

Side Effects in the Application of Polyamide 6 Barrier Materials for Fuel Tanks

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ABSTRACT: To reduce the pollution of air by minimizing evaporative emissions from fuel tanks, new plastic fuel tanks made of materials with excellent barrier properties have to be developed. Single-layer polyamide 6 tanks are one option to meet the requested low-hydrocarbon permeation rates for motorcycle vehicle tanks. Recently, some problems with respect to deposits in polyamide 6 tanks, blocked nozzles, tubing, and gasoline filters were observed. Thus, samples (precipitates) were taken from unused tanks after conditioning as well as of used tanks and filters after being in contact with gasoline for some time. By investigating the precipitates and deposits by means of infrared (IR) spectroscopy, the main constituents were identified to be cyclic caprolactam oligomers. Additional investigations on the extracted samples by mass spectroscopy allowed us to attribute specific features of the IR spectra to the individual cyclic oligomers (dimer, trimer, and tetramer). In addition, we could show that the crystalline precipitates and deposits in the fuel systems of used vehicles consist of mixtures of the cyclic dimer, trimer, tetramer, and even pentamer of caprolactam with varying contributions of the individual oligomers in dependence of the history of the part. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

During the last years, great efforts have been made to reduce the pollution of air by minimizing evaporative emissions from fuel tanks. The US Environmental Protection Agency (EPA) and the California Air Resources Board (CARB) have claimed drastically lowered limits for permeation rates of the fuel tanks of all vehicles driven by a gasoline engine.^{1–3} In Europe, new emission regulations for fuel tanks will be released soon by the Economic Commission of Europe. It is expected that the new limiting values for permeation rates of fuel tanks in Europe will be in accordance with the regulations of the EPA and CARB.^{2,4,5}

To reduce the emissions of hydrocarbons through the walls of fuel tanks by permeation with the aim to meet these new requirements, new plastic fuel tanks made of materials with excellent barrier properties had to be developed.⁶ New polyamide (PA) 6 and 6.6 materials were introduced by various companies such as DSM,⁷ Lanxess,^{3,8} or Rhodia,⁹ which can be applied as single-material sol-

utions for blow-molded tanks. These single-layer tanks provide a cost-effective alternative to coextruded multilayer plastic tanks with, for example, ethylene vinyl alcohol as permeation barrier layer.^{1,3,10–12} The barrier properties of the PA single-layer tanks are nearly as good as those of the coextruded multilayer tanks,^{12,13} and exceed those of standard HDPE tanks widely used in Europe.^{12–14} Although the barrier properties of the commonly used HDPE tanks could be drastically improved by fluorination techniques, the additional production step of fluorination is getting increasingly undesirable owing to environmental concerns and the cost-intensive and complex safety procedures needed in the handling of this aggressive gas.^{1,3,8,15} Compared to the metallic tank materials like sheet steel or aluminum, which still have a remarkable market share in the United States and Asia, polymeric single-layer tanks have the big advantages of less weight, the absence of corrosion problems, easier forming, and higher freedom in design.^{3,13,15}

Single-layer PA6 tanks showed, after being implemented in motorcycle vehicles now for a few years, some problems with

The additional Supporting information is the supplementary material of this article.

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Table I. List of the Investigated Samples

Sample	Code	FTIR	MS
Precipitates of tank 1	PT1	+	+
Precipitates of tank 2	PT2	+	+
Precipitates of tank 3	PT3	+	+
Crystalline residues of tank 4	PT4	+	n
Crystalline residues of tank 5	PT5	+	n
Polyamide 6 reference material	T	+	n
Residue from a blocked in-tank gasoline filter	PF1	+	+
Residue from a blocked in-tank gasoline filter	PF2	+	n
Residue from a blocked in-tank gasoline filter	PF3	+	n
Residue from a blocked nozzle	PN1	+	+

respect to deposits in the tanks, blocked nozzles, tubing, and gasoline filters.^{16,17} Thus, the present study deals with the identification of such substances isolated either from the gasoline, gasoline filters, and nozzles or from the crystalline precipitates on the inner surface of the tanks.

