# Effect of inherent PVC additives on hydrothermal dechlorination kinetics

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## Introduction

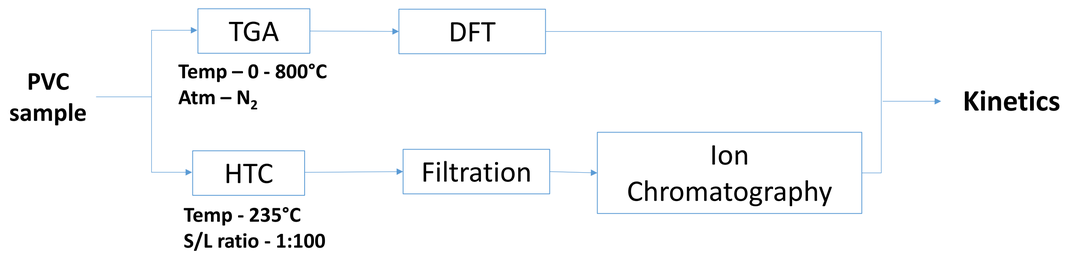
- PVC is comprised of various additives which affect its dechlorination behaviour
- Typical additives include heat stabilizers, fillers, plasticizers, and smoke suppressants
- The effect of these additives on hydrothermal dechlorination is largely unknown
- Interaction between these additives and particle size require investigation
- Understanding these effects is key in understanding dechlorination behaviour and aids chemical reaction control during chemical recycling efforts

## Aim and Objectives

- The aim of this study is to investigate the effect $ZnSt_2/CaSt_2$ stabilizer, filler agent ($CaCO_3$) and plasticizer ( Diisononyl phthalate) on hydrothermal dechlorination of poly (vinyl chloride)
- To highlight the effect of particle size on reaction mechanism

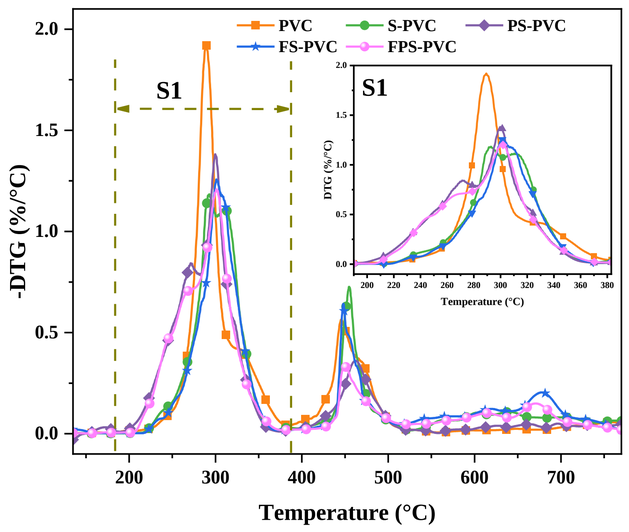
## Materials and methods

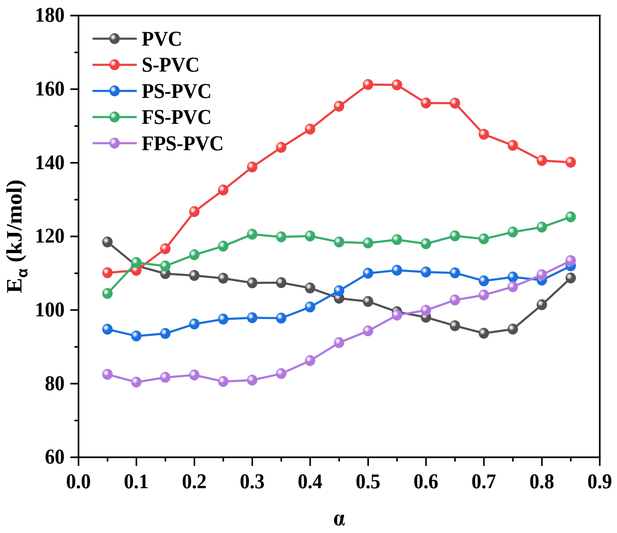
| PVC formulation | Additives (phr) | | | | |
|---|---|---|---|---|---|
| | PVC | $CaSt_2$ | $ZnSt_2$ | DINP | $CaCO_3$ |
| PVC | 100 | - | | | |
| S-PVC | 100 | 0.5 | 0.25 | | |
| FS-PVC | 100 | 0.5 | 0.25 | | 20 |
| PS-PVC | 100 | 0.5 | 0.25 | 50 | |
| FPS-PVC | 100 | 0.5 | 0.25 | 50 | 20 |




