

## STABILIZATION OF POLY (VINYL CHLORIDE) IN THE PRESENCE OF ACID RED4, MORIN AND METHYL BLUE

RIZWAN HUSSAIN\*  
FAZAL MAHMOOD\*

*SUMMARY: The stability of poly (vinyl chloride) when mixed with Acid Red4, morin and methyl blue in different concentrations has been studied by employing differential thermal analysis. It is evident from the results that the presence of these dyes imparts a stabilizing effect on the polymer. The stabilization effect has been reported as heat of reaction for the main decomposition process of PVC.*

*Key Words : Dyes, stability, PVC, heat of reaction, DTA.*

### INTRODUCTION

The worldwide production of poly (vinyl chloride)-PVC constitutes 30% of the total production of thermoplastics (1). The presence of chlorine in PVC hinders burning through formation of hydrogen chloride as it is incombustible (prevents access of oxygen to the combustion zone) and reacts with free radicals (acting as terminator for the combustion propagation reactions (2). Thus by virtue of its chemical nature PVC achieves the kind of flame retardancy which has to be induced in other plastics. Various inorganic compounds including antimony oxide (2), zinc borate (3), alumina trihydrate(4), molybdenum oxide (1), compounds of lead (1) etc have been used as fire stabilizers for PVC.

This paper aims at exploring the effects of cationic dyes namely Acid Red4, morin and methyl blue on the

thermal stability of PVC. The thermal degradation of these samples has been studied by employing differential thermal analysis.

### MATERIALS AND METHODS

#### Chemicals

Poly (vinyl chloride) : having molecular weight  $100000 \pm 200$ , particle size 100% passes through B.S. 60 mesh 74% passes 200 mesh. It was supplied by Formosa Plastics Corp., USA (cat. No. F-622) and used as such.

Acid Red4: Aldrich Cat. No. 21074-9.

Morin hydrate : Aldrich Cat. No. M8763-0.

Methyl Blue : Aldrich Cat. No. 86102-2.

#### Preparation of samples

PVC and the respective dyes were physically homogenized in a mechanical tumbler. The samples prepared had dye concentrations of 1.5 to 9.0% w/w with respect to the polymer.

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\* P.O. Box 1356, PINSTECH, Islamabad, Pakistan.

Figure 1: DTA curves of A=PVC; B=Acid Red4; C=Morin; D=Methyl Blue.

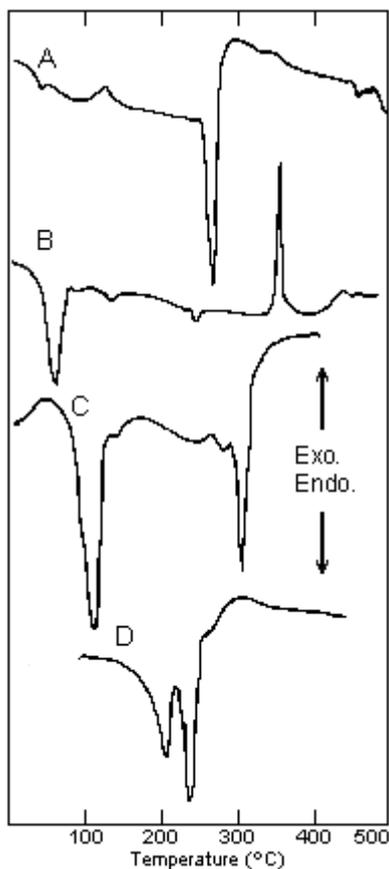
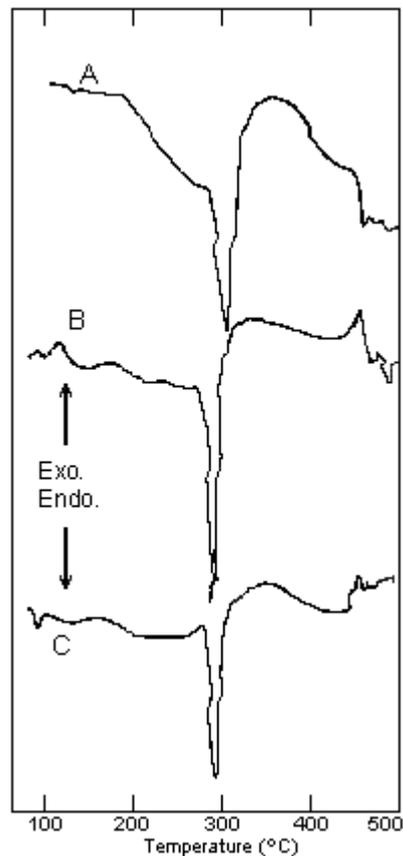


Figure 2: DTA curves of AR-PVC. A=7.5% AR-PVC; B=5.0% AR-PVC; C=2.5% AR-PVC.



