



# UNIVERSITY OF TRENTO

## Department of Industrial Engineering

Properties and characterization of materials (mod.2)

### Identification of a polymeric sample by FTIR and $^{13}\text{C}$ solid state NMR

Arduini Giacomo

Cresci Alex

Leso Sergio Maria

Pascolo Gaia

Rashtchian Morvarid

#### 1. Introduction

FTIR and NMR can be considered complementary spectroscopies<sup>[1]</sup>, the infrared spectroscopy can be used to define the functional groups, the NMR spectroscopy is used to identify the organic structure. The aim of the report was to perform a chemical and structural characterisation of a unknown polymer sample through the combination of FTIR and  $^{13}\text{C}$  solid state NMR. After the recognition of the polymer the NMR spectroscopy was used in order to study the same sample after an unknown process.

#### 2. Materials and Methods

##### *FTIR-ATR analysis*

The FTIR analysis was performed using a FT-IR Varian 4100 Excalibur equipped with a diamond crystal for attenuated total reflection (ATR). The wavenumber range of study was  $4000 \div 550 \text{ cm}^{-1}$ , 64 scans for sample with a spectral resolution of  $4 \text{ cm}^{-1}$ . The sample analysed was a transparent plastic bar of unknown compound. The OMNIC software was used to process data and correct the baseline.

The plastic bar was in rectangular shape with adhesive protection to protect the surface, the surface adhesive was

removed before the placing the bar on the diamond source of the ATR-IR spectrometer.

#### NMR analysis

The NMR analysis was carried using a Bruker Avance 400 WB Ultrashield equipped with double channel 4 mm CPMAS probe. The instrument acquired the spectrum under the following conditions:  $^{13}\text{C}$  frequency 100.46 MHz, 2 ms contact time, 8.5 KHz spinning speed, 5 s recycle delay and 512 scans.

The peak fitting and analysis were performed using OriginLab software and SciDaVis. The deconvolution for the peak was performed using Gaussian curves.

### 3.Experimental Results

FTIR-ATR spectrum is reported in Fig.1, the wavenumber range was  $4000 - 550\text{ cm}^{-1}$ . Characteristic peaks were recorded and assigned at 2967, 2912, 1730, 1425, 1251, 1096 and  $610\text{ cm}^{-1}$ .

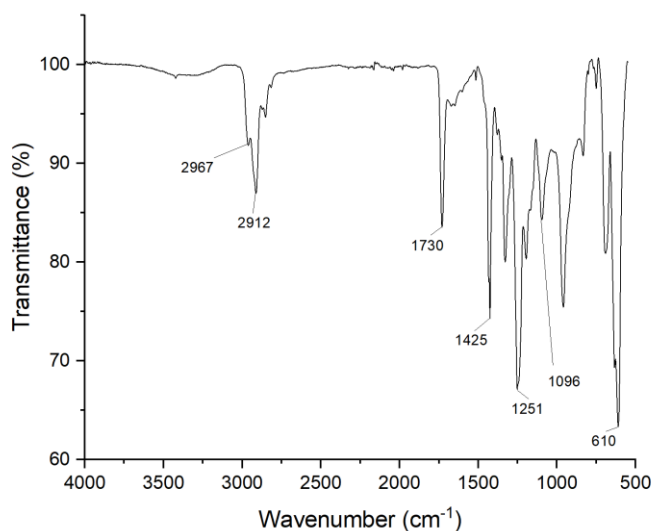


Fig.1- FTIR ATR spectrum of unknown sample with diamond crystal.

In Fig.2  $^{13}\text{C}$  NMR spectra are reported, Fig.2 (a) spectrum of the same unknown sample analysed under FTIR-ATR analysis.

The second spectrum in Fig.2 (b) represents the unknown sample after an unknown processing.

#### 4. Data Analysis

The spectrum of unknown sample shows peaks at  $2967\text{ cm}^{-1}$  and  $2912\text{ cm}^{-1}$  characteristic of asymmetric stretching vibration of  $\text{CH}_2^{[2]}$ . The peak at higher wavenumber is attributed of asymmetric stretching bond of C-H and the lower wavenumber peak to symmetrical stretching bond of C-H. The peak at  $1425\text{ cm}^{-1}$  is assigned to the C-H aliphatic bending bond  $^{[2]}$ . The peak at  $1250\text{ cm}^{-1}$  is attributed to the bending bond of C-H  $^{[2]}$ . Peak near  $1100\text{ cm}^{-1}$  correspond to C-C stretching bond  $^{[2]}$ . Peak at  $610\text{ cm}^{-1}$  correspond to C-Cl bond stretching vibration  $^{[4]}$ . The sample analysed was a poly vinyl chloride (PVC) bar. The peak at  $1730\text{ cm}^{-1}$  is characteristic of C=O stretching vibration  $^{[3]}$ , corresponding to residual traces of the plasticiser employed. The result of FTIR analysis are reported on Table 1.

