# Thermogravimetric evaluation of the antioxidants stability of biodegradable polymer containing natural phenolic antioxidants

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Horizon 2020
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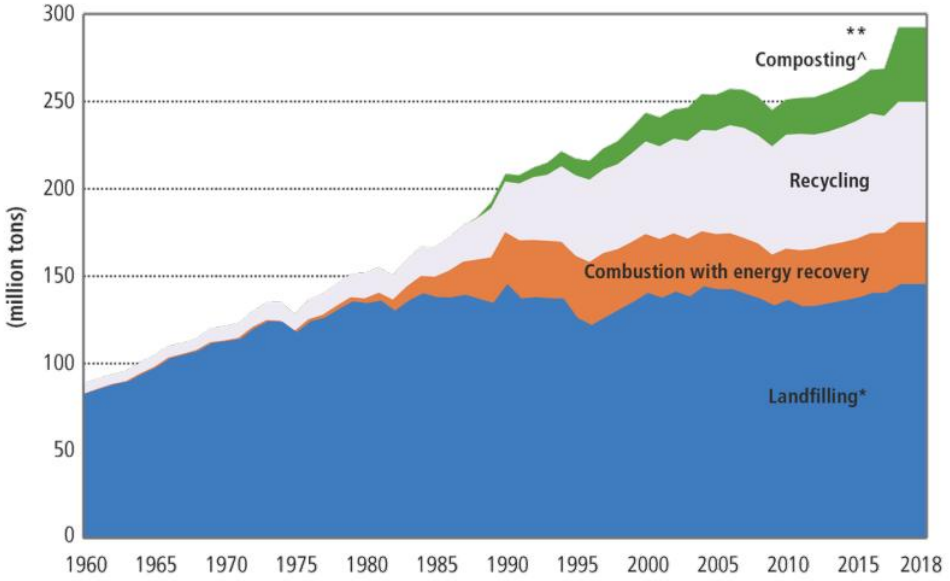
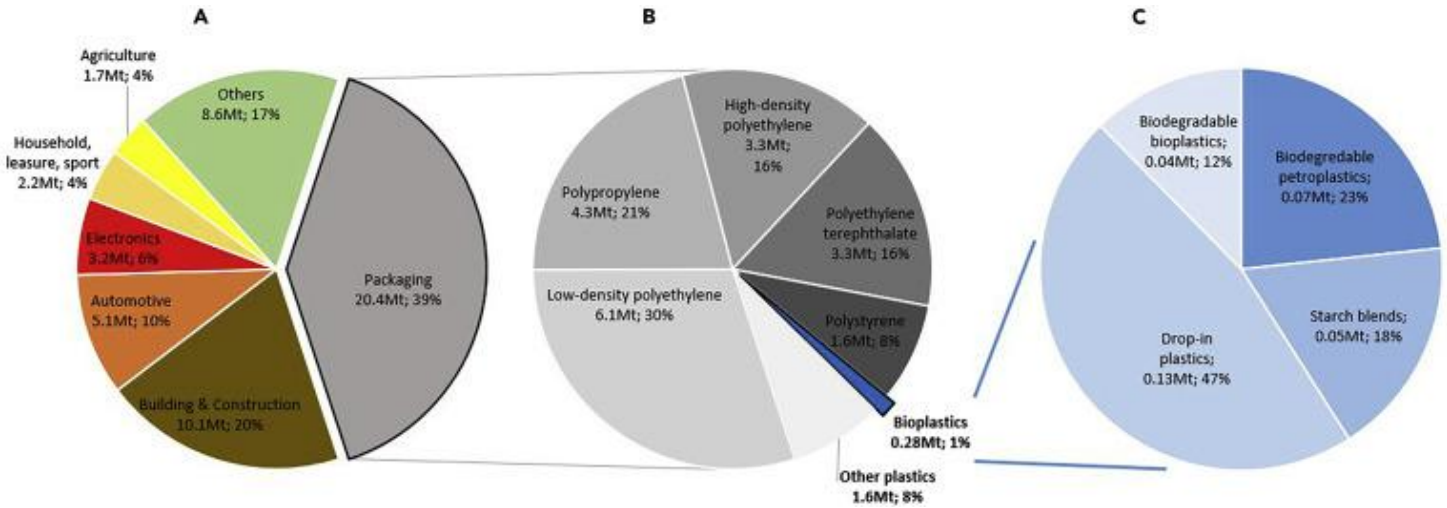
BBI JU

- End-of-life plastic makes up a large percentage of household and industrial waste
- Limited portion of plastic waste is recycled
- Bioplastics could find interesting application in packaging field

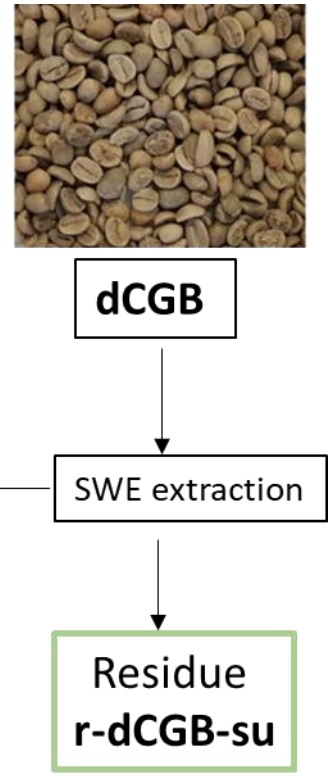



*EPA, Advancing Sustainable Materials Management: Facts and Figures Report, Data Tables, 2018*
*The Unintended Side Effects of Bioplastics: Carbon, Land, and Water Footprints; J. Brizga, K. Hubacek, K. Feng*

