

Degradation of Poly(vinyl chloride) onto KF-Al₂O₃

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γ -Alumina coated with potassium fluoride, KF-Al₂O₃ proved dehydrochlorination of poly(vinyl chloride), in tetrahydrofuran. The molecular changes was observed in the accuracy of polyene sequence distribution by using UV-Vis spectrophotometer. The increase of dehydrochlorination rate was investigated at different reaction times and amount of KF-Al₂O₃.

Key Words: KF-Al₂O₃, Poly(vinylchloride), Dehydrochlorination, UV-Vis spectroscopy.

INTRODUCTION

Poly(vinyl chloride) is widely used in industry and it exhibits easily modifiable mechanical properties. When processed, stored and used under normal conditions, it undergoes degradation¹. It is well known that poly(vinyl chloride) is easily transformed into conjugated polyenes by dehydrochlorination. The most critical feature is a decolouration of the sample. Therefore the reaction can be observed visually by the colour change in the polymer from yellow through orange, red, brown to black. The degradation of poly(vinyl chloride) results in a deterioration of some properties such as mechanical, electrical and thermal stability. Partial dehydrochlorination of PVC generates new double bonds, and thus increasing the availability of allylic chlorines in the backbone. The colour change during PVC degradation are investigated for most experimental investigation such as thermal-, photo-, mechanical- and chemical degradation¹⁻⁶. The simplest polyene spectrum for a diene which usually has only one absorption maximum. Trienes usually have three maxima and the higher polyenes usually have six main maxima. The effect of increasing the number of conjugated double bonds is to displace the spectrum to longer wavelengths; the increase in λ for each successive polyene decreases as the length of conjugation increases. The fundamental fact of PVC decomposition is the elimination of hydrogen chloride at rather low temperatures (about 100 °C) or under the influence of light in the first stage this reaction leads to the formation of one double bond⁷. Potassium fluoride on alumina (KF/Al₂O₃), is a solid supported reagent and it is used as a solid phase organic synthesis reagent⁸⁻¹¹. The versatility of potassium fluoride coated

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on alumina has been demonstrated in the recent literature which includes its accounts in the aldol and Michael reaction¹², condensation of sulfones with aldehydes¹³, olefin and acetylene forming elimination reactions¹⁴, metathesis of silylalkynes and cross-metathesis of silylalkyne and 1-alkyne¹⁵.

In this study, we investigated the formation of conjugated double bonds on the PVC chain in tetrahydrofuran using KF-Al₂O₃ as a solid base catalysis. The formation and length of polyenes was followed by an increase in absorbance in UV-VIS region by using UV-Vis spectrophotometer. It is observed conjugated polyene units according to different reaction times and conditions. Consequently, the shift in maxima of absorption peaks to longer wavelengths was observed due to continuous increase in reaction times.

EXPERIMENTAL

Solution of PVC samples, a commercial material (PETKIM-P38, Yarimca, Turkey), used in this study was prepared being dissolved in THF from Merck (Darmstadt, Germany). PVC-THF mixture (2.5 g/250 mL) remained to form the solution for a week in a dark bottle. Tetrahydrofuran (Merck) of analytical grade was purified as described¹⁶.

KF-Al₂O₃ reagent: The γ -alumina was used as aluminium oxide anhydrous (Merck). Typically, KF (20 g) (no dehydration is necessary) was dissolved in water (*ca.* 200 mL) in a 600 mL beher glass. γ -Alumina (30 g) was then added and the aqua sample was stirred with magnetic stirrer. The water in the bulk water was removed by rotary evaporation at *ca.* 60 °C at least 2 h. This impregnated alumina was then dried in vacuum dry oven at 75 °C for several hours¹⁷.