#### Differential thermal analysis

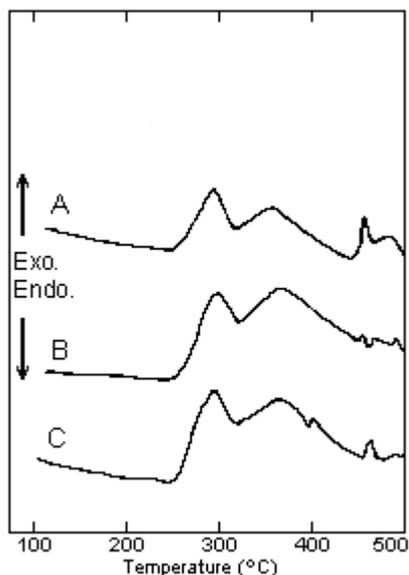
A DT 30 Thermal analyzer manufactured by Shimadzu (Japan) was used to record the DTA curves of 10-15 mg samples in dynamic nitrogen atmosphere with a gas flow rate of 20 ml/min. A linear heating rate of 10°C/min was maintained from ambient temperature to 500°C.  $\alpha$ -Alumina (Shimadzu) was used as reference material. The instrument was calibrated by recording the DTA curves of indium and zinc metals (5).

#### RESULTS AND DISCUSSION

The DTA curve of PVC reproduced in Figure 1 has a small endotherm at 70°C pointing towards the melting of the polymer. Crystalline transitions can be envisaged from small exotherm at 155°C. The main endothermic peak at 290°C represents the dehydrochlorination of PVC. It is followed by small peaks near 460°C.

The DTA curve of Acid Red4 (Figure 1) has a well defined endotherm in the temperature region of 55 to 105°C with a maximum at 95°C. This peak results from the dehydration of the dye. The large endotherm is followed by two very small endotherms appearing at 155°C and 265°C. The sharp exothermic peak at 360°C is indicative of decomposition of acid red dye. The DTA curves of polymer samples blended with different concentrations of Acid Red4 (Figure 2) show an interesting pattern. The DTA curves for PVC containing 2.5% and 5% of the dye have the main dehydrochlorination process occurring at 300°C. However in the DTA curves for 7.5% AR-PVC main endotherm appears at 315°C.

Figure 3: DTA curves of M-PVC. A=2.5% M-PVC; B=5.0% M-PVC; C=7.5% M-PVC.



The DTA curve of morin reproduced in Figure 1 has a sharp endotherm with a maximum at 145°C which is a consequence of the removal of water/solvent molecules from the dye. The second endotherm appearing at 330°C is indicative of the decomposition of the dye upon melting (6). The samples of PVC mixed with different concentrations of the dye (Figure 3) have a broad initial endotherm appearing at approximately 240°C. The second endotherm can be assigned to the decomposition of PVC. The temperature for maximum volatilization shifts from 305°C to 310°C as the dye concentration is increased. There is a shift of  $\pm 20^\circ\text{C}$  in this endotherm when compared to that of pure PVC (Figure 1).

The DTA curve of methyl blue (MB) has two well defined endotherms with maximal at 228°C and 265°C respectively. It is evident from the DTA curves in Figure 4 that the stability of PVC containing various percentages of methyl blue enhances as the amount of dye in the blend increases. The main endothermic peak representing the dehydrochlorination of PVC appearing at 290°C in the virgin polymer is shifted in the tempera-

ture region of 315°C to 330°C when methyl blue is blended with it.

