

Adsorption of simulants for chemical warfare agents on glass fibre reinforced nylon 6 studied by FTIR spectroscopy

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Director

Summary

The adsorption of vapours and liquids of triethyl phosphate (TEP), trimethyl phosphate (TMP), dimethyl methylphosphonate (DMMP), dichlorophosphate (MDCP) and phosphorus(V) oxychloride (TCP) on glass fibre reinforced nylon 6 was studied using Fourier transform infrared spectroscopy.

The purpose of the experiment was to gain information on the mechanisms of adsorption of chemical warfare agents on nylon 6. The organophosphorus compounds were used to simulate chemical warfare agents, especially nerve agents and halogenated agents. The interactions between TEP, TMP and DMMP and the nylon 6 surface were weak. Adsorption of MDCP and TCP on nylon 6 lead to degradation of the nylon 6 material.

Sammendrag

Adsorpsjon av væskeformig og gassformig trietyl fosfat (TEP), trimetyl fosfat (TMP), dimetyl metylfosfat (DMMP), diklorofosfat (MDCP) og fosforoksyklorid (TCP) på glassfiberforsterka nylon 6 har blitt studert ved bruk av Fourier transform infrarød spektroskopi (FTIR).

Målet med eksperimentet var å samle ny informasjon for å forklare mekanismene ved adsorpsjon av kjemiske stridsmidler på nylon 6. Organofosfatforbindelser ble benyttet for å simulere kjemiske stridsmidler, spesielt nervestridsmidler og halogenerte forbindelser. Vekselvirkningene mellom TEP, TMP og DMMP og nylon 6 var svake. Adsorpsjon av MDCP og TCP på nylon 6 førte til nedbrytning av nylon 6-materialet.

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Preface

This work was carried out as part of the summer internship of Line Rydså in 2011.

1 Introduction

Chemical warfare agents are compounds which poses a big threat on human beings when used. Nerve agents attack the nerve system and blister agents can harm skin and eyes. Ultramide polyamide 6 (nylon 6) is a commonly used material both in civilian and military equipment. It is important that mission-critical equipment used by military forces and first responders is resistant towards CWAs and easy to decontaminate so that their operations can be carried out as safely and quickly as possible. This work has therefore investigated the sorption mechanisms when the material is exposed to CWAs.

To find out how the simulants affect the nylon 6 material, Fourier transform infrared (FTIR) spectroscopy can be used. If some of the molecules' or the compounds' vibration frequencies shift to higher or lower wavenumbers and/or change in intensity, one can gain information about the mechanism occurring.

Previously, Li et al. [1] exposed a nylon 6,6 film to water. Li and co-workers observed decrease in peak frequency for the carbonyl (C=O) group, indicating strengthen hydrogen bonding. Observed increase in frequency for the NH-group in the presence of water showed the opposite.

In another study performed by Iwamoto et al. [2], a thin film of nylon 6 was dehydrated. The water interacted with the free amide groups. Peaks of increasing/decreasing intensities occurred around the amide I and II bands. Their height/depth reduced with dehydration, verifying that these interactions were due to water content. For the vibration in the amide II band (mainly due to N-H deformation), hydrogen bonding shifted the peak to higher frequencies. The opposite happened for the stretching at the amide I band (mainly C=O stretching). The frequency for the C=O group was observed to be larger when it was hydrogen bonded to water than with a NH-group. The hydrogen bonding between water and the amide groups of nylon 6 was stronger than between the amide groups within nylon 6 itself. The same was found for the NH group.

When blending nylon 6 with larger amounts of chitosan, Ma et al. found that the amide I band shifted to lower frequencies, indicating hydrogen bonding between the two components [3].

Kanan and Tripp [4] have examined the interactions between organophosphonates (DMMP, TMP, MDCP, TCP) and silica. The interactions between DMMP and silica were found to be hydrogen bonds between the oxygen atoms in both methoxy moieties of DMMP and the silanol (SiOH) groups on silica. Interactions with TMP found place through all three methoxy groups. Due to steric hindrance, the TMP molecule cannot adsorb through all three methoxy groups and the P=O group simultaneously. The observed changes in the P=O group in both TMP and DMMP change upon adsorption is explained by electronic effects. The hydrogen bonds between the methoxy modes and the silica surface reduce the methoxy groups' electron donating strength to the phosphorus atom, resulting in the reduction of the P=O group's frequency. MDCP interacted with

the silica surface through both the methoxy and phosphoryl (P=O) moieties, TCP was hydrogen bonded to the free silanol groups through the phosphoryl group.

In this work FTIR spectroscopy was used to examine how simulants of chemical warfare agents interact with glass fibre reinforced nylon 6. Simulants were used because of health, environment and safety reasons. These simulants were organophosphonates and halogenated organophosphonates. Infrared spectroscopy identifies characteristics such as functional groups in molecules. By analyzing exposed samples with FTIR spectrometry, it can be elucidated how the simulants adsorb on the surface of the polymer.

2 Theory and background

2.1 Molecular vibrations

Infrared (IR) radiation is used to identify certain functional groups and backbone characteristics within a molecule. IR radiation is passed through a sample. Molecules absorb this energy, and molecular vibrations and rotations are induced, occurring at different wavenumbers (noted $\tilde{\nu}$, expressed in cm^{-1}). Infrared spectra consist of bands, which correspond to the vibrations in the molecules. Different bonds are characterized as bands of specific frequencies and intensities. The intensities of the bands can be expressed as transmittance (T) or absorbance (A), as shown in equation (2.1) and (2.2) respectively [5].

$$T = \frac{I}{I_0} \quad (2.1)$$

$$A = \log_{10} \left(\frac{1}{T} \right) \quad (2.2)$$

Here, I is the radiant power transmitted and I_0 is the incident radiant power.

The vibration movements within the molecule are stretching or bending. The former is due to variation in bond length, whereas the latter concerns changes in bond angle [6]. Figure 2.1 presents the fundamental vibrations of the methylene group. Fundamental vibrations are those that involve no change in the centre of gravity of the molecule [5]. By following this scheme; bonds can stretch (ν) in-phase (symmetrical, s) or out-of-phase (asymmetrical, as) [6]. The bending modes are scissoring (δ , deformation), wagging (ω), twisting (τ) and rocking (ρ). The figure gives the values for where the fundamental vibration modes are expected to appear in the spectrum for the CH_2 -group.

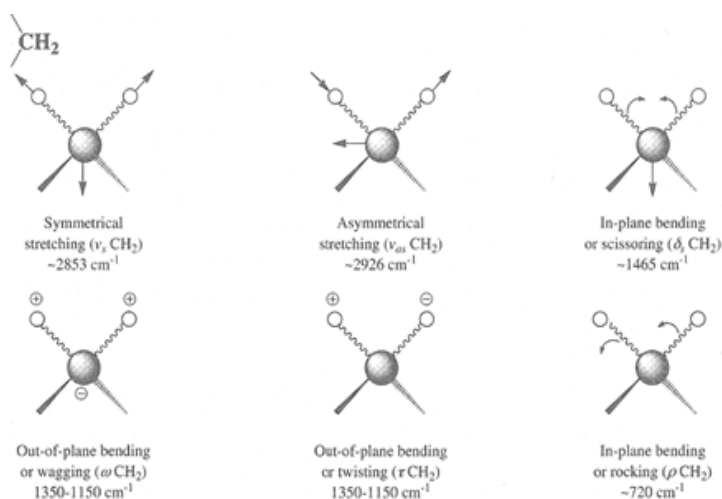


Figure 2.1 Fundamental vibrations of methylene. (+) and (-) indicate movement perpendicular to the plane of the page [5].

Only those vibrations that lead to changes in the dipole moment in the molecule can be observed in the IR spectrum [5]. The vibration frequency for the bond between two atoms is determined by the force constant of the bond and the masses of the concerning atoms, as explained in equation (2.3).

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f}{(M_x M_y) / (M_x + M_y)}} \quad (2.3)$$

Here, $\tilde{\nu}$ is the vibration frequency [cm^{-1}], c is the speed of light [cm/s], f is the force constant of the bond [g/s^2], and M_x and M_y are the masses [g] of atom x and y , respectively. Therefore, bonds will vibrate at different frequencies, and can be recognized in the IR spectrum [7]. Careful analysis of IR spectra allows one to find whether the backbone is linear or branched, saturated or unsaturated and aromatic or non-aromatic, or if specific functional groups, such as hydroxyl-, carbonyl- or amino functionality, are present or absent in the molecule. The IR spectrum obtained from a molecule is unique and therefore characteristic for the compound [7]. If spectra are acquired under similar conditions, they can be used for identification.