EXPERIMENTAL

Materials

The materials under investigation were precipitations and crystalline residues of tanks, nozzles, and filters, which we obtained from our customers for analysis. These samples have, in common that they all, stem from motorcycle vehicles equipped with PA6 tanks. All tanks were made of a black PA6. The tanks, however, originate from different batches produced within a period of several years (2008–2011). As PA6 reference material, we used a transparent PA6 foil (denoted as T) and compared it to the tank material of T1.

Samples PT1 and PT2 were grayish-white crystalline precipitates formed at the inner surfaces of tank T1 and tank T2 after conditioning. Tank T1 was unused and only conditioned with water vapor, whereas tank T2 was also first conditioned with water vapor but then filled with gasoline for test purposes. The water vapor conditioning of the tanks was performed at 67°C for 24 h at 100% relative humidity.

All other precipitation samples (PT3–5, PF1–3, and PN1) originate from used vehicles being claimed with defective fuel injection systems. The precipitate PT3 was a solid chunk of white-yellowish material, which was found in the PA tank T3 of a motorcycle. PT4 and PT5 were crystalline residues formed on the inner tank walls of tanks T4 and T5.

In addition, deposits from three blocked in-tank gasoline filters, agglomerated off-white to dark residues in appearance, were analyzed (named PF1–PF3 throughout the article; see Table I). We also investigated the residues from a blocked nozzle (yellowish-white substance), which is denoted as PN1 in the following. All of these clogged parts originate from used vehicles equipped with PA6 tanks.

All samples were investigated by means of FTIR spectroscopy; some of the precipitations were extracted and subjected to a mass spectroscopic analysis. A list of the samples under investigation is provided in Table I.

FTIR Spectroscopy

Transmission FTIR spectra were collected from the samples using a Bruker Hyperion 3000 infrared microscope equipped with a 15× Cassegrain objective and coupled to an Equinox 55 FTIR spectrometer. The material was pressed to a thin film using a Spectratech diamond microtransmission cell. A single element MCT detector with nitrogen cooling was used. The spectral resolution was 4 cm⁻¹ and in total 32 spectra were accumulated.

Mass Spectroscopy

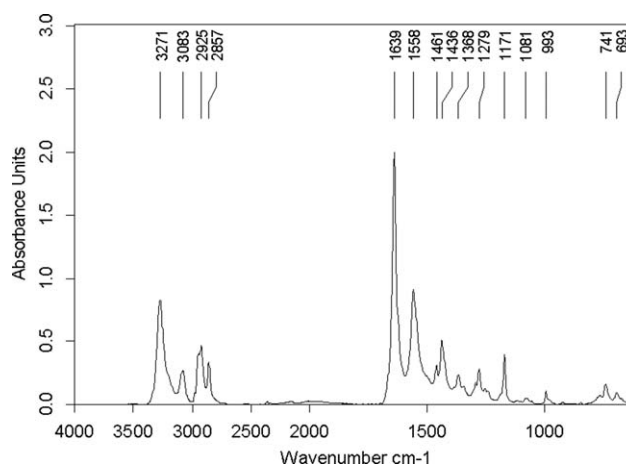
To identify the molecular mass, a small amount of the precipitates a/o residues was dissolved in pure methanol (*pro analysi*). The solution was filtered through a paper filter and analyzed by means of mass spectrometry (MS). A triple quadrupole mass spectrometer AB-Sciex Qtrap 5500 with atmospheric pressure chemical ionization (with positive molecule ionization) was used for the analysis. The methanol eluate was directly injected to the ion trap (heated nebulizer), scanning was performed using the linear ion trap modus at 1000 Da/s and 0.05 ms LIT fill time in a mass range *m/z* from 100 to 700 (1000) Da.