General procedure

Method-A: 10 mg/10 mL PVC/THF sample was added onto 1 g KF-Al₂O₃ in 50 mL dark bottle (sample no, 1-11). Thermal degradation was neglected during experiment, keeping the temperature constant at 20 °C. On the other hand, all test tubes were kept in a dark place to avoid the photodegradation of PVC. The catalytic effect of the molecular oxygen in air during experiments was neglected by means of dissolving the samples in THF solvent. The reaction mixture was stirred continuously by magnetic stirring. The changes of PVC solutions were investigated both by changing treatment time 1 g KF-Al₂O₃ catalysis and by changing amount of KF-Al₂O₃ catalysis for 24 h. After having observed the yellow-(dark) coloured solutions, the mixtures were filtered from KF-Al₂O₃ particulars. UV-Vis spectra of this solutions were investigated by spectrophotometric technique. The experimental conditions of dehydrochlorination were shown in Tables 1 and 2.

Method-B: 10 mg/10 mL PVC/THF sample was added onto 1 g KF-Al₂O₃ in 50 mL dark bottle (samples no. 3-5). The same reaction conditions were supplied as in the method-A. Poly(vinyl chloride) solution was added onto 1 g KF-Al₂O₃ and/or 10 mg trichloroacetic acid. The reaction mixture was stirred continuously by magnetic

TABLE-1
PVC/THF SAMPLES TREATED WITH 1 g OF KF-Al₂O₃ TO DIFFERENT TIMES

Sample No.	PVC/THF (mL) (10 mg/1 mL)	KF-Al ₂ O ₃ (g)	Time (h)
1	10	0.0	24
2	10	1.0	4
3	10	1.0	8
4	10	1.0	12
5	10	1.0	24
6	10	1.0	32
7	10	1.0	48
8	10	1.0	72
9	10	1.0	96
10	10	1.0	120
11	10	1.0	>>(30 days)

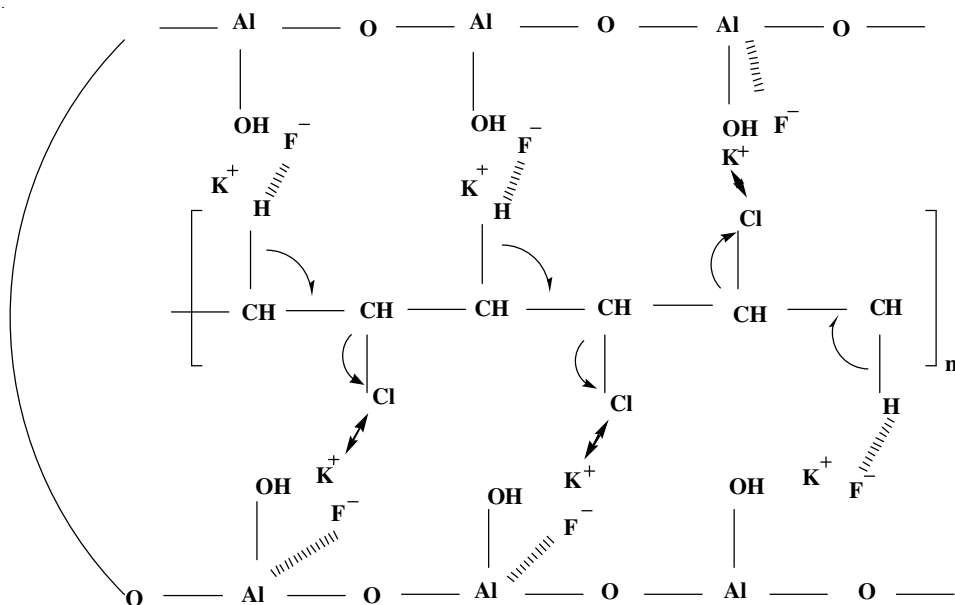
TABLE-2
PVC/THF SAMPLES TREATED WITH THE DIFFERENT
AMOUNTS OF KF-Al₂O₃ FOR 24 h

Sample No.	PVC/THF (mL) (10 mg/1 mL)	KF-Al ₂ O ₃ (g)
1	10	0.0
2	10	0.5
3	10	1.0
4	10	2.0
5	10	3.0
6	10	4.0

stirring for 96 h. After yellow-(dark) or colourless solutions, the mixtures were filtered from KF-Al₂O₃ particulars. UV-VIS spectra of this solutions were investigated by spectrophotometric technique. The experimental conditions of dehydrochlorination were shown in Table-3.

