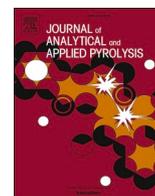




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Applicability of single-shot and double-shot Py-GC/MS for the detection of components in vinyl acetate-based emulsions used in modern-contemporary art

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ABSTRACT

This research explores the use of different pyrolysis-based techniques for studying the chemical composition of vinyl acetate (VAc) based emulsions widely used in modern-contemporary art and contributes to the understanding of their composition by the detection of different monomers and additives. For this purpose, six different commercial VAc-based emulsions from the early 21st century were analyzed for the first time by single-shot (SS) and double-shot (DS) pyrolysis – gas chromatography / mass spectrometry (Py-GC/MS). The results obtained were compared, and highlight the advantages of DS in comparison to SS for the analysis of VAc-based emulsions. Several different components assigned to plasticizers, surfactants, intermediates, and antioxidant families, were detected, mainly by the thermal desorption step of DS. The information gained by this research enriches the knowledge of the formulation of VAc-based emulsions, by considering for the first time a large variety of them. Moreover, it also points to the importance and the potential of DS Py-GC/MS for investigating these materials, which have been rarely explored with this technique.

1. Introduction

Vinyl acetate (VAc) based emulsions have been widely used in modern-contemporary artworks as binders for dyes/pigments in paints as well as adhesives. VAc is formed by the polymerization of vinyl acetate monomer, which is the reaction product of acetic acid and ethylene in the presence of zinc or tin salts [1]. Surfactants are also indispensable components in VAc-based emulsions, usually characterized by non-ionic polyethylene oxide (PEO) or polyethoxylated based compounds [2]. These emulsions also incorporate several additives in low concentrations to improve their chemical and physical properties, thus making their chemical composition quite complex. Depending on their type, additives can give VAc-based emulsions flexibility (plasticizers), increase resistance to light and heat degradation (stabilizers), and also

modify their colour (dyes, pigments). Nevertheless, their detailed formulation, including types of additives, is often kept secret by manufacturers. Thus, complete information regarding their chemical composition is still not readily available. To keep up to date with customers' demands and new "green" regulations, paint manufacturers are constantly improving their formulations giving rise to new VAc-based emulsions, which continue to be introduced in the market and used by contemporary artists. It is well known that the ageing chemical behavior of films based on VAc-emulsions is related not only to the environment in which they are exposed to and kept, but also to its chemical composition [3,4]. Therefore, the investigation of their chemical composition is critical to understanding and predicting their long-term stability and chemical behaviour and to better assess the condition of artworks in museum collections containing VAc-based emulsions. Three of the most

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common types of VAc-based polymers are poly(vinyl acetate) (PVAc) homopolymer, VAc copolymerised with VeoVa (Vinyl ester of Versatic acid) (p(VAc-co-VeoVa)), and ethylene vinyl acetate copolymer (p(E-co-VAc)).

PVAc homopolymer may also be modified with poly(vinyl alcohol) (PVAL) for thickening and stabilizing the emulsion to achieve the best viscosity qualities [5]. Generally, PVAL can serve different functions within the formulation, such as emulsifier and stabilizer [5]. Its low glass transition temperature ($T_g = -30\text{ }^\circ\text{C}$) allows it to also act as a plasticizer for VAc ($T_g = 30\text{ }^\circ\text{C}$). There is evidence of VAl being used as a plasticizer in the late 1920 s [6]. PVAc homopolymer can also be modified with phthalate-based plasticizers, among which dibutyl phthalate (DBP) and bis(2-ethylhexyl) phthalate (DEHP) are the most common. These external plasticizers were used in the early formulations, but by the 1940 s, there were already complaints regarding their chemical stability, especially regarding their migration towards the surface [7]. In the 1950 s, copolymerization with softer monomers, such as highly branched C_9 and C_{10} vinyl esters (VeoVa) and ethylene, appeared to solve the problem of plasticizer migration. However, phthalates have continued to be used in VAc emulsions. By the 1970 s and 80 s, more types of copolymers, such as VAc with butyl acrylate (n BA), 2-ethylhexyl acrylate (2-EHA), vinyl caprate, dibutyl maleate, were developed. Nonetheless, phthalate-based plasticizers have been found in paint formulations since the 2000 s [8]. VAc-based emulsion paints are thus generally characterized by a multi-component system consisting of monomers and different types of additives. Pyrolysis – gas chromatography / mass spectroscopy (Py-GC/MS) is one of the most used techniques for VAc-based emulsion characterization, also given its high sensitivity for identifying components such as additives that can be present in small quantities (3%) [9,10]. Several studies have been done on artistic VAc-based emulsions by Py-GC/MS in flash pyrolysis mode or also known as non-reactive pyrolysis, or single-shot (SS) mode, in which the sample is immediately pyrolyzed at high temperature under a stream of inert carrier gas [4,11–15]. One of these studies was enhanced by adding a few microliters of a derivatizing reagent onto the sample [12] to decrease the polarity of certain polar functional groups such as O-H, thus improving the volatility of the sample, and ultimately obtaining a higher resolved chromatogram with a better peak shape. Hexamethyldisilazane (HMDS) reagent type has been employed for the analyses of PVAc [1,12]. This type of reagent acts when in contact with the sample and during the pyrolysis step, converting polar functional groups to their respective silyl esters. This type of methodology is normally referred to as Py-GC/MS with derivatization. It has been demonstrated that the use of HMDS improved the detection of carboxylic acids such as acetic acid in PVAc resins and emulsions, as well as of copolymers such as butyl ester of butanedioic acid ascribed to the butyl maleate monomer, and external plasticizers such as diethyl phthalate (DEP) [1,12]. Nevertheless, one of the main drawbacks of using HMDS for the identification of PVAc is that the broad peak of the reagent eluted at low retention times may hinder the identification of benzene [12]. This is a problem, because benzene together with the acetic acid peak is useful to establish the full characterization of a VAc. On the other hand, the recombination and condensation products of benzene may be detected at higher retention times and considered as marker compounds for PVAc. The main disadvantage of Py-GC/MS with derivatization is that other typologies of additives not containing polar functional groups, but still present in low concentrations in VAc-based emulsions, cannot be fully identified at high temperatures. This disadvantage is overcome by another type of Py-GC/MS application, and it is represented by the double-shot (DS) mode. While the SS mode allows the polymer identification at high temperature conditions in one single step, the double-shot (DS) mode involves two steps for only one sample, thus combining the advantage of gaining information on both additives and polymer matrix: 1) thermal desorption (TD) for the analysis of volatile compounds also including additives at low temperature as the first step and 2) pyrolysis of the main polymer upon higher temperatures

Table 1

List of the investigated materials distinguished according to their commercial names, manufacturers, and year of purchase. The compositional information of each material is also reported here and acquired from the technical datasheet.

PVAc Pure Homopolymer	Sigma Aldrich - U.S.A	2020	PVAc pure homopolymer
Pliodisp 7580	Resiquímica – Chemical Resins - Sintra, Portugal	2020	Non-plasticized aqueous copolymer dispersion based on vinyl acetate and acrylic acid
Inart Glue	Inart – Cacém, Portugal	2020	Unknown
Mowilith LDM 1871	Celanese Corporation – Texas, U.S.A.	2017	Non-plasticized aqueous copolymer dispersion based on vinyl acetate and ethylene, stabilized with PVAL
Polidisp 1080	Resiquímica – Chemical Resins - Sintra, Portugal	2017	PVAc stabilised with PVAL, non-plasticised
Pliodisp 7252	Resiquímica – Chemical Resins - Sintra, Portugal	2020	Non-plasticized aqueous copolymer dispersion based on vinyl acetate and VeoVa
V2 Glue	Casa Ferreira Artigos para Belas Artes – Lisbon, Portugal	2020	Unknown

conditions as the second step. The use of Py-GC/MS in DS mode for studying additives and polymer matrices of synthetic resins and plastics has increased over the last twenty years [4,13–23]. Particularly, this method was used in a previous work on PVAc paints, by one of the authors, not only for the detection of additives in PVAc paints but also for revealing differences in the composition of the specimens before and after UV ageing, considering the detectable amount of acetic acid and DEP [4]. Nevertheless, despite the high potential of DS Py-GC/MS, it still represents an unstudied topic for investigating VAc-based emulsions in the field of science for modern-contemporary art as well as its comparison to conventional Py-GC/MS as SS for these materials is lacking. Furthermore, only specific case studies and some coloured paints containing VAc-based emulsion were analyzed by DS Py-GC/MS so far, thus not being highly representative of the variety that can be found in art collections.

1.1. Aim of the research

This research intends to highlight the comparison between single-shot (SS) and double-shot (DS) techniques of pyrolysis – gas chromatography / mass spectrometry (Py-GC/MS) for qualitatively elucidating the complex chemical formulation of vinyl acetate (VAc) based emulsions used in modern-contemporary art. For this purpose, a recently purchased large set of VAc-based emulsions from the early 21st century were analyzed by DS Py-GC/MS, and the results were compared with those obtained by conventional SS Py-GC/MS. The comparison between the SS and DS Py-GC/MS aims for a better understanding of the potentiality of DS for the analysis of VAc-based emulsion as well as enriching the knowledge on their chemical composition, which represents important data not only for conservation scientists and analytical chemists, but also for art-historians, conservators, and restorers.