## Results and Discussion

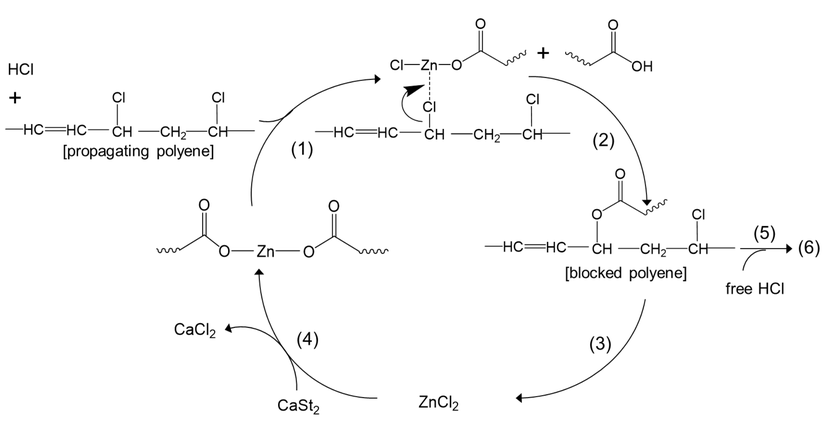
### 1. Thermal dehydrochlorination of various PVC-formulations



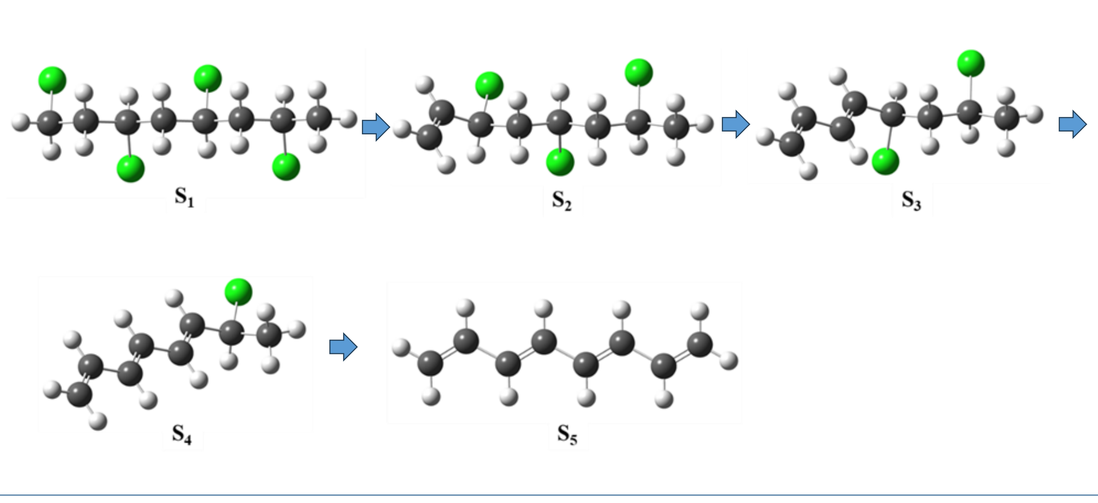




### 2. Thermal dehydrochlorination of stabilized PVC (S-PVC) using DFT

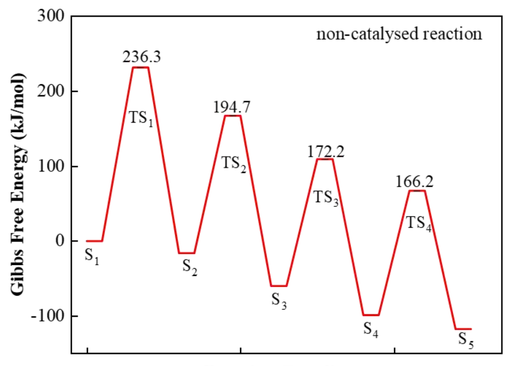
#### 2.1 Stabilization effect of Zn/Ca stearate stabilizer under mild conditions