TABLE-3
PVC/THF SAMPLES TREATED WITH 1 g OF KF-Al₂O₃
AND/OR TRICHLOROACETIC ACID FOR 96 h

Sample No.	PVC/THF (mL) (10 mg/1 mL)	KF-Al ₂ O ₃ (g)	TCA (mg)
1	10 mL PVC/THF	-	-
2	10 mL THF	-	1.0
3	10 mL THF	1.0	1.0
4	10 mL PVC/THF	1.0	1.0
5	10 mL PVC/THF	1.0	-
6	10 mL PVC/THF	-	1.0



Scheme: Possible schematic models of dehydrochlorination of PVC on KF-Al₂O₃

RESULTS AND DISCUSSION

At the end of each experiment studies, yellow-(dark) coloured solutions were filtrated and were analyzed by Shimadzu 1600-A model UV-VIS spectrophotometer at the range of 290-900 nm wavelength. Spectrums are given in Figs. 1, 3 and 5.

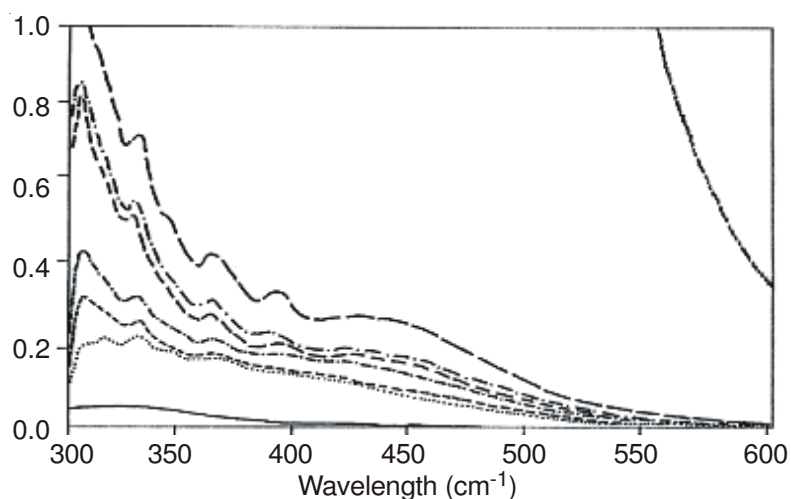


Fig. 1. UV-VIS spectra of PVC reacted with 1 g of KF/Al₂O₃ in THF up to different time (____) 0, (.....) 4, (-----) 8, (-.-.-.-) 32, (____) 72, (.....) 96, (____) 120, (____) >> 30 days

Decolouration observed during PVC degradation is due to the formation of conjugated polyene sequences, $-(CH=CH)_n$, (> 4 double bonds)³. The UV-Vis absorbance spectrums at various time intervals such as 4, 8, 32, 72, 96, 120 h and $>> 30$ days using 10 mg PVC/10 mL THF solution onto 1 g KF-Al₂O₃ samples were investigated and the increasing ratio and number of the polyenes distribution were observed in Fig. 1. In that, both the formation of conjugated polyenic sequences and the absorption shifted to the bathochromic region were observed by means of different treatment times in PVC samples. Consequently, when treatment time was increased, as a results of HCl release, conjugated polyenes having different distribution of chain lengths were observed in the samples.

Fig. 2 consists of change of absorbance values at different wavelengths in UV-Vis spectra of PVC treated with 1 g KF-Al₂O₃. Fig. 2 shows the absorption of conjugated double bonds at 295 nm are more than conjugated double bonds, at 320, 333, 352, 383, 408, 430 nm. So, it can be suggested that the probability of the most conjugate double bonds have observed at 295 nm regards to $n = 6$ polyenes.

