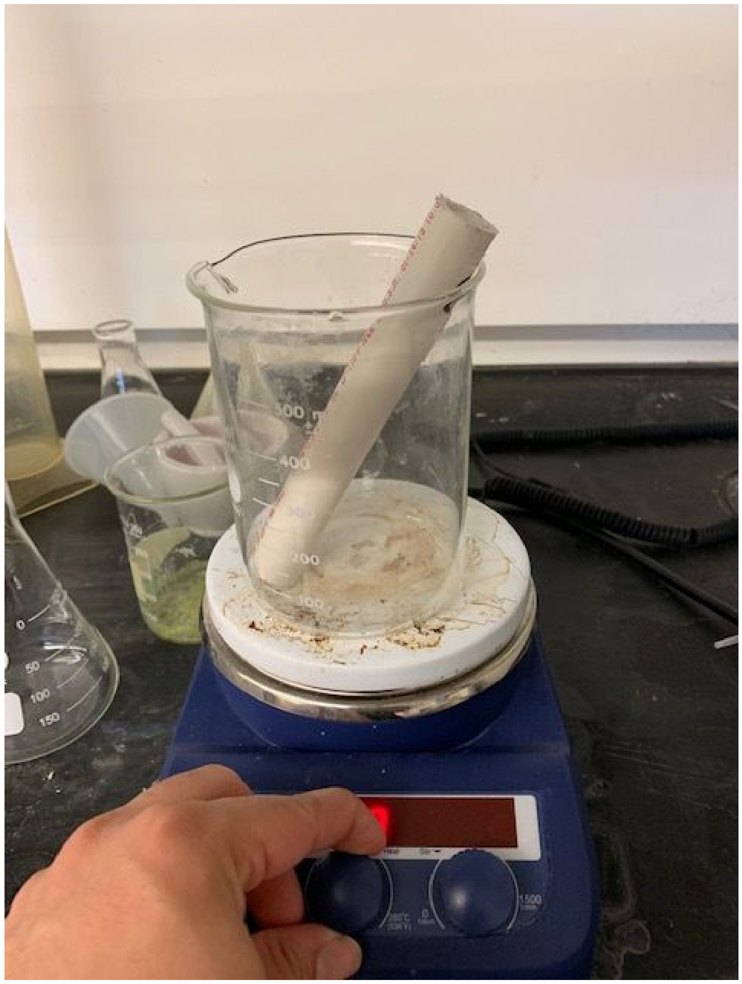
What is the Effect of Heat upon Thermoplastics Degradation?



Introduction:

In this study I investigated the role that heating plays upon thermoplastic in an isolated example that would be found in a landfill. Through the conversion of H_2 to CH_3 by methanogens,[1] the temperatures in landfills, especially on the water, attain the capability to reach extreme temperatures of 150 ºC (302 ºF) in marine hydrothermal systems and 77 °C (170 °F) as an upper limit for methane generation. [23]

I decided to study this topic after learning about the harmful effects that some pollutants can have on the atmosphere and the environment with the goal to relate my learning back to Chemistry in order to further understand it.Although similar research has been conducted by scientists S.A. Jabarin, and E.A. Lofgren in their paper examining the weight loss of volatile degradation products, decreasing inherent viscosity, and increasing carboxyl end group concentration ultimately however their procedure contained too many differences in addition to the specificity of only focusing on PETE plastic made it a good starting point to annoy my experiment off of.[4] I became interested in conducting my research upon a real world application in the environment, this would allow for my project to have a greater understanding by all people. My curiosity centered on the effect of the degradation that would occur in thermoplastic polymers at their melting point temperatures.

Safety: In this experiment, I wore goggles and gloves while performing the experiment under the fume hood, thus protecting my eyes and hands from any potential harm. In a previous study of 55 different polymer types, 29% of them were found to contain monomers that could be classified as carcinogenic, mutagenic[5] or toxic for reproduction[6]. Due to this risk, I took the precaution to close the

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[1]D.E. Holmes, J.A. Smith, (2016, November). Methanogens. Retrieved March 22, 2019, from https://www.sciencedirect.com/topics/agricultural-and-biological-sciences/methanogens

[2] Ferry, J. G. (1993). *Methanogenesis: Ecology, physiology, biochemistry & genetics*(15th ed.). New York: Chapman & Hall.