2. Experimental

2.1. Materials

In Table 1 the materials selected for this study with their relative commercial names, manufacturers, year of purchase and compositional information declared on the technical datasheet are reported. Six different commercial unpigmented VAc-based emulsions were recently acquired from emulsion manufacturers and purchased from fine arts

Table 2

List of the investigated materials distinguished according to the vinyl acetate-based emulsions type characterized within this study, and their additives name and type detected by single-shot (SS) and/or double-shot (DS) of Py-GC/MS. Py: pyrolysis; TD: thermal desorption.

Commercial Name	Vinyl acetate-based emulsions				Additives				
	Type	detected by Py-GC/MS		Name	Type	detected by Py-GC/MS			
		SS	DS			SS	DS	Py	
									Py
PVAc Pure Homopolymer*	poly(vinyl acetate) homopolymer PVAc	✓	✓						
Pliodisp 7580	poly(vinyl acetate) homopolymer PVAc	✓	✓	Bis(2-ethylhexyl) phthalate (DEHP)	Plasticizer			✓	
				Diethyl phthalate (DEP)	Plasticizer			✓	
				Diisobutyl phthalate (DiBP)	Plasticizer			✓	
				Di-n-octyl phthalate (DNOP)	Plasticizer			✓	
				2-Ethylhexyl benzoate (2-EHB)	Plasticizer			✓	✓
Inart Glue	poly(vinyl acetate) homopolymer PVAc	✓	✓	Diacetin	Plasticizer			✓	✓
				Diethylene glycol dibenzoate (DEGDB)	Plasticizer			✓	✓
				Dipropylene glycol dibenzoate (DPGDB)	Plasticizer			✓	✓
Mowilith LDM 1871	poly(vinyl acetate) homopolymer PVAc	✓	✓	Triethylene glycol (TEG)	Plasticizer			✓	✓
				1-Dodecanol	Surfactant / Precursor			✓	
				1-Chlorododecane	Intermediate			✓	
				1-Bromododecane	Intermediate			✓	
Polidisp 1080	poly(vinyl acetate) homopolymer PVAc	✓	✓	Vinyl alcohol (VAL)	Stabilizer			✓	
Pliodisp 7252	poly(vinyl acetate-co-vinyl versatate) copolymer p(VAc-co-VeoVa)	✓	✓	Di-t-butyl-4-butylphenol (Isonox 132)	Antioxidant			✓	
V2 Glue	poly(ethylene-co-vinyl acetate) copolymer p (EVA)	✓	✓	Diacetin	Plasticizer			✓	✓
				Vinyl alcohol (VAL)	Stabilizer			✓	✓

* Not in form of emulsion (see 2.1)

stores in Portugal: *Pliodisp 7580*, *Inart Glue*, *Mowilith LDM1871*, *Polidisp 1080*, *Pliodisp 7252*, and *V2 Glue*. Additionally, *PVAc Pure Homopolymer* ($M_w \approx 83,000$ g/mol) was included into this research as a reference of a pure homopolymer. Unpigmented VAc-based emulsions were considered for this study in order to focus on the investigation of their main additives' composition such as plasticizers, antioxidants, intermediates etc. thus excluding pigments. In the art field, it is fairly common for artists to use unpigmented emulsions and add their own pigments later on. Moreover, these materials were selected because of their wide use in the field of modern-contemporary art and their high commercial availability in Portuguese fine arts stores and distributors, thus reflecting the high demand for these materials in the artistic field. All the emulsions were cast on glass slides (average emulsion film thickness of 90 μm) with a film applicator and dried under room temperature and relative humidity conditions. *PVAc Pure Homopolymer* was in the form of beads. Consequently, it was dissolved in acetone in a 20/80 (w/v) proportion before the application on a glass slide. According to the technical datasheets, *V2 Glue* and *Inart Glue* are classified as white glues, without any specific information about their chemical formulations. On the other hand, *Polidisp 1080* is described as a PVAc emulsion with PVAL as a stabilizer, without the addition of any plasticizer. *Pliodisp 7252* is defined as a non-plasticized aqueous copolymer dispersion based on VAc and VeoVa, while *Pliodisp 7580* is a non-plasticized aqueous copolymer dispersion based on VAc and acrylic acid. Finally, *Mowilith LDM 1871* is described in the datasheet as a non-plasticized aqueous copolymer dispersion based on vinyl acetate and ethylene, stabilized with PVAL.

2.2. Pyrolysis – gas chromatography / mass spectrometry (Py-GC/MS)

For the pyrolysis – gas chromatography / mass spectrometry (Py-GC/MS) investigations, two different analytical procedures were selected: 1) Py-GC/MS analysis in single-shot (SS) mode; 2) Py-GC/MS analysis in double-shot (DS) mode, which is based on two steps analysis: a) thermal

desorption (TD) of the samples at a lower temperature to detect volatile compounds and b) pyrolysis (Py) of the same sample as the second step; for both procedures around 0.15 mg of each sample material was put in a sample cup (ECO-CUP Frontier Lab, Japan) and then analyzed.

For the analyses of the samples, the PY-2020iD pyrolyzer (Frontier Lab, Japan) combined with a GCMS-QP2010 Plus (Shimadzu, Japan) was employed. The GC/MS unit was equipped with a capillary column SLB-5 ms Supelco, U.S.A. (30 m length x 0.25 mm internal diameter x 0.25 μm film thickness) using bonded and highly cross-linked 5% diphenyl / 95% dimethyl siloxane. The capillary column was connected with a deactivated silica pre-column Rxi Guard Column Restek, U.S.A. (5 m length x 0.32 mm internal diameter). NIST 05 and NIST 05 s Library of Mass Spectra were available to identify the compounds.

For the Py-GC/MS analyses in SS mode the pyrolysis temperature was set at 600 °C, while the pyrolysis interface and the injector temperature were set at 280 °C and 250 °C, respectively. The DS Py-GC/MS parameters were as follows: For the TD step, the temperature was set at 100 °C, held for 2 min and increased by 20 °C/min to 250 °C and held there for 2 min. The second-step Py was carried out at 600 °C with the pyrolysis interface and the injector temperature at 280 °C and 250 °C, respectively, similarly to the SS. As generally advised by the system the pyrolysis interface temperature was set in Auto mode for the TD of DS with the upper temperature limit of 280 °C. In Auto mode the pyrolysis interface temperature is controlled 100 °C above the temperature of the pyrolyzer furnace. For instance it started from 200 °C and it rised up to the limit temperature of 280 °C. These temperature conditions for the DS were used according to a previous work conducted by one of the authors on PVAc paints [4] in which it is shown that those conditions were the optimal for gaining better reproducibility information.

The GC column temperature conditions for both SS and DS were as follows: initial temperature 40 °C, held for 5 min followed by a temperature increase of 10 °C/min to 290 °C for 3 min. The helium gas flow was set at 1 ml/min and the electronic pressure control was set to a

