

THE PYROLYSIS - GAS CHROMATOGRAPHY/MASS SPECTROMETRY STUDY OF FLAME-RETARDED HIGH-IMPACT POLYSTYRENE

ISTRAŽIVANJE POLISTIRENA VISOKE ŽILAVOSTI OTPORNOG NA GORENJE S PIROLITIČKOM -
PLINSKOM KROMATOGRAFIJOM / MASENOM SPEKTROMETRIJOM

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Abstract

High-impact polystyrene (HIPS) is widely used for electrical appliances, electronic instruments and building materials. Recently, the degradation of flame retarded plastics got into the focus of interest due to the increasing role of recycling of plastic waste. It is well known that polybrominated flame retardant that were mostly used may produce brominated dioxins during combustion. The oxidative degradation behaviour of brominated flame retardants is of interest since flame retarded plastics may be disposed in municipal waste incinerators or may be involved in accidental fires. It has been demonstrated that various analytical pyrolysis techniques are suitable for the analysis of organic products from flame retarded polymers. The pyrolysis - gas chromatography/mass spectrometry (Py-GC/MS) finds excellent use in the analysis of thermal degradation products of polymers. In the case of flame retarded polymers, such a study is of great importance in understanding the mechanism of flame retardancy.

To study the mechanism of thermal degradation of flame retarded HIPS polymer the phosphate and anhydrophobic fumed silica (Aerosil) were added into the samples. The thermal decomposition temperatures of HIPS samples were measured from the thermogravimetric analysis (TGA) carried out under inert atmosphere from ambient to 550 °C at different heating rates. For the characterization of the studied samples the pyrolysis–gas chromatography/mass spectrometry was used and carried out at 550°C. In Py-GC/MS analysis the pyrolysis temperature is essential factor because by rising the depolymerisation temperature of HIPS higher percentage of low molecular weight substances is obtained. The results indicate that thermal decomposition of HIPS samples are affected by the presence of flame retardant additives.

Key words: flammability of polymers, pyrolysis decomposition, polystyrene, flame retardants

Sažetak

Polistiren visoke udarne žilavosti (HIPS) ima široku upotrebu u električnim i elektroničkim uređajima te građevini. Zbog rastuće količine recikliranog plastičnog otpada u centar pažnje dolazi plastika koja sadrži usporivače gorenja. Poznato je da su se kao usporivači gorenja koristili polibromirani spojevi koji tijekom gorenja proizvode bromirane dioksine. Termo-oksidativna degradacija bromiranih spojeva je od posebnog interesa jer takva plastika može završiti u spalionicama komunalnog otpada ili može biti zahvaćena slučajnim požarom. Pokazalo se da su različite analitičko-pirolitičke tehnike vrlo pogodne za analizu organskih produkata nastalih toplinskom razgradnjom polimera koji sadrže usporivače gorenja. Jedna od takvih pogodnih metoda je i pirolitička - plinska kromatografija/masena spektrometrija (Py-GC/MS). Ova metoda naročito je pogodna za razumijevanje mehanizma djelovanja polimernih usporivača gorenja..

U ovom radu istraživanja je toplinska razgradnja uzoraka HIPS polimera pripremljenih s usporivačima gorenja, dodan je fosfatni usporivač gorenja uz nanopunilo siliku (Aerosil). Zatim, temperature toplinske razgradnje HIPS uzoraka određene su termogravimetrijskom analizom (TGA) u inertnoj atmosferi u temperaturnom intervalu od 25°C – 550°C pri različitim brzinama zagrijavanja. Ispitivani uzorci karakterizirani su pirolitičko -plinskom kromatografija/ masenim spektrometrom na temperaturi od 550°C. Kod Py-GC/MS analize temperatura pirolize je od iznimnog značaja budući se porastom temperature pirolize povećava udio depolimeriziranog HIPS-a u obliku niskomolekularnih tvari. Rezultati pokazuju da na toplinsku razgradnju uzoraka HIPS-a znatno utječu prisutni usporivači gorenja.

Ključne riječi: gorivost polimera, pirolitička razgradnja, polistiren, usporivači gorenja.