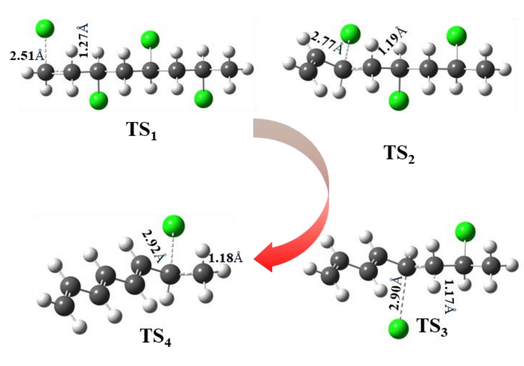


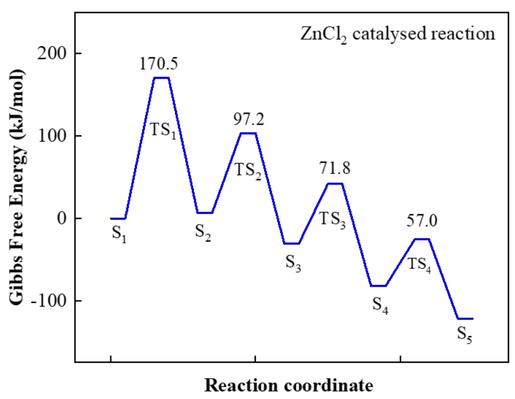

#### 2.2 Thermal decomposition path for HCl elimination: Effect of ZnCl$_2$ on dehydrochlorination

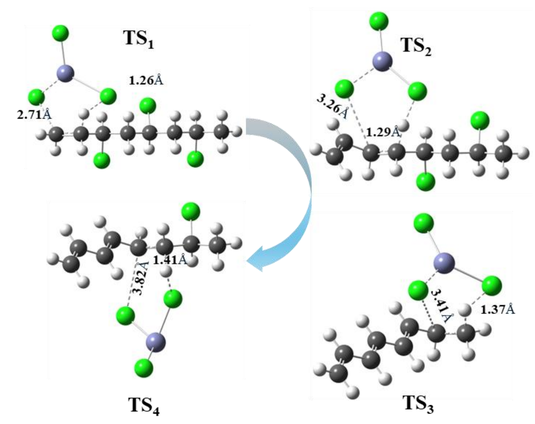



### Comparison between non-catalyzed and catalyzed dehydrochlorination



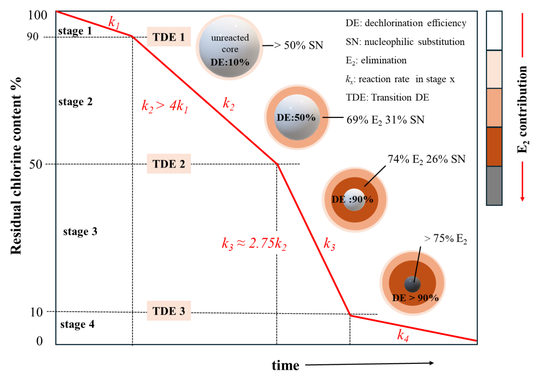



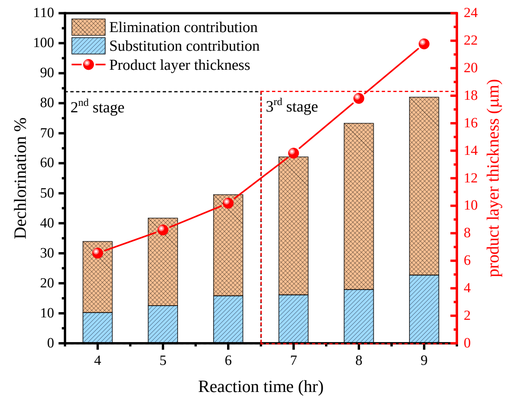

$ZnCl_2$ significantly reduces activation energy, and it shows synergy between the catalytic species and the increased conjugated length

### 2.3 Hydrothermal dechlorination mechanism and the effect of particle size

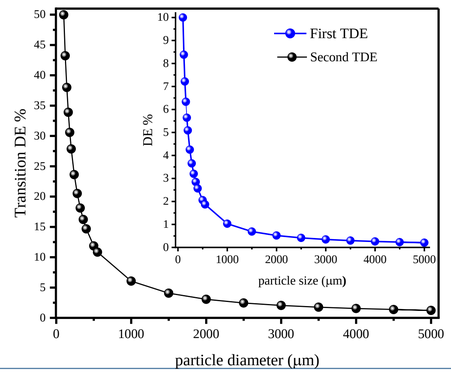
#### 2.3.1 Reaction mechanism of a 100μm particle