RESULTS AND DISCUSSION

FTIR Spectroscopy

FTIR Spectra of the precipitates in the tanks as well as the residues on filters and nozzle were recorded. The FTIR spectra of the precipitates of the tanks 1–3 (PT1, PT2, and PT3) and the residues on filter 1 (PF1) and the blocked nozzle (PN1) are shown in Figures 1–5. Figure 6 shows the spectrum of the reference sample PA6 in comparison to the spectrum of the tank material T1.

All spectra showed the characteristic bands of moderately long-chained amide species: CH₂— stretching vibrations (2940–2850 cm⁻¹); CH-deformation vibrations ($\nu_{\text{CH}} = 1480\text{--}1330\text{ cm}^{-1}$); NH-stretching vibrations ($\nu_{\text{NH}} = 3320\text{--}3070\text{ cm}^{-1}$), the amide I and II bands ~ 1640 and $\sim 1550\text{ cm}^{-1}$.¹⁸ However, by comparing the absorption maxima of the bands of the various samples, clear differences could be observed in respect to the absorption maxima of, for example, the ν_{NH} and the amide I and II bands. In comparison to the PA6 reference sample (Figure 6), which

**Figure 1.** FTIR spectrum of the sample PT1.

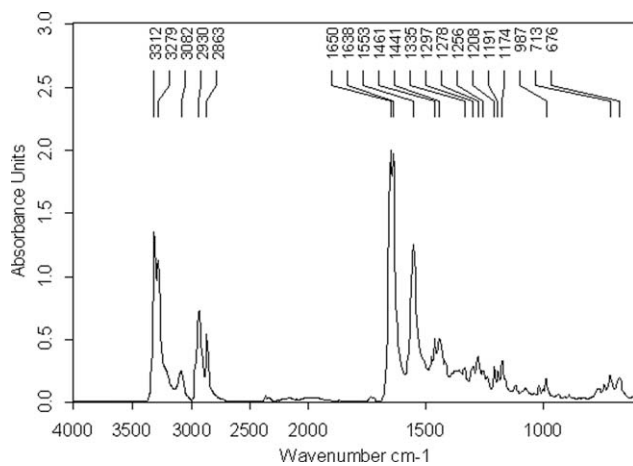


Figure 2. FTIR spectrum of the sample PT2.

showed one narrow band at 3300 cm^{-1} and one at 1641 cm^{-1} attributed to the ν_{NH} and amide I vibrations, respectively, the spectra of the precipitations exhibited maxima between 3312 and 3278 cm^{-1} (ν_{NH}) and 1650 and 1635 cm^{-1} (amide I). Some spectra showed two maxima (e.g., Figure 2, spectrum of PT2), indicating the coexistence of at least two contributing species. In addition, strong differences in the appearance and relative intensities of bands in the fingerprint region ($1300\text{--}700\text{ cm}^{-1}$) were noticed, indicating a higher degree of crystallinity for the precipitations in relation to the polymeric PA6 reference material. In accordance with spectroscopic databases (e.g., Ref. ¹⁹), we assigned the precipitations to oligomeric caprolactam species.

Mass Spectroscopy

Samples PT1-3, PF1, and PN1 were dissolved in methanol and subsequently analyzed by mass spectroscopy.^{20–22} Using the positive molecule ionization, all substances present in the extract, which can form positive ions, will be detected at a mass of the molecular mass +1. Besides the monomer, the cyclic caprolactam ($m + 1 = 114$), signals for the cyclic dimer ($m + 1 = 227$), the cyclic trimer ($m + 1 = 340$), the cyclic tetramer ($m + 1 = 453$), and even the cyclic pentamer ($m + 1 = 566$) were detected.²³ In