Hydrogen bonding modifies both the vibration frequency and the broadening of bands in the spectrum. Intermolecular hydrogen bonding is due to involvement of two or more molecules of same or different kind. Intramolecular hydrogen bonding occurs between sites within the same molecule. Both effects depend on temperature, whereas intermolecular hydrogen bonding is concentration dependent too [5].

The region with the greatest practical use spans the range of $4000 - 400 \text{ cm}^{-1}$ ($2500 - 25000 \text{ nm}$, longer wavelengths than visible light) [5]. Infrared spectroscopy is one of the most frequent used methods when examining polymers [8].

2.2 Fourier transform infrared spectroscopy

The concept of the Fourier transform infrared (FTIR) spectrometer is presented in Figure 2.2. The spectrometer uses radiation containing all IR wavelengths. The IR radiation is split into two beams [6]. Both beams pass through the sample, but one of them has a fixed length while the other one vary its length. The variation in path lengths results in a sequence of constructive and destructive interferences and hence variation in intensities. These variations result in an interference pattern, an interferogram, that is converted by Fourier transform into a conventional plot of absorption or transmittance versus wavenumber.

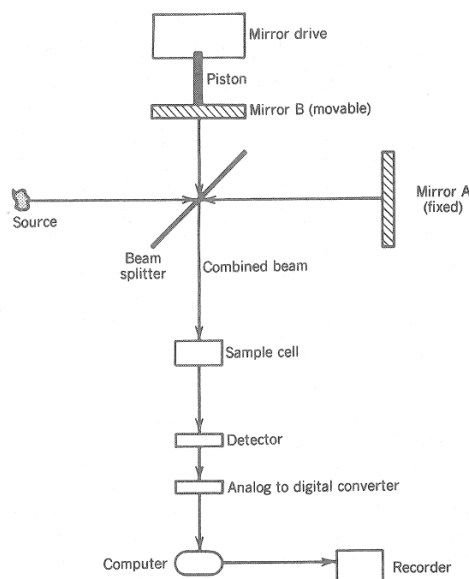


Figure 2.2 Schematic of a Fourier transform infrared spectrometer.

2.3 Ultramide polyamide 6 (nylon 6)

Nylon 6 is a polymer with structure shown in Figure 2.3. The polymer is often glass reinforced, containing up to 40 % glass fibre (silica) [9]. This makes the material more thermally stable [8]. Nylon is a member of the family of polyamides, which contain the amide functional group $(-\text{C}=\text{O})-\text{NH}$. They are thermoplastics, which means that they can easily be shaped into form by melting and hardening due to temperature [10]. One characteristic for nylon 6 is the strong interactions between neighbouring chains. Hydrogen bonding occur between the amide groups $(\text{C}=\text{O}$ and $\text{NH})$, and dipole-dipole interactions can also be of importance [1].

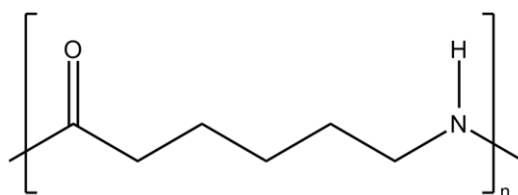


Figure 2.3 Repeating unit of nylon 6 [6].

2.4 Chemical warfare agents and simulants

Chemical warfare agents (CWAs) are chemicals used to injure or kill, to reduce one's resistance. They are classified by the effect they have on humans; as nerve, blister, choking, blood or incapacitating agents [11]. Figure 2.4 shows the structures of some nerve agents. Other warfare agents may include chlorine atoms. Compounds such as mustard, nitrogen mustard, lewisite (all blister agents), and phosgene and diphosgene (choking agents) contains chlorine.

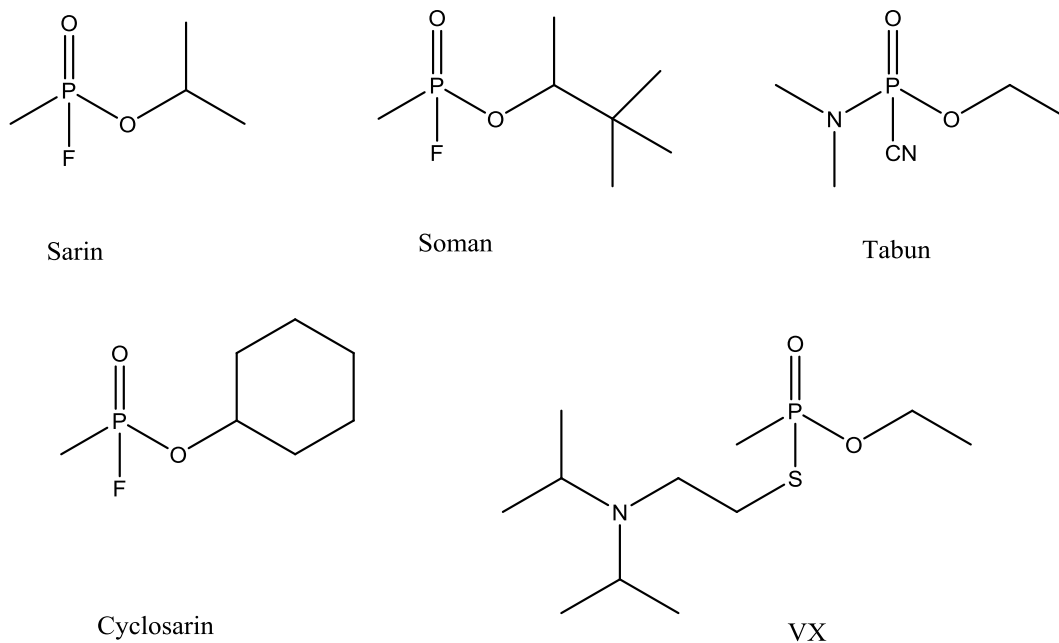


Figure 2.4 The nerve agents sarin (GB), soman (GD), tabun (GA), cyclosarin (GF) and VX.

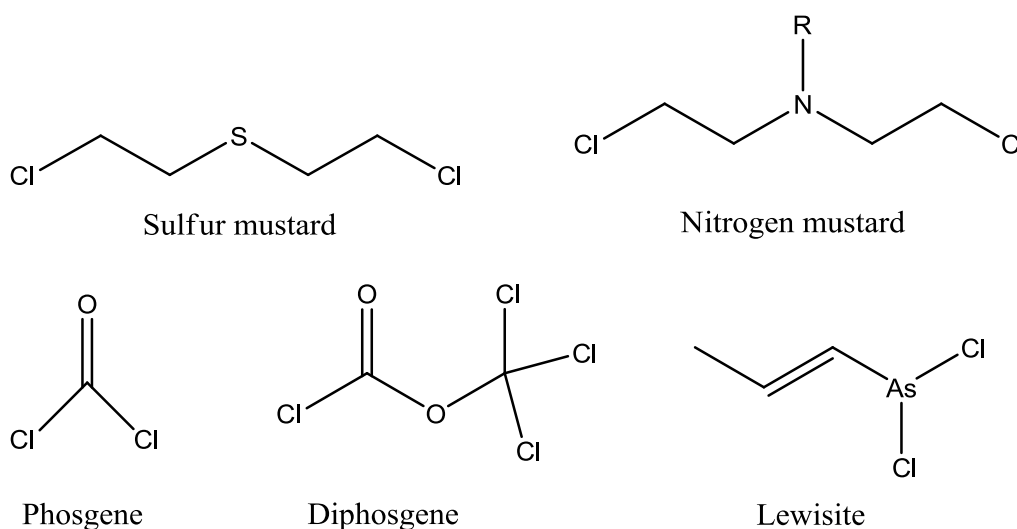


Figure 2.5 Structure of some chlorine-containing chemical warfare agents.

Since all these compounds are extremely dangerous to work with, chemical simulants are often chosen instead when examining the effects of chemical warfare agents. Chosen simulants in present study are triethyl phosphate (TEP), phosphorus(V) oxychloride (TCP), methyl

dichlorophosphate (MDCP), dimethyl methylphosphonate (DMMP), trimethyl phosphate (TMP), and tributylphosphate (TBP).