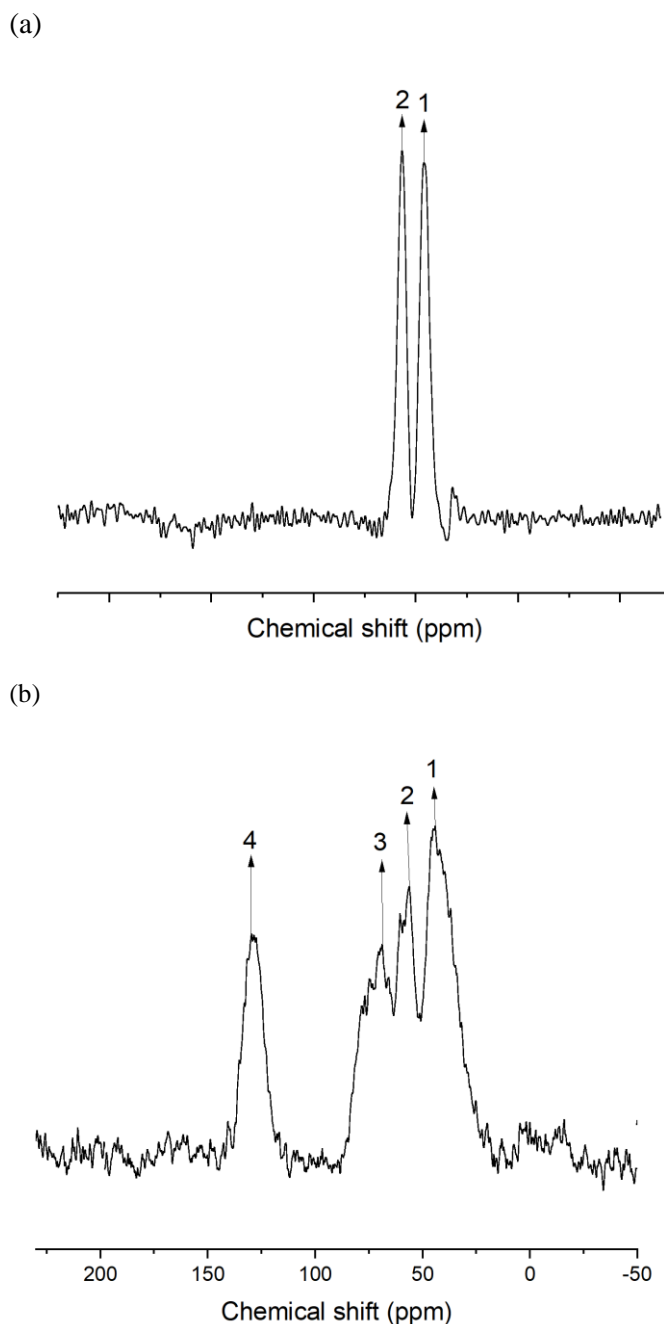


Fig.2 –  $^{13}\text{C}$  NMR spectra. (a) NMR spectrum of unknown sample, (b) NMR spectrum of unknown sample after treatment.

$^{13}\text{C}$  NMR was used to confirm the analysis done with ATR-FTIR and to study the PVC sample after unknown processing. Fig.2 (a) presents the  $^{13}\text{C}$  spectrum of poly-vinyl chloride. Clear peaks are present at 46 and 56 ppm, the peak at lower ppm can be identified as the chemical shift related to  $\text{CH}_2$  region  $^{[6]}$ , the peak at higher ppm can be identified as the  $\text{CHCl}$  region  $^{[6]}$ . Their relative height was equal, meaning the presence of the two regions in equal quantity. The  $^{13}\text{C}$  NMR spectrum gives the confirmation that the sample is pure PVC, with agreement of the results from infrared spectroscopy analysis.

Frequency (cm <sup>-1</sup> )	Functional Group	Assignment	Peak	Type of carbon	% Results
2967	CH <sub>2</sub>	Asymmetric stretching bond of C-H[2]	1	CH <sub>2</sub>	43.17
2912	CH <sub>2</sub>	Symmetric stretching bond of C-H[2]	2	CHCl	10.65
1730	CO	Stretching vibration of C=O[3]	3	CHO	27.21
1425	CH	C-H aliphatic bending bond[2,10]	4	C=C	18.97
1251	CH	Bending bond C-H[2,10]			
1096	C-C	C-C stretching bond [2,10]			
610	C-Cl	C-Cl stretching bond[4]			

Table 1- Analysis of peak finding after FTIR ATR analysis on unknown sample

Fig.2 (b) Report the <sup>13</sup>C NMR spectrum of PVC after unknown processing. Resonance peaks characteristic of PVC are still visible at 44 and 56 ppm but with a different intensity respect the Fig.2 (a) spectrum of pure PVC. Peaks at higher chemical shift are present, at 68 ppm and 129 ppm chemical shift. The peaks are characteristic respectively of the C-O region [6] and C=C region [6] .