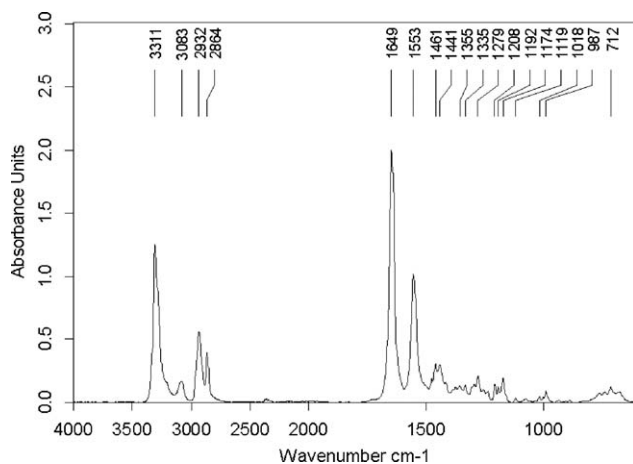


Figure 3. FTIR spectrum of the sample PT3.

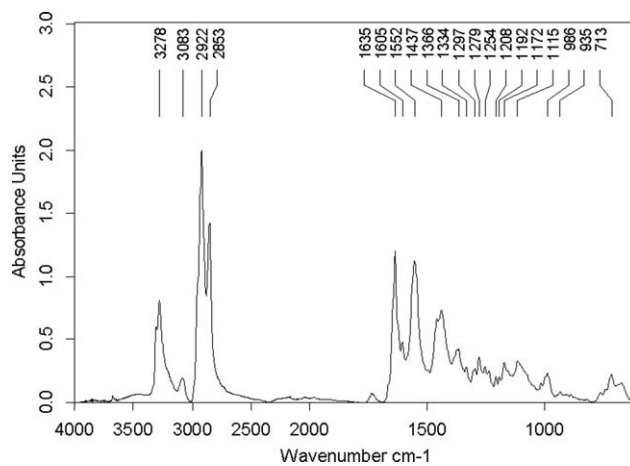


Figure 4. FTIR spectrum of the sample PF1.

Figures 7 and 8, the MS spectra of the extracted precipitations of the samples PT1, PT2, PT3, PF1, and PN1 are shown. The main constituents of these samples are listed in Table II.

Crosscorrelation Between the FTIR Absorptions and the Assignment by MS

Thus, after chemically identifying the constituents of part of the precipitates by MS, we tried to index the corresponding FTIR absorption bands and attributed them to the individual cyclic oligomers O2, O3, and O4. These results, together with the published literature data for caprolactam O1 and its cyclicdimer O2,¹⁹ are summarized in Table III. The melting points of the various oligomers, as published in Ref. ²³, are also listed in Table III.

With these assignments of specific infrared (IR) absorptions to individual oligomers, we aim to get a tool to identify the composition of an unknown precipitation just by recording its IR spectrum without being forced to run additional cost- and time-consuming extractions and MS analyses.

Based on the obtained assignments of the FTIR absorptions, we tried to qualitatively identify the principal constituents of the remaining four samples PT4, PT5, PF2, and PF3; the results are

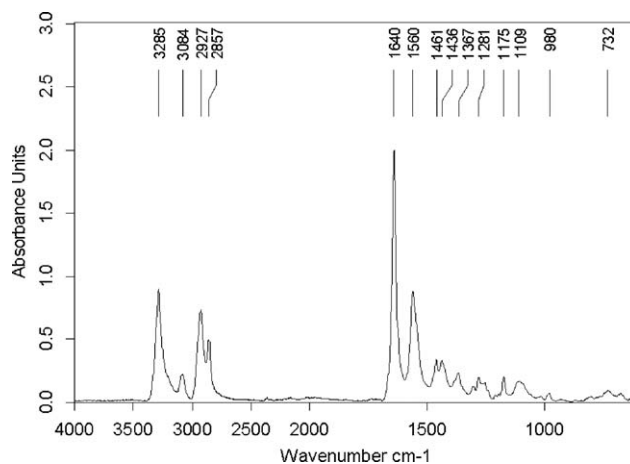


Figure 5. FTIR spectrum of the sample PN1.