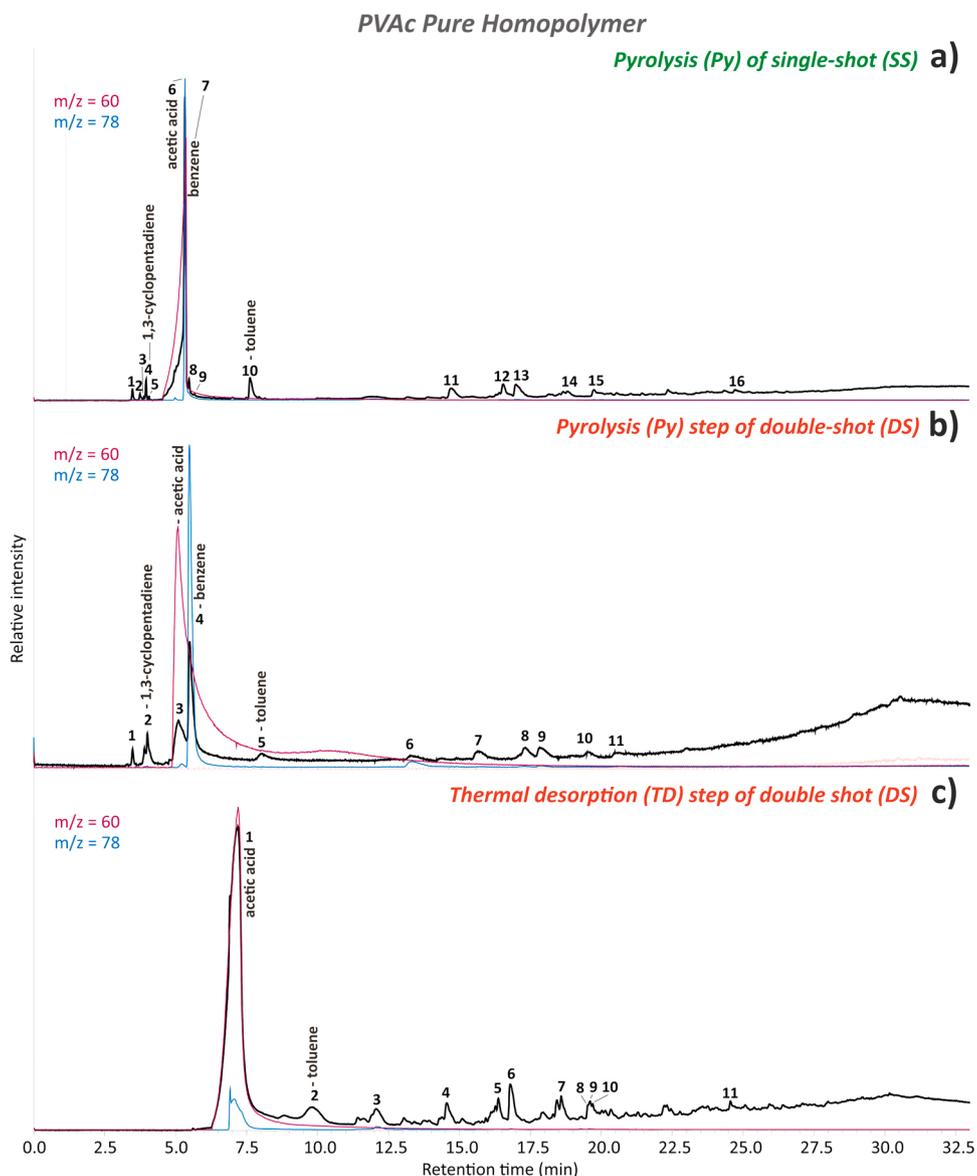


Fig. 1. Total ion chromatograms (TIC) of PVAc Pure Homopolymer acquired by the a) pyrolysis (Py) of single-shot (SS), b) pyrolysis (Py) step of double-shot (DS), and c) thermal desorption (TD) step of double-shot (DS). The numbered peaks of the TICs are listed and described in Table 3a, b, and c, respectively. Extracted ion chromatogram of the ion mass with $m/z = 60$ for acetic acid in pink and with $m/z = 78$ for benzene in blue, characteristic for PVAc.

constant flow of 31.7 ml/min, in split mode at 1:50 ratio for SS and Py of DS, while of 7.6 ml/min in split mode of 1:10 ratio for TD of DS. The mass spectra were recorded under electron impact (EI) ionization in positive mode at 70 eV and the temperature of the MS interface and the ion source were 280 °C and 200 °C, respectively. The mass spectrometer was scanned from $m/z = 50$ to $m/z = 750$.

3. Results and discussion

3.1. Vinyl acetate-based emulsions

The results obtained by this research allowed us to distinguish three different main classes of vinyl acetate-based emulsions, independently of the presence or absence of external plasticizers:

- poly(vinyl acetate) (PVAc) homopolymer
- poly(vinyl acetate-co-vinyl versatate) copolymer – p(VAc-co-VeoVa)
- poly(ethylene-co-vinyl acetate) copolymer – p(E-co-VAc)

Additionally, the complexity of the formulations considering the presence of several and different additives, was determined in some cases. All six commercial VAc-based emulsions and the PVAc pure homopolymer were analyzed with SS and DS techniques, and the results in terms of polymer and additive contents are reported in Table 2. These findings are hereafter presented and discussed.

3.1.1. Poly(vinyl acetate) (PVAc) homopolymer

A poly(vinyl acetate) (PVAc) homopolymer was identified and characterized in five of the seven analyzed samples by the Pyrolysis step (Py) at 600 °C of the single-shot (SS) and double-shot (DS) Py-GC/MS. These are the PVAc Pure Homopolymer and the VAc-based emulsions named Pliodisp 7580, Inart Glue, Mowilith LDM 1871, and Polidisp 1080. As shown in Fig. 1a for the PVAc pure homopolymer and described in Table 3a, the principal and characteristic pyrolysis products with Py of SS are represented by acetic acid (AA) (peak #6) and benzene (B) (peak #7) as the most dominant peaks, complemented by 1,3-cyclopentadiene (peak #4) and toluene (peak #10). This result is in agreement with those obtained through Py-GC/MS analyses reported in the literature [1,4,8,

Table 3

Main pyrolysis products obtained by **a)** pyrolysis (Py) of single-shot (SS), **b)** pyrolysis (Py) step of double-shot (DS), and **c)** thermal desorption (TD) step of double-shot (DS) of Py-GC/MS of the investigated PVAc Pure Homopolymer at their corresponding retention time (RT min) and mass to charge ratio (m/z) (base peak marked in bold).

a) Pyrolysis (Py) of single-shot (SS)			
Peak #	RT min	Compound name	m/z
1		1,3-Butadiene	54
2	3.48	Acetone	58
3	3.75	1,3-Pentadiene, (<i>E</i>)-	53, 67
4	3.89	1,3-Cyclopentadiene	66
5	3.96	Cyclopentene	53, 67
6	4.07	Acetic acid	60
7	5.04	Benzene	52, 78
8	5.33	1,3-Cyclohexadiene	51, 79
9	5.48	Cyclohexene	54, 67 , 82
10	5.67	Toluene	65, 91
11	7.63	Indene	58, 89, 115
12	14.73	Cycloprop[<i>a</i>]indene, 1,1a,6,6a-tetrahydro-	51, 64, 77, 89, 102, 115, 130
13	16.56	Azulene	51, 102, 128
14	17.01	Naphthalene, 1-methyl-	63, 115, 142
15	18.08	Biphenyl	76, 115, 154
16	19.76	Anthracene	76, 89, 152, 178
	24.74		
b) Pyrolysis (Py) step of double-shot (DS)			
Peak #	RT min	Compound name	m/z
1	3.45	1,3-Butadiene	54
2	3.99	1,3-Cyclopentadiene	66
3	5.10	Acetic acid	60
4	5.48	Benzene	52, 78
5	8.07	Toluene	69, 91
6	13.39	1,3,5,7-Cyclooctatetraene	51, 78, 104
7	15.67	Indene	58, 89, 115
8	17.32	Cycloprop[<i>a</i>]indene, 1,1a,6,6a-tetrahydro-	51, 64, 77, 89, 102, 115, 130
9	17.89	Azulene	51, 102, 128
10	19.62	Naphthalene, 1-methyl-	63, 115, 142
11	20.51	Biphenyl	76, 115, 154
c) Thermal desorption (TD) step of double-shot (DS)			
Peak #	RT min	Compound name	m/z
1	7.19	Acetic acid	60
2	9.82	Toluene	65, 91
3	12.07	1,3,5,7-Cyclooctatetraene	51, 78, 104
4	14.56	Indene	58, 89, 115
5	16.37	Cycloprop[<i>a</i>]indene, 1,1a,6,6a-tetrahydro-	51, 64, 77, 89, 102, 115, 130
6	16.79	Azulene	51, 102, 128
7	18.59	Naphthalene, 1-methyl-	63, 115, 142
8	19.58	Biphenyl	76, 115, 154
9	19.61	1,1'-Biphenyl, 2-methyl-	83, 115, 153, 168
10	19.70	Naphthalene, 1-ethyl-	63, 115, 141 , 156
11	24.55	Anthracene	76, 89, 152, 178

23–26] and based on thermal degradation mechanisms investigated by different types of techniques, including non-isothermal thermogravimetry (TGA) [27], thermal degradation [28], solid-state NMR, thermogravimetry coupled with mass spectrometry (TGA-MS) and differential

thermal analysis (TGA-DTA) [29]. Under thermal degradation, AA is first formed through deacetylation reactions via side-chain elimination from the polymer chain. This occurring process leaves an unsaturated polymer backbone or polyene. A further rearrangement reaction takes then place along the polyene backbone with the consequent formation of B.

Because the peaks of AA and B overlapped, their specific m/z values – 60 for AA and 78 for B – were plotted in the total ion chromatograms (TIC) to easily distinguish and better identify them. As shown in pink in Fig. 1a, the AA peak is much broader with a characteristic fronting peak shape, also typically observed in previous studies [1,4,8,23]. Additionally, AA starts to be eluted earlier than B but with a maximum peak at a slightly higher retention time (RT 5.37 min). On the other hand, the B peak is sharper and narrower and its maximum peak is detected at a lower RT (5.33 min).

The distinction between AA and B can be better observed with Py of DS (Fig. 1b), both in the TIC and in the extracted selected ion chromatograms for AA and B. Here the AA peak has a tailing shape in contrast to the characteristic fronting one found in the Py of SS. A dominant broad and intense peak of AA is produced during the TD of DS, while a much less intense one was registered for B (Fig. 1c). This result shows that AA is formed first at lower temperature conditions such as from 100 ° to 250 °C during TD of DS, and both B and AA can be found at a higher temperature such as 600 °C during the Py of DS and SS with better chromatographic discrimination in DS.

This pyrolytic behaviour can similarly be observed in *Pliodisp 7580* (Fig. 2a,b,c – Tab. S-4a,b,c). On the other hand, the detection of AA and B in *Inart Glue* followed a different pyrolytic pattern. In contrast to PVAc Pure Homopolymer and *Pliodisp 7580*, the AA and B peaks can be seen well-separated in the Py step of SS (Fig. 3a) whereas they overlap at the Py step of DS (Fig. 3b). Additionally, the production of AA at the TD of DS (Fig. 2c), in terms of peak area and intensity is relatively lower for *Inart glue*.

