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CHARACTERIZATION OF POLYOLEFINS WASTES BY FTIR SPECTROSCOPY

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Abstract: *In this paper the Fourier transform infrared spectroscopy (FTIR) method has been used to assess the degradation state (oxidation degree) of different polyolefinic plastic wastes from construction industry, separated in density fractions. Polyolefin oxidation has been identified and quantified by the presence of a strong absorption band assigned to carbonyl groups and its possible influence on the properties and behaviour of the polymer wastes has been critically assessed.*

Key words: *degradation, FTIR, polyolefin, recycling, waste.*

1. Introduction

Due to their low biodegradability, plastic wastes are a matter of great concern, due to their persistence in the environment. Land filling or incineration, as traditional methods dealing with the increasing waste production are no longer economically viable and possess a great environmental risk. Nowadays, a lot of attention has been focused on recycling of post-consumer plastics. Four major categories for recycling and reutilisation for plastic solid waste have been identified, based on their thermo-mechanical and compositional characteristics: re-extrusion (primary), mechanical (secondary), chemical (tertiary) and energy recovery (quaternary), each method being suitable for different areas of industry [2].

Statistical data regarding waste accumulation and recycling in Europe (2008) have shown that the recovery rate of post-consumer plastics has reached the value of 51.3%. More than half of the total amount of recycled plastics is represented by energy recovery and about 40% by mechanical recycling [17].

However, plastic recycling generally encounters some major drawbacks: first of all, it is desired that the materials obtained from plastic waste to possess mechanical strengths comparative to those of virgin polymers, which is extremely difficult due the wide range of structural properties of plastics, which impart different thermal behaviour, making blending of polymers extremely difficult. Secondly, degradation of the plastic material during its lifecycle caused by high temperature of initial processing or by environmental conditions (temperature, light radiation from different sources, humidity etc.) renders the identification and sorting of the polymer very difficult. Also, one must take into account that processing parameters of the polymer wastes may differ substantially from those of the corresponding virgin polymers.

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To overcome these drawbacks, the key issue is to accurately determine the characteristics of the polymeric waste used in new materials designing and production, namely its composition and degradation state (e.g. oxidation degree, polymerization degree and so forth).

According to the reference literature, for determining the waste composition along with the degree of degradation, different characterization methods such as: spectroscopy (NIR, FTIR, Raman), mechanical testing [3], [13], and thermal analysis (TGA and DSC) [9], [14] have been used, due to their sensitivity to material's properties alterations.

Molecular structure and morphology modifications (that occurs during the product life time or during the recycling operations) [7] could be determined by using the above-mentioned methods. The most suitable and sensible analysis for assessing polymer degradation is FTIR spectroscopy [14].

Studies regarding the degradation of polymers during their lifecycle have proven that generally, it involves two principal steps: abiotic and biotic degradation. The abiotic degradation involves the polymeric material degradation due to exposure to the outdoor conditions and is followed by microbial assimilation (biotic degradation) [6], [9], [15].

The first indication of the sample oxidation, assessed by visual observation (yellowing, cracking at the surface, gloss and transparency reduction), may be due to the formation of degradation products such as carbonyl, hydroxyl, and vinyl groups. They are considered the main initiators of polymers oxidation, by absorbing UV light and becoming free radical sources [10], [11].

The paper is focused on the statistical composition and degradation degree assessment of seven light density fractions of plastic wastes from the construction industry, obtained by sink-flotation method, by using the attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) method, in conjunction with specialized software and spectral databases. Polymer oxidation has been identified and quantified by the presence of a strong absorption band at ~ 1720 cm^{-1}, assigned to carbonyl groups vibration. For a quantitative approach of the degree of oxidation, the carbonyl index has been calculated, and its possible influence on the properties and behaviour of the polymer waste has been critically assessed.

2. Materials and Characterization Techniques

Plastic wastes originating from buildings and construction Industry (B&CW) have been used in this study. The plastic wastes samples have been kindly supplied in the frame of the European W2Plastics FP7 project and used without further processing. The samples have been received washed, cut and separated based on their density by sink flotation in seven fractions (0.89-0.90 g/cm^3; 0.90-0.91 g/cm^3; 0.91-0.92 g/cm^3; 0.92-0.93 g/cm^3; 0.93-0.94 g/cm^3; 0.94-0.95 g/cm^3; 0.95-0.96 g/cm^3) as it can be seen from Figure 1. The aforementioned density range (0.89-0.96 g/cm^3) has been chosen as being specific to polyolefins (PO). The studied fractions were assumed to consist only in PO, mainly polyethylene (PE) and polypropylene (PP).