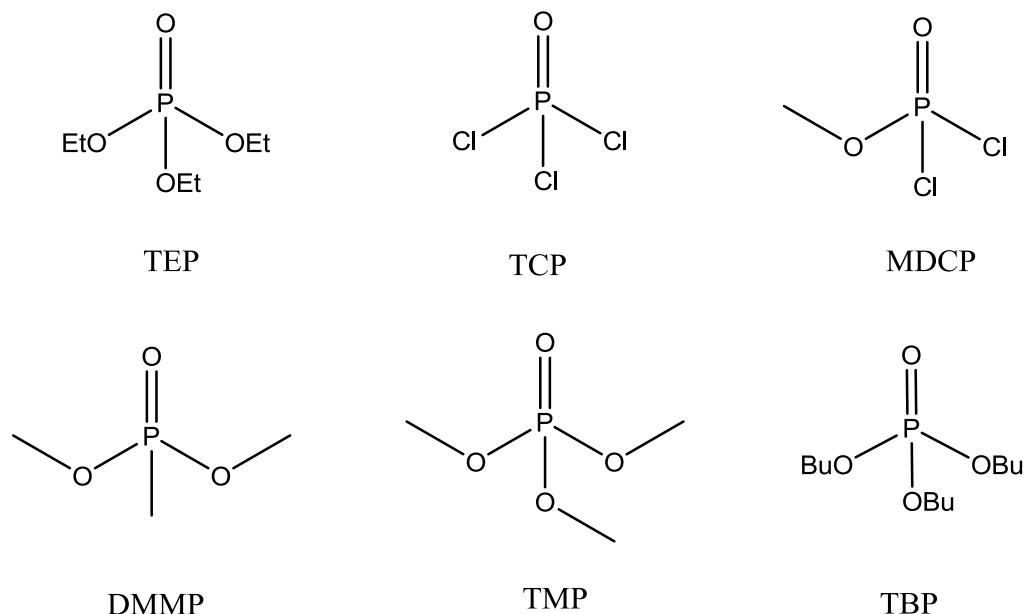


Figure 2.6 Structure of the chemical warfare simulants triethyl phosphate (TEP), phosphorus(V) oxychloride (TCP), methyl dichlorophosphate (MDCP), dimethyl methylphosphonate (DMMP), trimethyl phosphate (TMP), and tributylphosphate (TBP).

The compounds in Figure 2.6 contain P=O bonds and other bonds similar to those found in nerve agents such as P–O–C and P–C bonds. Some of them contain chlorine atoms too, which suggests that they are suitable as simulants for chlorinated CWAs, and sarin and soman since they are halogenated. These safer compounds simulate the different characteristics of the CWAs.

3 Experimental methods

3.1 Materials

A piece of *Ultramid*® B3ZG6 black 30564 polyamide (68-69,4 % nylon 6, 30 % glass (silica), 0,5-1,5 % carbon black and 0,1-0,5 % caprolactam – precursor for nylon 6) was received from BASF. The piece was filed, producing a fine powder. Half of it was dried at 105 °C for 36 hours, trying to reduce the surface hydroxyl groups.

Simulants used were methyl dichlorophosphate (MDCP), triethyl phosphate (TEP), trimethyl phosphate (TMP), dimethyl methylphosphonate (DMMP), tributyl phosphate (TBP), and phosphorus(V) oxychloride (TCP, trichloro phosphate), all purchased from Sigma-Aldrich.

3.2 FTIR instrument

All infrared spectra were collected at 4 cm^{-1} resolution in the range of $4000 - 600\text{ cm}^{-1}$ using a Bruker Vertex 70 FTIR instrument with KBr beam splitter, Specac GoldenGate ATR cell and an MCT detector cooled by liquid nitrogen to increase sensitivity. ATR spectra were recorded in absorbance. Each spectrum was obtained by averaging 32. All spectra were obtained at room temperature.

3.3 Exposure to simulant vapours

Exsiccators were used to expose powder of nylon 6 for vapours of the simulants. The powder was kept in Petri dishes on a grid above a beaker with the simulant. The atmosphere and walls inside the exsiccator were then saturated with vapour. The powder, both dried and non-dried, was exposed to simulant for periods of 1, 2, 7, 14 and 28 days before obtaining FTIR spectra of the powder. FTIR spectra were obtained from all simulants and unexposed powder as well, to eliminate sources of error due to changes over time. Nylon 6 was only exposed to TBP for 14 days.

3.4 Evaporation of simulant from exposed nylon 6

Non-dried powder exposed to simulant vapour for 28 days was left on the ATR-FTIR cell without pressure. Spectra were obtained frequently (time varies) to see how fast the simulant evaporated from the surface of the powder. This experiment was carried out for TEP, TMP and DMMP.

4 Results and discussion

A collection of all the spectra obtained in this experiment can be found in the appendices. Only those parts that contain important information are given below. There was only a small difference between the spectra of dried and non-dried nylon 6 powder (Figure A.8). Since the differences were small and did not seem to have an impact on the results, only non-dried nylon 6 powder is commented further.

4.1 Nylon 6 exposed to simulant vapour

The main results from the FTIR spectra of the exposure in the different simulants are given in Figure 4.1, Figure 4.3, Figure 4.4, Figure 4.5, Figure 4.6 and Figure 4.7, and the most important changes in these experiments are summarized in the tables (Table 4.1-Table 4.3) below the respective figures.

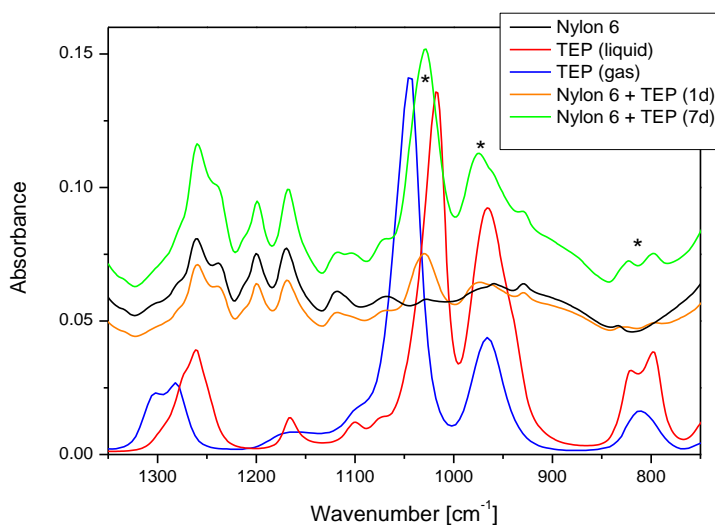


Figure 4.1 FTIR spectra of nylon 6 exposed to TEP for 1 (orange) and 7 (green) days.

Table 4.1 Shifting of infrared bands due to exposure of nylon 6 to TEP vapour.

	Peak / cm^{-1}	Peak / cm^{-1}	Peak / cm^{-1}	Peak cm^{-1}]
TEP gas	1044	967	812	812
TEP liquid	1018	965	821	798
Sample (7d)	1029	976	824	798
Difference (gas–sample)	15	-10	-12	15
Difference (liquid–sample)	-11	-11	-3	0

Figure 4.1 show the spectrum and Table 4.1 gives the peaks shift when nylon 6 is exposed to TEP. Increase in peak intensity means that more simulant has adsorbed on the polymer's surface. Since the peaks corresponding to the PO-C and P-OC bonds shift, it indicates that these bonds participate in the adsorption to the nylon 6 surface. The interactions are weak because the shifts in wavenumbers are small. The complete binding sequence cannot be fully understood from this, but from the analogy with Kanan and Tripp [4], a structure as the one given in Figure 4.2 can be suggested. It must be pointed out that this is only a guess made merely out little information, and must not be taken as the true adsorption mechanism. The ethoxy moieties interact weakly to the surface moieties in nylon 6. To figure out the exact details of the binding sequence, more studies must be performed.