[3] Long-term temperature monitoring of geomembranes at dry and wet landfills. (2005, June 13). Retrieved from
https://www.sciencedirect.com/science/article/abs/pii/S026611440500004X?via=ihub

[4] Jabarin, S. A., & Lofgren, E. A. (1984). Thermal stability of polyethylene terephthalate. *Polymer Engineering and Science,24*(13), 1056-1063. doi:10.1002/pen.760241311

[5] MUTAGENIC | meaning in the Cambridge English Dictionary. (n.d.). Retrieved from https://dictionary.cambridge.org/dictionary/english/mutagenic

hood in order to ensure that the toxic chemicals would be unable to escape; allowing ample time for the majority of the gas to leave the vent and the polymer to cool down to an appropriate temperature.

Background information:

The two major types of plastics are thermoset and thermoplastic, where the former will be irreversible affected by heat(melting/damaging). While “Thermoplastics are a class of polymers that can be softened and melted by the application of heat; they can be processed either in the heat-softened state (e.g. by thermoforming) or in the liquid state (e.g. by extrusion and injection molding).”[7]Although thermoplastics are recyclable, the vast majority of them never are” in the first global analysis of all plastics ever made—and their fate. Of the 8.3 billion metric tons that has been produced, 6.3 billion metric tons has become plastic waste. Of that, only nine percent has been recycled. The vast majority—79 percent—is accumulating in landfills or sloughing off in the natural environment as litter. If this present trend continues, we will easily reach 12 billion metric tons of plastic waste in landfills by the year 2050.[8] Unless we dramatically change our recycling habits the amount of plastic being lost in our landfills will continue to grow, huge amounts of it being capable of getting recycled. In September of 2018, the EPA estimated that approximately 20% of all landfill was made up of plastic.[9] This unfortunately leads to a severe situation, specifically in the case of propylene, in which products containing polypropylene degrade extremely slowly in landfills and can take an excess of 30 years to fully decompose. This has a catastrophic environmental impact; as it decomposes, it releases toxins such as lead and cadmium into biosystems. Previous studies have shown that cadmium containing some plastic products has the potential to seep into bio systems during decomposure, thus causing harm. The incineration of thermoplastics similar to Polypropylene releases dioxins and vinyl chlorides. Again, resulting in a negative

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[6] Toxicity of plastics. (2017, July). Retrieved March 27, 2019, from https://www.blastic.eu/knowledge-bank/impacts/toxicity-plastics/

[7] Thermoplastics. (n.d.). Retrieved March 22, 2019, from https://www.sciencedirect.com/topics/materials-science/thermoplastics

[8] A whopping 91% of plastic isn't recycled. (2018, December 20). Retrieved March 27, 2019, from https://news.nationalgeographic.com/2017/07/plastic-produced-recycling-waste-ocean-trash-debris-environment/

[9] Plastics: Material-Specific Data. (2018, July 19). Retrieved March 29, 2019, from https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plastics-material-specific-data

environmental impact.[10] Further study is required to measure the true impact of the incineration of plastics, but ultimately, if we continue to use thermoplastics we will need to dramatically improve our recycling strategies so that the harmful environmental impact of using them can be negated as best as possible. Technology is being developed and tested to make more thermoplastics available for recycling; where it is heated, extruded and made into pellets to be reused, but we will have to have dramatic strategies in place.[11][12]

Methodology - Apparatus:

- 7 100ml or greater flasks
- (Four pieces of each plastic with similar starting weights(all plastics can be found in the house easily or if necessary at a nearby food store)(any weight can be used as long as they are within one gram of each other as the change is being measured in each experiment not the ending weights.)
    - Polyethylene Terephthalate (PETE or PET)
    - High-Density Polyethylene (HDPE)
    - Polyvinyl Chloride (PVC)
    - Polycarbonate (PC)
- Digital Balance
- Digital Stopwatch
- Constant temperature producing hotplate
- Safety Glasses/Goggles
- Safety Hood / Fume Hood
- Scissors/Saw/What is necessary to slice through your plastic safely
- Prepared (1% 5% 10% 25% 50% 75%) 100ml solutions of methanol(can be any solution if necessary)
- Water