The FTIR spectra of the samples have been obtained using a FTIR spectrometer (Perkin Elmer BXII) working in Attenuated Total Reflectance (ATR) mode, performing a total of 4 scans with a 2 cm^{-1} resolution, in the 4000-600 cm^{-1} spectral region. From each density fraction, at least 25 representative samples have been selected based on their overall aspect (colour, gloss, transparency) - Figure 1.

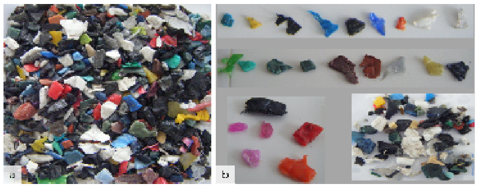


Fig. 1. *B&CW density fraction 0.95-0.96 g/cm^3 (a), picked samples for ATR-FTIR analysis from the same density fraction (b)*

The samples selected for FTIR analysis represent one tenth of the received fraction. For each selected piece of waste, FTIR analysis was conducted in three different points. All the coefficients calculated based on bands heights or areas are provided as mean values.

3. Results and Discussion

The ATR-FTIR spectroscopy analysis was used in this study as a qualitative (aiding polymers identification based on their specific absorption bands) and as well as a semi-quantitative method, assessing the polymers degradation degree by quantification of specific absorption bands assigned to carbonyl groups, and by carbonyl index calculation.

In order to discriminate between PE and PP the 3000-2750 cm^{-1} spectral region has been firstly taken into consideration, where PE presents two absorption bands assigned to -CH$_2$- asymmetric and symmetric stretching vibration, while PP presents four superimposed absorption bands corresponding to asymmetric and symmetric stretching vibration of methylene and methyl groups. Different features have been also observed in the 1470-1350 cm^{-1} domain, where absorption bands corresponding to scissoring vibration of the methylene group (1468 cm^{-1} in both PE and PP spectra) and to symmetric deformation of the methylene group (1377 cm^{-1} only in PP spectra). Supplementary, for PE, a doublet with the maxima at 730 and 720 cm^{-1} corresponding to bending and rocking vibrations of crystalline and amorphous methylene group is encountered [4], [6], [8].

All these spectral differences are helpful in discriminating between PE and PP in the IR spectra. Some representative FTIR spectra for each density fraction with the PE-PP repartition through the seven analyzed density fraction are presented in Figure 2. An overall view of the separated waste fractions, through the information revealed from the FTIR spectra analysis, reveals that in the 0.91-0.93 g/cm^3 and 0.95-0.96 g/cm^3 density fraction, a heterogeneous PE-PP mixture is encountered, while in the 0.89-0.91 g/cm^3 and 0.93-0.95 g/cm^3 and homogeneous composition has been found (consisting either in PP or PE, respectively).

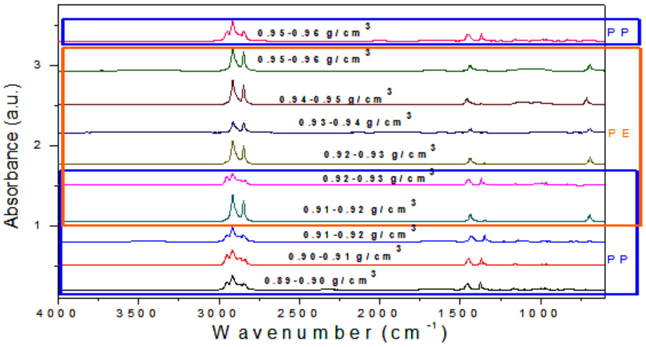
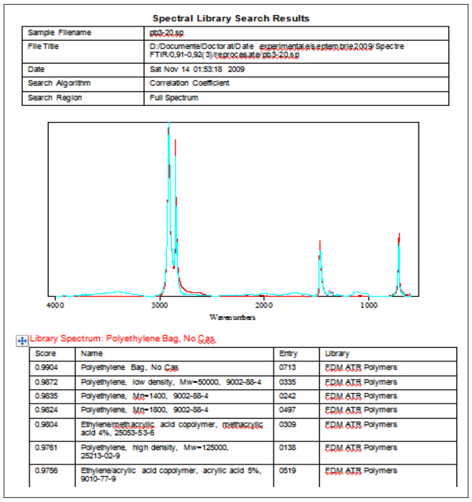


Fig. 2. *FTIR spectra of each density fraction (representative spectra) and the PP/PE repartition*

An accurate identification and quantification of the PP and PE occurrence for each density fraction has been performed by using specialized software (Essential FTIR - FDM Library) and spectral databases.