1. Introduction

In recent years, much attention has been paid to the possibility of recycling plastics by pyrolysis because of high amount of the Waste Electronic and Electrical Equipment (WEEE). Unfortunately, WEEE plastics often contain toxic brominated flame retardants, which make them particularly problematic to recycle [1]. Pyrolysis of plastic wastes is a proven process whereby polymers are converted into gas, oil, and char products that can then either be used as chemical feedstocks or as fuels. Knowledge of the thermal behaviour and the reactivity of polymers and their mixtures with flame retardants during pyrolysis, is very important for the effective design of flame retarded polymers, and the solid devolatilization is always a fundamental step. Thermal behaviour of plastics can be improved by knowing thermal degradation products obtained on pyrolysis. Looking at the large number of available flame retardant compounds on the market, it is important to understand differences in the performance of materials due to the chemical structure of the flame retardant [2]. In addition to halogen-containing organic types, flame retardants (FR) are based on inorganic minerals and nitrogen compounds among others, as well as products now available that are based on phosphorus [3]. A variety of phosphorous based chemicals with different physical and chemical properties can be used like: triaryl phosphates, resorcinol bis(diphenylphosphate) (RDP), tris(chlorpropyl)phosphate (TCPP), phosphinic acid derivatives, ammonium polyphosphate (APP), red phosphorus, diphenyl 2-ethylhexyl-phosphate (DPO). The flame retardant effect of the P-products cannot be described by a single mechanism. Typically, a P-based FR is designed to develop its activity in combination with the starting decomposition of the specific polymer it is used for. Phosphorus-based flame retardants are generally believed to act in the condensed phase, though a few of them have been found to act in the gas phase as well [4]. The classes of phosphorus-based FRs quoted above are mainly used in polyamides, polyesters, polyolefins and styrenics. The main area of application for the compounded materials is injection-moulded electrical and electronic (E& E) parts [5].

The aim of this study was to examine the effect of phosphorous flame retardant and its combination with silica nanofiller on the thermal decomposition reactions of HIPS polymers, in order to observe changes in thermal stability and in the composition of pyrolysis.

2. Experimental

Materials

Studied samples were prepared with high-impact polystyrene (HIPS, Doki 472, Dioki), melt flow rate 3.5 g/10min, content of butadiene rubber 8.5 mass-%, and with addition of diphenyl 2-ethylhexylphosphate (disflamoll DPO, Lanxess), phosphorus content of 8.6 mass-%, as flame retardant, and fumed silica (Aerosil R7200, Degussa) with 99.8 mass % SiO₂, structure modified with a methacrylsilane, was used as nanofiller.

Sample Preparation

The samples of HIPS with phosphate based flame retardant and anhydrophobic fumed silica were prepared by extrusion. The process was carried out on a Haake Rheorcord System 9000 twin-screw extruder (Haake, Karlsruhe, Germany), a co-rotating extruder with standard, non-intensive screw characteristics. Temperature profile in extruder was set to 190/200/210/220°C (from hopper to die) and screws rotation speed was set to 60 rpm.

The fractions of DPO flame retardant in HIPS were: 4 and 8 mass-% and Aerosil 4 mass-%, samples are denoted as PS, PS-8P and PS-4A-4P and were further characterized.

Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were carried out on ca. 10 mg HIPS samples using a TA Instruments SDT-2960 thermogravimetric analyzer under a flowing N₂ atmosphere from 25°C to 550°C at the heating rate of 5°C, 10°C, 15°C and 20°C / min.

Pyrolysis - Gas Chromatography/Mass Spectrometry (Py-GC/MS)

The pyrolysis of the studied samples was carried out in a Frontier Lab double-shot pyrolyzer PY-2010 iD. About 0.2 mg samples was pyrolyzed at 550 °C for 1 min in a quartz tube using helium as a carrier gas. Analysis of the volatile products was accomplished online with a GC/MS (Shimadzu GCMS-QP2010 plus) using Ultra ALLOY⁺-5 (5% diphenyldimethyl polysiloxane) metal capillary separation column (length 30m x 0.25mm i.d. x 0.25 mm film thickness). The pyrolysis interface and the GC injector were kept at 320 °C. GC Injection port was in constant pressure mode at 140kPa with split ratio 1/50. GC oven was programmed at 70°C with heating rate 20°C /min up to 320°C and then held for 3 min. The mass spectrometer operated at 1.06 kV in the EI mode. The mass range of 25-350 Da was scanned at scan speed 666. Peak identification was performed using a quadrupole mass-spectrometer.

