



IAU-ARAK

Effect of some additives on degradation of poly (vinyl chloride- co- vinyl

Mohamamd Taghi Taghizadeh *, Abbas Agha Bozorgi

Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

Received 20 January 2010; received in revised form 10 May 2010; accepted 15 May 2010

Abstract

The thermal decomposition of 86 % vinyl chloride 14 % vinyl acetate copolymer was studied by the conductometry technique in the presence of nitrogen. The kinetics of stability and thermal degradation of vinyl chloride- co- vinyl acetate (PVC- co- PVAc) copolymer with copper, copper oxide and tricalcium dicitrate (st) were investigated at various temperatures (150-180 °C) in solution. The rate coefficients for the degradation of the copolymer were determined. The energies of activation, determined from the temperature dependence of the rate coefficients for copolymer alone was 63.536 kJ mol⁻¹ and in the presence of copper, copper oxide and tricalcium dicitrate were 44.224, 55.594 and 110.332 KJ mol⁻¹, respectively. The results show that thermal stability was increased in the presence of tricalcium dicitrate, but its thermal stability was decreased in the presence of copper and copper oxide.

Keywords: Thermal degradation; Copolymers; Vinyl chloride-co-Vinyl acetate; Additive; Activation energies.

1. Introduction

PVC is commonly used as a thermoplastic because of its wide variability of properties allowing its application in rigid and soft products [1]. However, PVC has very poor thermal, thermo oxidative and light stability. The major chain degradation occurs by the elimination of HCl and simultaneous formation of conjugated double bond. Numerous stabilizers have been developed to neutralize the released HCl and prohibit further degradation by preventive reactions [2]. The kinetics and thermal degradation of PVC has been widely investigated over a range of temperatures. The thermal degradation has been shown to occur in two distinct stages by most investigators [3]. At lower temperatures (< 350 °C), the degradation proceeds almost exclusively by dehydrochlorination, where in chlorine radicals are liberated, and leading to a formation of the polymer chain. During dehydrochlorination, large amounts of HCl and small amounts of aromatics such as benzene, naphthalene, and anthracene are liberated. The liberated hydrogen chloride during the first stage is reported to auto catalyze the dehydrochlorination of polymer [4].

In the second stage, around 445 °C the backbone of the polymer chain undergoes structural disintegration, leading to the evolution of various aromatic compounds such as benzene, toluene, and other alkyl aromatics and finally yielding a residual char [5]. In the case of poly (vinyl acetate) (PVAc), the addition of poly (vinyl chloride) (PVC) affected the thermal stability of

*Corresponding author. Tel.: +98 411 3393137, fax: +98 411 3340191.
E-mail address: mtaghizadeh@tabrizu.ac.ir (M.T. Taghizadeh)

PVAc dramatically [6]. It has been reported that residual chlorine as high as 5% can be found in the PVC matrix after the dehydrochlorination stage [7]. Copolymer of vinyl chloride (VC) and vinyl acetate (VA) have achieved commercial importance and have been extensively used as fire extinguisher because of low moisture absorption and thermal expansion. It is also of considerable interest, however, to compare their degradation behavior with that of the homopolymers. Questions to which such a study might provide some answers include the following. Are the copolymers intermediate in stability between PVC and PVA; is there a maximum or minimum stability at any particular composition? Do the copolymers discolour in the same way as the homopolymers?

Although a copolymer often has superior physical properties to either of the related homopolymers, the thermal stability is often impaired. Lehrle and Robb [8] have shown that under the conditions of their experiments the main degradation products are acetic acid and hydrochloric acid and those they are produced in proportions corresponding to the proportion of the monomers in the copolymer. The pyrolytic stability of PVC- co- PVAc was investigated by Grassie et al. [9, 10] and it was concluded that introduction of PVAc reduces thermal stability of PVC and it becomes least stable at around 40 wt. % Poly (vinyl acetate) in the copolymer. The objective of the present study is 4- fold: (a) to study the thermal stability of (PVC- co- PVAc) copolymer; (b) to study the influence of the Cu and CuO on the thermal degradation of copolymer; (c) to study the influence of the Cu/St and CuO / St mixed on the thermal stability; (d) determination of the degradation rate coefficients, k , and the activation energy, E_a .

2. Experimental

2.1. Materials

Fine powders of PVC- co- PVAc (Sigma Aldrich. USA) contain vinyl chloride 86%, vinyl acetate 14 % (MW: 27000); tricalcium dicitrate from Fluka Company; copper, copper oxide, 1,2-dichloroethane (Purity 99 %) and methanol (Purity 99 %) were supplied from Merck Chemical Company, and they were used as received.

2.2. Sample preparation

The (PVC-co-PVAc) sample (0.2 g) was mixed thoroughly with an appropriate amount of additives. All samples formulations were prepared by mixing 100 parts copolymer, 1,2,3,4 parts of each sample: copper, copper oxide and thermal stabilizer in a mortar for each experiment and transferred into a degradation tube. The tube was connected to a source of nitrogen maintained at a flow rate of 180 ml/min. The degradation tube was then immersed in a thermostat oil bath controlled at 150, 160, 170, 180 °C [11, 12].

2.3. Degradation experiments

The volatile degradation products were swept into a water trap. Portions of the solution formed in 200 ml water were used for the estimation of acetic and hydrochloric acids. Evaluation of the stabilizing efficiency was carried out by measuring degradation rate using continuous conductometry determination of the evolved $\text{CH}_3\text{COOH}/\text{HCl}$ gas. Samples were collected at regular time intervals (5 min) for measuring conductivity. All data were performed on a Hanna HI 8819 Electrometer. The extent of degradation (conversion %) was calculated from the elimination of ratio $\text{CH}_3\text{COOH}/\text{HCl}$ evolved to the amount available in the copolymer [13].

2.4. UV- Visible absorption by degraded samples

Shimadzu 120-02 UV/Visible spectrophotometer was used in the analysis of degraded polymer samples in 1,2-dichloroethane solution for conjugated double bonds. The degraded copolymer samples dissolved readily in warm 1,2-dichloroethane.

