

## The influence of type and concentration of stabilisers on the thermal stability of plasticised poly (vinyl chloride)

M. Davallo\*

Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran.

Received: June 2011, Revised: July 2011, Accepted: August 2011

**Abstract:** The influence of a variety of stabilisers and its content on the thermal stability of plasticised poly (vinyl chloride), PPVC were investigated. Experimental results indicated that the type of stabiliser had a significant influence on the thermal stability of PPVC. However, after identifying the order of efficiency of the thermal stability of stabilisers added to PVC, it was found that addition of stabiliser and the amount of it can increase the thermal resistance of PPVC polymer.

**Keywords:** Thermal stability, Poly (vinyl chloride), Thermal degradation of PVC, Decomposition of PVC.

### Introduction

Despite of the versatility afforded from the excellent range of properties which are offered by plasticised poly (vinyl chloride), PPVC, major problem associated with this polymer is its instability to temperature and to photo-initiated chemical changes by the evolution of hydrochloride acid (HCl) followed by oxidation. On decomposition

process, the presence of evolved HCl gas worsens the consequences of the chemical reaction. HCl is a toxic product which has tendency to attack the surface of lower-grade steel tools in processing equipment. Formation of polyene (C=C) sequences during dehydrochlorination leads to progressive compound when degraded excessively. However, it has been recently proposed that

the low thermal stability of PVC is due to at least the presence of structural inhomogeneity in the molecules which accelerates the rate of dehydrochlorination by activating the carbon-chlorine (C-Cl) bonds in the system. Thus, such structural irregularities are thought to include initiator residue, chain unsaturation, branches, isomer and oxidation structures. The higher temperature is associated with a greater extent of degradation and it can also be seen that a greater degree of stabilization by increasing the concentration of stabilizer retards the development of chain-unsaturation sequences. Degradation of PVC due to evolution of HCl is shown by the following mechanism:



The liberated HCl accelerates further decomposition and if oxygen is present it would increase the reaction and moreover it causes both chain scission and cross-linking. It also can accelerate the colour formation of PVC. In this work, a variety of stabilisers on the thermal stability of PPVC were first studied and order of efficiency of thermal stability of stabilisers were identified. Then the concentration of stabiliser which gave the greater thermal efficiency was determined.

## Experimental

### Materials

#### *Types of stabiliser on the thermal stability of PPVC*

The PVC used in this study is a suspension resin with solution viscosity k-value of 65 (from Arvand Petrochemical Co, Iran). Eight different types of stabiliser (referred to as 1, 2, 3, 4, 5, 6, 7 and 8) used in this study which were compatible with PVC, all were with industrial grade (from Ciba-Geigy). The additives used are shown in Table 1. The PVC compounds formulations are shown in Table 2. These are based on a dialkyl phthalate (DAP) plasticised formulation, (with an industrial grade), but without the fillers. All compounds were added with pigment.

#### *Sample preparation*

A high speed laboratory mixer (Fielder 8L) was used to mix PVC and the additives. To produce moulded flat sheet, the dry compounds of PVC and additives were first sheeted on a two roll-mill before being compression moulded at the set temperature of 160 °C. Samples (2 cm<sup>2</sup>) for degradation testing were cut from the compressed sheet prepared for each compound and then were placed in a preheated oven at 180 °C. Samples of each compound were removed at varying time intervals (e.g 1, 5, 10, 15, 30, 60, 120 and 180 mins) and their colour changes were observed as a function of time.

Table 1 Types of additives used.

Additives	Types
Stabiliser-1	No stabiliser
Stabiliser-2	Liquid Ba/Cd
Stabiliser-3	White lead
Stabiliser-4	Mixed Cd/Ba/Zn
Stabiliser-5	Dibutyl tin dilaurate
Stabiliser-6	Calcium stearate
Stabiliser-7	Mixed Cd/Ba
Stabiliser-8	Zinc stearate
Plasticiser	DAP
Lubricant	Cadmium stearate

Table 2 PVC compounds.