PROLIFIC

- Protein and bioactive molecules extraction from agri-food waste
- Polyphenols with intersting properties
- Antioxidant properties evaluation:
  - Thermogravimetric analysis
  - ABTS assay



# Kinetics Methods

- “Model-free” kinetic analysis
- Two main assumption:
  - Degradation reaction can be described only by one kinetic equation for the degree of conversion (α)
    $$\frac{d\propto}{dt} = A\exp\left(-\frac{Ea}{RT}\right) f(\propto)\ sd$$
  - The reaction rate at a constant value of conversion is only a function of temperature

- Kissinger-Akahira-Sunose (KAS) equation

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(-\frac{AR}{g(x)Ea}\right) - \frac{Ea}{RT_m}$$

Plot: $\ln\left(\frac{\beta}{T^2}\right)$ vs $\left(\frac{1}{T}\right)$

- Flynn-Wall-Ozawa (FWO) equation

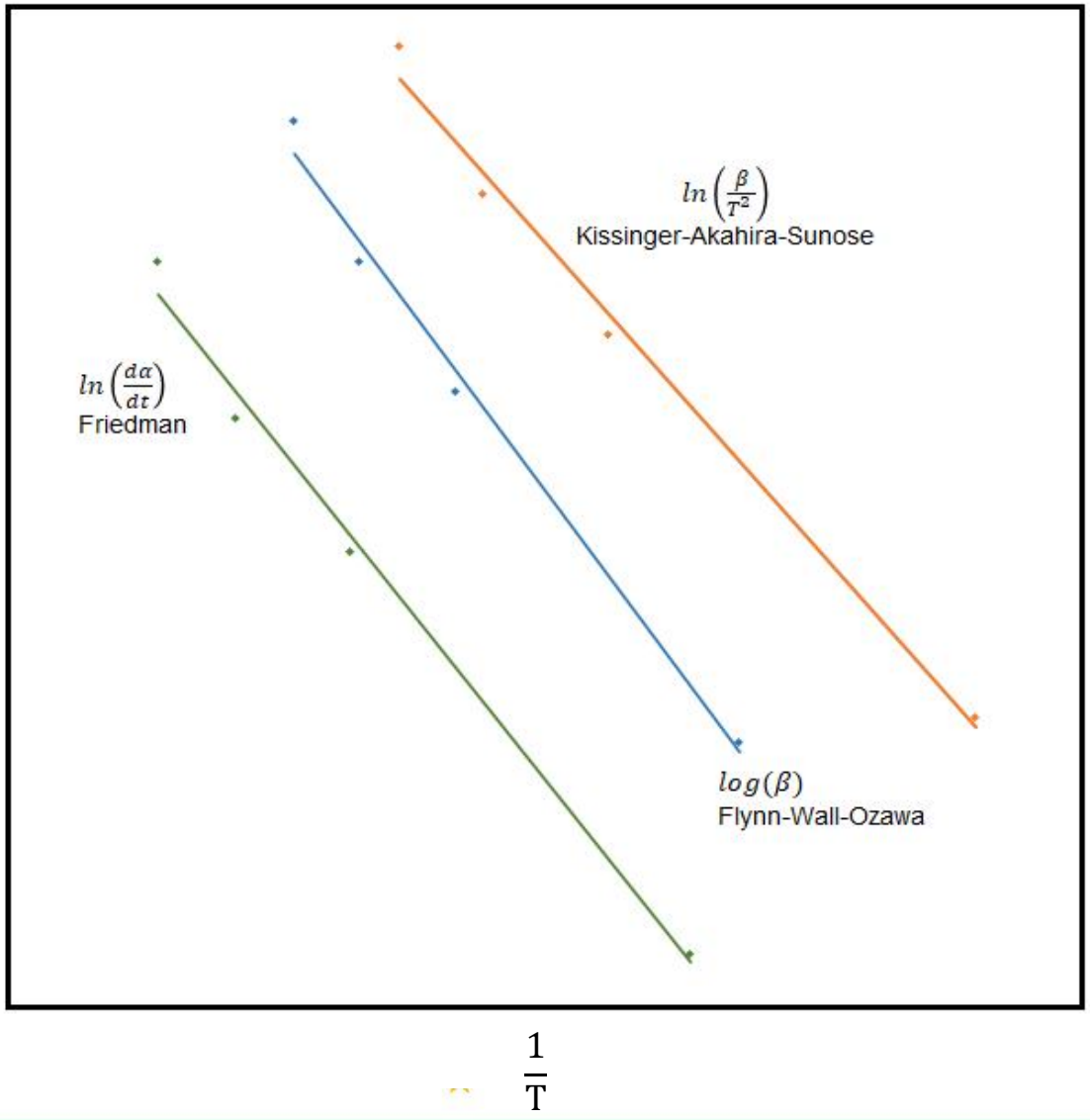
$$\log(\beta) = \ln\left(-A\frac{Ea}{Rg(\propto)}\right) - 2{,}315 - 0{,}4567\frac{Ea}{RT}$$