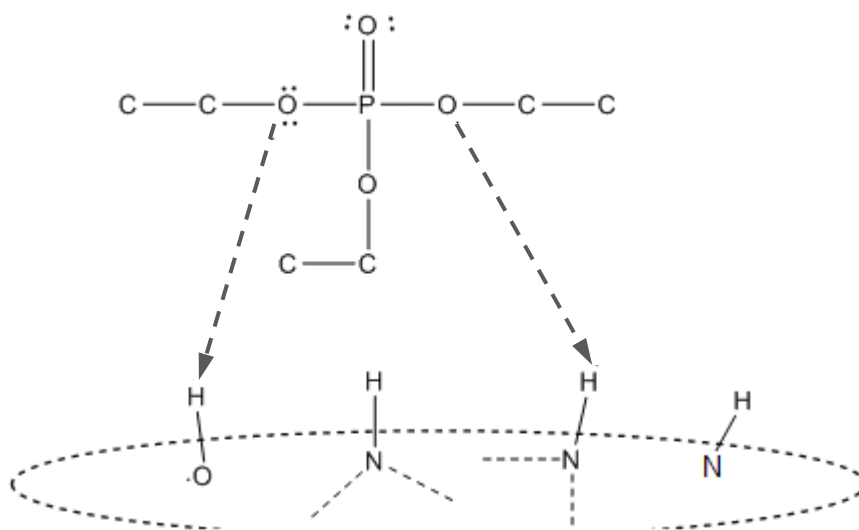


Figure 4.2 A suggestion for the interaction between TEP and nylon 6 upon exposure. The dashed arrows indicate weak interactions.

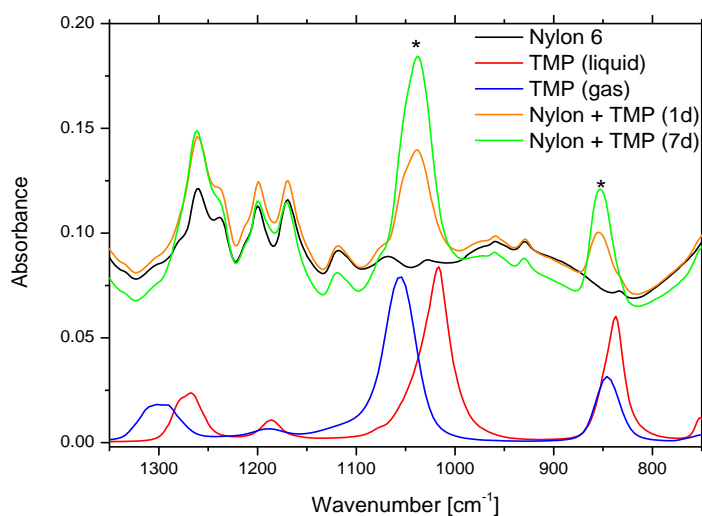


Figure 4.3 FTIR spectra of nylon 6 exposed to TMP for 1 (orange) and 7 (green) days.

Table 4.2 Shifting of infrared bands due to exposure of nylon 6 in TMP vapour

	Peak / cm ⁻¹	Peak / cm ⁻¹
TMP gas	1056	846
TMP liquid	1017	837
Sample (7d)	1038	853
Difference (gas-sample)	18	-7
Difference (liquid-sample)	-11	-16

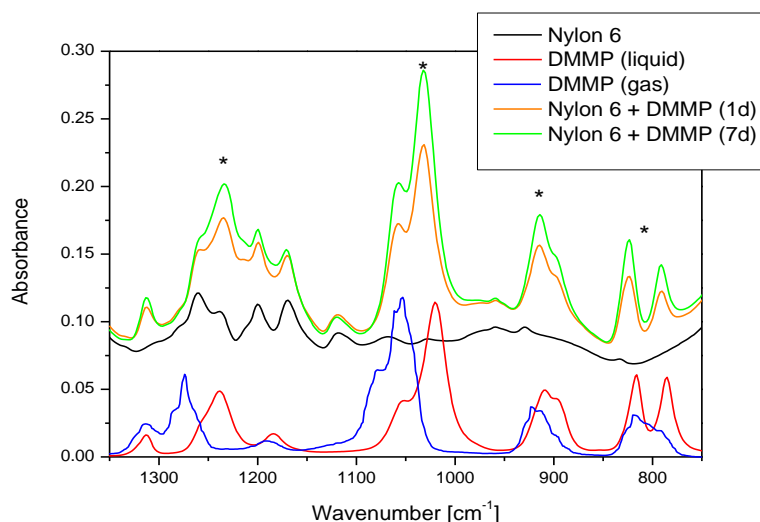


Figure 4.4 FTIR spectra of nylon 6 exposed to DMMP for 1 (orange) and 7 (green) days.

Table 4.3 Shifting of infrared bands due to exposure of nylon 6 in DMMP vapour.

	Peak / cm^{-1}	Peak / cm^{-1}	Peak / cm^{-1}	Peak / cm^{-1}	Peak / cm^{-1}
DMMP gas	1277	1053	922	817	817
DMMP liquid	1239	1020	909	816	785
Sample (7d)	1234	1032	914	824	791
Difference (gas – sample)	43	21	8	-7	26
Difference (liquid– sample)	5	-12	-5	-8	-6

Figure 4.3 and Table 4.2 show spectrum and peaks shift for nylon 6 exposed to TMP. Figure 4.4 and Table 4.3 gives the spectrum and shifts for nylon 6 exposed to DMMP. The same explanation can be used for the experiment with TMP and DMMP as for the one with TEP.

TBP was too little volatile, so the experiments gave no results of importance (see spectra in Figure 4.5). This simulant will therefore not be discussed further.

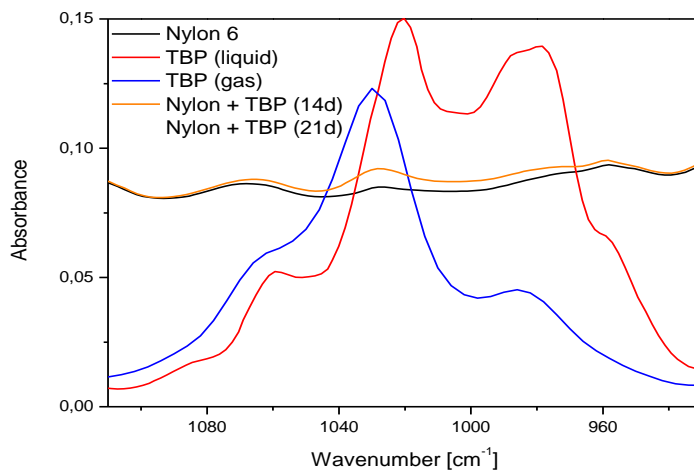


Figure 4.5 FTIR spectra of nylon 6 exposed to TBP for 14 (orange) days.

Since there are no simple changes in band positions, no table as for the other simulants is included for MDCP and TCP. Nylon 6 turned in to a viscous liquid when exposed to MDCP and TCP; see spectra in Figure 4.6 and Figure 4.7, respectively. It is clearly seen from the spectra as well that the chlorine containing simulants degrade the material completely.

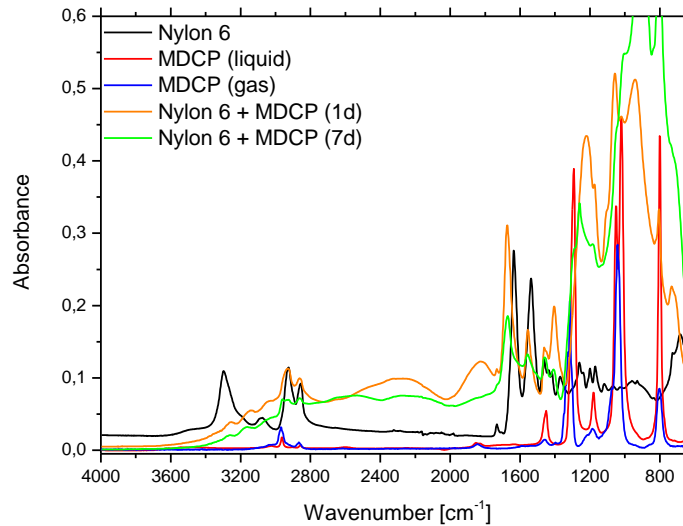


Figure 4.6 FTIR spectra of nylon 6 exposed to MDCP for 1 (orange) and 7 (green) days.