3. Results and Discussion

3.1. Effect of flame retardants on the thermal stability

The TG analysis was used to examine the changes in the overall thermal decomposition of pure HIPS polymer and HIPS samples with phosphorous flame retardants. The thermal decomposition first evolved formation of phosphate species and phosphoric acid that can stabilize polymer macroradicals resulting in a cross-linked phosphate structure [6]. The maximum degradation temperatures (DTG_{max}) of all studied samples are summarized in Table 1. It is shown, as the heating rate is increased (5,10,15,20°C/min) that T_{max} is shifted to higher temperatures and the thermal stability of HIPS increases and particularly significant increase is observed for the sample in the presence of phosphorous flame retardant (DPO) and silica nanofiller (Aerosil). On the other hand the presence of phosphorous flame retardants alone does not modify the thermal stability as compared to pure HIPS polymer.

Table 1 - Temperatures of the maximum rate of decomposition (DTG_{max}) of HIPS polymer and flame retarded HIPS samples

Samples	5	10	15	20	Char
	°C/min	°C/min	°C/min	°C/min	
	DTG _{max} °C				mass-%
PS	414.5	423.4	432.0	436.0	1.3
PS-8P	411.1	423.2	429.9	435.7	0.5
PS-4A-4P	422.9	434.8	437.9	446.2	6.7&3.2

The mass loss (TG) and the rate of mass change (DTG) of pure and flame retarded HIPS samples are shown in Figures 1 a)-c). The mass losses started at 300°C and 350 °C and are almost complete at approximately 450 °C. The weight losses show that degradation of HIPS polymer occurs almost totally in one-step process as can be concluded by the presence of only one peak in DTG. Although, in Figures 1b) and c) it can be observed thermal degradation starts for the samples PS-8P and PS-4A-4P at 378°C and 314°C, respectively and that indicate different mechanism of degradation due to presence of additives and their different chemical bonds and formation of low molecular structured products during the pyrolysis. The DTG curves of PS-4A-4P sample show shift from 5 to 11 °C higher temperature with increase of heating rate. Similar effect was observed in case of char formation (Table 1), increase of char formation was found with lower heating rate (5°C/min) of 6.7 mass-% and for the higher heating rate is 3.2 mass-%. Note the DTG peak of PS -8P sample have lower content of formed char due to presence of phosphorous flame retardant also indicating different decomposition process.