Plot: $\log(\beta)$ vs $\left(\frac{1}{T}\right)$

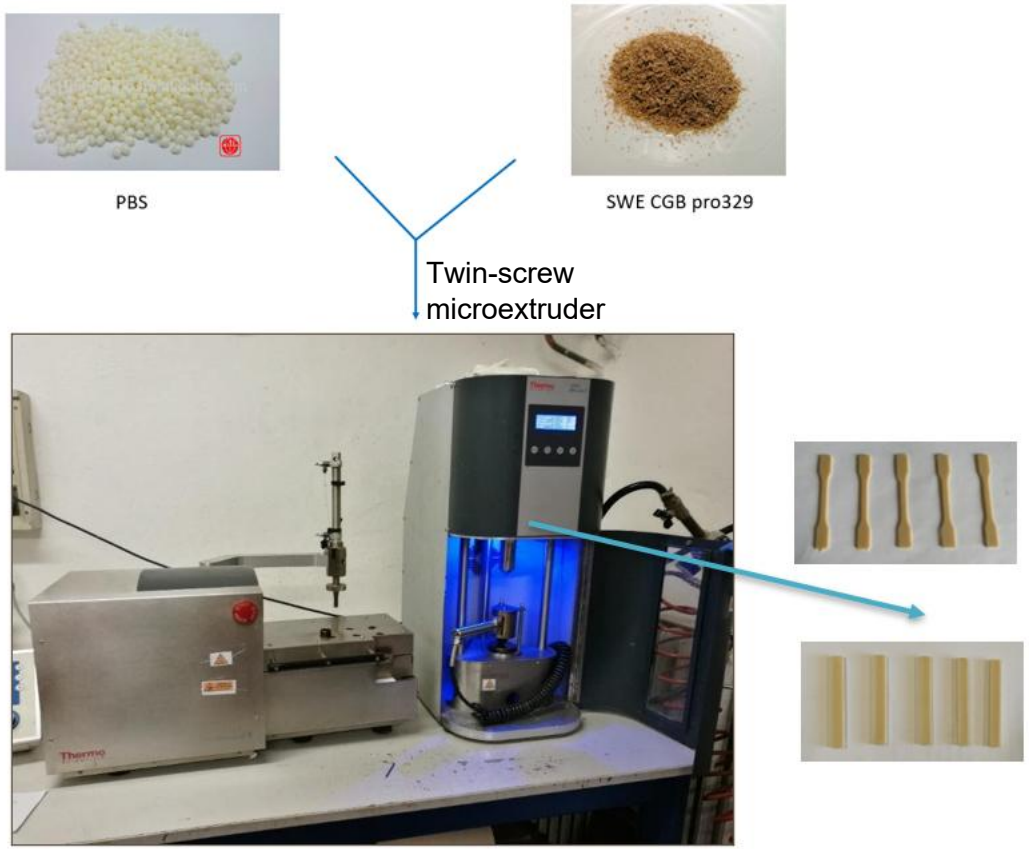
- Friedman equation

$$\ln\frac{d(\alpha)}{dt} = \ln[Af(\alpha)] - \frac{E_a}{RT}$$

Plot: $\ln\left(\frac{d\alpha}{dt}\right)$ vs $\left(\frac{1}{T}\right)$

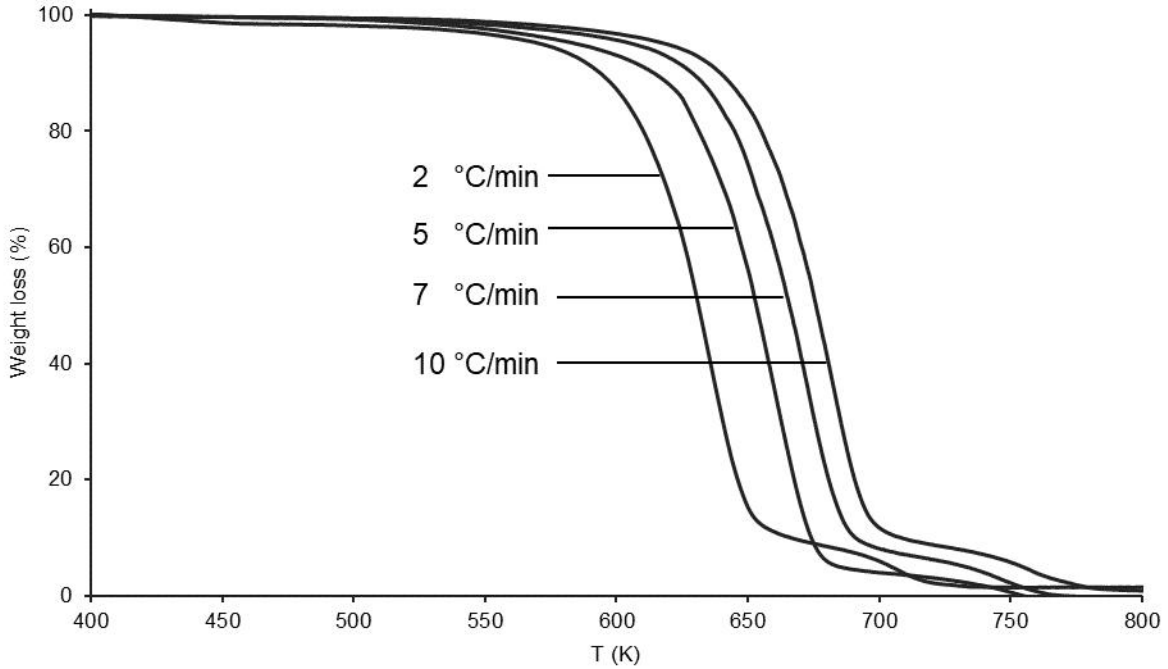


# Sample preparation



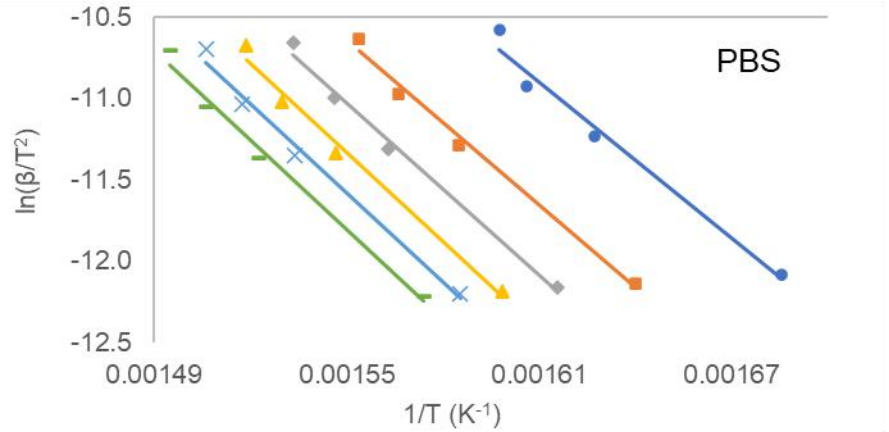

- Samples:
  - PBS
  - PBS + 1 wt% polyphenols
  - PBS + 3 wt% polyphenols
  - PBS + 5 wt% polyphenols
- Activation energy was calculated and compared