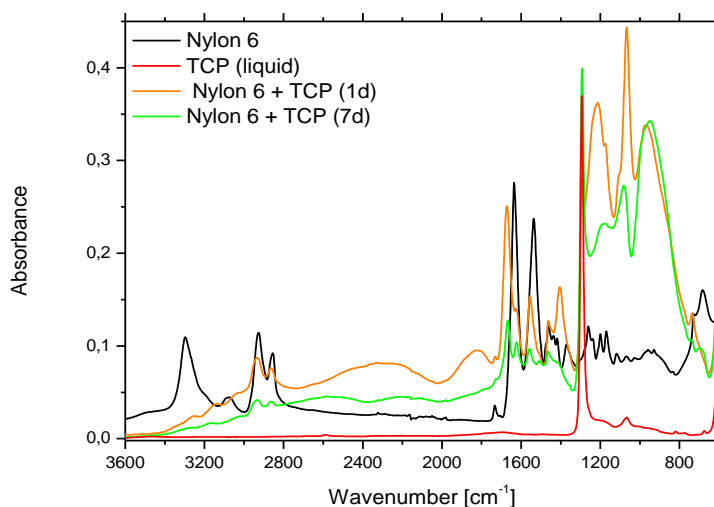


Figure 4.7 FTIR spectra of nylon 6 exposed to TCP for 1 (orange) and 7 (green) days.

4.2 Evaporation of stimulant from exposed powder

In Figure 4.8-Figure 4.10, the evaporation of simulant from the exposed samples is shown. This experiment was not executed for TCP and MDCP due to the full degradation effect they had on nylon 6. In the appendices graphs are included that show the spectra over a larger wavenumber interval than those beneath. The FTIR spectra shown under is mostly concentrated around one particular bond, the PO-C bond around 1030 cm^{-1} . In this way, the evaporation of the different simulants can be compared more easily. Under each graph there is a table showing how the peak positions changes as more simulant evaporates. The FTIR spectra in this section are normalized such that all graphs meet in the hollow at approximately 1590 cm^{-1} . This band is chosen because it changes little over time. This is done for easier comparison of the intensities of the bands.

Figure 4.8 shows the recorded spectra when TEP evaporates from nylon 6. The intensities of the bands show that the simulant is evaporating off the nylon 6 surface. The shifts in vibrational frequency of the bands are insignificant.

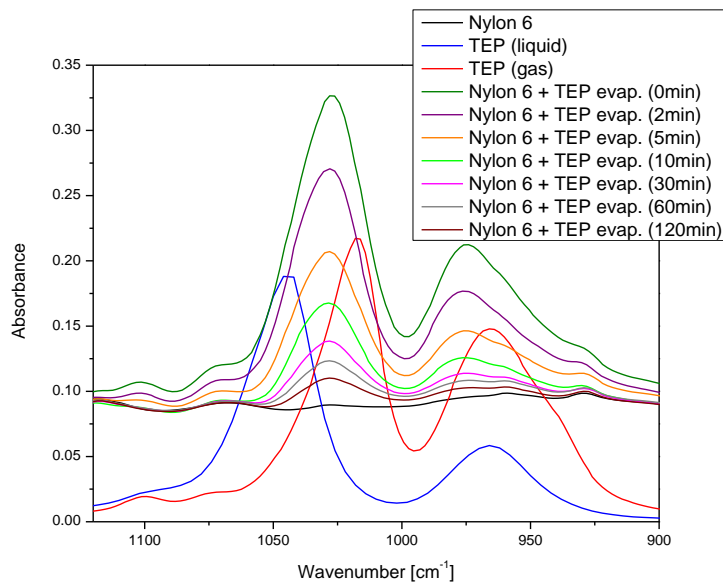


Figure 4.8 FTIR spectra of nylon exposed to TEP for 28 days (green) and left to evaporate.

Figure 4.9 gives the FTIR spectra when TMP evaporates from nylon 6. The P-OC band at 853 cm^{-1} shifts to 860 cm^{-1} after 120 minutes, which is higher than for liquid (837 cm^{-1}) and gaseous (837 cm^{-1}) TMP. The PO-C band shifts from 1037 cm^{-1} to 1034 cm^{-1} .

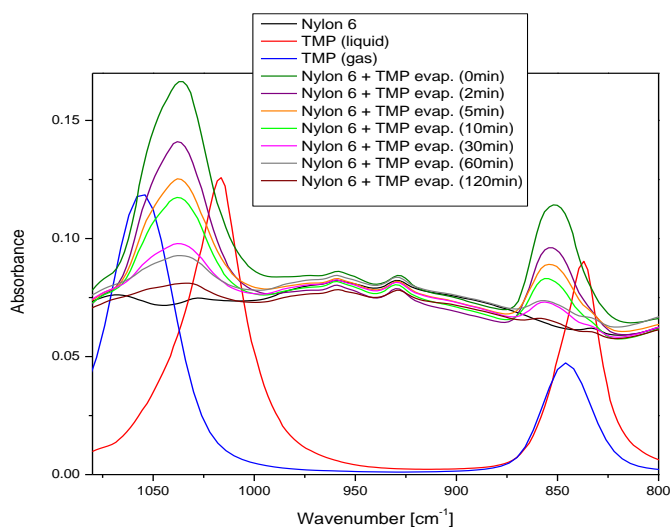


Figure 4.9 FTIR spectra of nylon exposed to TMP for 30 days (green) and left to evaporate.

Figure 4.10 shows the spectra taken when DMMP evaporates from the nylon 6 surface. The P=O and P-CH₃ bands shift towards higher wavenumbers, which is closer to those for liquid and gaseous DMMP ($1239/1274$ and $909/922$ for P=O and P-CH₃, respectively). The PO-C band shows insignificant shifts.

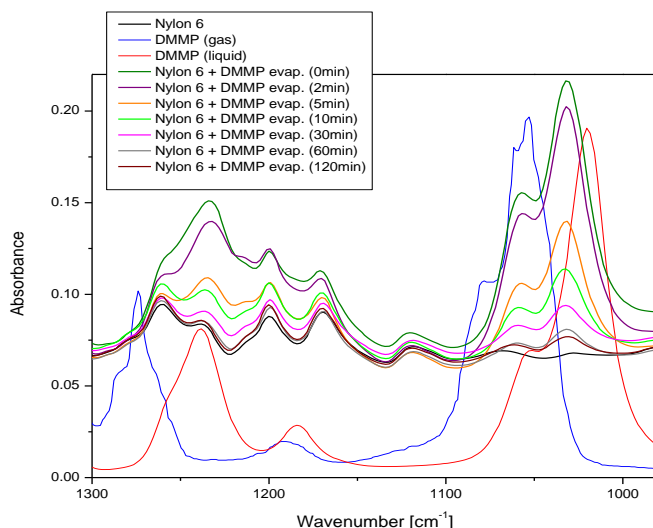


Figure 4.10 FTIR spectra of nylon exposed to DMMP for 29 days (green), and left to evaporate.

5 Conclusion

This study has examined the adsorption of simulants for chemical warfare agents on glass fibre reinforced nylon 6 by using Fourier transform infrared spectroscopy. The simulants used were triethyl phosphate (TEP), trimethyl phosphate (TMP), dimethyl methylphosphonate (DMMP), methyl dichlorophosphate (MDCP) and phosphorus(V) oxychloride (trichlorophosphate, TCP). The adsorption was followed for 28 days with spectra taken after 1, 2, 7, 14 and 28 days.

The trend of the adsorption was seen already after one day. The repeated measurements over time showed very small shifts in the wavenumbers only indicating that the interactions did not change over time. When exposing glass fibre reinforced nylon 6 to the vapour of TEP, TMP and DMMP, shift in peaks for adsorbed simulant relative to peaks for liquid and gaseous simulant were observed. This indicates weak interactions between groups in the simulant molecules and surface groups in nylon 6.

For TEP and TMP only bands related to the methoxy/ethoxy moieties of the simulant molecules shifted in the FTIR spectra upon adsorption. For TEP and TMP the interaction with nylon 6 is most likely to happen with the oxygen atom in the methoxy/ethoxy moieties. For DMMP all groups may take part in the interaction. The adsorption of simulants on the surface of glass fiber reinforced nylon 6 was independent of nylon 6 being dried or not. The chlorine containing simulants MDCP and TCP degraded the polymer material almost instantaneously, making it viscous and not suitable for further use. Further studies are needed in order to fully elucidate the adsorption mechanisms and the nature of the interactions.