2.5. IR Spectra were recorded by Fourier transform infrared

Spectrophotometer (FT-IR) using the FT-IR Shimadzu model 4300 Japan in the range 500-4000 cm^{-1} at 25 °C. All the samples were mixed with KBr for These analyses.

3. Results and discussion

3.1. The UV/Visible absorption spectra of copolymer samples degraded in N_2 at 180 °C for 120 min

The UV/Visible absorption spectra of copolymer samples degraded in N_2 are generally regarded as not providing accurate or reliable information on the level of instauration in the copolymer, however, such spectra can be useful in providing a basis for assessing the relative effectiveness of additives in stabilizing and non-stabilizing copolymer against degradation.

The absorption pattern indicates that longer conjugated bond systems are present in copolymer samples degraded in the presence of copper and copper oxide than in the copolymer samples degraded in presence of tricalcium dicitrate. It is known that each absorbance maximum in the spectra of degraded polymer corresponds to one polyene sequence with a given length. The combined effect of these reagents would reduce the amounts of HCl evolved leading to the formation of short polyene sequences absorbing in the ultra violet region as shown in Fig. 1 (cases b, e, f). The color has been ascribed to the formation of polyene sequences long enough to absorb in the visible region (cases c, d). Hence the remarkable absence of initial coloration of the polymer sheets stabilized with a mixture of tricalcium dicitrate with copper and copper oxide is clue to the formation of short polyene sequence during the induction period. Therefore, tricalcium dicitrate exerts a stabilizing effect on the thermal degradation and copper and copper oxide exerts an accelerating effect on the thermal degradation.

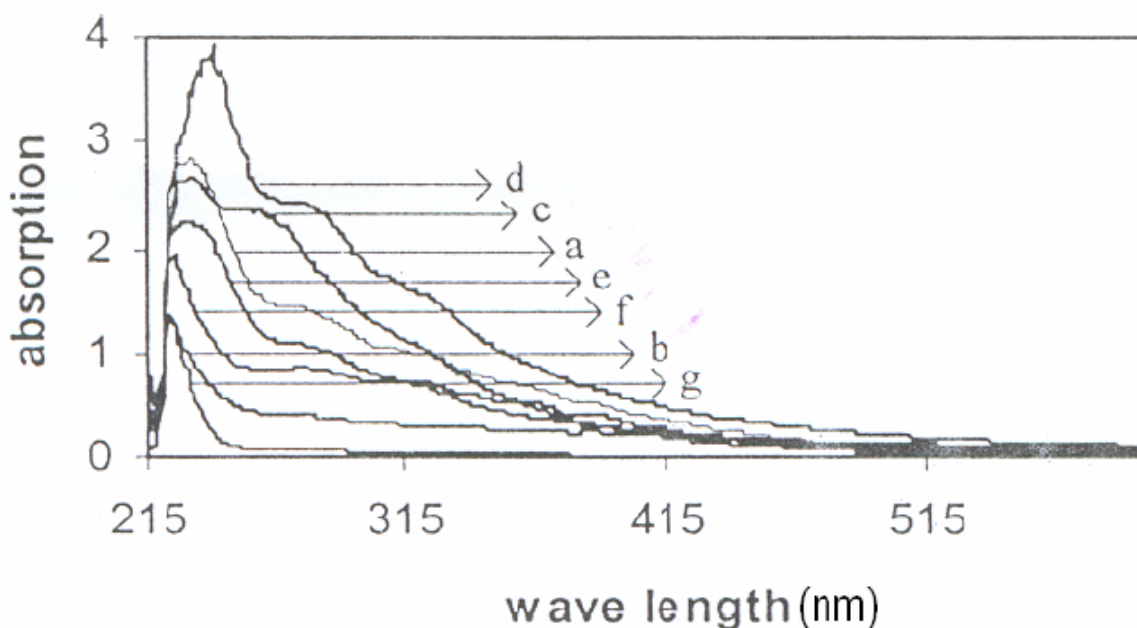


Fig. 1. UV-Visible spectra of (PVC- co- PVAC) copolymer thermally degraded in N_2 at 180 °C for 120 min, with respects of 100:1, 100:1:1 (a) pure Cop.; (b) Cop/ St; (c) Cop./ CuO; (d) Cop./ Cu; (e) Cop./ St/CuO; (f) Cop./ St/Cu; (g) Cop. initial.

3.2. FT-IR spectra of degraded copolymer samples

The FT-IR spectrum of initial copolymer and degraded copolymer in the presence of additives in N_2 at $180\text{ }^\circ\text{C}$ for 120 min is shown in Fig. 2. In this study attention was focused on the range in the absorption pattern in six main regions: (a) stretching vibration of the O-H group between 3436 and 3455 cm^{-1} ; (b) Stretching vibration of the C=O at about 1740 cm^{-1} ; (c) Stretching vibration of the C=C at about 1638 cm^{-1} ; (d) Stretching vibration of the C-O at about 1237 cm^{-1} ; (e) Stretching vibration of the C-H at about 1433 cm^{-1} ; (f) Stretching vibration of the COO^- group between 1500 - 1600 cm^{-1} .