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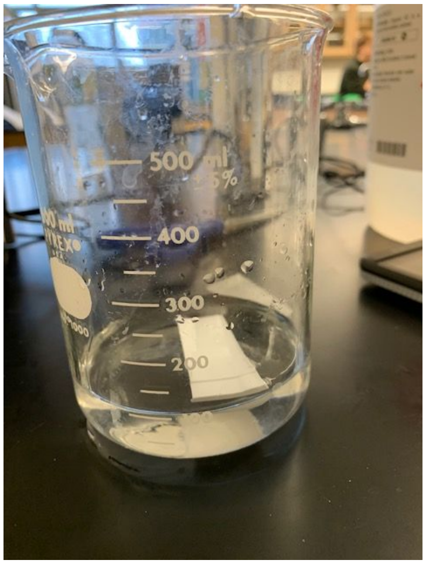
[10] LeBlanc, R. (2001). Polypropylene Recycling - An Introduction. Retrieved from https://www.thebalancesmb.com/an-overview-of-polypropylene-recycling-2877863
[11] Plastic Biodegradation in Landfills. (2005, May 22). Retrieved March 27, 2019, from http://green-plastics.net/posts/45/plastic-biodegradation-in-landfills/
[12] Ohsol, E. Perlmutter, A.(1979) United States Patent #3750600A - Disposal of thermoplastic materials. (4/2/19). Retrieved from https://patents.google.com/patent/US3750600A/en

Experimental Procedure:

1. Create six different 100ml solutions of methanol at 1% 5% 10% 25% 50% 75% and respectively in the 100ml+ flask
2. To determine the density range of each substance place the polymer in progressively higher percent density(by volume) solutions until it sinks. for example if it floated in 5% and sinked in 1% you would be able to tell that it fell under the range of 989.6-981.5g/l. The equivalent for each percentage based upon my equations are:998.2 g/l is 1%, 989.6 g/l is 5%, 981.5 g/l is 10%, 959.2 g/l is 25%, 915.6 g/l is 50%, 859.2 g/l is 75%.(numbers calculated for methanol)(Measuring them in this way before the scale would be ultimately made redundant by greater scientific tools)
3. Record this range as predictor/reference point for future results.
4. Clean the flask, allowing time to dry or drying by hand.
5. Prepare the hotplate for the heating of the plastics, setting it to 150 degrees celsius (or as close as possible if a temperature controlling hotplate can not be found)
6. While the hotplate is heating up cut your different plastics into comparably sized pieces, once cut measure on the scale and record your results.
7. Once hotplate is adequately heated, place the plastic in your flask on the hot plate allowing to heat for five minutes(timed by digital stop watch)
8. Once the timer goes off, leave the plastic in the flask moved to the side with metal tongs. Approx. 10 minutes.