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Appendix A FTIR reference spectra of pure compounds

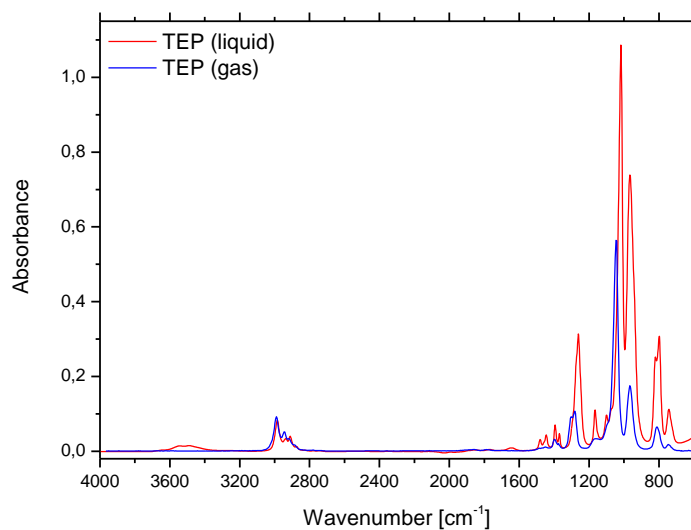


Figure A.1 FTIR spectra of TEP in liquid (red) and gas (blue) phase.

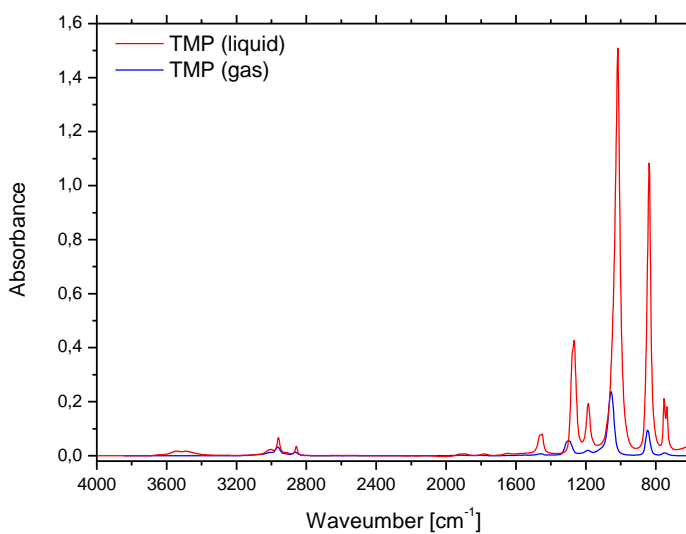


Figure A.2 FTIR spectra of TMP in liquid (red) and gas (blue) phase.

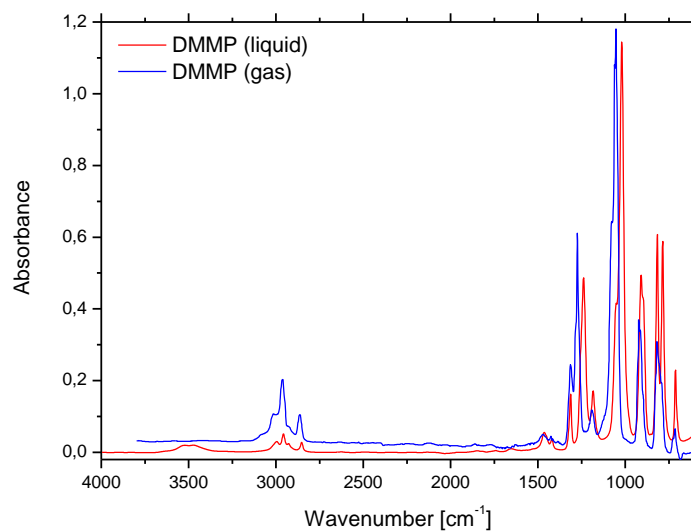


Figure A.3 FTIR spectra of DMMP in liquid (red) and gas (blue) phase.

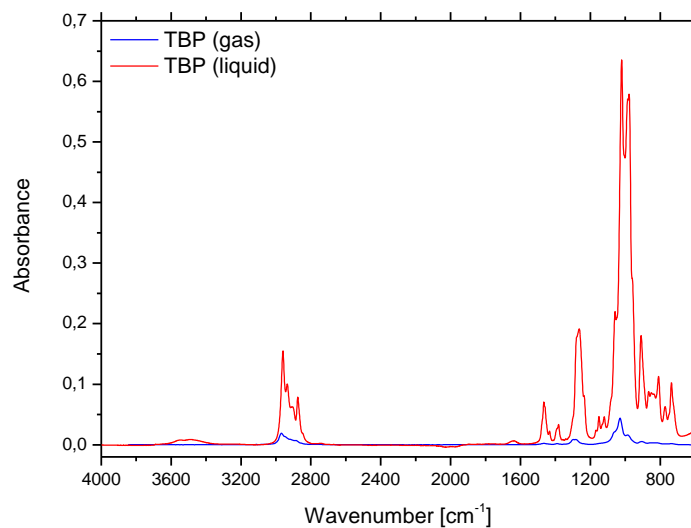


Figure A.4 FTIR spectrum of TBP in liquid (red) and gas (blue) phase.

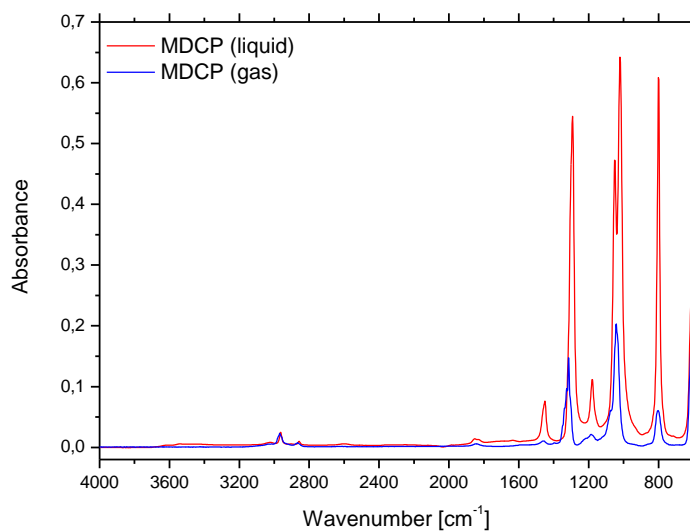


Figure A.5 FTIR spectra of MDCP in liquid (red) and gas (blue) phase.

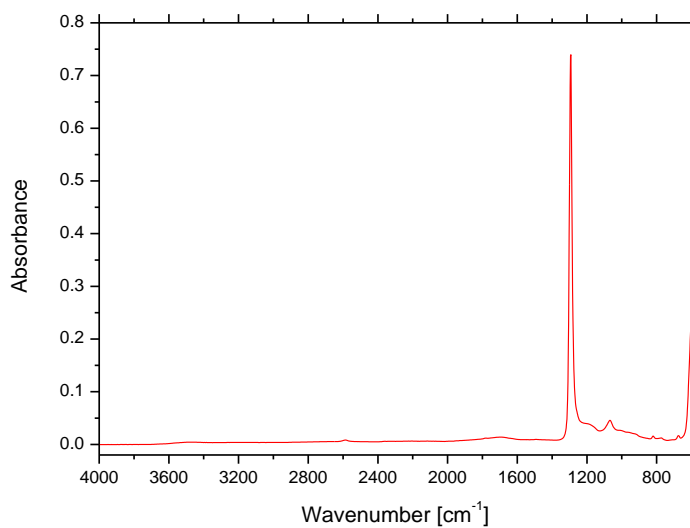


Figure A.6 FTIR spectrum of TCP in liquid phase.

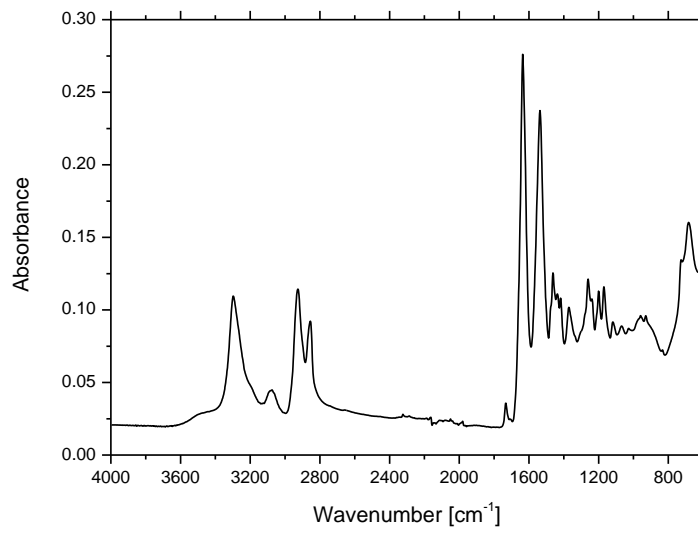


Figure A.7 FTIR spectrum of unexposed nylon 6.