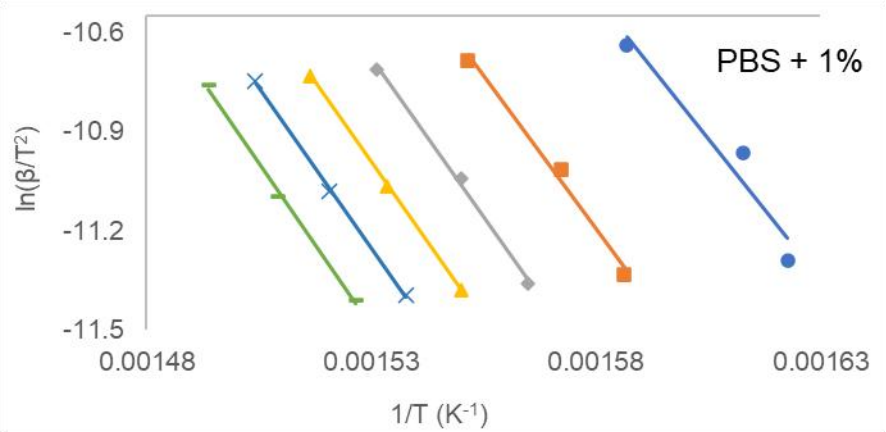
# Thermogravimetric analysis parameters

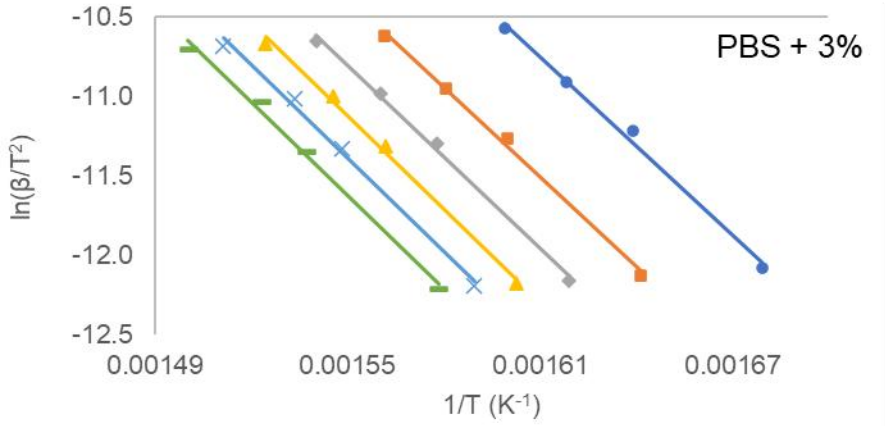


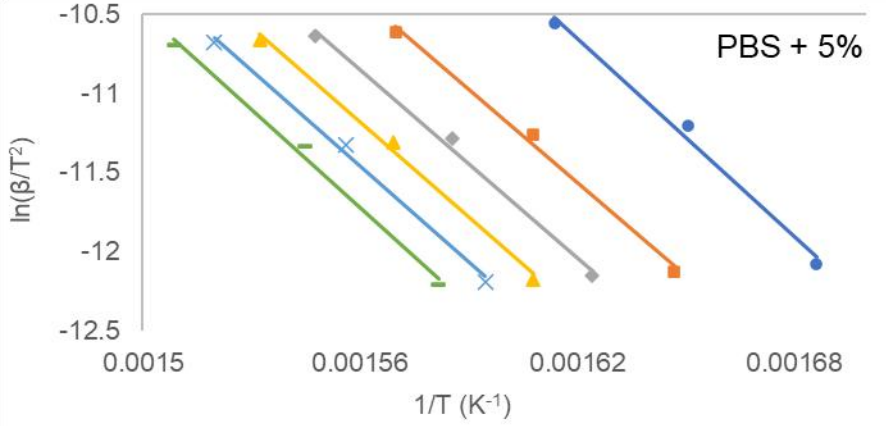

- Samples weight: 5 ± 0.5 mg
- Air flow: 50 mL/min
- Temperature rate: 2-5-7-10 °C/min
- Temperature range: 300-900 K

# KAS (Kissinger-Akahira-Sunose)




α = 0.1 0.2 0.3 0.4 0.5 0.6

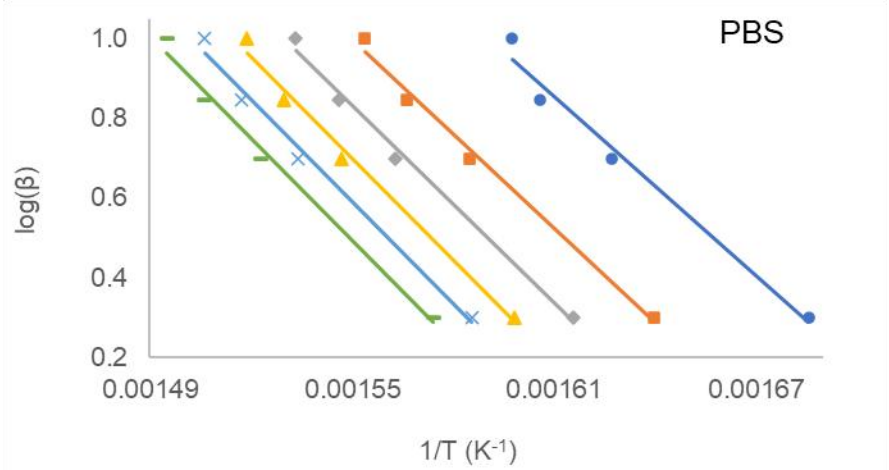
# KAS (Kissinger-Akahira-Sunose)

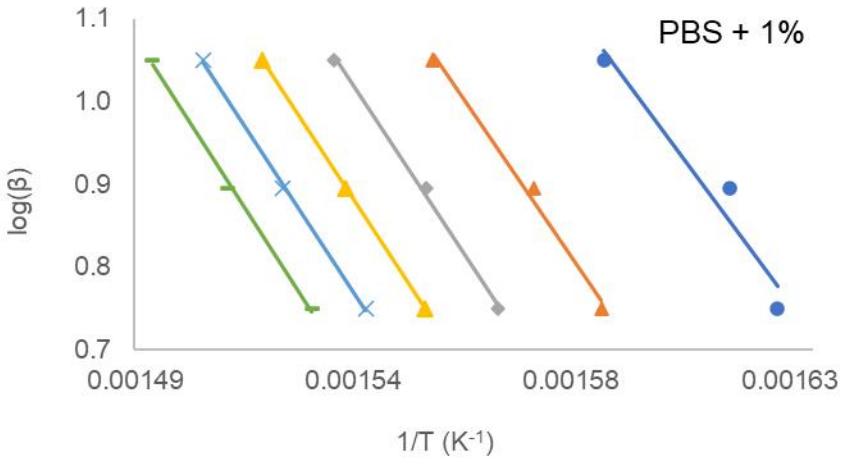
| Conversion | PBS | | PBS + 1% polyphenols | | PBS + 3% polyphenols | | PBS + 5% polyphenols | |
|---|---|---|---|---|---|---|---|---|
| | Ea [KJ/mol] | $R^2$ | Ea [KJ/mol] | $R^2$ | Ea [KJ/mol] | $R^2$ | Ea [KJ/mol] | $R^2$ |
| 0.1 | 133 | 0,9778 | 141 | 0.9384 | 156 | 0,9932 | 175 | 0,9911 |
| 0.2 | 140 | 0,9900 | 153 | 0.9897 | 157 | 0,9964 | 164 | 0,9943 |
| 0.3 | 147 | 0,9910 | 161 | 0.9967 | 161 | 0,9966 | 165 | 0,9944 |
| 0.4 | 152 | 0,9881 | 161 | 0.9999 | 163 | 0,9954 | 166 | 0,9949 |
| 0.5 | 152 | 0,9876 | 161 | 0.9991 | 163 | 0,9941 | 168 | 0,9951 |
| 0.6 | 153 | 0,9884 | 164 | 0.9969 | 163 | 0,9931 | 172 | 0,9934 |

