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Short communication

An investigation about the solid state thermal degradation of acetylsalicylic acid: polymer formation

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Abstract

An investigation about the thermal degradation of acetylsalicylic acid (ASA) is performed. It is verified that the thermal degradation of ASA produces not only salicylic acid (SA) and acetic acid (AA) as products but also an ASA polymer, which is transparent and solid. And also verified that the temperature in which the polymer is obtained influences its physical consistence (solid or semi-solid). Furthermore, the ASA polymer is very stable from a thermic point of view, as verified by TG and DSC analysis. X-ray diffraction patterns obtained for the ASA polymer show that it exhibits a low crystallinity.

Keywords: Acetylsalicylic acid; Thermal degradation; Polymer

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1. Introduction

Thermal analyses have been successfully employed in the food and pharmaceutical industries, for example to evaluate the chemical purity of substances [1,2]. As typical examples, could be mentioned in the studies performed for ascorbic acid samples [3,4].

Some previous studies have investigated the thermal degradation of acetylsalicylic acid (ASA) [5,6]. However, a complete characterization of the formed residues, clarifying the ASA thermal degradation mechanism is still lacking. The aim of this work is to perform such study.

2. Experimental

Acetylsalicylic acid (SANOFI) was used without further purification.

The thermogravimetric curves were obtained in the range 30–1200 °C on a Shimadzu TGA-50 apparatus under dry air, humid air and nitrogen. A sample of 4 mg, a gas flow of 50 $cm^3\,min^{-1}$, and a heating rate of 10 $°C\,min^{-1}$ was employed. The DSC curves were obtained in the range 30–500 °C on a Shimadzu DSC-50H apparatus under nitrogen atmosphere, with a heating rate of 10 $°C\,min^{-1}$ and a gas flow of 50 $cm^3\,min^{-1}$.

The infrared spectra were obtained in KBr discs in the range 4000–400 cm^{-1} by using a FTIR BOMEM apparatus model MB 102. The X-ray diffraction patterns (powder method) were obtained on a Phillips PW 1710 apparatus by using Cu Kα radiation.

3. Results and discussion

In order to evaluate the effect of atmosphere on the thermal decomposition of ASA, TG curves under nitrogen, dry air and humid air were obtained, and are shown in Fig. 1. The respective TG data are summarized in Table 1.

The TG curves obtained for ASA exhibit two mass loss steps as follows: (1) release of salicylic acid (SA) and acetic acid (AA), with the formation of an intermediary compound and (2) thermal degradation of the intermediary compound.

As can be verified, the mass loss percentage associated with the first mass loss step increases in the order: humid air > dry air > nitrogen. Hence, it can be concluded that water plays a prominent role in the formation of the thermal degradation intermediary, and so, the thermal degradation of

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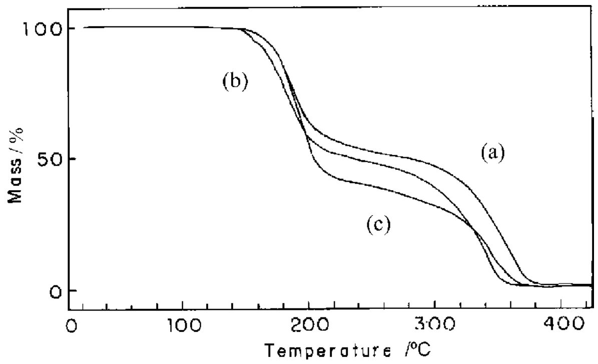
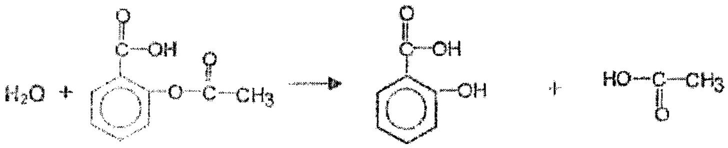


Fig. 1. TG curves for ASA under different atmospheres: humid air (a), dry air (b) and nitrogen (c).

ASA giving salicylic and acetic acids is a hydrolysis process, as follows:



In order to clarify the nature of intermediary products formed in the thermal degradation of ASA, a detailed investigation was performed.

By using the Shumadzu thermobalance, an ASA sample was heated until 180 °C (at 10 °C min^{-1}) and this temperature was maintained for 20 min. Formation of a crystalline solid residue on the panel walls was observed. The performed infrared analysis confirmed that this product was salicylic acid.