#### 2.3.2 Mechanism contribution for a 100μm particle



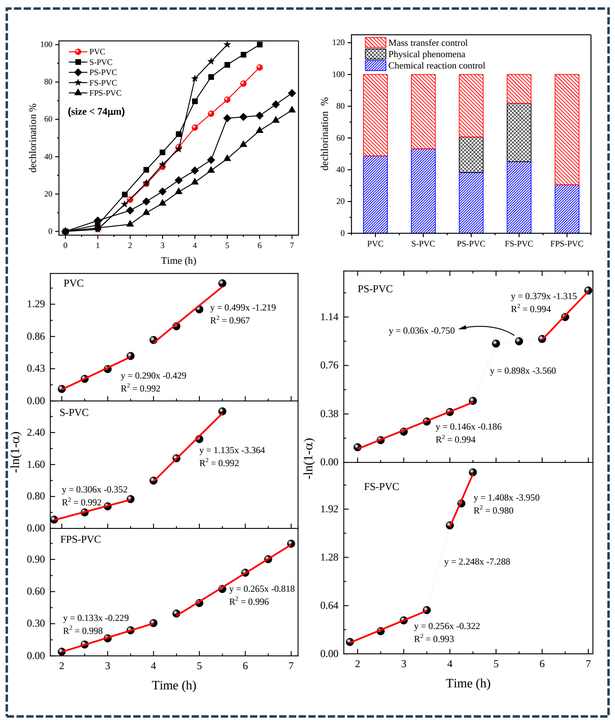

#### 2.3.3 Particle size effect on mechanism



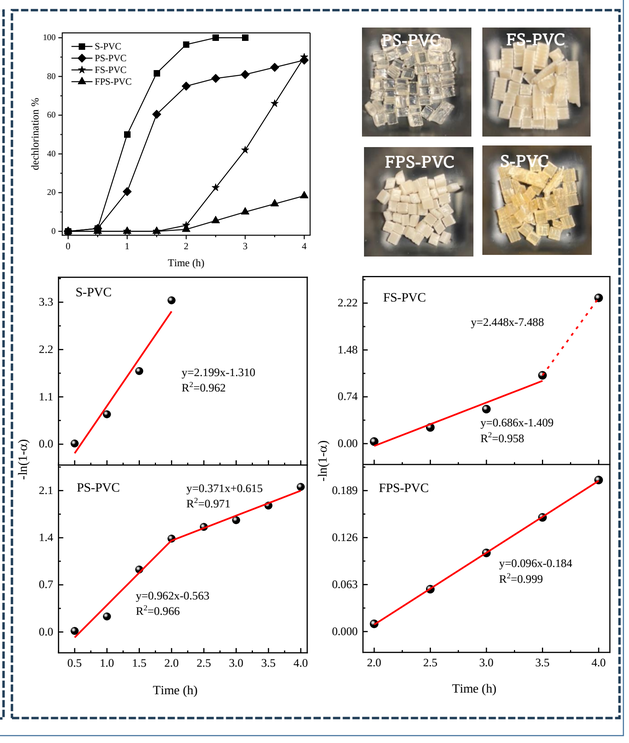

- Reaction rate changes at TDE of 10%,50%, and 90%
- Dechlorination rate increases with elimination contribution
- Dechlorination is product layer controlled [product layer thickness is proportional to elimination contribution]
- As particle size increases, $TDE_1$ and $TDE_2$ become insignificant, allowing the reaction to proceed rapidly, approaching the level of thermal dehydrochlorination.

### 2.4 Hydrothermal dechlorination of different PVC formulations [ 74μm vs 2mm particle size]

#### 2.4.1 Effect of additives for powdered PVC




#### 2.4.2 Effect of additives for large PVC pieces




## Conclusion

1. $ZnSt_2$, $CaCO_3$ and large particle size increase reaction rate
2. $ZnSt_2$ is hydrolyzed to $ZnCl_2$ which lowers the activation energy of both the initiation and prorogation stages of dechlorination
3. Plasticizer decreased dechlorination rate for smaller particles but has an opposite effect for lager particle size

**Acknowledgements**

We extend our thanks to Riken Technos Corporation for preparing different PVC formulations used in this study