9. Remeasure on the digital scale again, once the time has passed, recording the data.



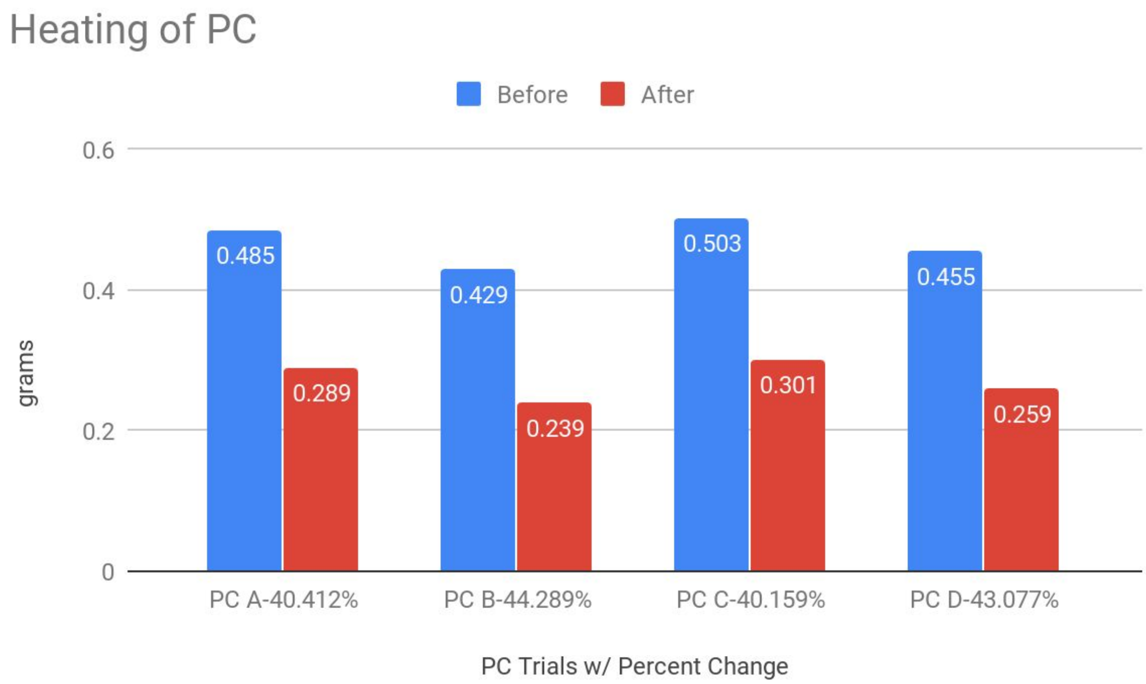
Raw Data:

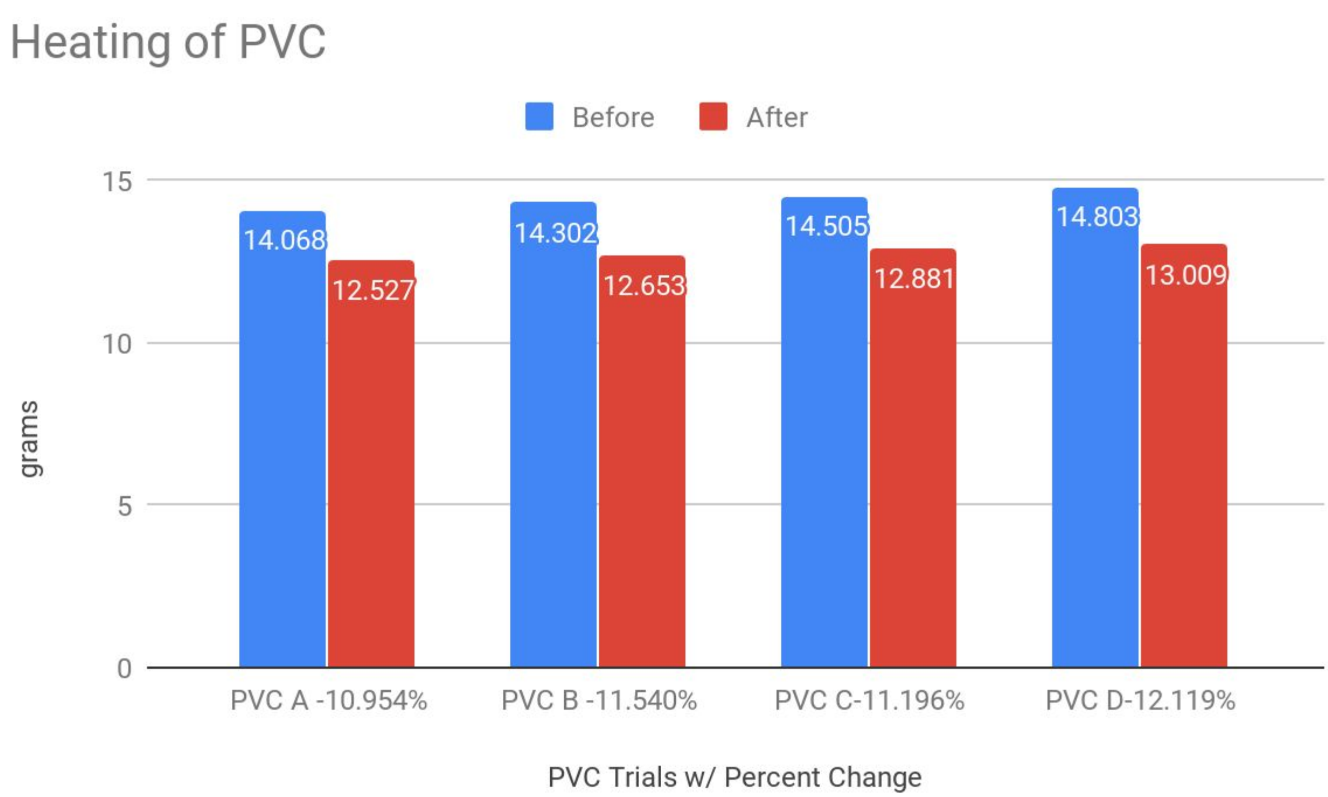
Effect of Heat upon Thermoset Plastics (before and After Heating with Percent Change and Standard Error included):(Error bars pictured in graphs but too small to appear)