To improve the performed investigation, a 500 g ASA sample was heated in an electric furnace under air atmosphere (10 °C min^{-1}) from room temperature to 155 °C, with this temperature been maintained for 20 min. It was observed that, when the sample was cooled to room temperature, the obtained product was transparent, with semi-solid aspect. When the same operation was repeated for another 500 mg sample, taking 180 °C as the upper limit temperature, the cooled product was a transparent solid. The 155 and 180 °C temperatures were chosen to take into account of the thermal degradation profile exhibited by ASA (TG curves).

Table 1
TG data summary for the solid state thermal degradation of ASA under three different atmospheres

Atmosphere	T_1 (°C)	T_2 (°C)	T_p (°C)	Δm (%)
N_2	163	203	187	48.4
	310	376	357	50.7
Dry air	155	208	182	51.4
	294	355	343	48.8
Humid air	162	211	192	60.2
	295	365	348	40.2

T_1, T_2 and T_p are the initial, final and "peak" temperature of the thermal degradation process, respectively. Δm is the experimental mass loss.

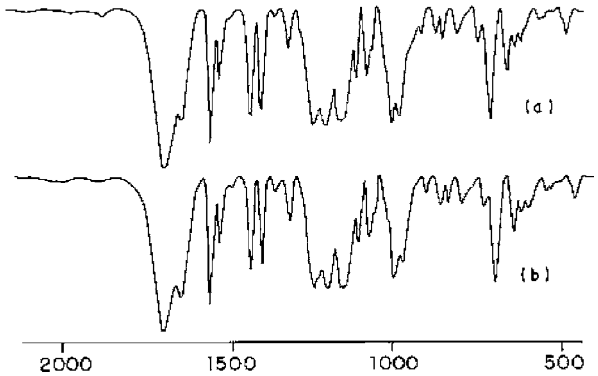


Fig. 2. Infrared spectra for the transparent residues generated by the thermal degradation of ASA for 20 min at (a) 150 °C and (b) 180 °C.

The infrared spectra obtained for the two residues are shown in Fig. 2. The main bands are those at 1749, 1500–1300 and 750 cm^{-1} attributed to the C=O, C–O and C–H vibrations, respectively. The obtained X-ray diffraction patterns for the same residues are shown in Fig. 3. As can be verified, both residues exhibit low crystallinity.

In order to investigate the ASA thermal degradation mechanism, TG and DSC analysis or the transparent residues were performed. The TG curves (10 °C min^{-1}, N_2 atmosphere) for SA, ASA and transparent residue from ASA thermal degradation at 180 °C are shown in Fig. 4. As can be verified, the thermal degradation profiles of the three samples are very different, with the transparent solid residue, exhibiting a higher thermal stability, showing that it is not merely a mixture of SA and ASA but indeed a new compound. The obtained DSC curves, shown in Fig. 5 confirm this hypothesis.

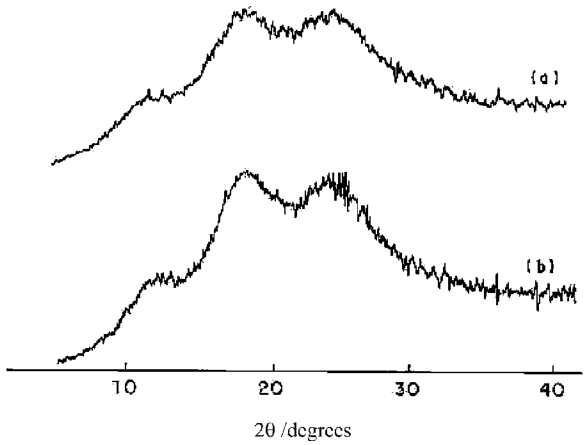


Fig. 3. X-ray diffraction patterns for the transparent residues generated by the thermal degradation of ASA for 20 min at (a) 150 °C and (b) 180 °C.