Each FTIR spectrum of the polymer waste from the mentioned density fractions has been compared with reference spectra from the FTIR FDM Library spectral database (organic polymers, polymers and coatings). The software displays a number of compounds, of whose FTIR spectra resemble more or less the spectra of the analysed sample, associated with correlation coefficients. A higher correlation coefficient has the significance of a better match between the spectra of the sample and the compared reference.

In Figure 3 an example of comparison report provided by the aforementioned software is presented.



Spectral Library Search Results

Sample Filename	pb3-20.sp
File Title	D:/Documente/Doctorat/Date experimentale/septembrie2009/Spectre FTIR/0,91-0,92(3)/reprocesate/pb3-20.sp
Date	Sat Nov 14 01:53:18 2009
Search Algorithm	Correlation Coefficient
Search Region	Full Spectrum

Library Spectrum: Polyethylene Bag, No Cas

Score	Name	Entry	Library
0.9904	Polyethylene Bag, No Cas	0713	FDM ATR Polymers
0.9872	Polyethylene, low density, Mw=50000, 9002-88-4	0335	FDM ATR Polymers
0.9835	Polyethylene, Mn=1400, 9002-88-4	0242	FDM ATR Polymers
0.9824	Polyethylene, Mn=1800, 9002-88-4	0497	FDM ATR Polymers
0.9804	Ethylene/methacrylic acid copolymer, methacrylic acid 4%, 25053-53-6	0309	FDM ATR Polymers
0.9761	Polyethylene, high density, Mw=125000, 25213-02-9	0138	FDM ATR Polymers
0.9756	Ethylene/acrylic acid copolymer, acrylic acid 5%, 9010-77-9	0519	FDM ATR Polymers

Fig. 3. *Essential FTIR-FDM Library example of an identification report*

The report contains data related to the spectra that are to be compared, data related to the reference spectra, and also the correlation coefficients. The highest correlation coefficient was chosen in order to identify the components for each density fraction. The correlation coefficients for the compared samples range between 0.79 and 0.99. This range has been considered acceptable due to the presence of other small-molecular compounds in the analysed samples, such as additives (dyes, pigments, plasticizers, stabilizers, fillers) as well as due to possible oxidation degree associated to the polymer aging. Their presence is observed in PO spectra as new absorption bands besides PO characteristic ones.

The percentual (numerical) composition of each density fraction has been determined by dividing the number of samples that were identified as one of the two components (PE or PP) with the total number of the samples taken into analysis (25). The composition of each density fraction is depicted in Figure 4. The repartition of PE and PP through the seven density fractions after software identification is similar with the one presented in Figure 2, obtained after PO characteristic absorption band visualisation. In the last fraction (0.95-0.96 g/cm^3) a small amount of PP (16%) has been identified, probably due to the presence of different additives or degradation products in the waste structure that are lowering/increasing the POs density, and making their separation difficult. It is appreciated that the use of characteristic software in conjunction with spectral databases for components identification is more reliable, especially with larger amount of samples taken into consideration, and reduces analysis time.

In order to determine the samples degree of degradation, the region of (1850-1630) cm^{-1} where carbonyl group's absorption band appears in case of POs oxidation, was investigated. All FTIR spectra present a weak absorption band in the investigated interval, which indicates the macromolecular chains oxidation. The POs and POs mixtures are known to degrade following Norrish degradation mechanism (type I and II in competition) [5], [11], [12], leading to chain scission and crosslinking. During POs degradation, hydroxyl (-OH at 3650-3200 cm^{-1} - a broad absorption band), carbonyl (-C=O at 1850-1630 cm^{-1}), methylene (-C=C- at 1680-1620 cm^{-1} - weak absorption band) and vinyl (-CH=CH$_2$ at 908 cm^{-1}) groups are the main degradation products that form.