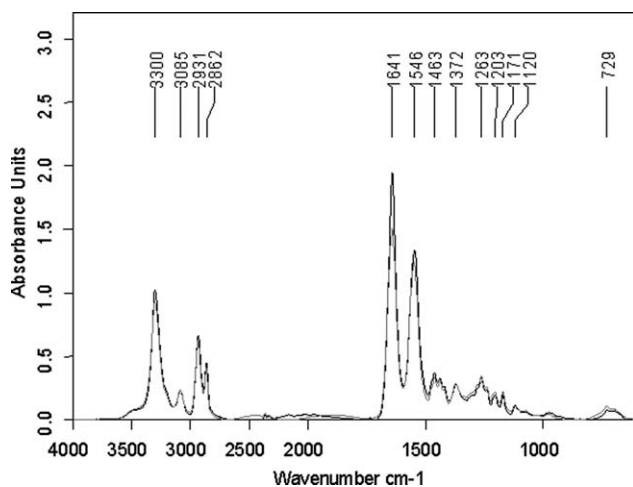


Figure 6. FTIR spectra of the reference PA6 colorless film (gray line) and of the tank T1 material (black line).

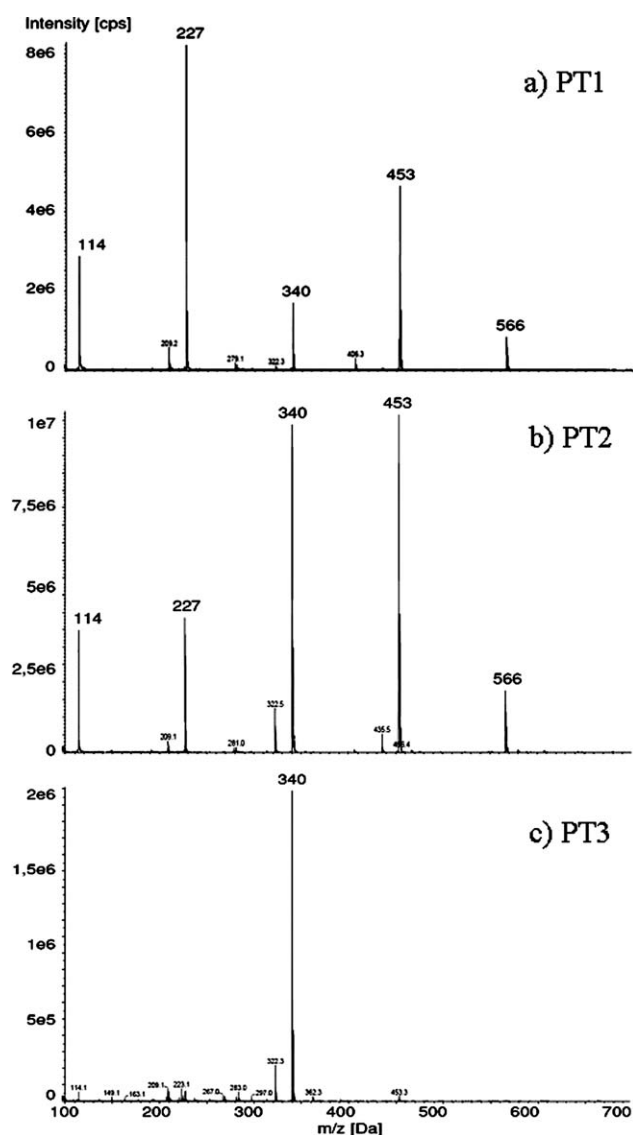


Figure 7. Mass spectra of the extracted precipitations (a) sample PT1, (b) sample PT2, and (c) sample PT3.

