.05
0
0
10
20
30
40
0.86
0.43
0

Fig. 7


α
HDPE weight loss percentage
Time (years)
298 K
(a)
0
0.2
0.4
0.6
0.8
1
0
0.05
0.1
0.15
0.2
0
4
8
12

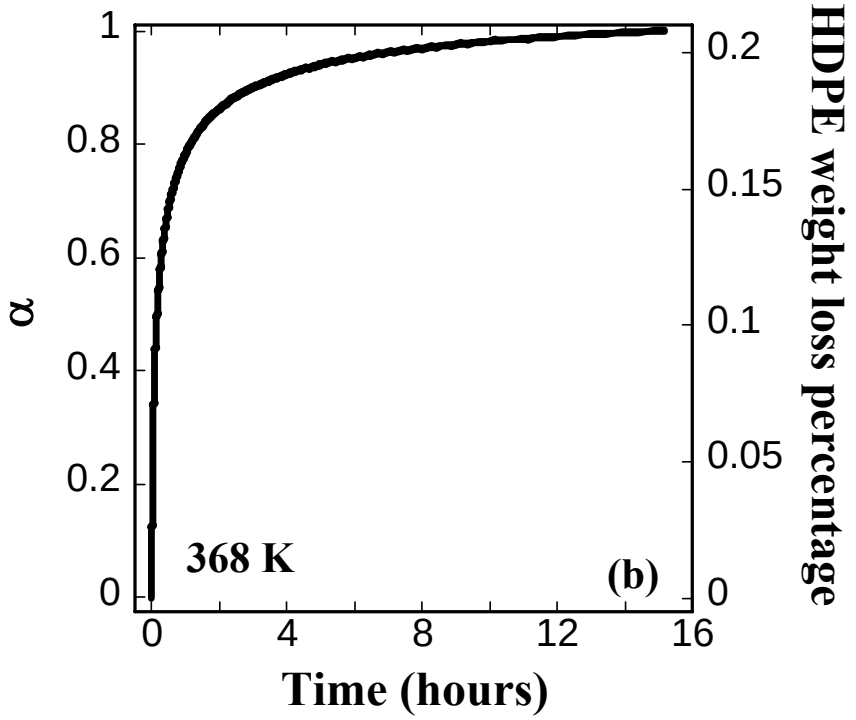

α
HDPE weight loss percentage
Time (hours)
368 K
(b)
0
0.2
0.4
0.6
0.8
1
0
0.05
0.1
0.15
0.2
0
4
8
12
16

Fig. 8