Concerning *Mowilith LDM 1871*, an additional pyrolytic pattern for AA and B was observed (Fig. 4). The shape, conformation, and RT of AA and B in the TIC registered at the Py of SS is comparable to that for PVAc Pure Homopolymer and *Pliodisp 7580* (first maximum peak detection of B and then AA) (Fig. 4a). On the other hand, the TIC at the Py step of DS (Fig. 4b) shows a similar pattern to *Inart Glue* (first maximum peak detection of B followed by AA) (Fig. 3a). The TD of DS shows an additional different pattern with a double band for the AA and a tiny one for the B eluted earlier (Fig. 4c). Finally, similarly to *Inart Glue* and *Pliodisp 7252*, the AA and B peaks in *Polidisp 1080* – both in the total ion chromatograms (TICs) and in the extracted ion chromatograms – are distinguishable in the Py of SS (first detection of the maximum peak of AA and then B) and DS (first detection of the maximum peak of B and then AA) (Fig. 5a,b). On the other hand, in the TD of DS (Fig. 5c) the profile of their extracted ion chromatograms was similar to the one obtained in *Mowilith LDM1871* (Fig. 4c).

It is possible that the yield of AA and B changes because of the interactions between AA and other products during the pyrolysis, e.g. related to additives, which could lead to changes in the AA and B peak area and shape as well as retention time. It also has to be considered that the thermal degradation of polyvinyl compounds is a polymer-specific reaction depending on the co-effects of other factors such as chemical structure, degradation initiating defect structures, and the configuration and conformation of the polymer chain. Alternatively, the rate of deacetylation of PVAc and the thermal degradation of PVAc cannot be ascribed to possible different molecular weights and chain lengths of the PVAc polymer according to previous studies [28,30]. Therefore, further investigations would be of interest and necessary for finding a satisfactory explanation for the differences in the yield of AA and B under pyrolysis at low and high-temperature conditions and without derivatization, which may hinder the identification of B.

The pyrolysis of PVAc Pure Homopolymer was also based on the formation of unsaturated and aromatic hydrocarbons pyrolysis products

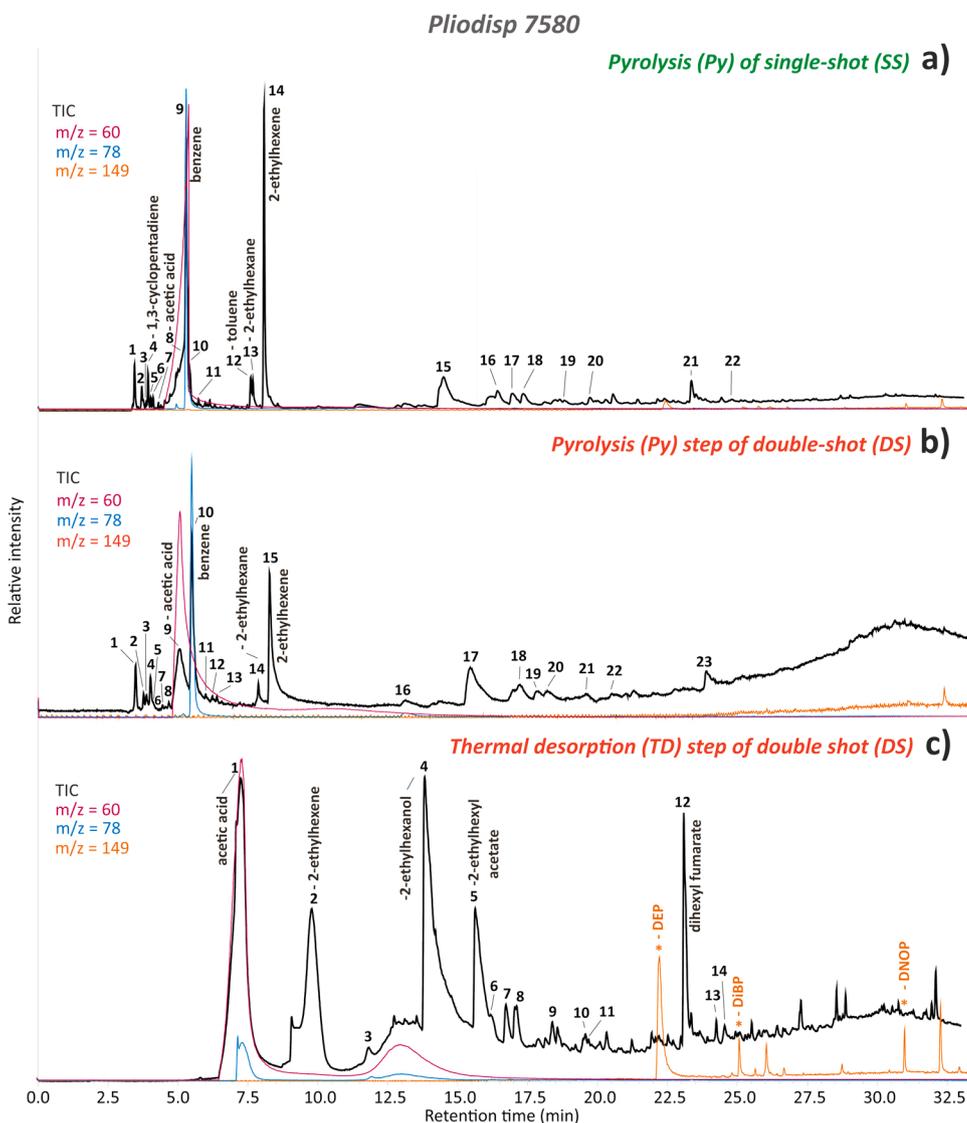


Fig. 2. Total ion chromatograms (TIC) of **Pliodisp 7580** acquired by **a)** pyrolysis (Py) of single-shot (SS), **b)** pyrolysis (Py) step of double-shot (DS), and **c)** thermal desorption (TD) step of double-shot (DS). The numbered peaks of the TICs are listed and described in Tabs. S-4a, b, and c, respectively. DEP: Diethyl phthalate; DIBP: Diisobutyl phthalate; DNOP: Di-n-octyl phthalate. Extracted ion chromatogram of the ion mass with $m/z = 60$ for acetic acid in pink and with $m/z = 78$ for benzene in blue, characteristic for PVAc, while $m/z = 149$ in orange characteristic for phthalate-based plasticizers.

(peaks #8–16 – Fig. 1a, Table 3a) at higher RT due to the breaking of the carbon chain containing double bonds. Particularly, the pyrolysis products such as naphthalene,1-methyl (peak #14), biphenyl (peak #15), and anthracene (peak #16), can be ascribed to the recombination and condensation reactions of the original benzene molecules. The above-mentioned peaks were also detected at the Py step of DS (Fig. 1b and Table 3b) and TD of DS (Fig. 1c and Table 3c). The same type of pattern can be observed for *Pliodisp 7580*, *Inart Glue*, *Mowilith LDM 1871*, and *Polidisp 1080* in Fig. 2a,b and Tab. S-4a,b, Fig. 3a,b and Tab. S-5a,b, Fig. 4a,b and Tab. S-6a,b, and Fig. 5a,b and Tab. S-7a,b, respectively. No additional information was obtained in the TD step of DS for the *PVAc Pure Homopolymer* (Fig. 1c and Table 3c) whereas further components such as additives were found for *Pliodisp 7580*, *Inart Glue*, *Mowilith LDM 1871*, and *Polidisp 1080*. These are described and discussed hereafter.

3.1.1.1. Additives in poly(vinyl acetate) (PVAc) homopolymer. While in the *PVAc Pure Homopolymer* no additional components were detected by SS or DS Py-GC/MS, specimens of *Pliodisp 7580*, *Inart Glue*, *Mowilith LDM 1871*, and *Polidisp 1080* were characterized by different types of additives, such as plasticizers.

3.1.1.1.1. Phthalates- and benzoic acid ester-based plasticizers in *Pliodisp 7580*. The plasticizer bis(2-ethylhexyl) phthalate (DEHP) was identified and characterized in *Pliodisp 7580* (Fig. 2, Tab. S-4). Typical

pyrolysis products of DEHP [31–33] were registered in the TIC obtained in the Py of SS and of DS, such as 2-ethylhexane (peak #13 – Fig. 2a, peak #14 – Figs. 2b) and 2-ethylhexene (peak #14 – Fig. 2a, peak #15 – Fig. 2b). The TD of DS lead to the formation of additional peaks of DEHP such as 2-ethylhexanol (peak #4 – Figs. 2c), 2-ethylhexyl acetate (peak #5 – Fig. 2c), dihexyl fumarate (peak #12 – Fig. 2c), and p-toluic acid, 2-ethylhexyl ester (peak #13 – Fig. 2c), which helped to confirm the presence of such phthalic-based plasticizer.

DEHP is a typical external plasticizer for VAc-based emulsions, frequently present in amounts between 20% and 50%, for improving the chemical and mechanical properties of the polymer after the film has been formed [1]. Vinyl-based polymers are typically characterized by the combination of a series of different phthalate-based plasticizers, and therefore screening methods such as Py-GC/MS have been tested over the last years to successfully identify them in plastics [34,35].