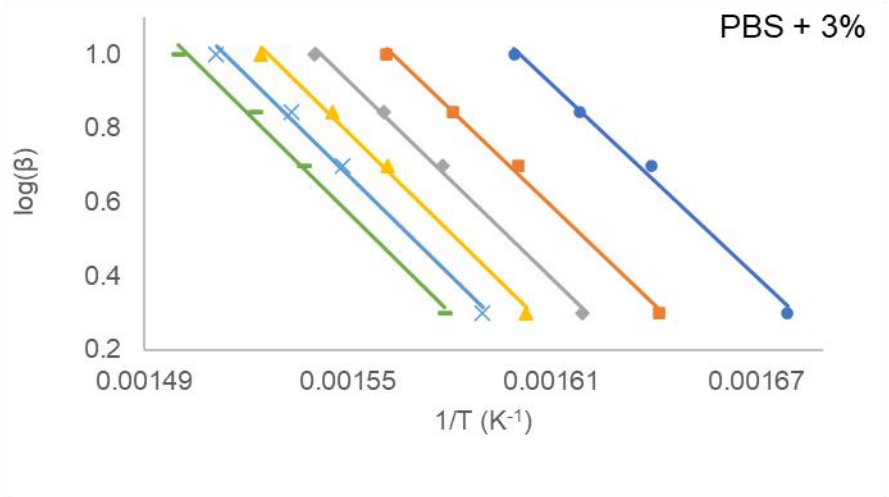
- Average Ea increase with polyphenol amount
- High correlation coefficent ($R^2$)

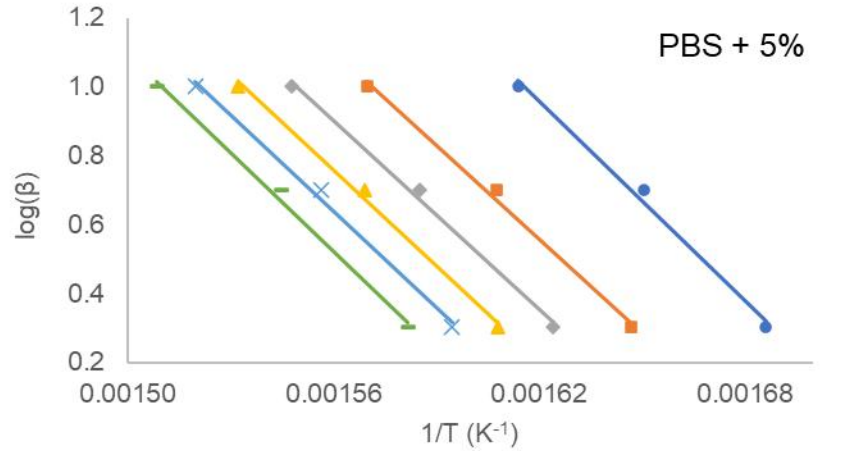
| | PBS | PBS + 1% polyphenols | PBS + 3% polyphenols | PBS + 5% polyphenols |
|---|---|---|---|---|
| Average Activation energy [kJ/mol] | 146 | 157 | 160 | 168 |