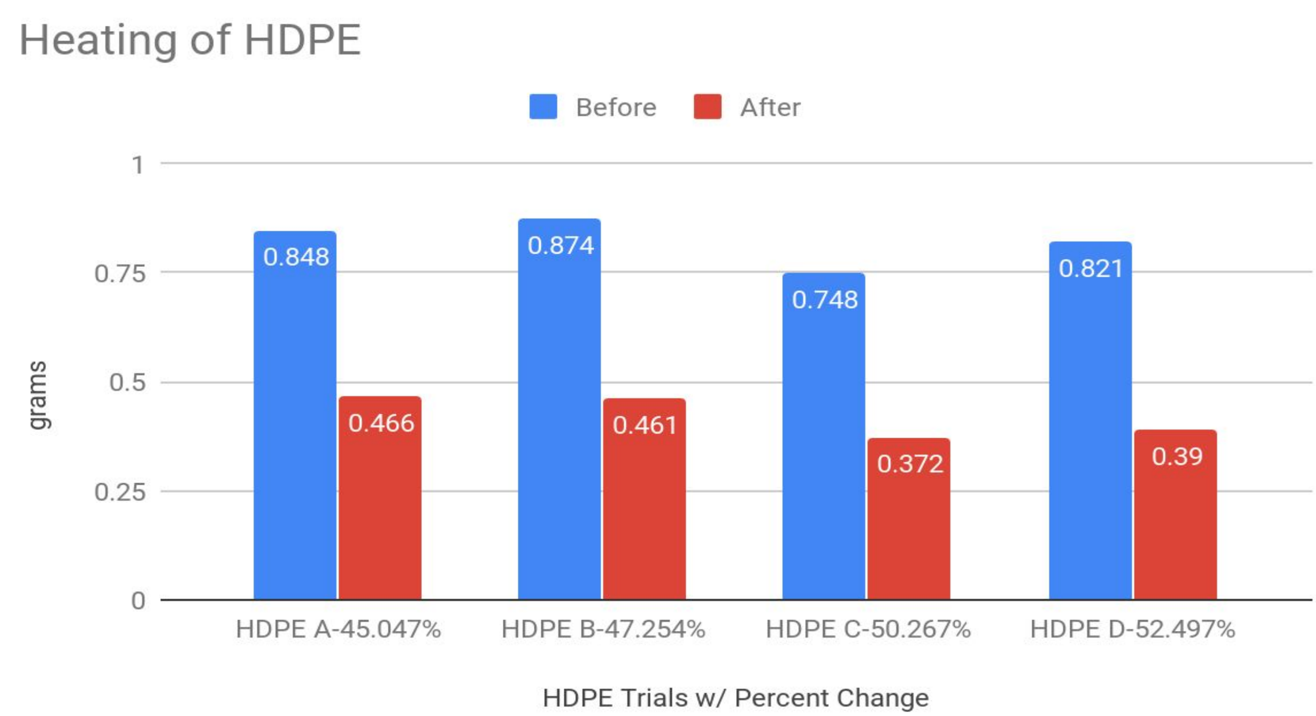
	Before	After	% Change
PVC A	14.068±0.078	12.527±.054	-10.954
PVC B	14.302±0.078	12.653±.054	-11.530
PVC C	14.505±0.078	12.881±.054	-11.196
PVC D	14.803±0.078	13.009±.054	-12.119
PETE A	0.388±.001	0.371±.007	-4.381
PETE B	0.391±.001	0.303±.007	-22.506
PETE C	0.395±001	0.335±.007	-15.190