In this study, the extracted ion chromatogram of the ion mass with $m/z = 149$, typical for phthalate-based plasticizers, was obtained in the SS and DS to confirm the presence of the phthalates in *Pliodisp 7580*. This procedure highlighted the presence of diethyl phthalate (DEP), diisobutyl phthalate (DiBP), and di-n-octyl phthalate (DNOP) only in the TD of DS (Fig. 2c – Tab. S-4c), thus highlighting the advantage of the DS Py-GC/MS.

Another type of plasticizer found in the *Pliodisp 7580* is the benzoic

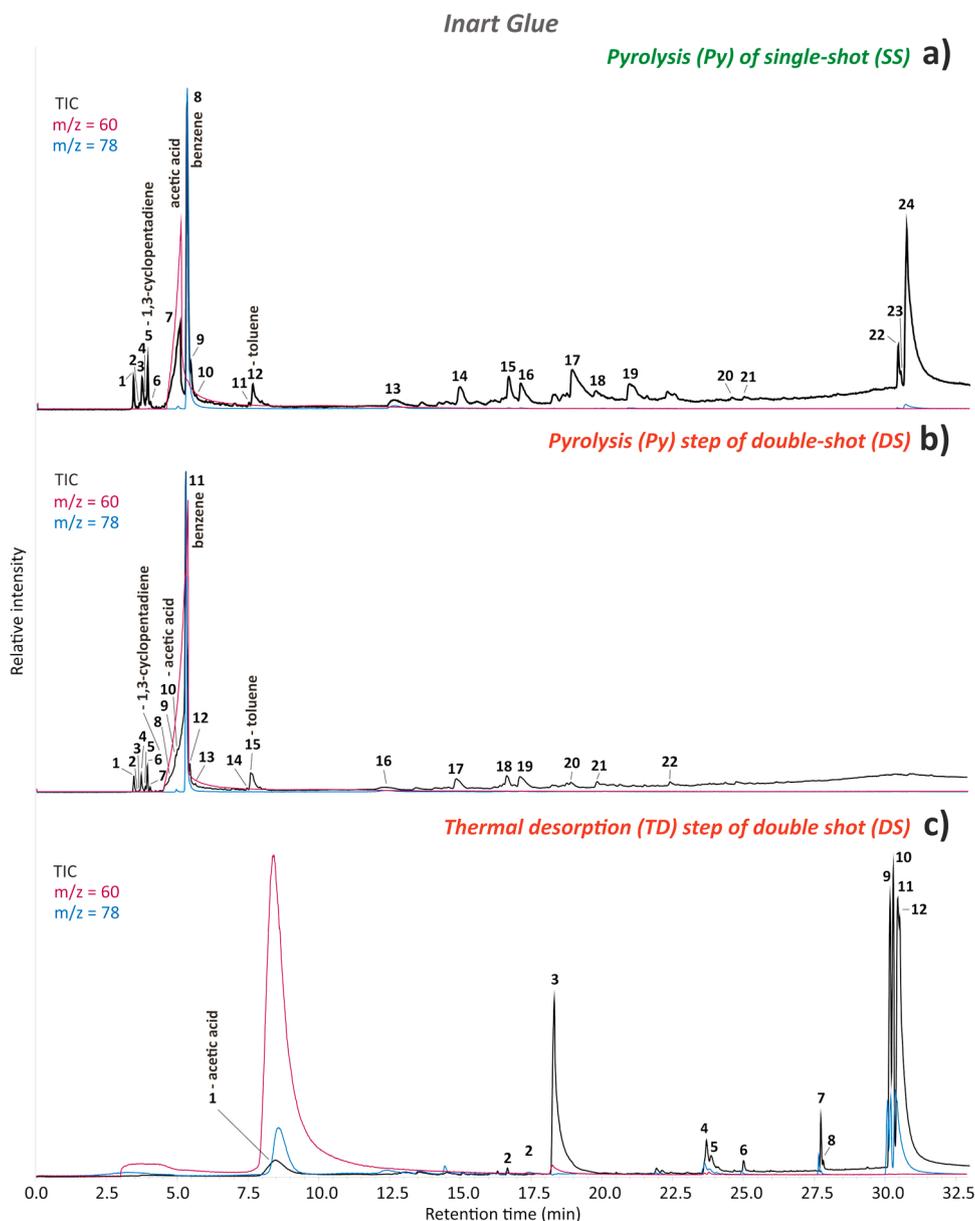


Fig. 3. Total ion chromatograms (TIC) of **Inart Glue** acquired by a) pyrolysis (Py) at of single-shot (SS), b) pyrolysis (Py) step of double-shot (DS), and c) thermal desorption (TD) step of double-shot (DS). The numbered peaks of the TICs are listed and described in Tabs. S-5a, b, and c, respectively. Extracted ion chromatogram of the ion mass with $m/z = 60$ for acetic acid in pink and with $m/z = 78$ for benzene in blue, characteristic for PVAc.

acid ester type 2-ethylhexyl benzoate (2-EHB). This compound was registered in the Py of SS and DS as peak #21 and 23, respectively (Fig. 2a,b). No additional information was obtained in the TD step of DS (Fig. 2c and Tab. S-4c). The peaks detected are mainly compounds deriving from PVAc homopolymer (peaks #1,3,6,7,9,10,11,14) and DEHP (peaks #2,4,5,12,13).

3.1.1.1.2. *Diacetin, diethylene glycol dibenzoate (DEGDB), and dipropylene glycol dibenzoate (DPGDB) in Inart Glue.* In the *Inart Glue* sample, peaks related to pyrolysis products of different types of plasticizers were identified in the Py of SS at retention times (RT) higher than 16.90 min (Fig. 3a). Those are represented by peak #17 (1,2,3-propanetriol, diacetate) originated by the diacetyl plasticizer, peaks #19, 24, and #22,23 formed because of diethylene glycol dibenzoate (DEGDB) and dipropylene glycol dibenzoate (DPGDB) plasticizers, respectively. Diacetyl is a plasticizer that provides tackiness to emulsions, making it more suitable for glues [36]. Blends of dibenzoate esters, such as DEGDB and DPGDB, have been used since the 1940 s as external plasticizers

[37].

The peaks of those pyrolysis products are better resolved and more intense in the TD of DS (peaks #3, 9, 10, 11, 12, Fig. 3c) than those registered in the Py of SS. Particularly, diacetyl is likely to be better detected in the TD step of DS at lower temperature conditions than in the Py step of DS and SS. The peaks #4–8 in the TD step of DS (Fig. 3c and Tab. S-5c) may be formed by the chemical rearrangements of the detected plasticizers under the used pyrolysis conditions.

3.1.1.1.3. *Triethylene glycol (TEG) and lauryl-based intermediates in Mowilith LDM 1871.* Triethylene glycol (TEG) type of plasticizer was detected in *Mowilith LDM 1871* at the TD step of DS according to the small intense peaks #5 and 6 with m/z 87, 91, 133, 169 (Fig. 4c).

By plotting its corresponding single ion mass profile $m/z = 87$ in the TIC of SS and DS it was possible to better observe the contribution of its main marker compounds predominantly in the TD of DS (Fig. 4c). In a similar way, these contributions could be also highlighted in the Py of DS (Fig. 4b) whereas it was otherwise not noticeable in the Py of SS. TEG