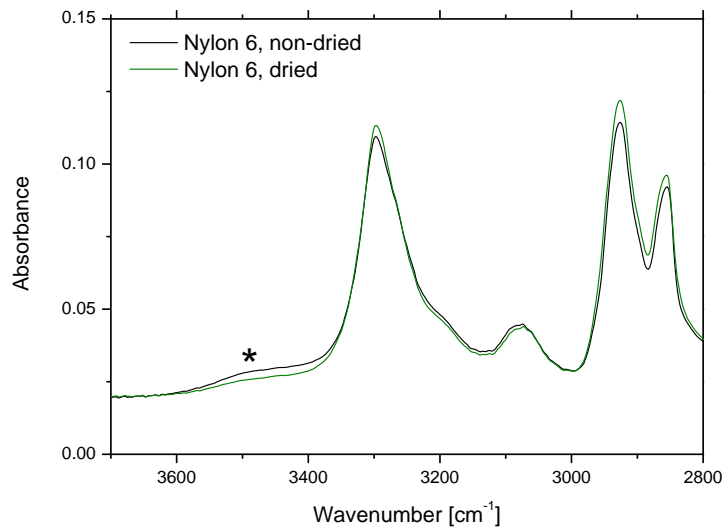


Figure A.8 FTIR spectrum of nylon 6 after drying.

Appendix B FTIR spectra from adsorption experiments

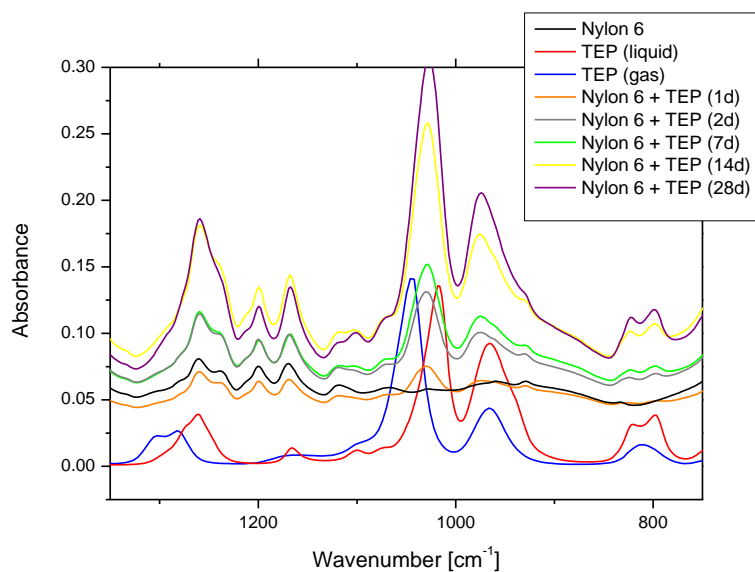


Figure B.1 FTIR spectra of nylon 6 exposed to TEP for 1, 2, 7, 14 and 28 days.

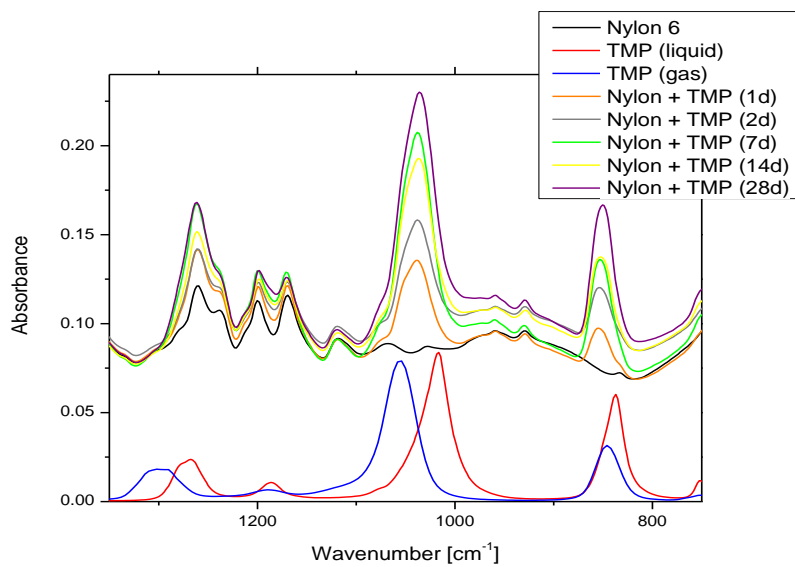


Figure B.2 FTIR spectra of nylon 6 exposed to TMP for 1, 2, 7, 14 and 28 days.

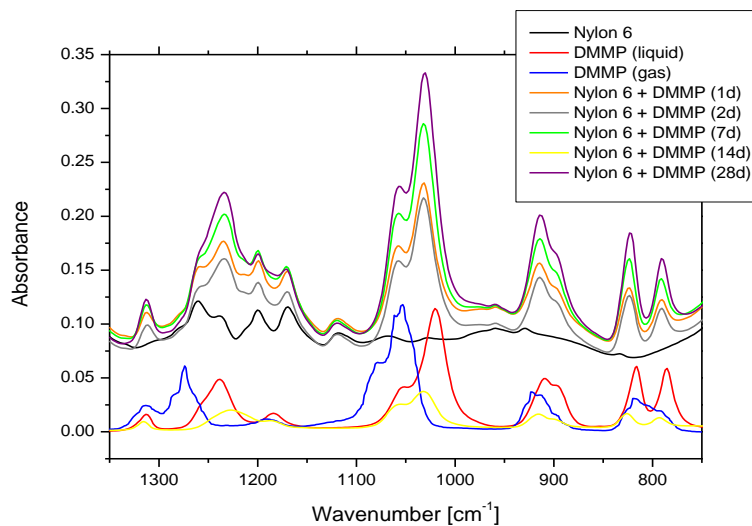


Figure B.3 FTIR spectra of nylon 6 exposed to DMMP for 1, 2, 7, 14 and 28 days.

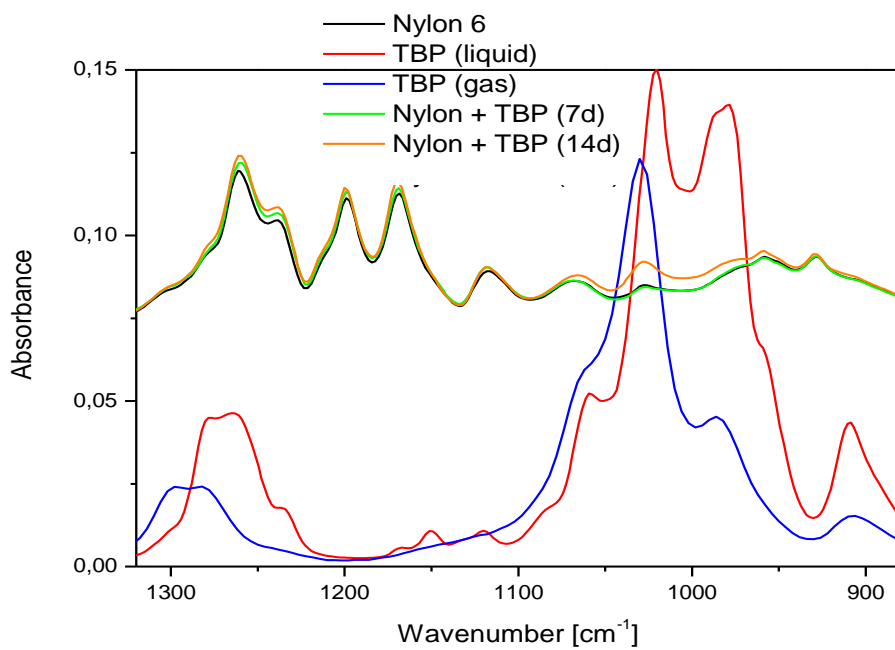


Figure B.4 FTIR spectra of nylon 6 exposed to TBP for 7 and 14 days.