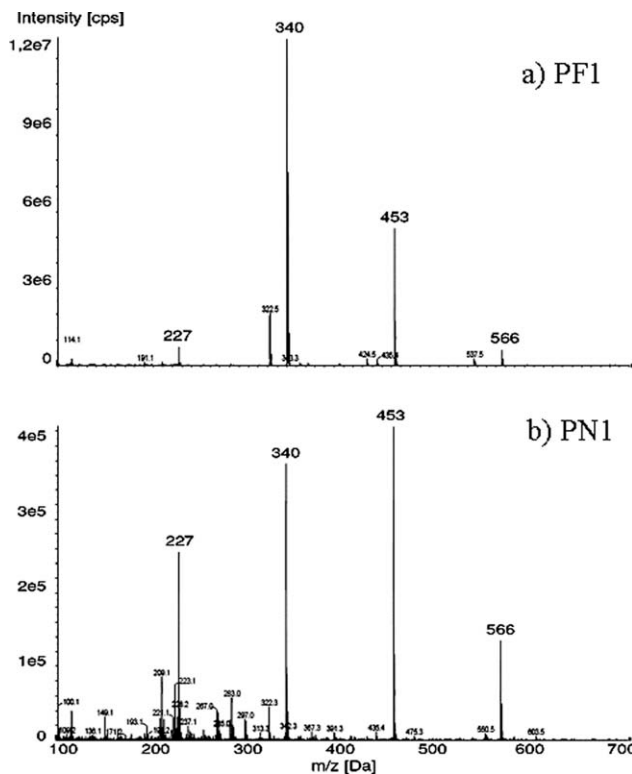


Figure 8. Mass spectra of the extracted precipitations (a) sample PF1 and (b) sample PN1.

summarized in Table IV. The IR-spectra of these samples are given as supplementary material to this paper. It has to be noticed, however, that it is only possible to get information about the main components of the unknown samples with this experimental approach. Owing to the fact that the bands of the different oligomers have very close absorption bands, overlapping is possible and a clear attribution is a demanding task.

DISCUSSION

From the presented experimental data, it can be concluded that the precipitates and crystalline residues that were found in PA6 tanks, blocked filters, and nozzles of motorcycle vehicles (possessing a PA6 tank) contained cyclic caprolactam oligomers as

Table II. Main Constituents of the Samples, Investigated by Means of MS^a

Sample	Code	Main species in the extract
Precipitations of tank 1	PT1	O2 + O3 + O4 + O5
Precipitations of tank 2	PT2	O2 + O3 + O4 + O5
Precipitations of tank 3	PT3	O3
Precipitations from a blocked in-tank gasoline filter	PF1	O3 + O4
Precipitations from a blocked nozzle	PN1	O2 + O3 + O4 + O5

^aO1, the monomer; O2, the cyclic dimer; O3, the cyclic trimer; O4, the cyclic tetramer; and O5, the cyclic pentamer.

Table III. Selected Vibration Modes (cm^{-1}), Characteristic for the Cyclic Oligomers O1–O4 and PA6

	O1 (Ref. 19)	O2 (Ref. 19)	O2	O3	O4	PA6
M.p. ($^{\circ}\text{C}$) (Ref. 22)	69.5	348	348	244	256-257	220
ν_{NH}	3296	3268	3271	3311	3278	3300
$\nu_{\text{CH}_2\text{asym}}$	2966, 2939, 2929	2954, 2939, 2923, 2912	2953, 2925, 2941, 2910	2932	2928	2931
$\nu_{\text{CH}_2\text{sym}}$	2856	2858	2857	2864	2850	2862
Amid I	1658	1639	1639	1649	1638	1641
ν_{CH_2}	1487, 1467, 1441, 1438, 1418	1464, 1448, 1438	1436	1460, 1440	1439	1463
ν_{CH_2} rock	824, 806	742	740	712	676	729

principal constituents. The identification as cyclic oligomers was performed via FTIR spectroscopy, the assignment of specific IR absorptions to the individual oligomers O2, O3, and O4, however, was possible only via parallel investigations of the extracted samples with mass spectroscopy. The correlation of the abundance of individual cyclic oligomers as determined by MS, with the appearance of specific features in the IR spectra allowed us to derive a tool to identify the main constituents of unknown precipitates just by recording their IR spectrum. This point is of significant relevance for the rapid identification of unknown substances (e.g., precipitates) with respect to the fact that FTIR spectroscopy is a well abundant, low priced, and most of all a mobile spectroscopic method.