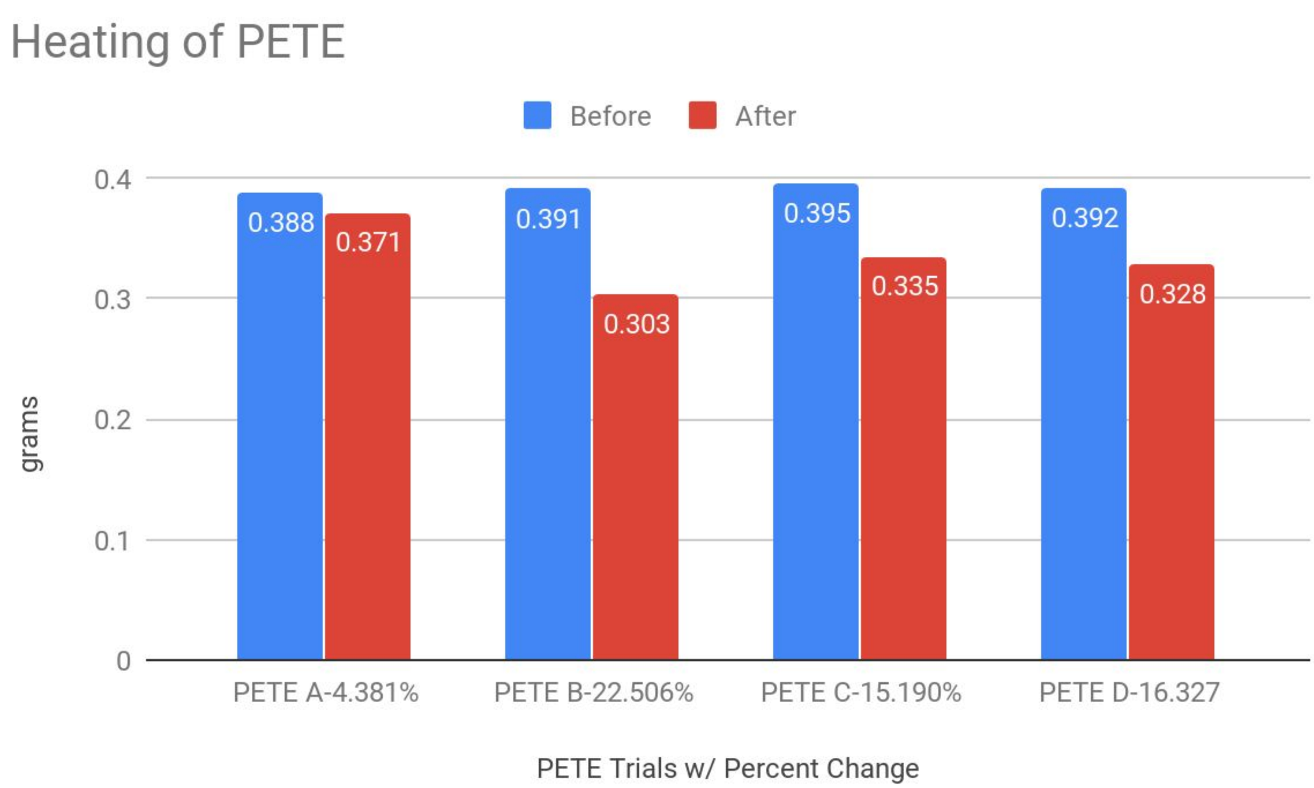
PETE D	0.392±.001	0.328±.007	-16.327
HDPE A	0.848±.014	0.466±.012	-45.047
HDPE B	0.874±.014	0.461±.012	-47.254
HDPE C	0.748±.014	0.372±.012	-50.267
HDPE D	0.821±.014	0.39±.012	-52.497
PC A	0.485±.008	0.289±.007	-40.412
PC B	0.429±.008	0.239±.007	-44.289
PC C	0.503±.008	0.301±.007	-40.159
PC D	0.455±.008	0.259±.007	-43.077
PP A	0.802±.008	0.569±.016	-29.052
PP B	0.82±.008	0.666±.016	-18.780
PP C	0.881±.008	0.72±.016	-18.275
PP D	0.828±.008	0.625±.016	-24.517
PVC Average	14.42	12.77	-11.442
HDPE Average	0.823	0.422	-48.730
PP Average	0.833	0.645	-22.569
PETE Average	0.392	0.334	-14.601
PC Average	0.468	0.272	-41.880