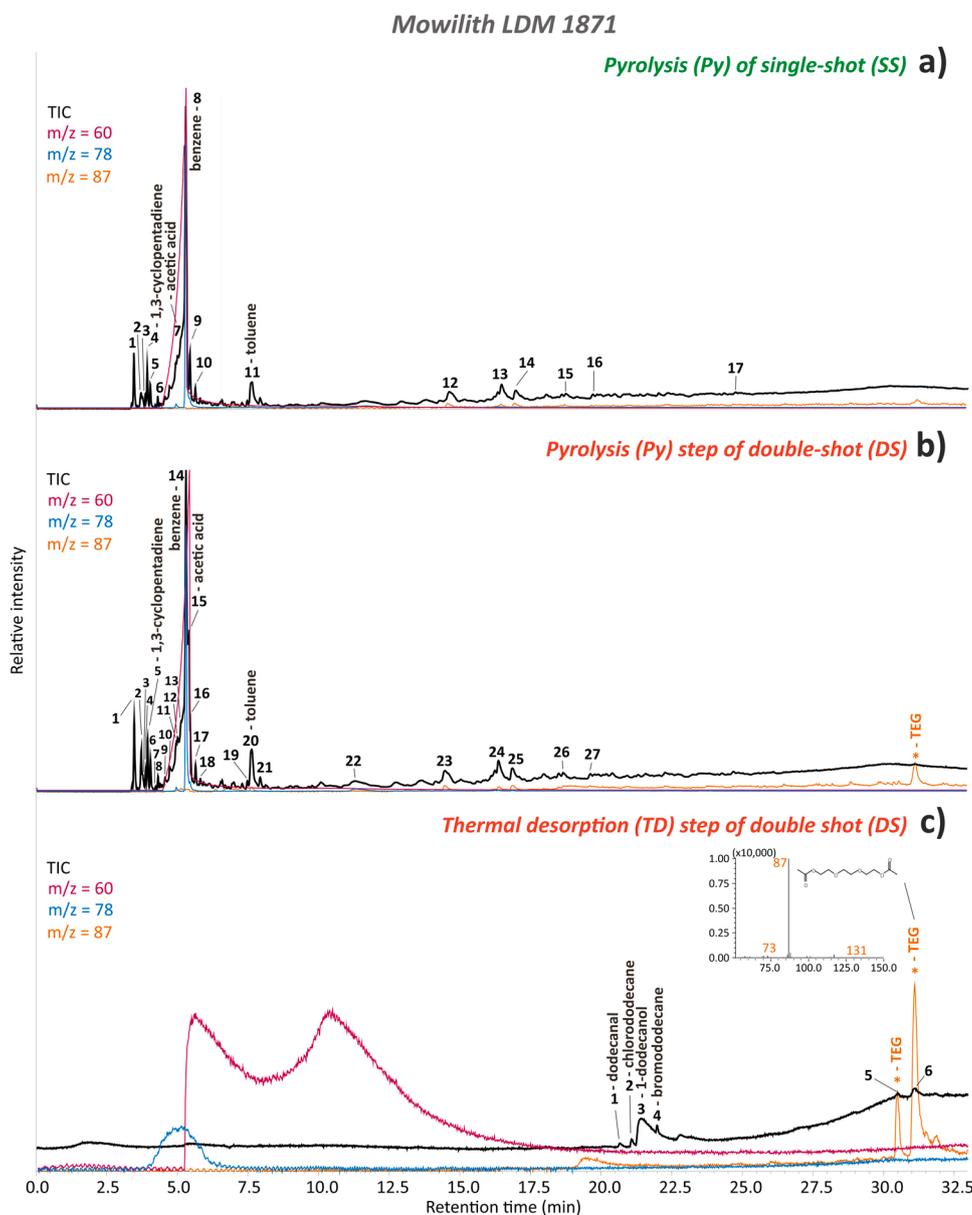


Fig. 4. Total ion chromatograms (TIC) of **Mowilith LDM 1871** acquired by the **a)** pyrolysis (Py) of single-shot (SS), **b)** pyrolysis (Py) step at of double-shot (DS), and **c)** thermal desorption (TD) step of double-shot (DS). The numbered peaks of the TICs are listed and described in Tabs. S-6a, b, and c, respectively. Extracted ion chromatogram of the ion mass with $m/z = 60$ for acetic acid in pink and with $m/z = 78$ for benzene in blue, characteristic for PVAc, while $m/z = 87$ in orange for triethylene glycol (TEG) with its corresponding mass spectrum.

is a relatively common plasticizer for vinyl resins [38] and has been used at least since the 1950 s [39]. 1-Dodecanol was detected by the TD of DS. This additive is also known as lauryl alcohol, and among its different uses, it is typically employed for making surfactants. Moreover, 1-Dodecanol is used as a precursor of 1-chlorododecane or lauryl chloride and 1-bromododecane or lauryl bromide types of intermediate for producing surfactants, which were detected as peak #2 and 4 (Fig. 4c, Tab. S-6c), respectively.

3.1.1.1.4. Vinyl alcohol (VAL) in Polidisp 1080. The presence of VAL as a stabilizer in *Polidisp 1080* was indicated only by the TIC obtained by TD of DS. As peaks of relative low intensity shown in the TD step of DS in Figs. 5c, 2-butenal (peak #1), furan, 2-ethyl-, (peak #2), and 2,4-hexadienal, (*E,E*)- (peak #3) were the only products detected and identified, which are all related to VAL [40].

Indeed, the main pyrolysis products of VAL are generally related to unsaturated aldehydes and molecules containing oxygen atoms [40]. The absence of those products in the TICs obtained at higher temperature conditions such as during pyrolysis may point to the lower concentration of VAL in comparison to VAc.

3.1.2. Poly(vinyl acetate-co-vinyl versatate) copolymer – *p*(VAc-co-VeoVa)

In *Plidisp 7252*, the pyrolysis products of VAc at the Py of SS were found together with the presence of hexanoic acid, 2-ethyl-, methyl ester and neodecanoic acid (peaks #14 and 15, respectively – Fig. 6a, Tab. S-8a). Those two pyrolysis products derived from VeoVa (Vinyl ester of Versatic Acid) as a synthetic sterically hindered carboxylic acid with a long, highly branched alkyl chemical structure started to be used in the 1960 s. VeoVa is a softer monomer than VAc and therefore copolymerized to VAc through a process known as “internal plasticization” or addition polymerization [22] for increasing hydrophobicity and UV resistance [41].

The Py of DS results in a better fragmentation of the VeoVa fragments resulting in several further peaks as #19, 21–26 depicted in Fig. 6b and listed in Tab. S-8b. The pre-thermal treatment of the sample during the TD of DS permitted, in this case, to have the more straightforward identification and characterization of VeoVa in the following Py step of DS. In the TD of DS nonanoic acid, 4,6-dimethyl-, methyl ester (peak #3) and neodecanoic acid (peak #4) were characteristic for VeoVa, while the following other unassigned peaks #6, 7, 9 with $m/z = 87$ as base peak are related to isomers of a vinyl ester compound with a highly

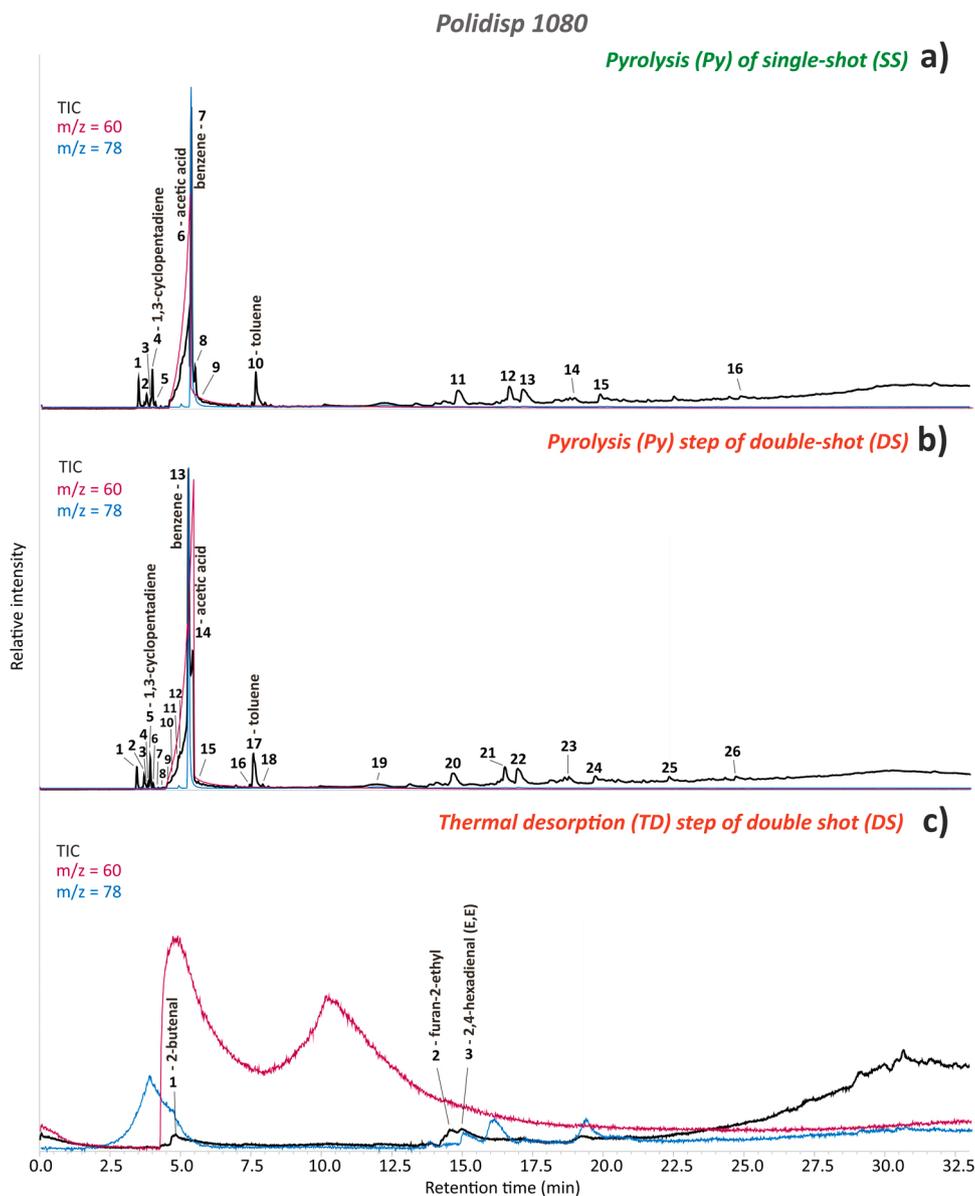


Fig. 5. Total ion chromatograms (TIC) of **Plodisp 1080** acquired by **a)** pyrolysis (Py) of single-shot (SS), **b)** pyrolysis (Py) step of at of double-shot (DS), and **c)** thermal desorption (TD) step of double-shot (DS). The numbered peaks of the TICs are listed and described in Tabs. S-7a, b, and c, respectively. Extracted ion chromatogram of the ion mass with $m/z = 60$ for acetic acid in pink and with $m/z = 78$ for benzene in blue, characteristic for PVAc.

branched C10 side group such as VeoVa (Fig. 6c).