# FWO (Flynn-Wall-Ozawa)




α = 0.1 0.2 0.3 0.4 0.5 0.6

# FWO (Flynn-Wall-Ozawa)

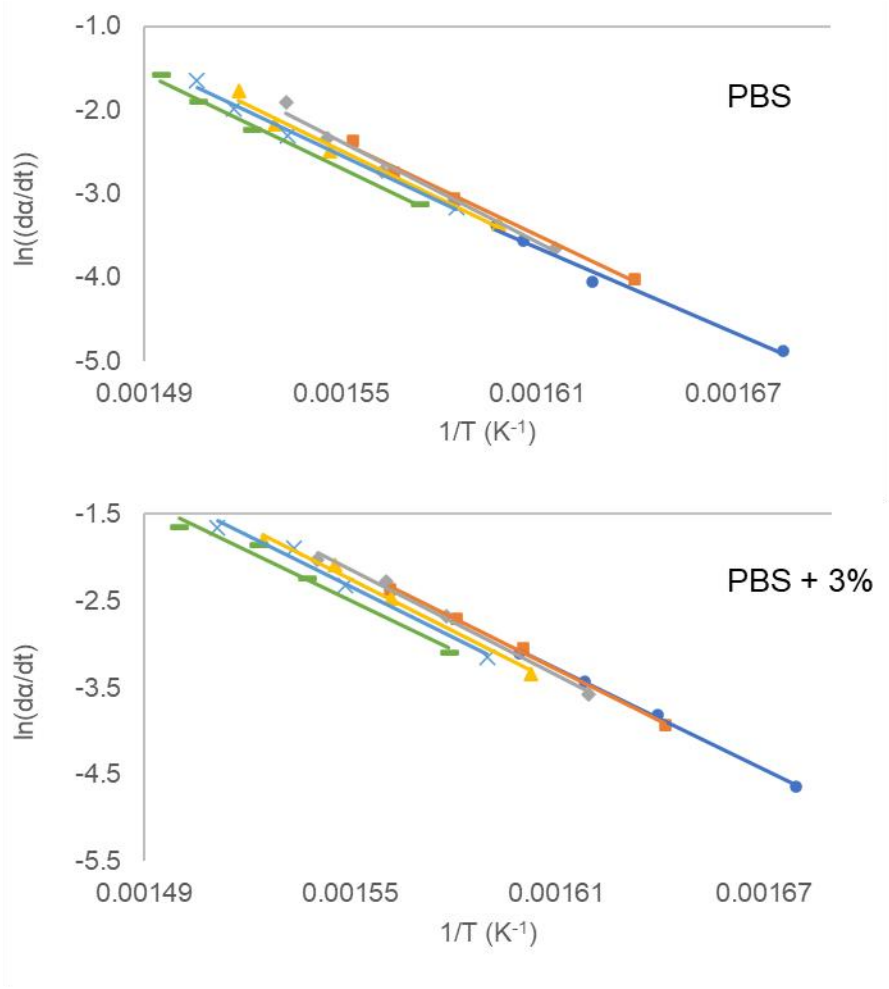


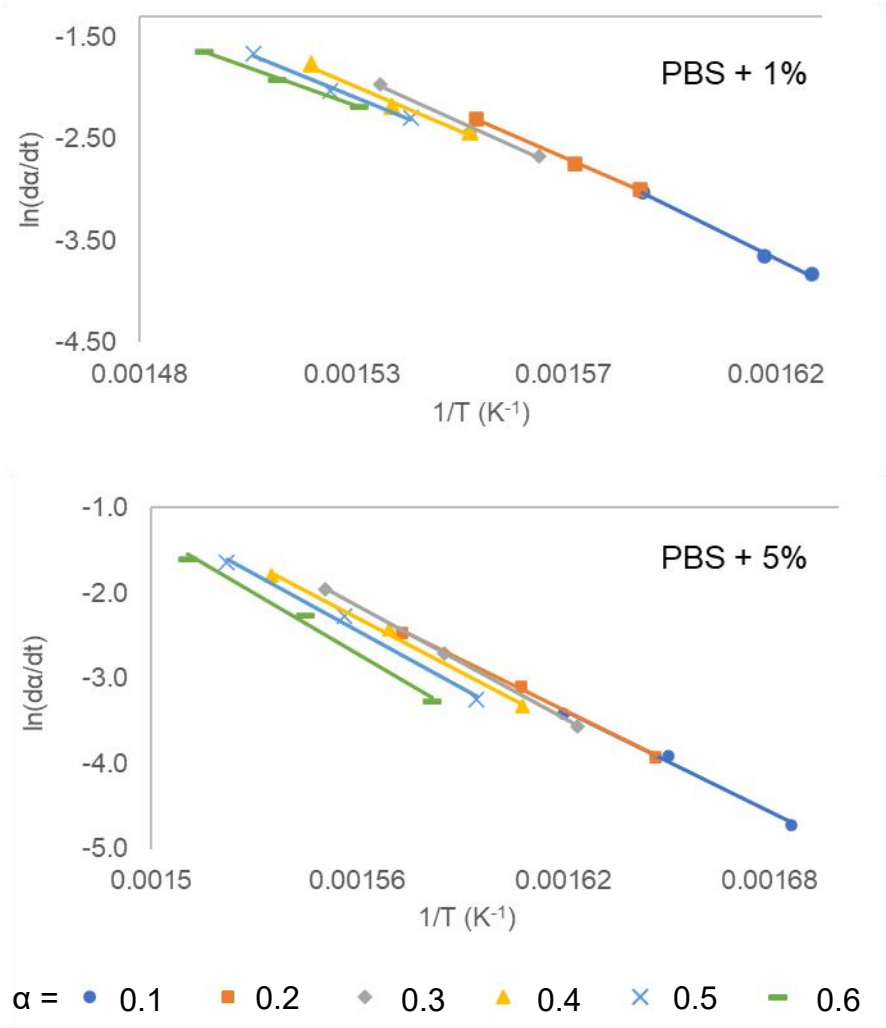
| Conversion | PBS | | PBS + 1% polyphenols | | PBS + 3% polyphenols | | PBS + 5% polyphenols | |
|---|---|---|---|---|---|---|---|---|
| | Ea [KJ/mol] | $R^2$ | Ea [KJ/mol] | $R^2$ | Ea [KJ/mol] | $R^2$ | Ea [KJ/mol] | $R^2$ |
| 0.1 | 136 | 0.9806 | 144 | 0.9462 | 158 | 0.9939 | 176 | 0.9921 |
| 0.2 | 143 | 0.9913 | 156 | 0.991 | 159 | 0.9941 | 165 | 0.9950 |
| 0.3 | 150 | 0.9921 | 162 | 0.9971 | 163 | 0.9924 | 167 | 0.9951 |
| 0.4 | 154 | 0.9895 | 163 | 0.9999 | 165 | 0.9939 | 168 | 0.9955 |
| 0.5 | 155 | 0.9891 | 164 | 0.9992 | 165 | 0.9987 | 170 | 0.9957 |
| 0.6 | 156 | 0.9898 | 167 | 0.9972 | 165 | 0.9979 | 174 | 0.9942 |

- Ea are in good agreement
- FWO Activation energy higher than KAS's Ea

| | | PBS | PBS + 1% polyphenols | PBS + 3% polyphenols | PBS + 5% polyphenols |
|---|---|---|---|---|---|
| FWO | Average Activation energy [kJ/mol] | 149 | 159 | 162 | 170 |
| KAS | Average Activation energy [kJ/mol] | 146 | 157 | 160 | 168 |

# Friedman


PBS
ln((dα/dt))
-1.0
-2.0
-3.0
-4.0
-5.0
0.00149
0.00155
0.00161
0.00167
1/T (K-1)
PBS + 3%
ln(dα/dt)
-1.5
-2.5
-3.5
-4.5
-5.5
0.00149
0.00155
0.00161
0.00167
1/T (K-1)