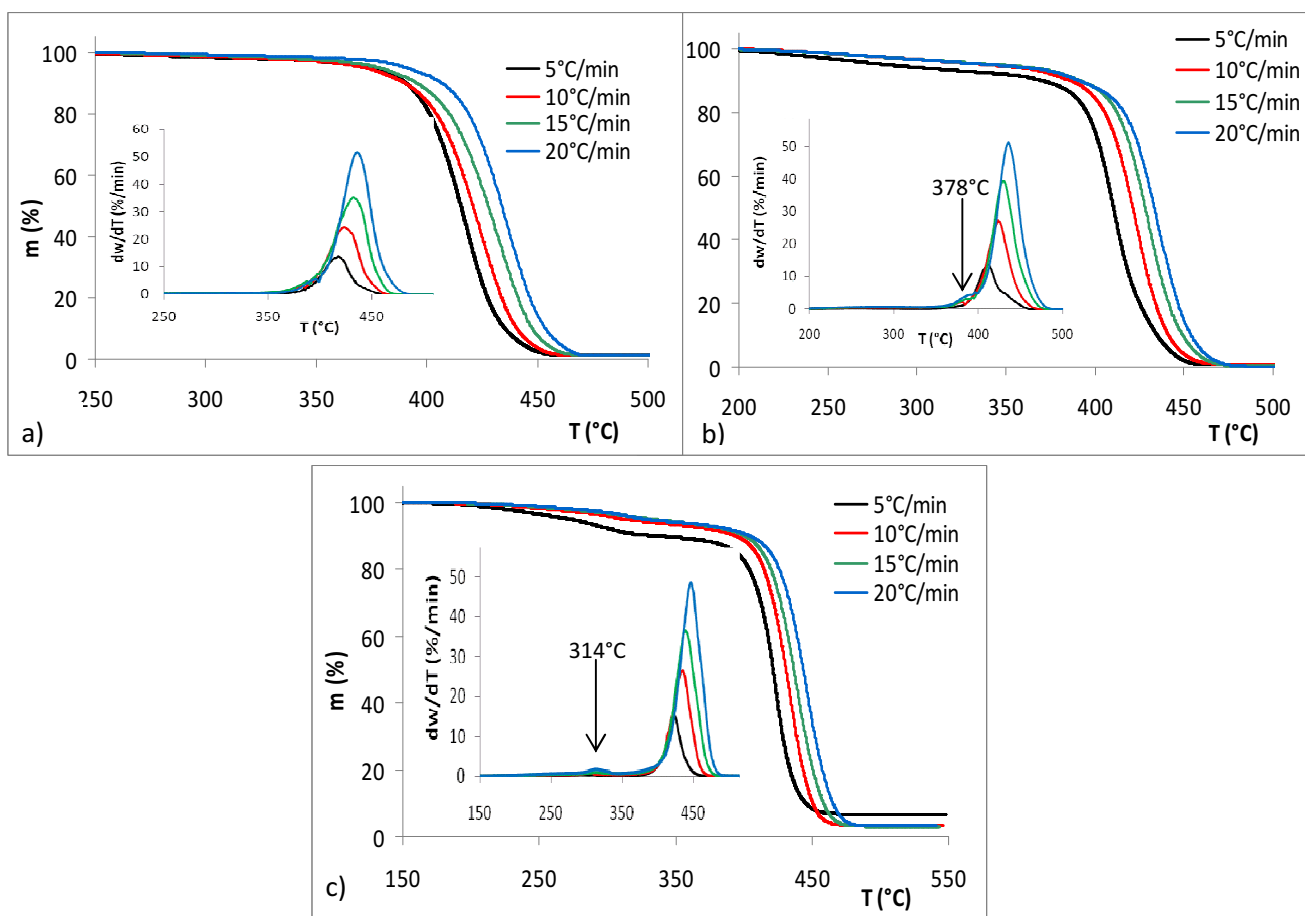
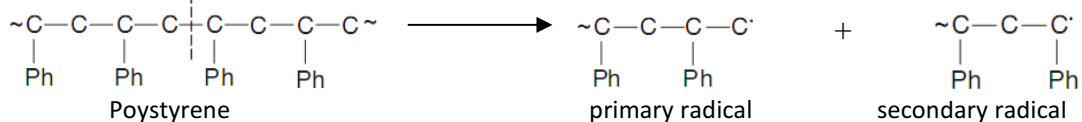


Figure 1 -TG curves and corresponding DTG curves of: a) pure PS, b) PS-8P and c) PS-4A-4P recorded at different heating rate.

3.2. Pyrolysis - Gas Chromatography/Mass Spectrometry Analysis

In order to explain the stabilizing effect of phosphorous flame retardants on HIPS polymer we have to consider the structure and composition of flame retarded HIPS samples and the interaction of various products; macro- and micro-radicals produced from the studied samples, which may give rise to different cross-products and thus play an important role in stabilization. HIPS thermally degrade mainly to monomer with some dimer and trimer that is initiated by a random scission of the polymer main chains at elevated temperatures to give primary and secondary macroradicals. Both macroradicals depolymerize to the monomer.