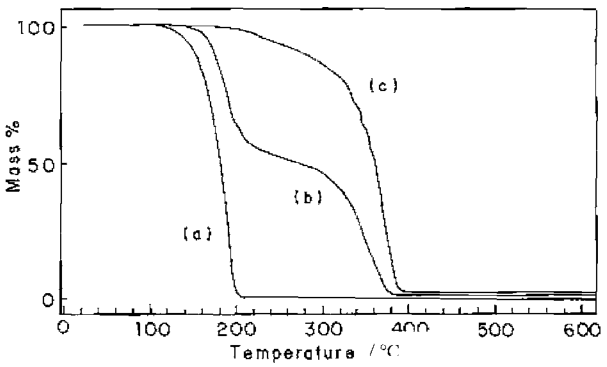


Fig. 4. TG curves for: (a) SA, (b) ASA and (c) the transparent residue generated by the thermal degradation of ASA for 20 min at 180 °C.

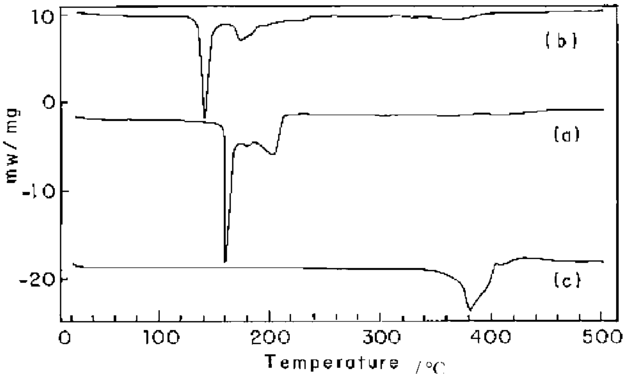


Fig. 5. DSC curves for: (a) SA, (b) ASA and (c) the transparent residue generated by the thermal degradation of ASA for 20 min at 180 °C.

Table 2
Elemental analysis results for the residues of ASA thermal degradation at different temperatures and time intervals

Sample	T (°C)	t (min)	C (%)	H (%)	O (%)
ASA	–	–	60.0	4.4	35.5
AS	–	–	60.9	4.3	34.8
Residue 1	150	0	59.9	4.4	35.7
Residue 2	150	10	60.5	4.3	35.2
Residue 3	150	20	61.8	4.2	34.0
Residue 4	150	30	59.9	4.4	35.7
Residue 5	150	60	62.5	4.3	33.2
Residue 6	180	0	57.9	4.5	37.7
Residue 7	180	10	61.6	4.4	34.0
Residue 8	180	20	63.1	4.2	32.7
Residue 9	180	30	59.9	4.4	35.7
Residue 10	180	60	66.2	4.4	29.4
Residue 11	210	0	61.3	4.3	34.3
Residue 12	210	10	64.4	4.1	31.5
Residue 13	210	20	63.7	3.9	32.4
Residue 14	210	30	61.7	4.4	33.9
Residue 15	210	60	67.3	3.8	28.9
Residue 16	240	0	61.8	4.3	34.0
Residue 17	240	10	65.9	3.9	30.2
Residue 18	240	20	67.1	3.0	29.9
Residue 19	240	30	67.6	3.7	28.6
Residue 20	240	60	68.7	3.7	27.7

The oxygen percentages are calculated values.