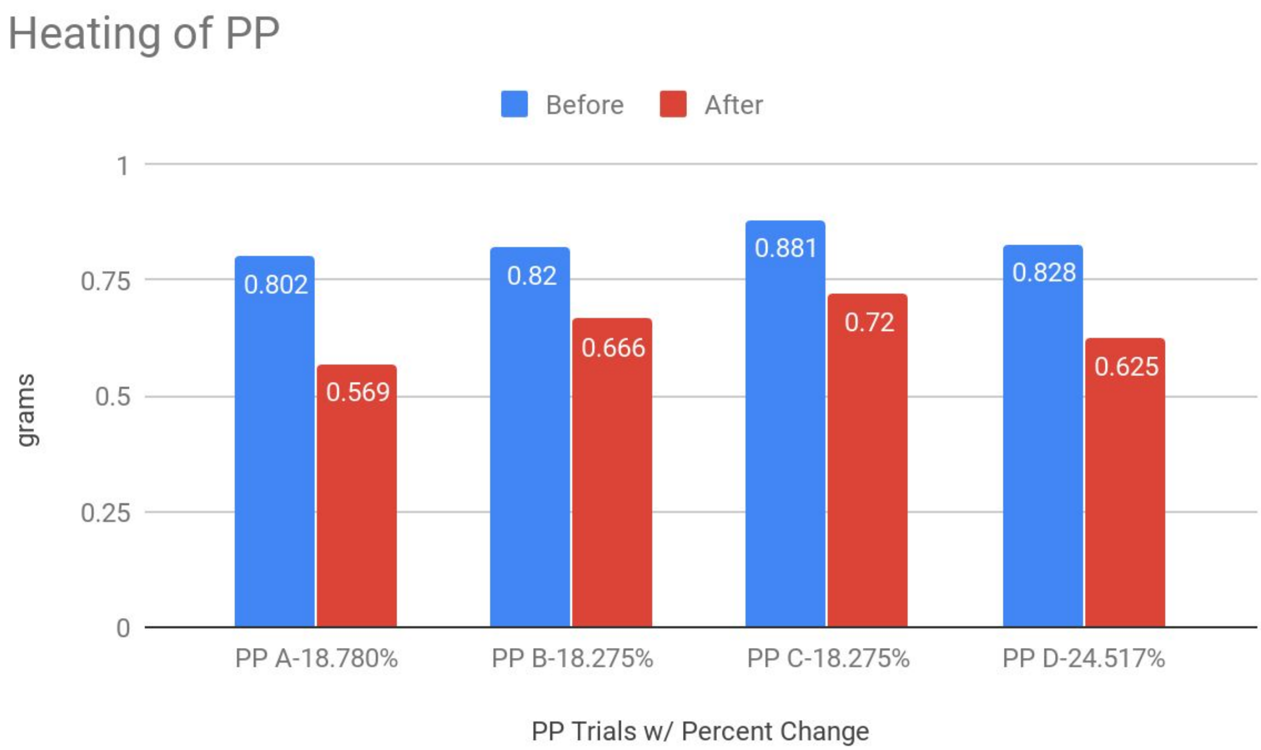
Data Processing






Heating of HDPE
Before
After
1
0.75
0.5
0.25
0
grams
0.848
0.466
0.874
0.461
0.748
0.372
0.821
0.39
HDPE A-45.047%
HDPE B-47.254%
HDPE C-50.267%
HDPE D-52.497%
HDPE Trials w/ Percent Change