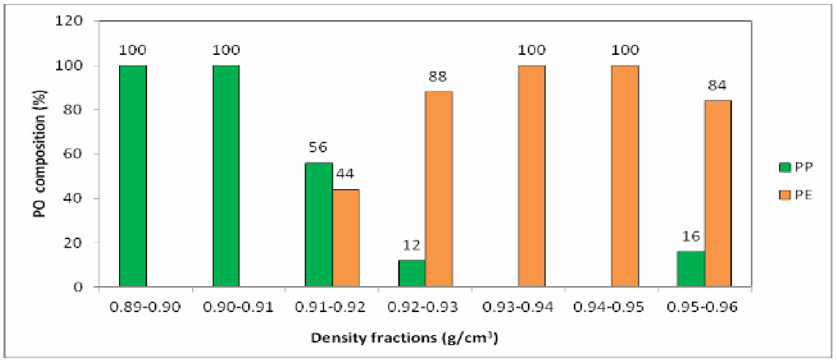


Fig. 4. *Composition of the B&CW density fractions determined via FTIR analysis*

Zooming in on the carbonyl regions in the ATR-FTIR spectra allows us a better observation of the absorption bands changes of the PO wastes. In Figure 5 four samples spectra (zoom in carbonyl region) are presented, each one representing four different density fractions (Figure 5a and b corresponding to PP; Figure 5c and d corresponding to PE).

The differences between spectra, mainly in the carbonylic region were assigned to different oxidation products that could form, due to different degradation stages of the wastes samples. The degradation differences that appear even in the same polymer type may be related to the presence of different additives in the polymeric matrix (especially the presence of thermal or UV-light stabilizers, may influence the reduction of the products' oxidation), storage conditions during products life-time and also at the end-of their life (humidity, light, temperature, oxygen content, microorganisms presence, are increasing the degradation probability).

Another important aspect that must be brought into discussion is the variability of the components' properties (molecular weight, chain branching, viscosity and so forth). According to literature [1], [16], various carbonyl containing species can be found in this wave number region, such as: γ-lactones (1797 cm^{-1}), lactones (1778 cm^{-1}), per-esters (1774 cm^{-1}), peracids (1754 cm^{-1}), aldehydes (1740 cm^{-1}), ester (1739 cm^{-1}), ketone (1727-1716 cm^{-1}), carboxylic acid (1703-1698 cm^{-1}), α,β-keto-aldehydes (1648 cm^{-1}), carboxylate (1592 cm^{-1}). Most of these absorption bands have been found in the analysed POs wastes spectra either as weak absorption bands, or as shoulders in the strong C=O absorption band. For all samples, an absorption band centered in the region 1655-1630 cm^{-1} corresponding to alkenes C=C stretch is observed. For PP spectra, several differences have been observed: FTIR spectra from Figure 5b present a sharper absorption band centered at 1650 cm^{-1} with smaller shoulders, while in Figure 5a a broad absorption band (1680-1550 cm^{-1}), have been observed where several absorption bands are overlapped. A more intense absorption band related to the presence of the double bond in comparison with the intensity of the bands related to carbonyl groups, suggests

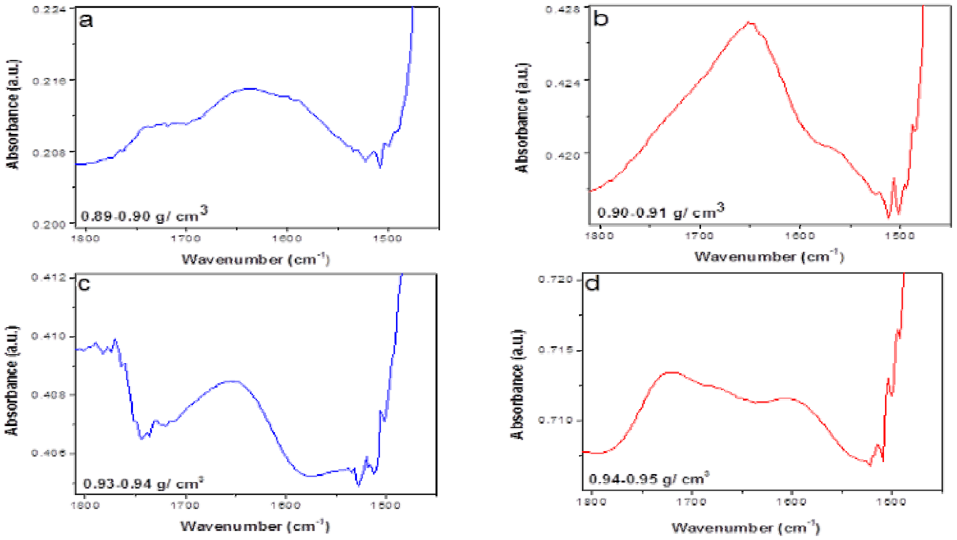


Fig. 5. *Carbonyl region detail for FTIR spectra of sample representing different density fractions: a) 0.89-0.90 g/cm^3; b) 0.90-0.91 g/cm^3; c) 0.93-0.94 g/cm^3 and d) 0.94-0.95 g/cm^3*