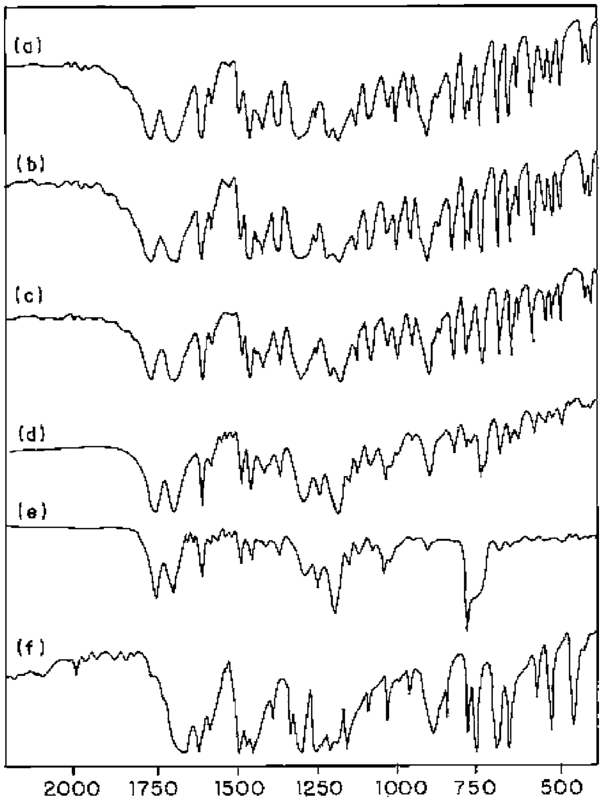


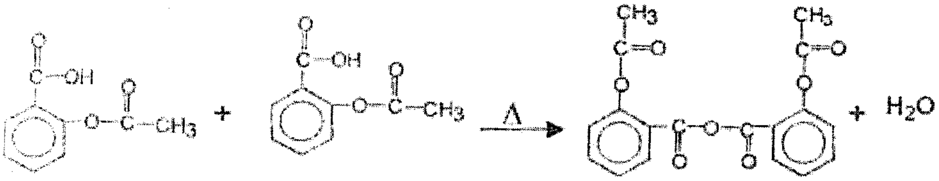
Fig. 6. Infrared spectra for: (a) ASA, the residues of ASA thermal degradation for 20 min at (b) 150 °C, (c) 180 °C, (d) 210 °C, (e) 240 °C and (f) SA.

Table 3
Thermal stability evaluation of the ASA thermal degradation residues (m_1 and m_2 are the initial and final residue sample masses, respectively)

T (°C)	t (min)	m_1	m_2	Δm (%)
150	0	2.00	2.00	0.00
150	10	1.99	1.94	2.50
150	20	2.00	1.88	6.00
150	30	2.00	1.75	12.50
150	60	2.00	1.67	16.50
180	0	2.00	1.99	1.00
180	10	2.00	1.84	8.00
180	20	2.00	1.62	16.50
180	30	2.00	1.41	29.50
180	60	1.43	0.97	32.50
210	0	2.00	1.82	9.00
210	10	2.00	1.53	23.50
210	20	2.00	1.48	26.00
210	30	2.00	1.67	32.50
210	60	2.00	1.35	32.50
240	0	2.00	1.71	14.50
240	10	2.00	1.41	29.50
240	20	2.00	1.34	33.00
240	30	2.00	1.30	35.00
240	60	2.00	1.24	38.00

Hence, it is verified that in the ASA thermal degradation, salicylic and acetic acids are formed and released in the first thermal degradation step, but these are not the only products formed. With a first look, one could propose that the two mass loss steps observed on the TG curve of ASA are due to the processes: ASA(s) → SA(s)+AA(g) and SA(s) → SA(g). However, the mass percentage of the solid residue after the first mass loss step is not that expected by using this simple mechanistic proposal, and proved with the present data, a new compound, that is not SA, AC or ASA is formed.

The formation of ASA dimmers can be proposed, as follows:



The water molecules formed could react with non-dimmerized ASA molecules giving SA and AA as products or with the formed dimmers, starting a polymerization process. Based on the obtained results for the samples decomposed at 150 °C (semi-solid) and 180 °C (solid), both transparent, could be supposed that the polymerization process is well developed at 180 °C.

In order to improve the characterization of the polymeric residues from ASA thermal degradation, the residues formed at 150, 180, 210 and 240 °C (heating rate of 10 °C $\min^{-1}$, N_2 atmosphere) were studied by infrared spectroscopy and CHN elemental analysis.

The infrared spectra to the samples obtained at the considered temperatures after heating for 20 min are shown in Fig. 6. For comparison, the infrared spectra for ASA and SA are also shown. As can be verified in Fig. 6, the infrared spectra of the transparent solid residues are very closely related with those for ASA. It was evident that the solid transparent residues are indeed ASA polymer. The residues heated at 240 °C for long time, which exhibits a yellowish aspect, suggesting that they are starting their thermal decomposition.

The elemental analysis results are summarized in Table 2. As a general result, it is observed that the carbon content of the residues increase with an increase on both the temperature and the time interval.

In order to evaluate the thermal stability of the formed residues the mass variation for residue samples heated at 150, 180, 210 and 240 °C for 0, 10, 20, 30 and 60 min were measured. The obtained results are summarized in Table 3. As can be verified, at higher temperatures and time intervals the mass losses are most significant. However, even after 60 min at 240 °C, 62% of the polymer mass is still stable.

4. Conclusions

Based on the obtained experimental results it can be concluded that ASA thermal degradation produces not only SA and AA as products but also an ASA polymer, which is transparent and solid. It is also verified that the temperature in which the polymer is obtained influences its physical consistence (solid or semi-solid). Furthermore, the ASA polymer is very stable from a thermic point of view, as verified by TG and DSC analysis.

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