The effect of phosphorous flame retardant (DPO) on the product distribution of HIPS was studied by Py-GC/MS. The volatile products were separated by GC and different ions produced were detected by MS that are presented at mass spectra in Figure 2. The intensity of peaks in pure HIPS can be compared with flame retarded HIPS samples, which were pyrolyzed at 550 °C. In the case of flame retarded samples some new peaks appear with different intensities. The variations of intensities with additives (DPO, Aerosil) for some major pyrolysis products of HIPS i.e., benzene, toluene, styrene, a-methyl styrene, diphenyl propane, styrene-dimer and -trimer, compositions are given in Table 2. Higher intensities of the main degradation products like styrene- dimer and trimer from PS-4A-4P sample are observed and indicate reduction of their decomposition into simpler products. This show that yields of styrene related to polymer mass was affected by the additives examined. The yields of

styrene dimer and trimer decomposition result in formation of benzene, toluene, ethylbenzene, alpha-methylstyrene and other minor decomposition products. It can be concluded that allyl cleavage of vinyl terminated polymer chains can be prevented by formation of the more stable macroradicals. Further on, it has been reported [7] that small amounts of C1–C4 hydrocarbons are also produced during the pyrolysis of HIPS that increased thermal stability by reduced monomer, dimer, trimer by enhancing hydrogenates like 1,3-Butadiene that were detected in the present work. Styrene products are formed in a free radical process which proceeds by elimination from the secondary macroradical of HIPS. Styrene oligomers are thought to form by a backbiting radical mechanism of the secondary macroradical [8]. Alternative or additional reaction path promoted by some additives may alter the pyrolysis product distribution.

Table 2 - Relative area of Py-GC/MS peaks of the pyrolysis products from HIPS and samples with DPO (PS-8P) and with DPO plus Aerosil (PS-4A-8P)

Peak no	Compounds name	T= 550 °C	Retention time	PS	PS-8P	PS 4A-4P
		MS ion	t _R (min)	Intensity		
	1,3-Butadiene	54.39.28	1.03	-	10	9
1	Benzene	78.28	1.21	1	1	1
2	Toluene	92.91.65	1.63	3	8	12
3	Ethylbenzene	106.91.28	1.91	1	1	2
4	Stiren monomer	104.103.78	2.16	72	99	99
5	2-Phenylpropene	118.117.28	2.63	1	2	6
6	α-methylstyrene	118.117.103	2.70	-	-	4
7	Indane	116.115	7.28	1	1	1
8	1-Buthyl benzene	28.91	7.48	1	1	1
9	Stiren dimer	208.104. 91	7.90	21	26	36
10	Benzene,(1-methyl-3-butenyl)	105.91.77	7.94	-	2	-
11	Aromatic polyphosphate	106.91.77	7.96	-	-	2
12	H-Indene, 1-methyl	130.115.91	8.90	-	2	2
13	Isomer of phosphoric acid, tri(2-isopropylphenyl)ester	28.91.118	9.11	-	1	1
14	1-Butenyl benzene	28.91	9.53	2	1	1
15	Stiren trimer	312.117. 91	11.68	63	54	63
16	Cresyl diphenylphosphate	340.77.65	11.77	-	10	5

In addition, indenenes appear in small amounts among the pyrolysis products. The indenenes are a flammable polycyclic hydrocarbon composed of a benzene ring fused with a cyclopentene ring. The alteration of decomposition mechanism of polystyrene macroradicals can be explained by the interaction of radical sites with ionic species of flame retardants resulting in indene formation. During this process hydrogen elimination was initiated by phosphoric acid where it is obviously facilitate hydrogen shift leading to cyclization and aromatization of the aliphatic chain segments forming indene compounds. The facilitated formation of a macromolecule containing a phenylindane segment as a chain end group (in present work, 2-Phenylpropene) could be the source of the increased formation of indene derivatives. The formation of methylphenylindene is observed in the presence of phosphorous flame retardants, Table 2.