These findings, that cyclic caprolactam oligomers were deposited on the inner surface of PA6 tanks, are strongly supported by a study on gasoline, stored over 14 months in a PA6 tank, which was performed by Mr. Harald Vogel (Petro Lab GmbH, Speyer). He found that caprolactam oligomers were partially dissolved in gasoline after a long storage period. In addition, he could detect particles dispersed in the fluid phase (gasoline) in the tank. The FTIR spectrum of these dispersed compounds is shown in Figure 9(a) in comparison to a PA6 reference spectrum. By comparing this FTIR spectrum of the dispersed particles with our spectra of the precipitations taken from the inner tank walls of a PA6 tank (for PT1, see Figure 9(b)), a perfect agreement could be obtained. In agreement with our assign-

ments, the dispersed particles consisted of a mixture of O2, O3, O4, and O5 with the cyclic dimer as main constituent.

It is a well-known fact that PA6 materials contain a remarkable content of monomer (caprolactam) as well as linear and cyclic oligomeric compounds²⁴ which can be extracted from the polymeric materials by, for example, low-molecular-weight alcohols such as methanol or ethanol.^{24,25} The concentration of the oligomers in the PA matrix depends on the polymerization conditions but is also driven by a thermodynamic equilibrium. This

Table IV. Principal Constituents of the Samples PT4, PT5, PF2, and PF3 as Determined from Their FTIR Spectra

Sample	Code	Main species of the precipitations identified via their IR absorptions
Residues from a blocked in-tank gasoline filter	PF2	O2
Residues from a blocked in-tank gasoline filter	PF3	O3 + O4 + aliphatic compound
Crystalline residues of tank 4	PT4	O2
Crystalline residues of tank 5	PT5	O2

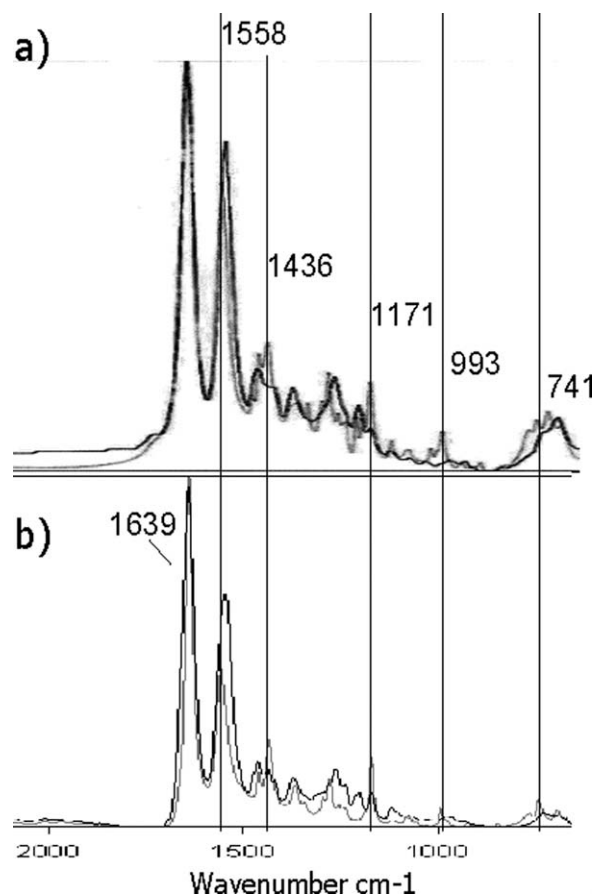


Figure 9. (a) Spectral comparison between the FTIR spectrum of the dispersed substance in gasoline (gray curve) and the reference PA (black curve). (b) Spectral comparison of the precipitations PT1 (gray curve) and PA6 (black curve).