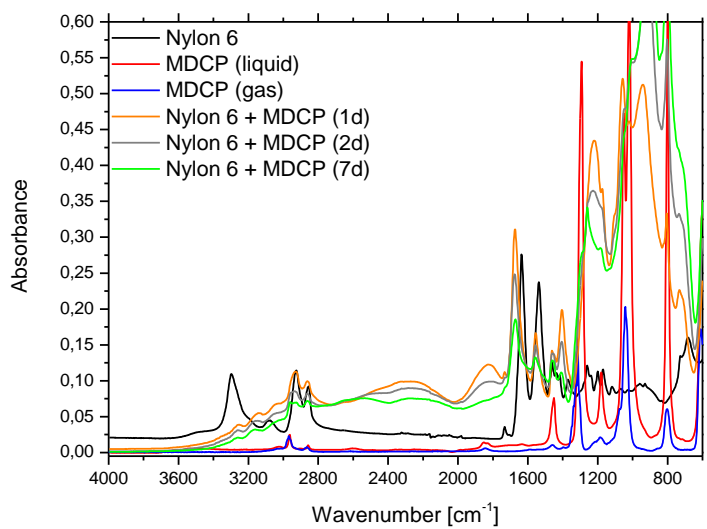


Figure B.5 FTIR spectra of nylon 6 exposed to MDCP for 1, 2 and 7 days.

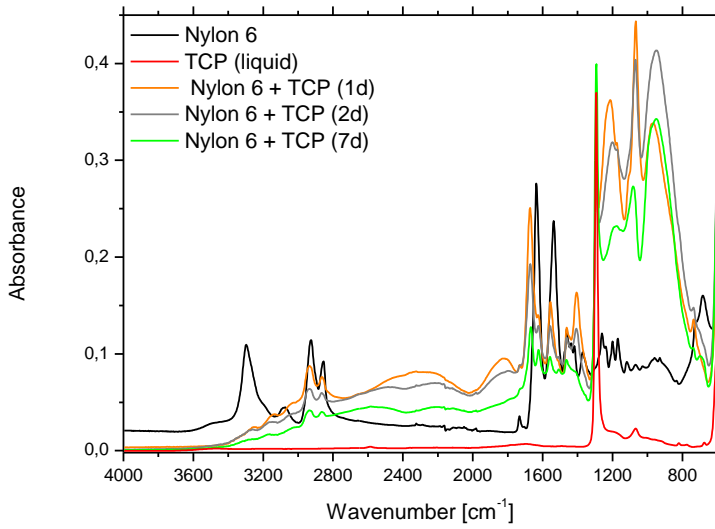


Figure B.6 FTIR spectra of nylon 6 exposed to TCP for 1, 2 and 7 days.

Appendix C FTIR spectra from evaporation experiments

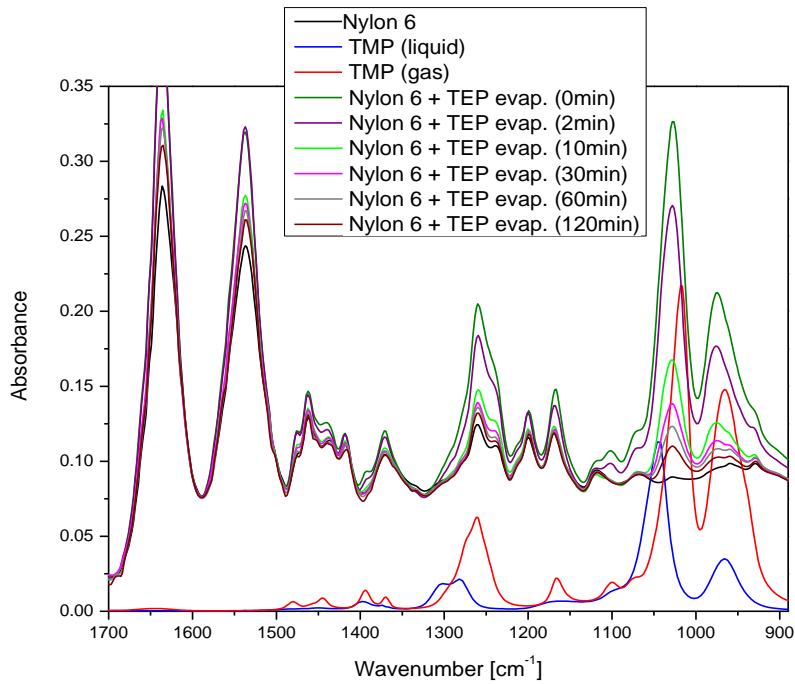


Figure C.1 FTIR spectra of nylon 6 exposed to TEP for 28 days and left to evaporate for 0, 2, 5, 10, 20, 30, 60 and 120 minutes.

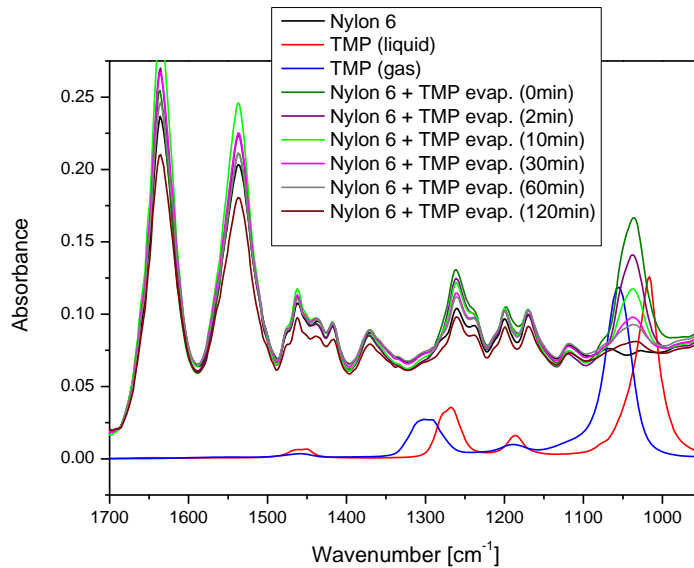


Figure C.2 FTIR spectra of nylon 6 exposed to TMP for 30 days and left to evaporate for 0, 2, 5, 10, 20, 30, 60 and 120 minutes.

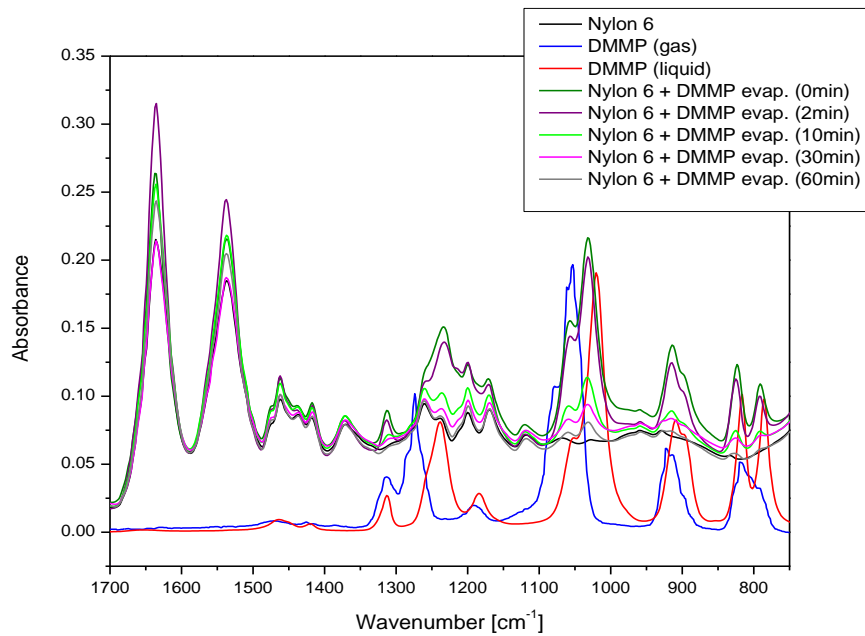


Figure C.3 FTIR spectra of nylon 6 exposed to DMMP for 29 days and left to evaporate for 0, 2, 10, 30, and 60 minutes.