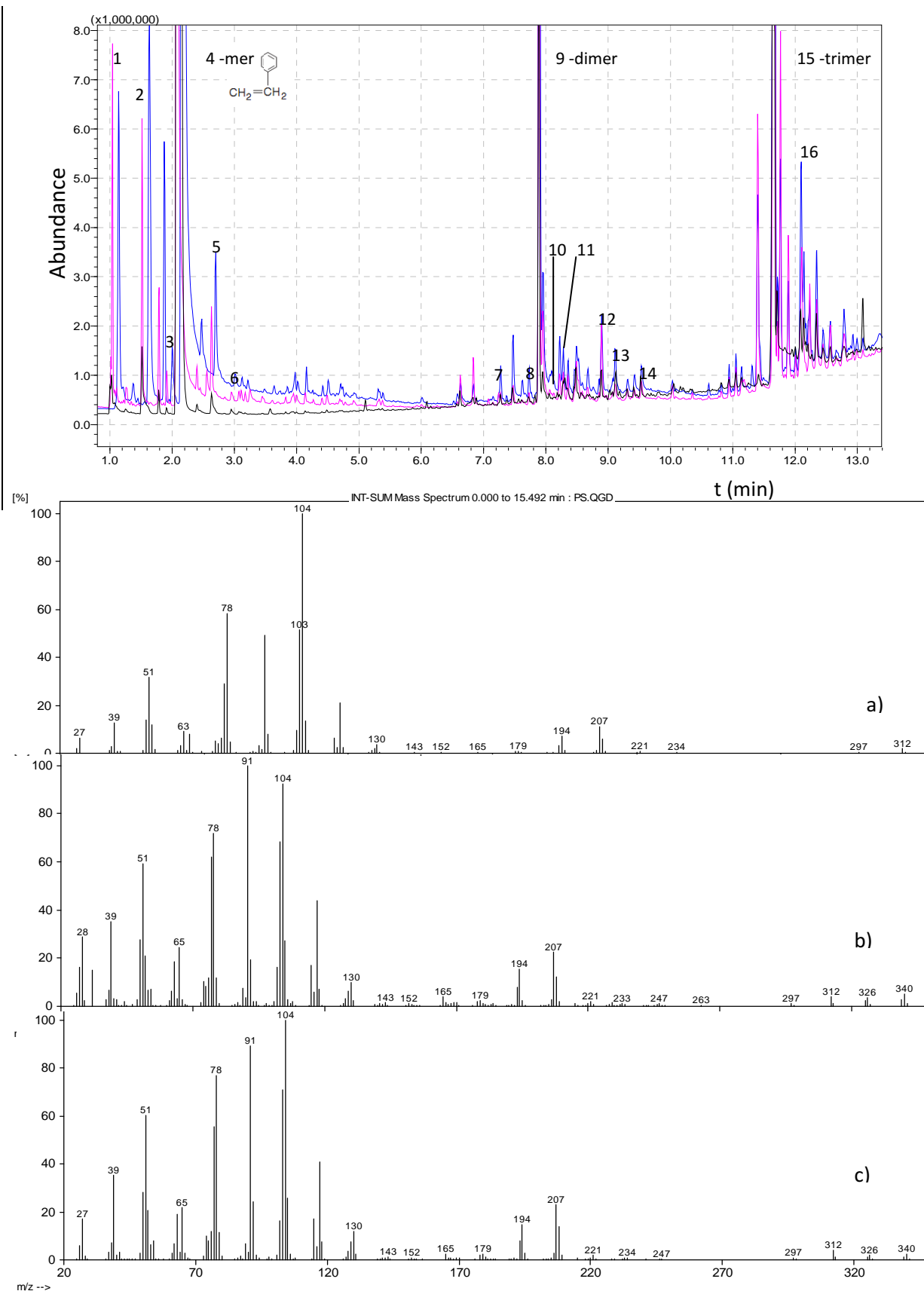


Figure 2 -Pyrolysis total ion chromatograms of the studied samples: PS-8P(red), PS-4A-4P (blue) in comparison with pure PS (black) and corresponding mass spectra: a) pure PS, (b) PS-8P and c) PS-4A-4P sample, respectively, pyrolyzed at 550 °C.

Conclusions

The T_{\max} for HIPS and flame retarded HIPS samples increases with higher heating rates which is due to less exposure to heat as degradation time is reduced in the case of higher heating rates. The T_{\max} of the studied samples has been calculated from the DTGA curves and from results it can be concluded that sample PS-4A-4P shows increased thermal stability due to the presence of additives, phosphorous flame retardant in combination with silica nanofiller.

The results of Py-GC/MS analysis show that HIPS samples give mainly styrene monomer, benzene, toluene, some dimers and trimers as volatile products and some phosphorous co-products but also show that in flame retarded samples some new peaks appear with different intensities and that yields of styrene related to polymer mass was affected by the additives examined.

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