Ingredient	PVC1	PVC2	PVC3	PVC4	PVC5	PVC6	PVC7	PVC8
PVC	100	100	100	100	100	100	100	100
Stabiliser-1	-	-	-	-	-	-	-	-
Stabiliser-2	-	2	-	-	-	-	-	-
Stabiliser-3	-	-	2	-	-	-	-	-
Stabiliser-4	-	-	-	2	-	-	-	-
Stabiliser-5	-	-	-	-	2	-	-	-
Stabiliser-6	-	-	-	-	-	2	-	-
Stabiliser-7	-	-	-	-	-	-	2	-
Stabiliser-8	-	-	-	-	-	-	-	2
DAP	50	50	50	50	50	50	50	50
Lubricant	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

The numbers indicates parts per 100 resin (phr) in the formulations.

The influence of concentration of stabiliser on the thermal stability of PPVC After identifying the order of thermal stability efficiency of stabilisers added to PVC, samples (prepared as mentioned above) with formulations which are shown in Table 3 were used. Samples for degradation testing were cut (2 cm<sup>2</sup>) from the compressed

sheet prepared for each compound and then were placed in a preheated oven at 180 °C. Samples of each compound were removed at varying time intervals (e.g 2, 10, 20, 30, 40, 80, 120 and 180 mins) and finally their colour changes were observed as a function of time.

Table 3 PVC compounds.

Ingredient	PVC1	PVC2	PVC3	PVC4	PVC5
PVC	100	100	100	100	100
DAP	50	50	50	50	50
Stabiliser (White lead)	0	1	2	4	8
Lubricant	0.5	0.5	0.5	0.5	0.5

The numbers indicate parts per 100 resin (phr) in the formulations.

## Results and Discussion

### *Types of stabiliser on the thermal stability of PPVC*

The thermal stability of PPVC samples tested are shown in Table 4. As it can be seen from Table 4, PVC2, PVC3, PVC5, and PVC8 indicated to have better thermal stability in comparison with other PVC. These PVC materials degrade in slower rate compared with those which changed colour from clear to brown/red and finally to black with increasing temperature. It is proposed that mechanism of dehydrochlorination are either due to ionic or radical reaction. According to Shapro, the radical reaction is said to occur to a larger extent with increasing temperature being dominant at higher temperature. Due to the extended polyene sequences they are able to bind hydrogen chloride with formation of carbanium salt, as shown below:



This reaction results in further intensifica-

tion of colour. By adding a stabiliser system which is able to bind HCl, this in effect can retard the thermal degradation of PPVC<sup>13,14</sup>. However, of those PPVC samples mentioned above, the PPVC that was stabilised with white lead (PVC3) observed to degrade slower compared to others.

### *The influence of concentration of stabiliser on the thermal stability of PPVC*

The thermal stability of prepared PPVC compounds are shown in Table 5. As it can be seen from Table 5, by increasing amount of stabiliser of PPVC, thermal stability of PPVC is improved. Thus, colour formation during degradation of PPVC can be suppressed by the amount of stabiliser added to the polymer [13]. For example, the polymer which contains no stabiliser in its composition degraded very rapidly in a matter of just a few minutes. Whereas the polymer which contains higher amount of stabiliser (PVC5) has better thermo-stability so has degraded very slowly and its colour changed to brown not black for a given time of 180 mins. Hence, the order of thermal stability of polymers are as follows:



Table 4 Thermal stability of PPVC samples.

Sample	PVC1	PVC2	PVC3	PVC4	PVC5	PVC6	PVC7	PVC8
Time (mins)								
1	Clear	Clear	White	Clear yellow	Clear yellow	Clear	Clear	Clear
5	Clear	Clear	White	Clear	Clear	Clear	Light yellow	Clear
10	Orange yellow	Yellow	Grey white	Yellow	Light yellow	Yellow brown	Yellow	Yellow
15	Red	Yellow brown	Grey brown	Black	Orange yellow	Red brown	Yellow	Black
30	Brown	Yellow brown	Grey brown	Black	Orange yellow	Red brown	Yellow	Black
60	Brown	Black	Grey Brown	Black	Black	Black	Black	Black
120	Black	Black	Brown	Black	Black	Black	Black	Black
180	Black	Black	Black	Black	Black	Black	Black	Black