Concerning the acetic acid (AA) and benzene (B) pyrolytic profile – including retention time (RT min), peaks separation and shape – the TIC of Plodisp 7252 was similar to the one evidenced in Inart Glue both in SS and DS. AA and B peaks are well resolved and can be easily distinguished in SS, whereas they overlap in Py of DS. Similarly to the other VAc-based emulsions, the extracted ion chromatograms of the ion mass $m/z = 60$ for AA and $m/z = 78$ for B were performed on the TICs (Fig. 6, a,b,c). Also, in this case, this procedure allowed a clear detection of those fundamental pyrolysis products for VAc.

3.1.2.1. Additive in p(VAc-co-VeoVa). In the TD of DS of *Plodisp 7252*, an additional component was found besides the AA and B of VAc and neodecanoic acid of VeoVa: di-*t*-butyl-4-butylphenol (peak #5, Fig. 6c). This compound is assigned to Isonox 132 [42], a type of common antioxidant for paints but also heat stabilizer for polyurethane foams, supplied by SI Group, Inc. (Schenectady Chemical Co.). Moreover, peak #1 of sulfur dioxide SO_2 in the Py of DS suggests the presence of sulfated

end caps of ionic surfactant such as lauryl sulfate, usually used in the stabilization of PVAc dispersions [43,44]. Unfortunately, no other products which may have been related to such surfactant types and which may have confirmed their presence were detected.

3.1.3. Poly(ethylene-co-vinyl acetate) – p(E-co-VAc)

Another type of vinyl acetate-based emulsion was detected. The V2 glue sample was characterized and identified as a copolymer of ethylene and vinyl acetate – p(E-co-VAc). As for the other samples based on a PVAc, acetic acid (AA) (peak #15 – Fig. 7a,b) and benzene (B) (peak #13 – Fig. 7a,b) represent the most dominant peaks in the pyrolysis (Py) of single-shot (SS) and double-shot (DS). These were complemented by 1,3-cyclopentadiene (peak #4 – Fig. 7a,b), toluene (peak #19 – Fig. 7a, peak #20 – Fig. 7b) and aromatic hydrocarbons at later retention times (Fig. 7a,b, Tab. S-9a,b). Similar to *Mowilith LDM 1871*, the AA and B peaks are well distinguishable in the total ion chromatograms (TICs) and the extracted ion chromatograms obtained by the Py of SS and DS (first detection of the maximum peak of B and then AA) (Fig. 7a,b).

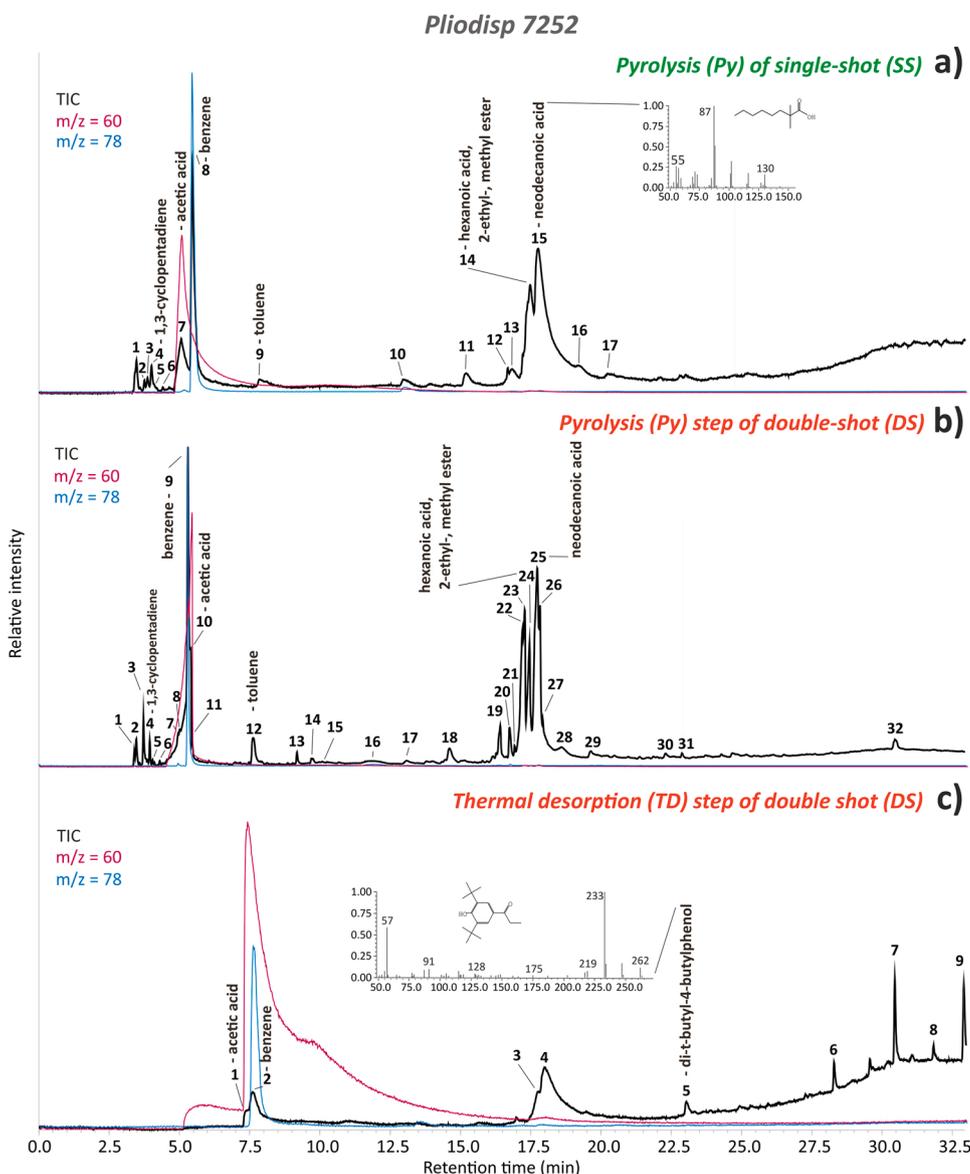


Fig. 6. Total ion chromatograms (TIC) of **Pliodisp 7252** acquired by **a)** pyrolysis (Py) of single-shot (SS), **b)** pyrolysis (Py) step at of double-shot (DS), and **c)** thermal desorption (TD) step of double-shot (DS). The numbered peaks of the TICs are listed and described in Tabs. S-8a, b, and c, respectively. Extracted ion chromatogram of the ion mass with $m/z = 60$ for acetic acid in pink and with $m/z = 78$ for benzene in blue, characteristic for PVAc. Additionally, mass spectrum of neodecanoic acid and di-*t*-butyl-4-butylphenol are depicted in a) and c), respectively.

Additionally, the profile of their extracted ion chromatograms from the TD of DS (Fig. 7c) was comparable to the one obtained in *Mowliith LDM1871* (Fig. 4c) and *Pliodisp 1080* (Fig. 5c).

The identification and characterization of ethylene in the sample, whose presence was suggested by the FTIR-ATR analyses done during this research and reported elsewhere [7,8], was not straightforward. Generally, the PLOT type of column, which has a polystyrene divinylbenzene (DVB) stationary phase, is better suitable for the separation of hydrocarbons and small hydrocarbon pyrolysis products [45–49]. Nevertheless, the presence of ethylene was confirmed by extracting the specific m/z values of 57 as an important marker compound of aliphatic hydrocarbons from the obtained total ion chromatogram (TIC) of the Py of DS and SS, and by comparing those results with the ones described in the literature [40]. Fig. 8 shows the pyrolytic profile of the aliphatic hydrocarbons ($m/z = 57$), including several alkenes and alkanes from 7 up to 22 carbons. The detection of those fragment molecules, which were identified in the Py of SS and DS (Fig. 8), implies the use of ethylene.

3.1.3.1. Additive in p(E-co-VAc). Similar to *Inart Glue*, diacetin plasticizer was clearly identified in the TD of DS (Fig. 7c) of *V2 Glue* as well as

in the Py of SS (Fig. 7a). The TD step only revealed the detection of 1,2,3-propanetriol, diacetate (peak #4), which is shown in Fig. 7c. Moreover, the detection of the very small intense peaks of 2-butenal (peak #1), furan, 2-ethyl- (peak #2), and 2,4-hexadienal, (*E,E*-) (peak #3) at the TD of DS (Fig. 7c) points that p(E-co-VA) in *V2 glue* is stabilized with VAL, which was also found in *Pliodisp 1080* as previously discussed (see Section 3.1.2).