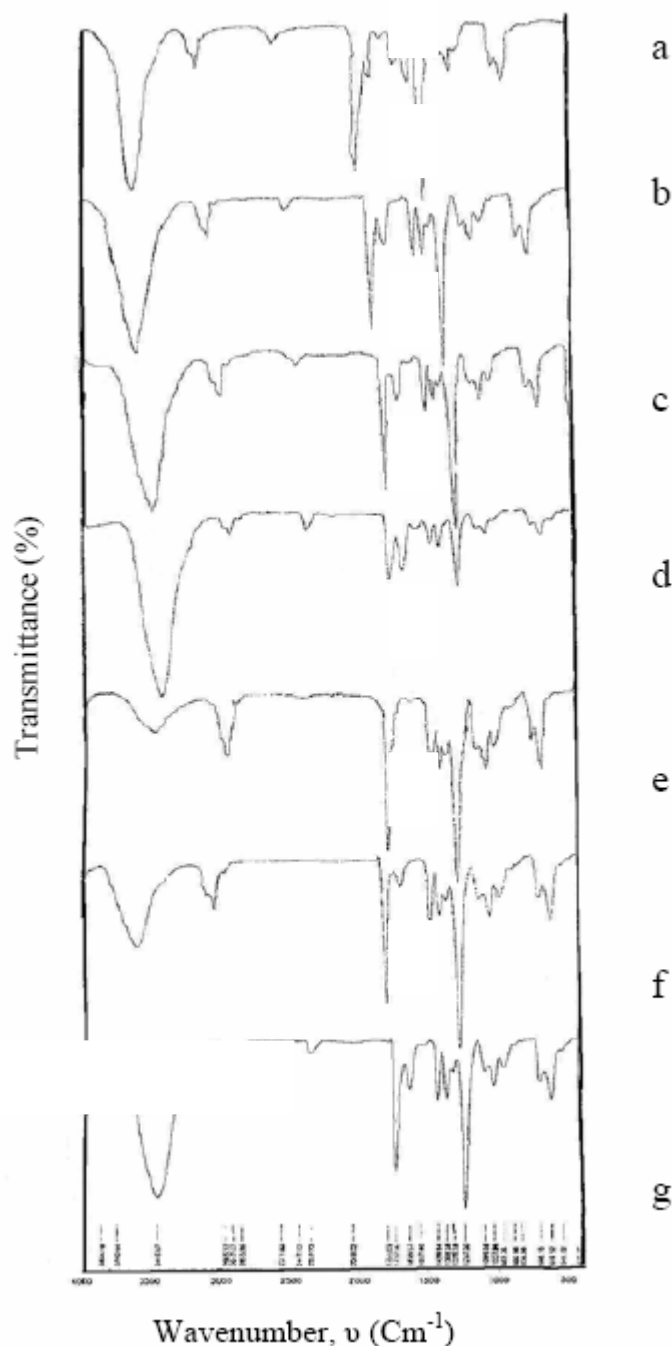


Fig. 2. FT- IR spectrum of (PVC- Co- PVAC) copolymer initial and degraded at $180\text{ }^\circ\text{C}$ in N_2 for 120 min with respect copolymer to additive (100/1) in the presence of materials: (a) initial; (b) degraded; (c) Cu; (d) CuO; (e) St; (f) St/CuO; (g) St/Cu.

The spectral range $1500\text{-}1600\text{ cm}^{-1}$ contains absorption band of the anti-symmetric stretching vibration of the COO^- group. The FT-IR spectrum unstabilized copolymer degraded at $180\text{ }^\circ\text{C}$ for 120 min did not show absorption within this region. The absorption by $\text{C}=\text{O}$ group in the range $1690\text{-}1750\text{ cm}^{-1}$ is characteristic of absorption bands of esters, carboxylic acids and ketones. The spectral range $1600\text{-}1650\text{ cm}^{-1}$ contains absorption band of the anti-symmetric stretching vibration of the $>\text{C}=\text{C}<$ group in conjugation and bonds at 3436 cm^{-1} attributed to O-H are strong but in the presence of St are rather weak. In the presence of Cu and CuO bands at 1433 cm^{-1} and 1237 cm^{-1} attributed to C-H and C-O, respectively, are very weak. The FT-IR studies on the interaction of copolymer with tricalcium dicitrate show that this material stabilizes copolymer against thermal degradation by replacing labile chlorine atoms in copolymer.

3.3. Effect of amount of materials

3.3.1. Degradation of PVC with different amount in the absence of stabilizer

Data of degradation (conversion %) of copolymer with different amount in the absence of stabilizer are shown in Fig. 3. The obtained rates of degradation of copolymer were (0.0216, 0.0398, 0.0650 and 0.0834) for the amount of 0.2, 0.3, 0.4 and 0.5 g copolymer, respectively. It is observed that with increasing the amount of copolymer, the rate of elimination of $\text{CH}_3\text{COOH}/\text{HCl}$ increase.

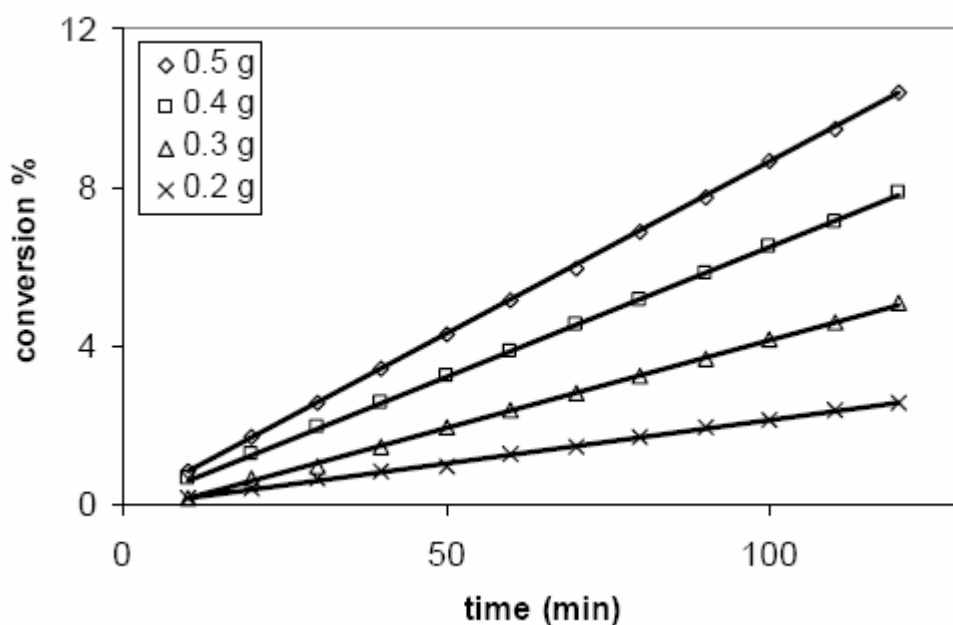


Fig. 3. Conversion (%) of copolymer at $180\text{ }^\circ\text{C}$ for various amounts of copolymer in the absence of additive.