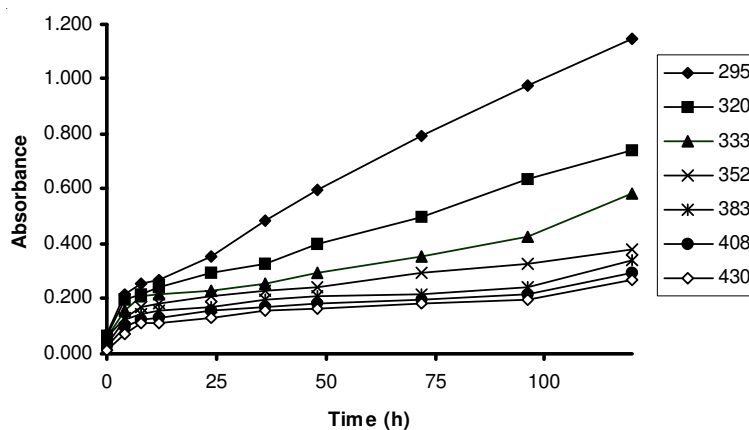


Fig. 2. Change of absorbance values at different wavelengths in UV-Vis spectra of PVC modified with 1 g of KF-Al₂O₃

The change of absorbance at different wavelengths for different amounts at 24 h are shown in Fig. 3. As seen from the Fig. 3, the highest increase of absorbance values are observed onto 1 g KF-Al₂O₃. Thus, it may be presumed that the possibility of crosslinking has been decreasing absorbance values through increasing the amount of KF-Al₂O₃ as a solid bases catalysis (Fig. 4).

Poly(vinyl chloride) degradation rate is strongly influenced by structural defects concentration, such as HCl formation or addition any strong Lewis acid or base, oxygen inducing auto-oxidation. The effect of hydrochloric acid or trifluoroacetic acid, on thermal degradation of PVC has been investigated in previous studies^{18,19}. In these studies, it was claimed that HCl occurs during degradation accelerated dehydrochlorination. In the same studies, trifluoroacetic acid was added in the reaction.

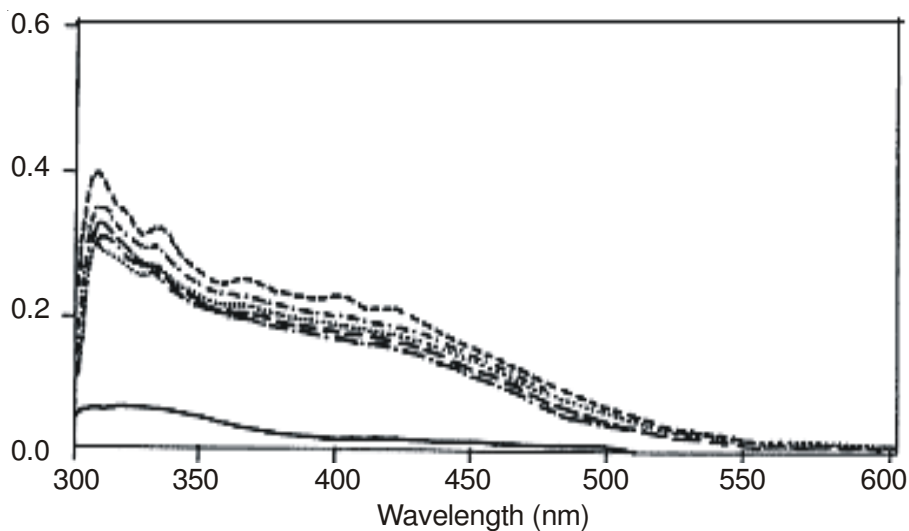


Fig. 3. UV-Vis Spectra of reacted with the different amounts of $\text{KF}/\text{Al}_2\text{O}_3$ in THF for 24 h (____) 0 g, (.....) 0.5 g, (-----) 1 g, (-.-.-.-) 2 g, (_____) 3 g, (____) 4 g of poly(vinyl chloride)

medium and observed that shifting wavelength off-500 nm. So this evidence showed that increasing the product of conjugate polyens in the acidic medium. In present study, we investigated the catalytic effect of $\text{KF}-\text{Al}_2\text{O}_3$ and/or trichloroacetic acid (TCA). The catalytic effect of $\text{KF}-\text{Al}_2\text{O}_3$ was observed as a solid bases catalyst. Otherwise, when trichloroacetic acid was added in PVC samples, it could be dehydrochlorination (Fig. 5). According to UV-Vis absorption spectra, the absorption maxima in the formation of conjugated polyene sequences and these sequences lengths move