4. Conclusions

This study explored the applicability of double-shot (DS) as compared to the single-shot (SS) Py-GC/MS for detecting components in VAc-based emulsions used in modern-contemporary art for the first time. Generally, three different classes of VAc-based emulsions were successfully characterized in the analyzed samples: PVAc homopolymer, poly(vinyl acetate-co-vinyl versatate) copolymer – p(VAc-co-VeoVa), and poly(ethylene-co-vinyl acetate) copolymer – p(E-co-VAc). More precisely, the DS technique of the Py-GC/MS applied to the identification and characterization studies of different VAc-based emulsions from the early 21st century allowed the detection of chemical multi-components in a more precise and detailed way than by the SS method in terms of additives detection, peak shape, and relative

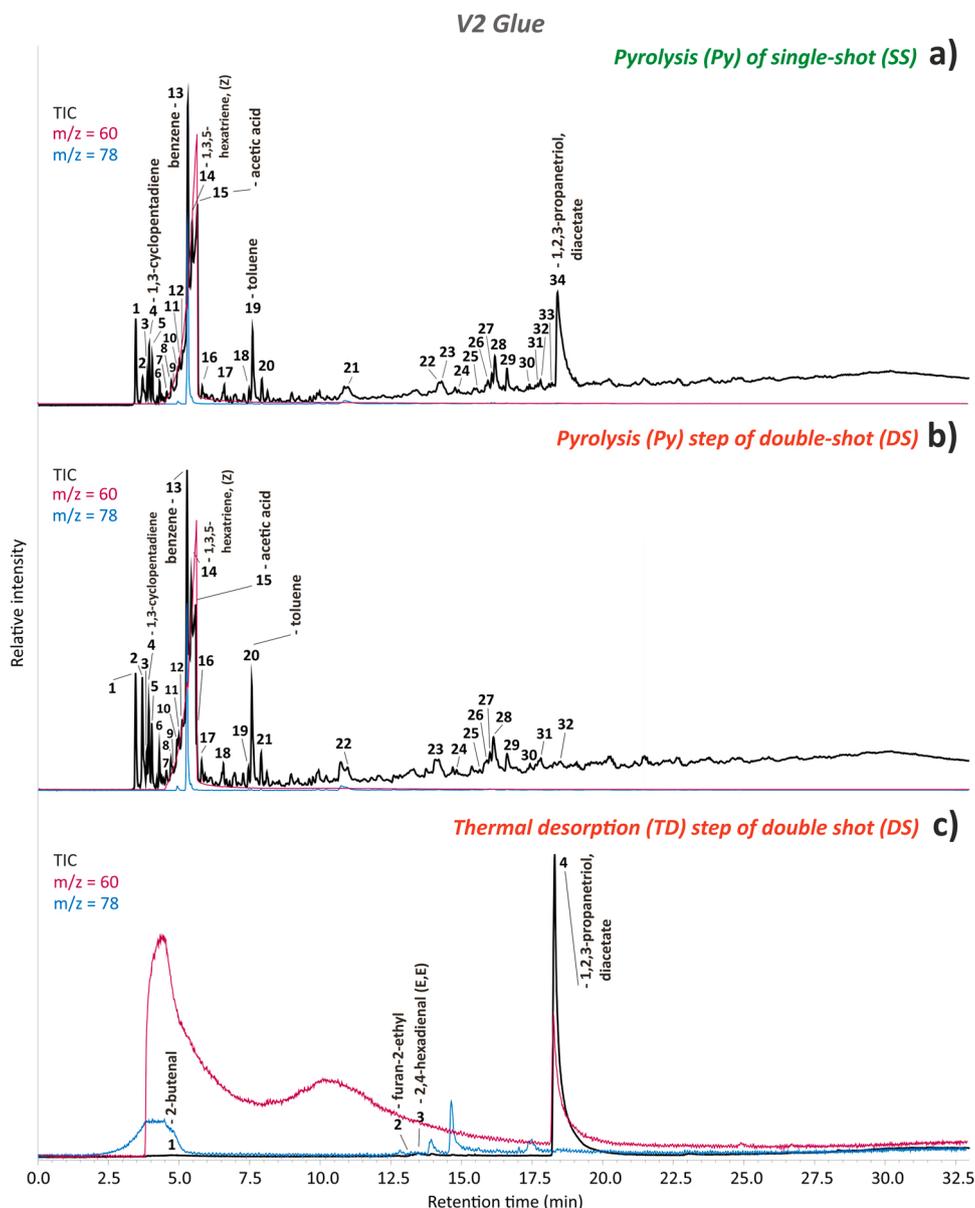


Fig. 7. Total ion chromatograms (TIC) of V2 glue sample acquired by a) pyrolysis (Py) of single-shot (SS), b) pyrolysis (Py) step of double-shot (DS), and c) thermal desorption (TD) step of double-shot (DS). The numbered peaks of the TICs are listed and described in Tabs. S-9,a, b, and c, respectively. Extracted ion chromatogram of the ion mass with $m/z = 60$ for acetic acid in pink and with $m/z = 78$ for benzene in blue, characteristic for PVAc.

abundance. Several classes of additives such as stabilizers, antioxidants, intermediates, plasticizers were mostly identified by DS. Depending on the analyzed material, the comparison between the SS and DS technique results shows four main evidences for the analytical characterization of VAc based emulsions: 1) the vinyl alcohol (VAI) type of stabilizer in the PVAc homopolymer was fully evidenced only at the TD step of DS according to the of 2-butenal, furan, 2-ethyl-, and 2,4-hexadienal, (*E,E*)-thermal desorbed compounds; 2) the detection of some additives such as di-*t*-butyl-4-butyl phenol (Isonox 132) antioxidant, 1-dodecanol surfactant/precursor, and 1-chlorododecane and 1-bromododecane types of intermediate was only possible by the TD step of DS; 3) the possibility of detecting some marker peaks of phthalate-based plasticizers (diethyl phthalate - DEP, diisobutyl phthalate - DIBP, and di-*n*-octyl phthalate - DNOP) and triethylene glycol (TEG) plasticizer by plotting their mass profile in the thermal desorption chromatogram ($m/z = 149$, $m/z = 87$, respectively), otherwise unnoticed by plotting the total ion chromatograms (TICs) of the SS; 4) the detection of some marker compounds of different types of plasticizer originated from diacetin, diethylene glycol

dibenzoate (DEGDB) and dipropylene glycol dibenzoate (DPGDB) was better and clearer achieved by the TD of DS. Particularly, diacetin is likely to be better detected in the TD step of DS than in the SS. All of the four analytical observations by the DS method above mentioned highlight the respective advantages of this technique applied in this study in comparison to the SS mode and the potential significance of its application in the field of modern-contemporary art for the analysis of VAc-based emulsions.

Declaration of Competing Interest

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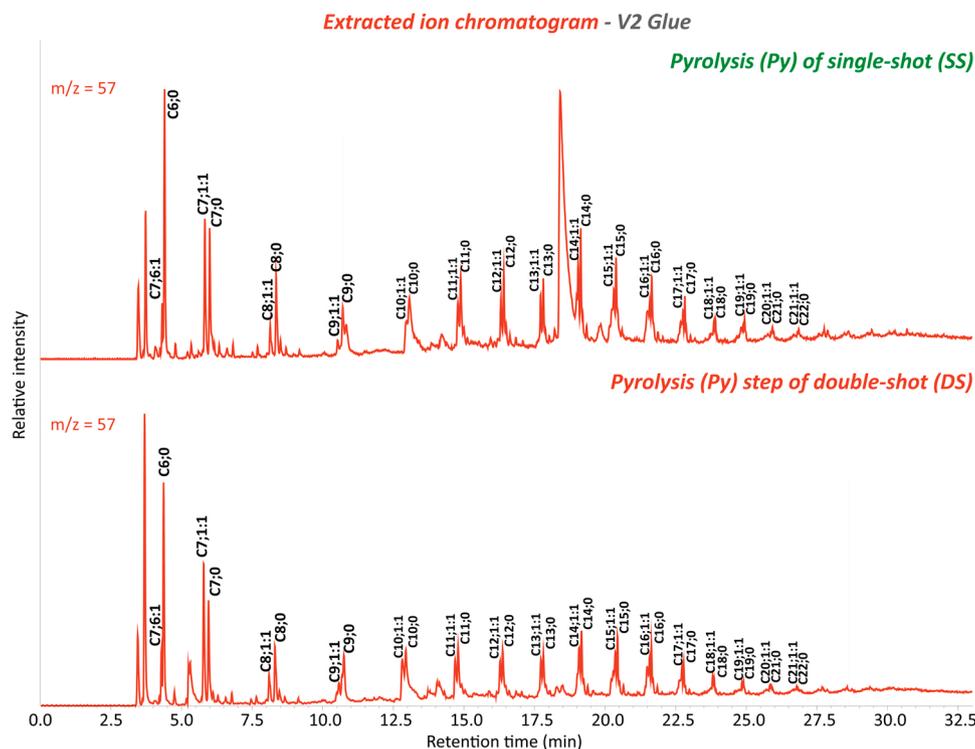


Fig. 8. Extracted ion chromatograms of the ion with m/z 57 in the V2 glue total ion chromatogram (TIC) obtained by pyrolysis (Py) of single-shot (SS) and pyrolysis (Py) step of double-shot (DS) (Fig. 7a,b), characteristics for aliphatic hydrocarbons as pyrolysis products of ethylene-based monomers.

hereby reported, which included non-financial support.

Data Availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jaap.2022.105782](https://doi.org/10.1016/j.jaap.2022.105782).

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