The heat of reaction for the main endothermic peak representing the dehydrochlorination of PVC was determined to quantify the effect of dyes on the polymer. The heat of reaction ( $\Delta H$ ) were calculated using the relationship (5) :

$$\Delta H_x = A_x/A_s \cdot m_s/m_x \cdot \Delta H_s$$

where, A=area of the peak; m = mass of the sample taken for DTA;  $\Delta H$  = heat of reaction ; s = reference material and x = sample.

The areas of the peaks were determined by the method described by Hodany (7). The results are presented in Table 1. The  $\Delta H$  for the dehydrochlorination of PVC sample is 39.4 J/g which is increased when the polymer is mixed with the dyes. The results presented in Table 1 depict that the M-PVC is the least stable.

Figure 4: DTA curves of MB-PVC. A=2.5% MB-PVC; B=5.0% MB-PVC; C=7.5% MB-PVC.

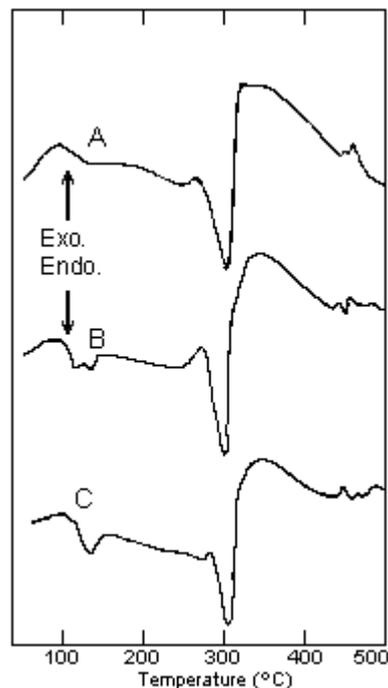
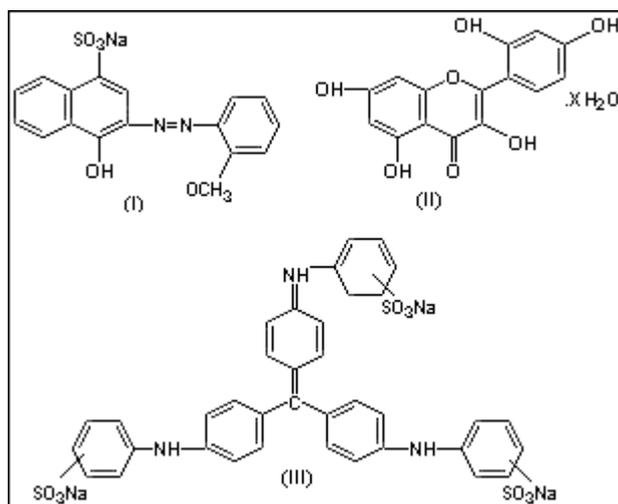


Figure 5: I=Acid Red4; II=Morin; III= Methyl Blue.



Whereas maximum stability is evident in AR-PVC samples. This is also evident from the DTA curves of these samples. It can be explained on the basis of the electron withdrawing groups (8) present in the dyes (Figure 5). MB contains two electron withdrawing groups namely  $\text{NH}_3^+$  and  $\text{SO}_3\text{Na}^+$  making it more prone for

bonding with. C-Cl of PC especially the amine group has greater tendency for attracting the electrons. AR contains  $\text{SO}_3\text{Na}^+$  group along with two electron donating groups i.e., OH and  $-\text{OCH}_3$  attached to the rings which decrease the electron withdrawing effect of  $\text{SO}_3$  group. Thus the possibility of its reaction with the alkyl halide (PVC) is lesser than that of MB. The dye structure of morin contains five OH (electron releasing) groups attached to the rings which drastically reduced the possibility of bonding between the polymer and the dye molecules when compared to that for MB and AR.

In light of the preceding discussion it can be concluded that the stability of PVC when mixed with dyes is as follows :



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Table 1: The heat of reactions for the polymer samples.

w/w% of dye in PVC	Heat of reaction (J/g)
PVC	39.4
2.5 % AR	52.1
5.0 % AR	52.3
7.5 % AR	62.6
2.5 % M	45.2
5.0 % M	45.2
7.5 % M	63.5
2.5 % MB	159.2
5.0 % MB	145.9
7.5 % MB	134.7

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Correspondence:

Rizwan Hussain

P.O. Box 1356,

PINSTECH, Islamabad,

PAKISTAN.