Table 5 Thermal stability of prepared PPVC samples

Sample	PVC1	PVC2	PVC3	PVC4	PVC5
Time (mins)					
2	Transparent	No change	No change	No change	No change
10	Red brown	Yellow brown	Yellow straw	Straw	Light straw
20	Dark brown	Toffee brown	Orange yellow	Straw	Light straw
30	Black	Mid-brown	Tan	Orange yellow	Straw
40	Black	Darker brown	Light brown	Orange yellow	Straw
80	Black	Chocolate brown	Dark Brown	Light brown	Dark straw
120	Black	Black	Dark Brown	Brown	Light brown
180	Black	Black	Dark Brown	Brown	Light brown

## Conclusions

From this experiment the need of a heat stabiliser can be derived from the explanation of the thermal damage of PPVC as follows:

1. A heat stabiliser should be capable of preventing the dehydrochlorisation reaction or

at least should be able to retard this reaction.

2. The stabiliser should shorten polyene sequences and destroy carbanium salts formation.
3. From experimental observation it was possible to conclude that PPVC stabilised

with white lead observed to degrade slower compared with others.

4. Having examined the discolouration of PPVC, it can be stated that addition of stabiliser and the amount of addition can prevent or minimise the effects of thermo-oxidation of PPVC polymers.

### References

1. Farhat, M.; Siddiqui, MN.; Journal of Analytical and Applied Pyrolysis; 74: 282; 2005.
2. Yarahmadi, N.; Jakubowicz, I.; Hjertberg, T.; Polymer Degradation and Stability; 82: 59; 2003.
3. Mikiya, I.; Kazukiyo, N.; Polymer Degradation and Stability; 92: 1692; 2007.
4. Mengeloglu, F; Karakus, K.; Sensors; 8: 500; 2008.
5. Wang, C.; Zhang, Y.; Polymer Test; 23: 299; 2004.
6. Bayer, G.; Polymer Advanced Technology; 19: 485; 2008.
7. Wang, D.; Wilkie, CA.; Journal of Vinyl Additive Technology; 8: 238; 2002.
8. Du, J.; Wang, D.; Wilkie, CA.; Wang, J.; Polymer Degradation and Stability; 79: 319; 2003.
9. Gong, F.; Feng, M.; Zhao, C.; Zhang, S.; Yang, M.; Polymer Degradation and Stability; 84: 289; 2004.
10. Constache, MC.; Wang, D.; Heidercker, MJ.; Manias, E.; Wilkie, CA.; Polymer Advanced Technology; 17: 272; 2006.
11. Constache, MC.; Heidercker, MJ.; Manias, E.; Gupta, RK.; Wilkie, CA.; Polymer Degradation and Stability; 72: 1753; 2007.
12. Liu, J.; Chen, G.; Yang, J.; Polymer; 49: 3912; 2008.
13. Sombatsompop, N.; Sungsanit, K.; Thongpin, C.; Polymer Engineering Science; 44: 487; 2004.
14. Hjertberg, T.; Sorvik, EM.; Thermal Degradation of PVC, in Degradation and Stabilisation of PVC ed. by Owen, ED; Elsevier Applied Science: New York; 1984.

## اثر نوع و غلظت پایدار کننده ها بر روی پایداری گرمایی پلی (وینیل کلرید) نرم

\*

دانشکده شیمی، دانشگاه آزاد اسلامی واحد تهران شمال ایران.

دریافت: بهمن 1389 : پذیرش: تیر 1390

**چکیده:** اثر پایدار کننده های متعدد و مقدار آن در پایداری گرمایی پلی (وینیل کلرید) نرم مورد بررسی قرار گرفت. نتایج تجربی نشان داد که نوع پایدار کننده ها اثر قابل ملاحظه ای بر پایداری گرمایی پلی (وینیل کلرید) نرم دارد. پس از تشخیص ترتیب توانایی پایداری گرمایی پایدار کننده ها ی افزوده شده به پلیمر، آزمایش ها نشان دادند که افزودن پایدار کننده ها و مقدار آن می تواند مقاومت گرمایی پلی (وینیل کلرید) نرم را افزایش دهد.

**واژه های کلیدی:** پایداری گرمایی ، پلی (وینیل کلرید)، تخریب گرمایی PVC، تجزیه PVC.