3.3.2. Effect of the stabilizer amount tricalcium dicitrate (St) on the efficiency of stabilization

Data of elimination of $\text{CH}_3\text{COOH}/\text{HCl}$ of copolymer (0.2 g) stabilized by tricalcium dicitrate in different amounts (0.002-0.008g) are shown in Fig. 4. They indicate that the rate of elimination of $\text{CH}_3\text{COOH}/\text{HCl}$ decrease with the increasing of $[\text{St}]/[\text{poly}(\text{VC-co-VAc})]$ ratio.

3.3.3. Effects of the Cu and CuO amounts on the degradation of copolymer

Data of elimination of $\text{CH}_3\text{COOH}/\text{HCl}$ of copolymer (0.2 g) in the presence of Cu and CuO amounts in different amounts (0.002-0.008 g) are shown in Figs. 5, 6. They indicate that the rate of degradation increase with the increasing of $[\text{CuO}]/[\text{poly}(\text{VC-co-VAc})]$ and $[\text{Cu}]/[\text{poly}(\text{VC-co-VAc})]$.

co-VAc)] ratios. The data for non-stabilized blank sample and those of the samples stabilized and unstabilized with various compounds are also given for comparison in Fig. 7.

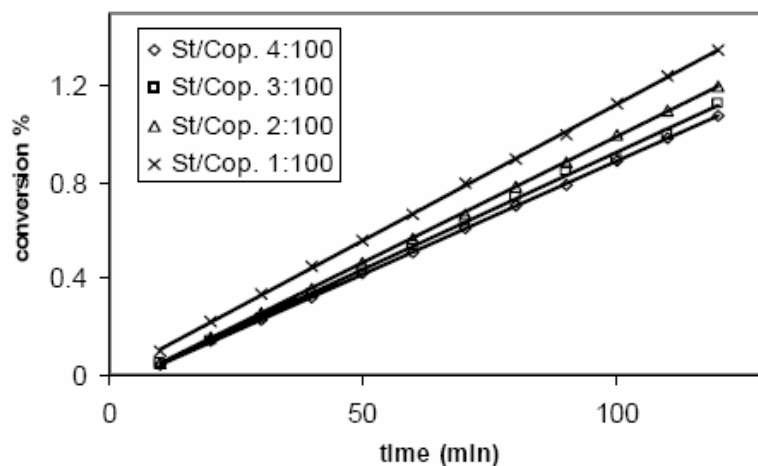


Fig. 4. Conversion (%) of copolymer at 180 °C with 0.2 g of copolymer for various amounts of St (g).

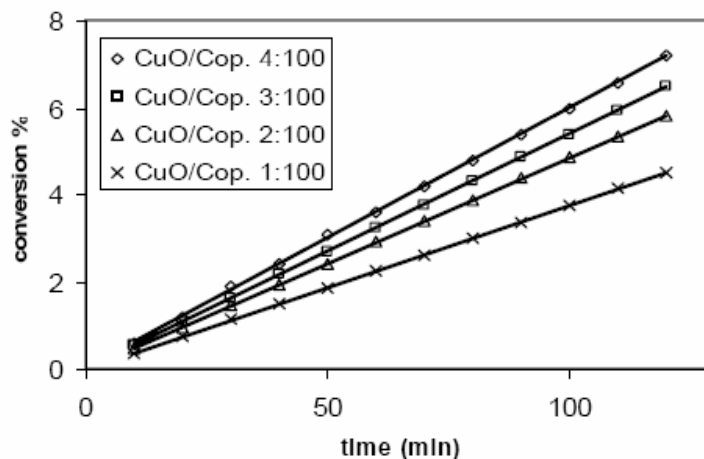


Fig. 5. Conversion (%) of copolymer at 180 °C with 0.2 g of copolymer for various amounts of Cu (g).

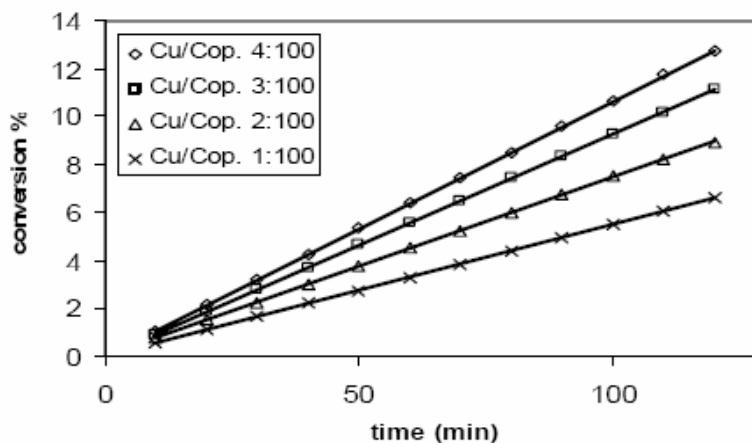


Fig. 6. Conversion (%) of copolymer at 180 °C with 0.2 g of copolymer for various amounts of CuO (g).

It can be seen from this Figure that the investigated tricalcium dicitrate (st) exhibits a greater stabilizing efficiency compared to that of copolymer blank, but Cu and CuO are able to destabilize the polymer to a lesser extent compared to that copolymer blank.