PBS + 1%
ln(dα/dt)
-1.50
-2.50
-3.50
-4.50
0.00148
0.00153
0.00157
0.00162
1/T (K-1)
PBS + 5%
ln(dα/dt)
-1.0
-2.0
-3.0
-4.0
-5.0
0.0015
0.00156
0.00162
0.00168
1/T (K-1)
α = 0.1 0.2 0.3 0.4 0.5 0.6

# Friedman

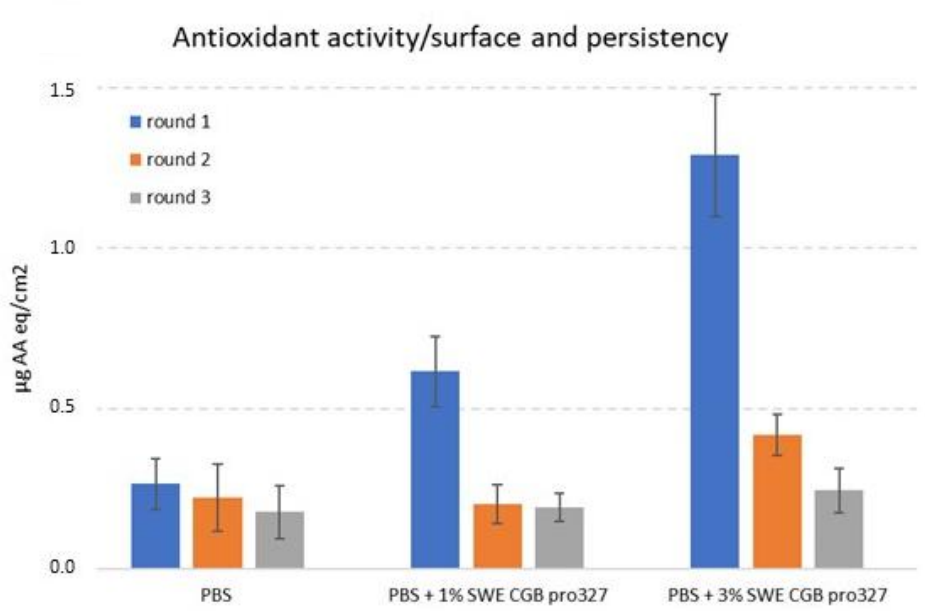


| Conversion | PBS | | PBS + 1% polyphenols | | PBS + 3% polyphenols | | PBS + 5% polyphenols | |
|---|---|---|---|---|---|---|---|---|
| | Ea [KJ/mol] | $R^2$ | Ea [KJ/mol] | $R^2$ | Ea [KJ/mol] | $R^2$ | Ea [KJ/mol] | $R^2$ |
| 0.1 | 141 | 0.9869 | 191 | 0.9942 | 160 | 0.9981 | 165 | 0.9915 |
| 0.2 | 154 | 0.9918 | 174 | 0.9987 | 163 | 0.9975 | 164 | 0.9983 |
| 0.3 | 168 | 0.9813 | 166 | 0.9879 | 169 | 0.9898 | 182 | 0.9990 |
| 0.4 | 159 | 0.9821 | 156 | 0.9861 | 167 | 0.9920 | 174 | 0.9961 |
| 0.5 | 153 | 0.9882 | 156 | 0.9853 | 164 | 0.9816 | 183 | 0.9928 |
| 0.6 | 158 | 0.9918 | 137 | 0.9978 | 159 | 0.9741 | 196 | 0.9905 |

- Ea trend confirmed
- Ea similar to KAS and FWO methods

| | | PBS | PBS + 1% polyphenols | PBS + 3% polyphenols | PBS + 5% polyphenols |
|---|---|---|---|---|---|
| Friedman | Average Activation energy [kJ/mol] | 155 | 162 | 164 | 172 |
| FWO | Average Activation energy [kJ/mol] | 149 | 159 | 162 | 170 |
| KAS | Average Activation energy [kJ/mol] | 146 | 157 | 160 | 168 |

# ABTS assay comparison




- Original PBS, PBS + 1% extract, PBS + 3% extract were tested
- PBS + 3% extract show higher antioxidant property
- Antioxidant activity trend was confirmed

# Conclusion

| Method | PBS | PBS + 1% polyphenols | PBS + 3% polyphenols | PBS + 5% polyphenols |
|---|---|---|---|---|
| KAS Ea [kJ/mol] | 146 | 157 | 160 | 168 |
| FWO Ea [kJ/mol] | 149 | 159 | 162 | 170 |
| Friedman Ea [kJ/mol] | 155 | 162 | 164 | 172 |

- Activation energy was successfully evaluated by thermogravimetric analysis
- Thermal degradation of PBS stabilized with natural antioxidants can be kinetically described in terms of the apparent activation energy (Ea)
- High Correlation coefficient ($R^2$) values
- Increase in antioxidant activity as the additive content of extracts increased
- Addition of 5% polyphenols results in increased stabilization of PBS
- Polyphenols extracted from coffee can be employed as antioxidants for packaging polymers
- Kinetic analysis proved to be a simple and fast method

Thank you for your attention!

https://www.prolific-project.eu/

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