the Norrish I type degradation mechanism. Figure 5b, reveals that PP sample is in a much advanced degradation state as PP from Figure 5a, due to the higher content in C=C. PE spectra also present some differences: in Figure 5c the double bound evidences the main absorption band in the region, and it presents small shoulders corresponding to different carbonyl species, while PE described by Figure 5d presents a broad absorption band with four maxima centred at 1724, 1680, 1650, 1606 cm^{-1}, with similar intensities. It seems that PE characterized by the spectrum from Figure 5d is in an advanced stage of degradation as the one from 5c.

Due to the fact that the different carbonyl species absorption bands are not totally separated, the total area of carbonyl groups absorption band, between 1850 and 1630 cm^{-1} has been used for the carbonyl index (CI) calculation - Equation (1):

$$CI = \frac{A_{1850-1650}}{A_{PO}}. \tag{1}$$

The CI has been calculated as the ratio between the absorbance area of carbonyl groups and the absorbance area of a specific band for the PO (used as internal reference) encountered at 1380 cm^{-1} in the case of PE, and at 2700-2750 cm^{-1} for PP, respectively [8]. The results are presented in Table 1 (average values of CI for each component of the density fractions). The CI$_{\text{average}}$ was calculated taking into consideration the components percent for each density fraction determined earlier.

Relatively low CI values have been obtained. Samples containing mainly polyethylene exhibit a carbonyl index around 1, by comparing with the ones with a higher percentage of PP, where all carbonyl indexes were above 0.7. Normally this means that PE containing fractions are more degraded than PP based fractions.

But taking into account that PP has to be more sensitive to oxidation (due to the tertiary carbon presence), and that carbonyl groups could act as weak points inducing new oxidative processes, the functionalized

Table 1

Calculated Carbonyl Index (CI) for the analyzed building and construction wastes (B&CW)

Density fraction [g/cm^3]	**CI$_{PP}$**	**CI$_{PE}$**	**CI$_{average}$**
0.89-0.90	0.45	-	0.45
0.90-0.91	0.46	-	0.46
0.91-0.92	0.49	0.76	0.61
0.92-0.93	0.28	1.26	1.14
0.93-0.94	-	1.13	1.13
0.94-0.95	-	0.94	0.94
0.95-0.96	0.45	1.16	1.05

polymer can further degrade following two competitive degradation mechanisms. If the PP degradation will lead to chain scission, crosslinking or even CO release, the carbonyl group species will be consumed, lowering the calculated CI, in case which the results may lead to wrong conclusions. In fact, the best conclusion that may be drawn here is that only ATR-FTIR analysis is not enough for determining the degradation stage of the waste, due to the complexity of the POs degradation mechanism. Unfortunately, FTIR analysis is characterizing only a thin layer from the material's surface (the penetration depth being in the microns range).

A correlation of the FTIR analysis with other methods that could identify the structural changes within the polymer (DSC, XRD, MFI, Rheology, and Chromatography) may be necessary.

4. Conclusions

FTIR spectroscopy is a sensitive method that can be used to identify the components from analyzed samples (building and construction waste). The use of specialised software combined with spectral databases, is less time-consuming, and more reliable.

A statistical composition of the seven light density fractions has been performed. Most of the POs fractions present a good PE and PP separation. PP is the main component in the density range of 0.89-0.92 g/cm^3, while above 0.92 g/cm^3 density the main component is PE.

All samples present signs of degradation, CI$_{average}$ ranges from 0.45 to 1.14.

ATR-FTIR analysis alone is not enough for determining the degradation stage of polymers due to possible CO release. Its correlation with other methods that could evidence the chains scission, crosslinking or crystallinity alteration, such as DSC, XRD, MFI, Rheology, and Chromatography is required. The present paper presents the early stages of a complex study related to characterisation of the different density fractions separated from polymer wastes, the final aim of the study being their recycling by plastic composites manufacturing.

Acknowledgements

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