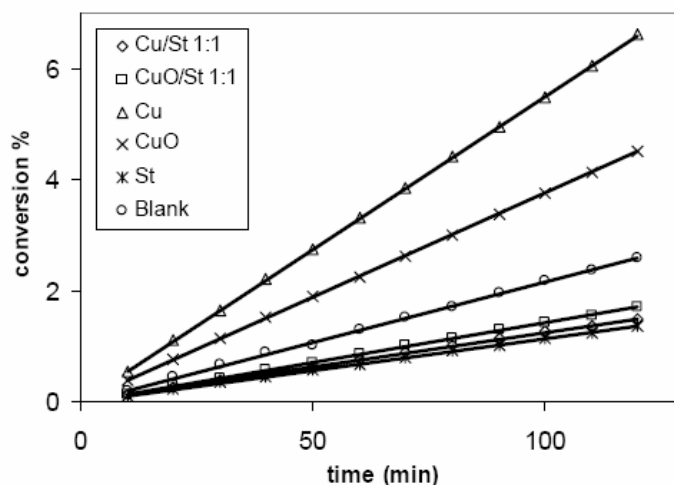


Fig. 7. Conversion (%) of copolymer in the presence of additives at 180 °C with 0.2 g of copolymer and 0.002 g of additives.

The greater stabilizing efficiency are illustrated not only by lower rates of dehydrochlorination during the subsequent stages of degradation reaction, but also by the longer induction periods (T_s) during which no detectable amounts of hydrogen chloride gas are liberated (Table 1).

Table 1

Dehydrochlorination data at 180 °C with 0.2 g copolymer containing 0.002 g of additives.

Additive system	T_s (min)	$R \times 10^2$ (conversion %/min)
Non	5.5	2.16
St	9	1.12
CuO	0.9	3.76
Cu	0.5	5.55
St + CuO	4	1.23
St + Cu	0.4	1.42

The introduction of OH and CO₂H group and other materials of the stabilizer resulted in an appreciable improvement in both T_s and the rate of dehydrochlorination. The results show that the St is a stabilizing compound, but Cu and CuO are unstabilizing compound on the copolymer.

3.3.4. Stabilizing of thermally degraded copolymer using mixed stabilizer

The results of degradation of thermally degraded copolymer at 180 °C in N₂ in the presence of the mixed stabilizer are shown in the Figs. 8 and 9. The results clearly reveal the greater stabilizing efficiency of these mixed stabilizers.

3.4. Temperature effect on the rate of degradation of copolymer

The extents of degradation of copolymer in the absence of stabilizer and in the presence of tricalcium dicitrate at various temperatures are shown in Figs. 10 and 11. It can be seen that the extent of degradation at temperatures between 150-180 °C is linear.

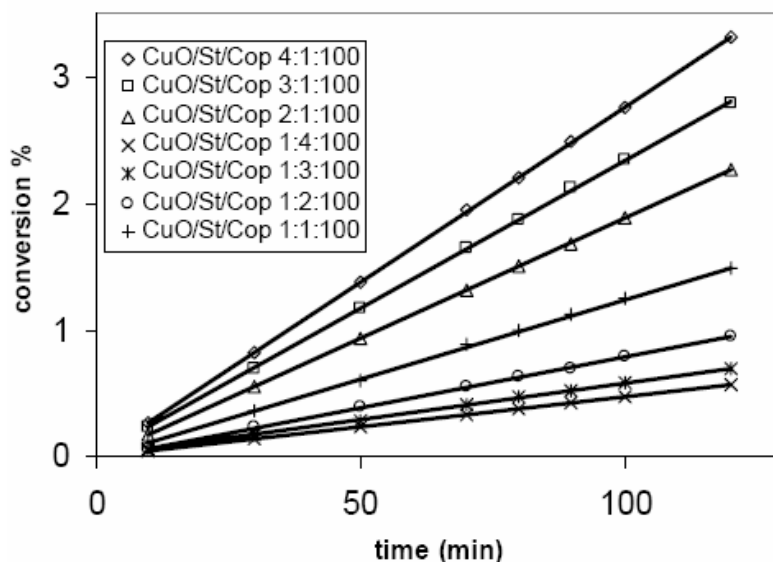


Fig. 8. Conversion (%) of copolymer at 180 °C with 0.2 g of copolymer for various amounts of mixed stabilizer (CuO/St).

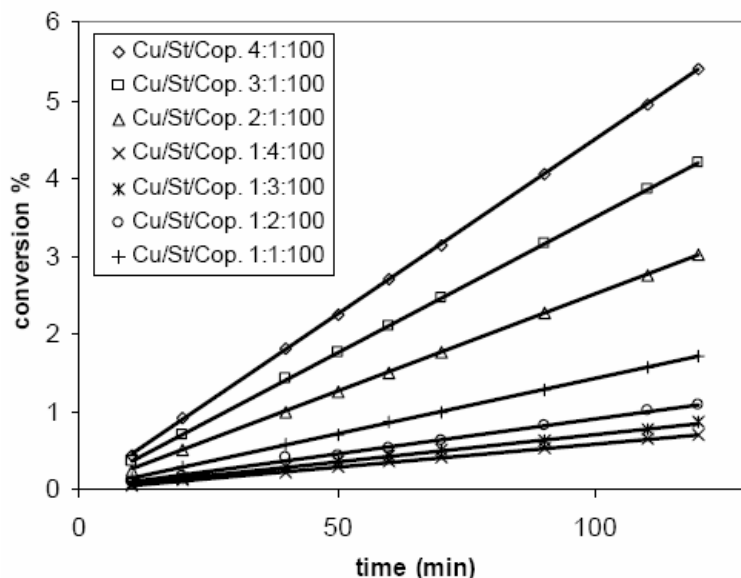


Fig. 9. Conversion (%) of copolymer at 180 °C with 0.2 g of copolymer for various amounts of mixed stabilizer (Cu/St).

The values of the required time for dehydrochlorination to attain 1% conversion, t_{DH} , for all additives are shown in Table 2. The results in table 2 show that tricalcium dicitrate exerts stabilizing effect on the degradation of copolymer.

The values of t_{DH} ranged from 50 min at 180 °C to 280 min at 150 °C, compared with the values obtained for degradation in the absence of stabilizer, these results indicate that this stabilizer has a deleterious effect on the stability of copolymer. It can be seen from Fig. 2 that, the copper and copper oxide, has an accelerating effect on the degradation of copolymer. From Table 2, it seems that tricalcium dicitrate is more effective on the stability of copolymer. Therefore it would be expected that the stabilizing effect of this compound on the degradation of copolymer should increase with increase in carboxylic group or alcohol group [14]. The results in Table 2 are consistent with this suggestion.