Heating of PETE
Before
After
0.4
0.3
0.2
0.1
0
grams
0.388
0.371
0.391
0.303
0.395
0.335
0.392
0.328
PETE A-4.381%
PETE B-22.506%
PETE C-15.190%
PETE D-16.327
PETE Trials w/ Percent Change



	Z Scores(z =x–x¯/σ) Before and After Heating	
	Before	After
PVC A	-1.127	-1.105
PVC B	-0.376	-0.525
PVC C	0.274	0.521
PVC D	1.229	1.109
PETE A	-1.212	1.308
PETE B	-0.173	-1.112
PETE C	1.212	0.0267

PETE D	0.173	-0.223
HDPE A	0.465	0.907
HDPE B	0.943	0.803
HDPE C	-1.375	-1.0417
HDPE D	-0.032	-0.669
PC A	0.520	0.602
PC B	-1.193	-1.170
PC C	1.071	1.028
PC D	-0.401	-0.461
PP A	-0.906	-1.190
PP B	-0.380	0.329
PP C	1.421	1.174
PP D	-0.140	-0.313

Example Calculations(Completed for PVC before trials):

1. Add all four trials results together - Divide the sum by ‘n’, being the number of trials

   14.068(Trial A)+14.302(Trial B)+14.505(Trial C)+14.803(Trial D)=57.678 which then is divided by n(4) to get 14.4195(mean)

2. next to find the standard deviation each individual value from each trial (14.068,14.302,14.505, and,14.803) are added together and then divided by n-1(3) resulting in 0.05784025 for Trial A, 0.01311025 for Trial B, 0.01288225 for Trial C, 0.05832225 for Trial D
3. From here the standard deviation can divided by n(4) which equals your standard error above or below your values. --- (0.3118445125/4)= ±0.078
4. Alternatively from step 3 each individual trial original result can be subtracted from the mean and then divided by the standard deviation giving the Z scores.

   (14.068-14.4195)/0.3118445125 =-1.127, (14.302-14.4195)/0.3118445125=-0.376, (14.505-14.4195)/0.3118445125=0.274, (14.803-14.4195)/0.3118445125=1.229

Data Uncertainty

a. Using the formula ($z = x - \bar{x} / \sigma$), I found that my Z scores show that my data is within +/- 2 standard deviations away from the mean. This demonstrates that my data can be seen as conforming to the mean that was found, thus leading to little uncertainty in terms of outliers in my data. Additionally I found that my standard error for the different trials was ±.078 ±.054 for PVC before and after, ±.001, ±.007 for PETE before and after, ±.014, ±.012, for HDPE before and after, and ,±.008, ± .007, for PC before and after and ±.008, .016 for PP before and after. this level of standard error demonstrates that although there is uncertainty, the highest being for PVC no value is high enough to make my data unreliable to any significant degree.

Conclusion:

According to my processed data, degradation that can occur in plastics can in this example range from -52.497% to -10.95% percent change before and after heating respectively. This massive range demonstrates that some plastics are likely to degrade to the extent that a large portion of their mass is lost, reaching over 50 percent in some cases. This data although not able to be compared to any other results due to the simplicity of the experimental procedure, it however can be compared in regards to the observations recorded in the quite similar experiment performed by Sergei V. Levchik and Edward D. Weil that although performed under combustion not simply heat thermoplastics are prone to be resistant to charing additionally release toxic chemicals and become malleable[13]

Although not a new discovery it illustrates in a clear way to the scientific community as well as the general population the concerning implications of continuing to use plastics in such a frivolous way. Further experimentation would need to take place at a larger scale in order to properly conclude what is being released; however, as Thermoplastics are heated, both in experimentation, and in the reformation/recycling of plastics, toxins among other particles are released into the atmosphere in small quantities.Performing these experiments in the future with more temperatures at play, but a specific plastic, may yield more promising results. This could allow for the study of the effect of a specific temperature, rather than the generic temperature taken that fell under the melting point of all of these plastics. Allowing for proper analysis of plastics in a more individualized manner.

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[13] Levchik, S. V., & Weil, E. D. (2004). A review on thermal decomposition and combustion of thermoplastic polyesters. *Polymers for Advanced Technologies,15*(12), 691-700. doi:10.1002/pat.526