The presence of 56 ppm peak with a lower intensity than the peak at 44 ppm led to the conclusion that the process carried on the sample reduce the presence of CHCl region leading to the elimination of the halogen chloride. The C-Cl was substituted by the C-O functional groups, the unknown process was a oxidise reaction.

The formation of C=C double bonds can be a result of degradation of PVC.

Peak number	Chemical shift (ppm)	Carbon atom
1	46	CH <sub>2</sub>
2	56	CHCl
3	68	C-O
4	129	C=C

Table 2- NMR peak assignment of pure PVC and after dehydrochlorination PVC.

The unknown process can be identified as a recycling process [7] . The removal of C-Cl bond and the presence of C=C bonds are typical results of dehydrochlorination[8] . In order to recycle PVC the halogen and the carbon fractions need to be separated. Dehydrochlorination process is the initial phase of thermal degradation of PVC and results in a polyene sequence [9] .

The semiquantitative analysis, reported on Fig.3 of the after-process PVC report that in the sample the presence of C-Cl bonds is of 10.65%. A hypothesis is that the dehydrochlorination process was not effective, in the literature the process can achieve the removal of C-Cl bond of 98% using ionic liquid[9] . Semiquantitative results are reported in Table 3.

Table 3- Semiquantitative analysis performed with peak convolution, OriginLab software.

## 5. Conclusions

The FTIR and <sup>13</sup>C NMR of unknown sample report the same results, the unknown sample was pure PVC. The after-process PVC studied in the second NMR was poly vinyl chloride after dehydrochlorination, the process is used as a end of life process for PVC in order to remove the halogen from the carbon fraction. The semiquantitative analysis report that the remaining halogen group was 10.65% confirming the reduction after dehydrochlorination but not effective to reduce the halogen content at value of 2-3% achievable with other techniques, for example in ionic liquid[9] .

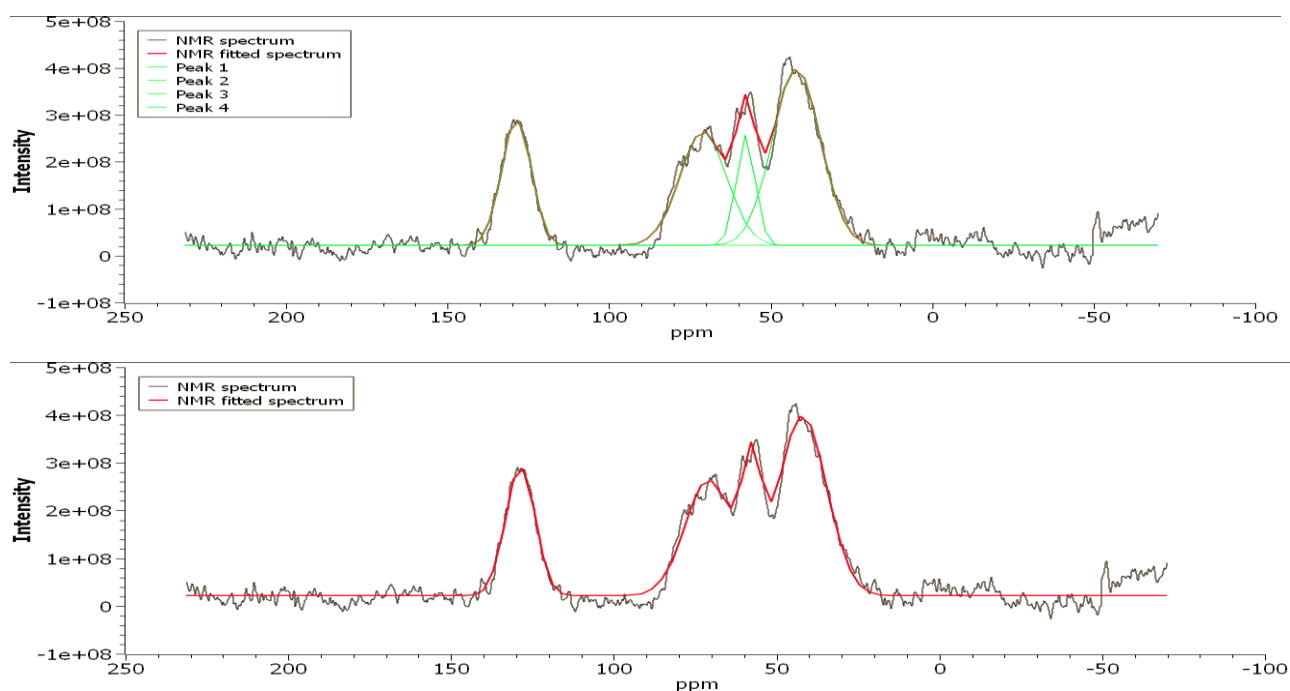


Fig. 3 – Semiquantitative analysis performed using peak convolution, the fitted curve were Gaussian like. The fitted spectrum gives good results.

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