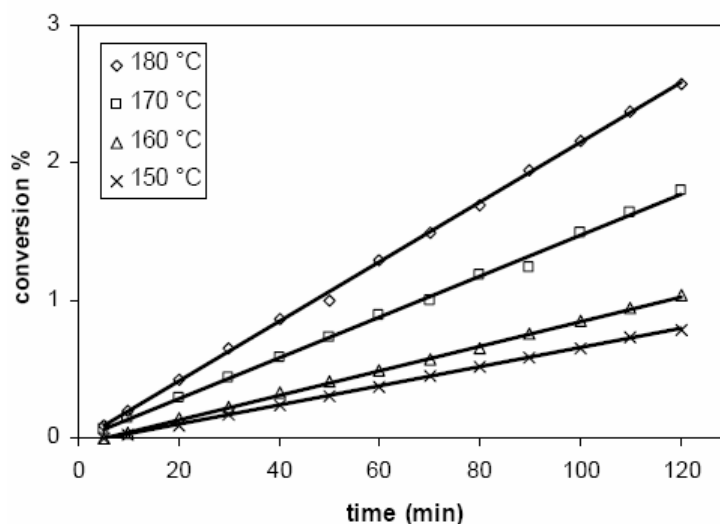


Fig. 10. Conversion (%) of copolymer in the absence of stabilizer at different temperature with 0.2 g of copolymer.

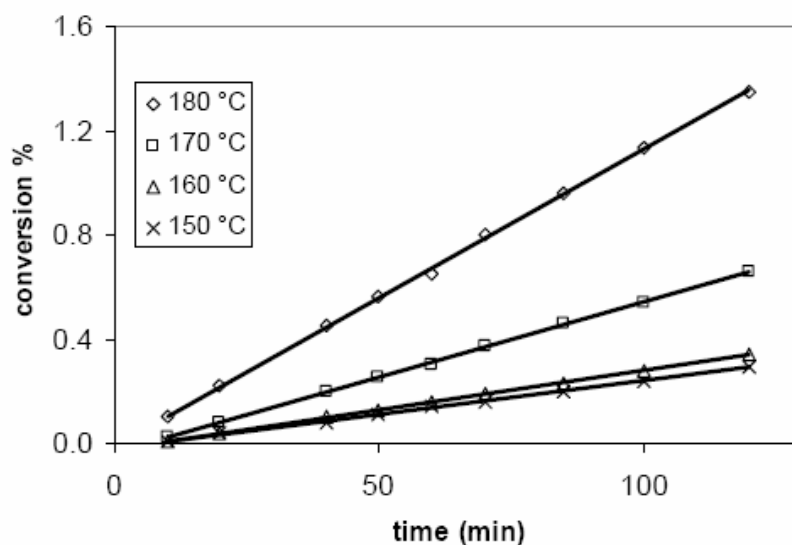


Fig. 11. Conversion (%) of copolymer in the presence of 0.002 g tricalcium dicitrate at different temperature with 0.2 g of copolymer.

Table 2

The values of t_{DH} in the presence and absence of additives with 0.2 g copolymer and 0.002 g additives.

Temperature (°C)	t_{DH} / min					
	Tricalcium dicitrate	Copper oxide	copper	Copper oxide- tricalcium dicitrate	Copper. tricalcium dicitrate	Non
150	280	87	55	260	192	175
160	260	64	33	240	168	120
170	180	41	28	160	112	70
180	90	32	18	80	70	50

3.5. Kinetics of degradation of copolymer

3.5.1. Determination of reaction order with respect to copolymer in the absence of stabilizer

Results of degradation of copolymer with various amounts of copolymer in the absence of additives are given in Table 3 and depicted in Fig. 3. The results indicate that the rate of elimination of CH₃COOH/HCl increases with the increasing of the amount of copolymer. In these conditions the rate equation is as follows:

$$R = Kw_{cop}^{\alpha} \quad (1)$$

The plot of ln (R) vs. ln (w_{cop}) is linear and presented in Fig. 12. The slope of the line is 0.98 nearly equal to unit.

Table 3

Effect of various amount of copolymer in the absence of additives on the rate of hydrochlorination of copolymer at 180 °C.

Copolymer (g)	R×10 ² (conversion %/min)
0.2	2.16
0.3	3.98
0.4	6.50
0.5	8.34

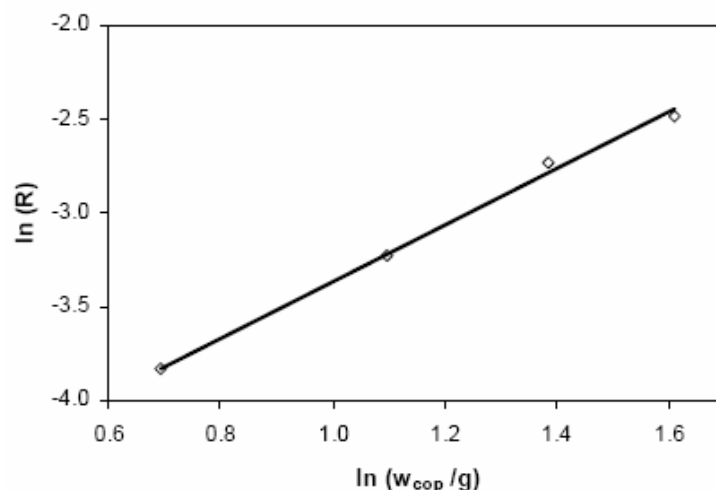


Fig. 12. ln (R) vs. ln (w_{cop}) in the absence of additive at 180 °C.