means that oligomers are formed back after extraction especially at elevated temperatures and high humidity.^{26,27} It is also known that these low-molecular-weight cyclic oligomers (particularly the cyclic dimer) can raise problems during the processing of PA6 as they might form depositions on rolls in foil production or precipitate in the forming tools of injection molding processes.^{24,28} Furthermore, it was found that water and alcohols are very effective in extracting cyclic oligomers from PA6 matrices.²⁵ Thus, the extraction of oligomers from the tank walls by gasoline in general and ethanol and water in specific might be an important side effect, when PA6-fuel tanks are applied. This was first realized by Liu et al.¹⁶ who stated that about 5 wt % of the PA material consists of cyclic oligomers which might be extracted when ethanol-rich fuel is used, leading to a contamination of the fuel with the oligomers.

According to various guidelines and regulations of the European Parliament^{29,30} and technical standards,^{31,32} the amount of ethanol in the fuel will steadily increase to 5% (E5) and 10% (E10) in the near future. This means that polymeric materials used within the fuel transport systems of vehicles might face additional challenges owing to this change in the gasoline composition.

In the case of PA6 fuel tanks, we could show that besides the extraction of the cyclic oligomers from the PA6 tank material by liquid gasoline (as it was the case for, e.g., the samples tanks 3, 4, and 5 which were in use in motorcycles for some time), the presence of water and/or alcohols in the gas phase (as it was the case in the conditioning of tanks 1 and 2) could also lead to the formation of surface precipitates. These findings are in good agreement with a fundamental study on the crystallization of cyclic oligomers on PA6 surfaces after exposure to water and alcohol vapor by Fujiwara.²⁵ He could show that the composition of the precipitates is strongly dependent on the type of vapor the PA6 is exposed to: while water vapor favors the migration of the cyclic dimer (O2) and tetramer (O4) to the surface, the cyclic trimer (O3) is the favored oligomer upon extraction with ethanol vapor.²⁵ The relative amounts of O2, O3, and O4 in our samples are, therefore, a hint that both water and ethanol (from the gasoline) are the main driving forces for the formation of the precipitates. Thus, it is obvious that the precipitation PT1 should consist mainly of O2 and O4 as the tank material was conditioned only with water vapor, whereas PT2 consists of O2, O3, and O4 as a result of the superimposition of the effects of conditioning with water and prolonged contact with ethanol-containing gasoline. Thus, the exact constitution of the precipitations from vehicles with defective fuel-injection systems will be highly dependent on the exact history of the tank inner surface, for example, contact with water vapor and/or gasoline (e.g., ethanol vapor therein) and their duration, temperature, etc.

As gasoline fuel contains significant amounts of ethanol (up to 10% in E10) and also some water, the damp phase above the fluid phase will contain significant amounts of ethanol and/or water damp. According to Ref. [25], this damp can induce the migration and subsequent crystallization of the oligomers on the inner tank walls during prolonged periods of stay. By the time, the tank is filled again or there is some mechanical activity, this oligomeric

mixture is dissolved or dispersed in the gasoline and might be transported and deposited to the in-tank filters and eventually to the whole fuel system, especially the nozzle.

CONCLUSIONS

Samples were taken from the fuel transport systems of motorcycle vehicles that showed precipitates and deposits in the single-layer PA6-fuel tanks as well as on blocked nozzles, tubing, and gasoline filters. Crystalline precipitates on the inner tank walls were formed during conditioning of the PA6 tanks with water vapor. The deposits in tanks, filters, and nozzles were collected from vehicles being claimed with defect fuel injection systems.

By investigating the precipitates and deposits by means of FTIR and MS, the main constituents could be identified to be cyclic caprolactam oligomers. Parallel investigations with both analytical methods (FTIR and MS) allowed us to attribute the obtained spectral features to individual cyclic oligomers O2–O5. Furthermore, a tool to identify the oligomeric composition of formed deposits just by IR spectroscopic measurements could be developed. It could be shown that the composition of the precipitations found in defect fuel systems of motorcycle vehicles exhibiting PA6 tanks is dependent on the history of the parts.

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