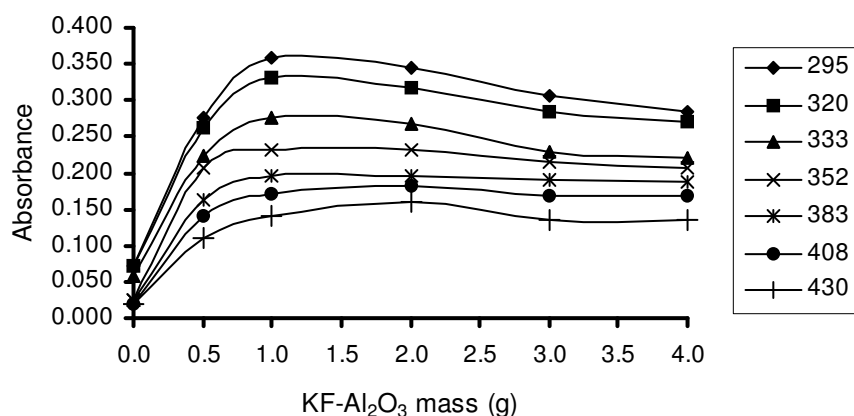


Fig. 4. Change of absorbance values at different wavelengths in UV-Vis spectra of PVC samples reacted with $\text{KF}-\text{Al}_2\text{O}_3$ for 24 h

to longer wavelengths their concentration increased. As soon as trichloroacetic acid was added in KF-Al₂O₃-PVC samples, the gas was emitted from the reaction medium due to KF-Al₂O₃ and colouration was not observed in PVC samples (Fig. 5). Colourless product showed that the catalytic effect of KF-Al₂O₃ solid bases catalyst was inhibited by trichloroacetic acid. This trend is also confirmed by spectrophotometric data which doesn't have any absorption peaks (Fig. 5).

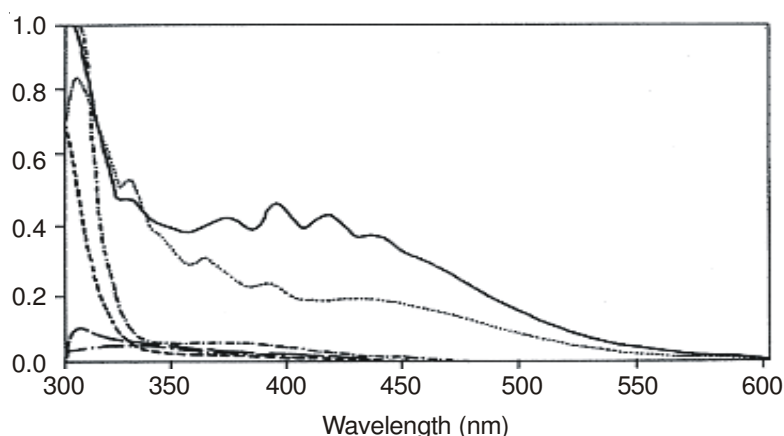


Fig. 5. UV-Vis spectra of PVC modified conditions for 96 h; (—) PVC, (—) TCA, (---) KF-Al₂O₃ + TCA, (---) KF-Al₂O₃ + PVC + TCA, (.....) KF-Al₂O₃ + PVC, (—) TCA + PVC

Conclusion

KF-Al₂O₃ as a solid catalysis can be used to degradate the PVC polymer which has acidic proton and α -leaving group like PVC without any effect of temperature. KF-Al₂O₃, only when its ratio of catalysis and catalytic time are adjusted, can be suggested as a chemical agent for chemical degradation of PVC without any effect of temperature and oxygen.

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