3.5.2. Determination of reaction order with respect to additive at constant amount of copolymer

The rate of degradation depends on the amount of additive and copolymer as following:

$$R = Kw_{cop}^{\alpha} \cdot w_{add}^{\beta} \quad (2)$$

$$R = K' w_{add}^{\beta} \quad (3)$$

The plot of ln (R) vs. ln (w_{add}) is linear and for additive is plotted in Fig. 13. The slope of the lines gives the orders with respect of additive. Experimental values of degradation for all additives are given in Table 4 and depicted in Figs. 4, 5, 6. From the data of Table 4 the reaction order with respect to tricalcium dicitrate, copper oxide and copper were determined -0.15 , 0.37 and 0.48, respectively. These results show that tricalcium dicitrate has negative order, therefore, it exhibited a stabilizing efficiency but two the others have positive orders, and accelerate the degradation of copolymer.

Table 4

Effect of additives amount on the rate of degradation of copolymer at 180 °C with 0.2 g copolymer.

W_{add}/g	$R \times 10^2$ (conversion %/min)		
	St	CuO	Cu
0.002	1.12	3.76	5.55
0.004	0.95	4.85	7.50
0.006	0.83	5.40	9.27
0.008	0.77	6.00	10.68

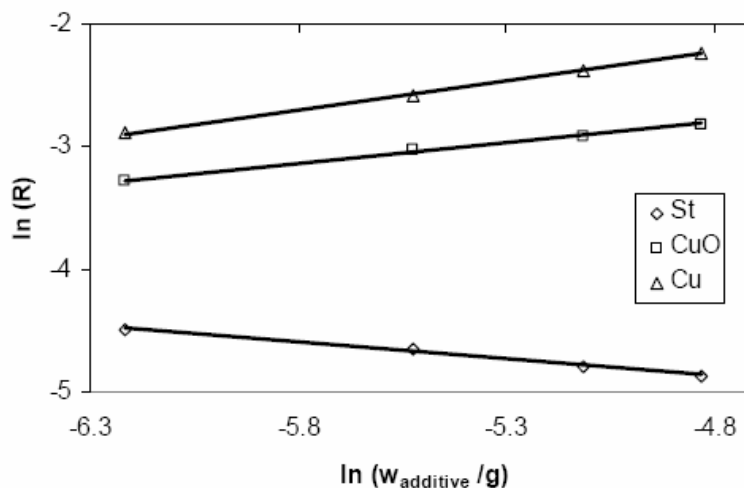


Fig. 13. $\ln(R)$ vs. $\ln(w_{\text{add}})$ at 180_ °C.

3.5.3. Determination of reaction order with respect of mixed stabilizer at constant amount of copolymer

Results of degradation of copolymer with various amounts of additives at constant amount of copolymer are given in Table 5 and depicted in Figs. 8, 9. The results indicate that the rate of elimination of $\text{CH}_3\text{COOH}/\text{HCl}$ increases with increase in amount of stabilizer. In these conditions the rate equations are as follows:

$$R = K w_{\text{cop}}^{\alpha} \cdot w_{\text{st}}^{\beta} \cdot w_{\text{CuO}}^{\gamma} \quad (4)$$

$$R = K w_{\text{cop}}^{\alpha} \cdot w_{\text{st}}^{\beta} \cdot w_{\text{Cu}}^{\gamma} \quad (5)$$

From equation (4-3) at constant amounts of copolymer and stabilizer, the plot of $\ln(R)$ vs. $\ln(w_{\text{CuO}})$ is linear and plotted in Fig. 14. The slope of the line is 0.83, which suggests that the order of the reaction with respect to copper oxide is 0.83. From same equation at constant amounts of copolymer and copper oxide, the plot of $\ln(R)$ vs. $\ln(w_{\text{st}})$ is linear and plotted in Fig. 14.

Table 5

Effect of mixed additive amount on the rate of dehydrochlorination of copolymer at 180 °C with 0.2 g copolymer.

w/g	$R \times 10^2$ (conversion %/min)	
	St/Cu	St/CuO
0.002/0.002	1.23	1.42
0.004/0.002	0.78	0.88
0.006/0.002	0.58	0.70
0.008/0.002	0.46	0.58
0.002/0.004	1.87	2.52
0.002/0.006	2.33	3.50
0.002/0.008	2.95	4.45

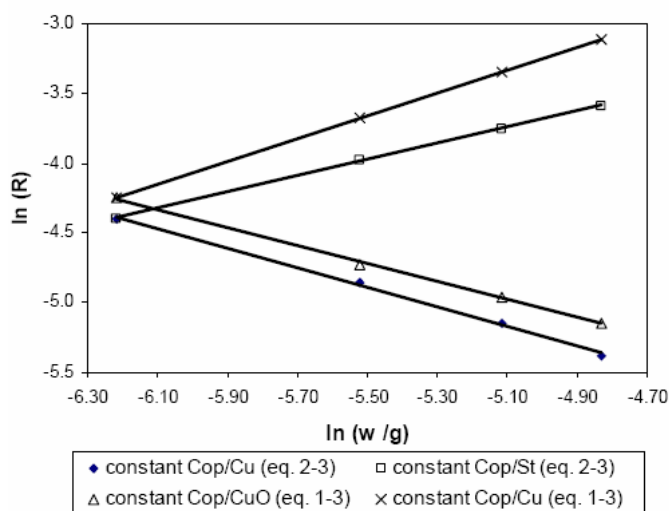


Fig. 14. $\ln(R)$ vs. $\ln(w_{\text{mixed additive}})$ at 180 °C.

The slope of the line is -0.64, which suggests that the order of the reaction with respect to tricalcium dicitrate is -0.64, which suggests that the order of the reaction with respect to stabilizer is -0.64. From equation (5-3) at constant amounts of copolymer and stabilizer, the plot of $\ln(R)$ vs. $\ln(w_{\text{Cu}})$ is shown in Fig. 12 and the slope of this line is 0.56, and from same equation at constant amounts of copolymer and copper, the plot of $\ln(R)$ vs. $\ln(w_{\text{st}})$ is shown in Fig. 14. The plot of this line is -0.70 which suggests that the orders of the reaction with respect to copper and stabilizer are 0.56 and -0.70, respectively.

Table 6

The effect of temperature on the rate coefficients of degradation of copolymer.

Compound	k (mol g ⁻¹ min ⁻¹)				E_a (KJ mol ⁻¹)
	Temperature (K)				
	423	433	443	453	
St/ Cop	0.0015	0.0027	0.0055	0.0110	110.352
CuO/Cop	0.0122	0.0157	0.0247	0.0361	55.594
Cu/ Cop	0.0182	0.0364	0.0482	0.0551	44.224
St/CuO/Cop	0.0017	0.0033	0.0061	0.0127	80.590
St/Cu/Cop	0.0037	0.0057	0.0093	0.0145	72.314
Cop	0.0067	0.0092	0.0152	0.0223	63.536

3.6. Calculation of activation energy

The degradation of copolymer was carried out at different temperature (Figs. 10 and 11). It was observed that the degradation of copolymer increases with increasing temperature. The degradation rate coefficients were obtained from the rate of degradation is listed in Table 6.

The variation of the rate coefficients with temperature follows Arrhenius behavior and is shown in Fig. 15. The activation energies, E_a , of the copolymers, obtained from the slopes of the lines in Fig. 15, are listed in Table 6. The results of Table 6 show that the variation of the rate coefficients and activation energies of degradation of copolymer. The degradation rate coefficients are lower and activation energies are higher at the presence of stabilizer, compared to the absence of stabilizer. This daringly indicates that the polymer with stabilizer is more stable than the polymer alone.

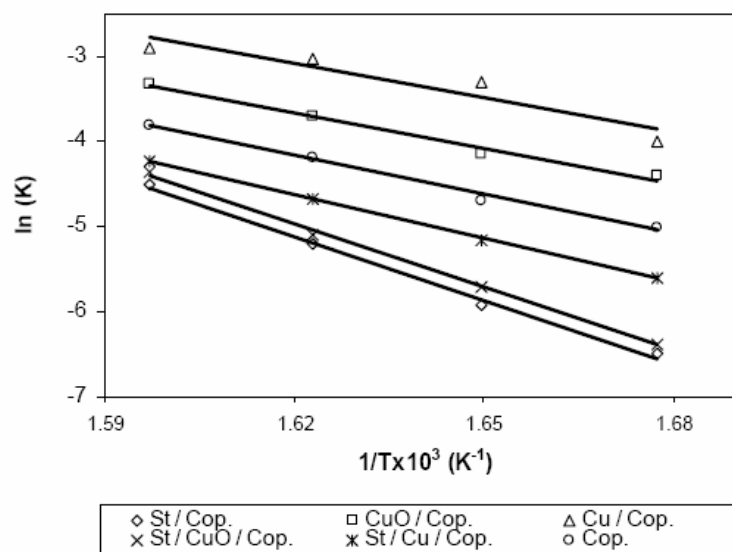


Fig. 15. Arrhenius plot of temperature dependence of the rate coefficient K for the compounds. Legend: compounds Cop-St (\diamond), Cop- CuO (\square), Cop- Cu (\triangle), Cop- St- CuO (\circ), Cop- St- Cu (\ast).

Experimental data indicate that the increased degradation of the copolymer in the presence of Cu and CuO is due to the formation of metal chlorides during the dehydrochlorination of copolymer. These results indicate the high reactivity of chlorine radical of hydrogen chloride formed leading to the destabilization of copolymer.

4. Conclusions

The results from this study have provided qualitative and quantitative data on the stabilizing effect tricalcium dicitrate on the thermal degradation of (PVC- co- PVAc) copolymer. The addition of Cu and CuO increases the degradation rate of copolymer and can be attributed to the Lewis acidity of the Cu and CuO. The catalytic activity of the St is higher than the Cu and CuO for the degradation of copolymer. It was observed that in the presence of Cu and CuO during the degradation of copolymer, indicating the formation of metal chlorides from Cu, CuO and liberated chlorine from copolymer degradation. The kinetics of thermal degradation of copolymer with additives was investigated at various temperatures in solution and thermo gravimetrically in the presence of nitrogen. Length of the induction period, T_s , the rate of dehydrochlorination (R_{DH}), and t_{DH} , were used to compare the stability efficiency. The degradation rate coefficients were determined. The energies of activation determined from the temperature dependence of the rate coefficients.

References

- [1] F.W. Biumeyer, Textbook of Polymer Science, John Wiley, 1994.
- [2] D. Braun, B. Bohringer, S. Kommerling, Appl. Macromol. Chem. Phys. 216 (1994) 1-19.
- [3] D.L. Gerrad, W.F. Maddams, Macromolecules 14 (1981) 1356-1359.
- [4] T. Hejertberg, E. Sorvik, J. Appl. Polym. Sci. 22 (1978) 2415-2426.
- [5] E.P. Chang, R. Salovey, J. Polym. Sci, Polym. Chem. Ed. 12 (1974) 2927-2944.
- [6] G. Sivalingam, R. Karthik, G. Madras, Ind. Eng. Chem. Res. 42 (2003) 3647-3656.
- [7] M. Blazo, E. Jakab, J. Anal. Appl. Pyrolysis 49 (1999) 125-143.
- [8] R.S. Lehrle, J.C. Robb, Nature 183 (1959) 1671-1680.
- [9] N. Grassie, I.F. McLaren, Eur. Polym. J. 6 (1970) 679-686.
- [10] N. Grassie, I.F. McLaren, I.C. Mc Neill, Eur. Polym. J. 6 (1970) 865-877.
- [11] X. Ruijian, Polym. Degrad. Stab. 28 (1990) 323-330.
- [12] G. Spiliopolos, M. Statheropoulos, G. Parissakis, Eur. Polym. 25 (1989) 989-991.
- [13] T. Mirokawa, Kagaku to Kogyo (Osaka) 41 (1967) 169-188.
- [14] N.G. Gaylard, A. Takahashi, J. Polym. Sci. 8 (1970) 37-48.