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In situ ATR-FTIR Spectroscopy of Poly(ethylene terephthalate) Subjected to High-Temperature Methanol

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Summary: In situ ATR-FTIR (attenuated total reflection Fourier transform infrared) spectroscopy combined with a high-pressure cell has been applied to measure IR spectra of polymers subjected to superheated or near-critical methanol (100–200 °C). Spectra of poly(ethylene terephthalate) (PET) have been measured under exposure to high temperature methanol using this ATR-FTIR approach to understand at a molecular level the recycling process of PET. The evolution of the structure and the morphology of the polymer has been studied during the methanolysis. The quantity of trans PET conformer is generally used as a tracer of the crystallinity of PET. During depolymerisation of PET the evolution of crystallinity and of trans conformer appears to be different. The dependence of the rate constant on reaction temperature was correlated by Arrhenius plot, which shows activation energy of 5.8 kJ/mol.

Keywords: alcoholysis; FT-IR; infrared spectroscopy; methanol; poly (ethylene terephthalate); polymer recycling; supercritical fluids

Introduction

Poly(ethylene terephthalate) PET is one of the most common consumer plastics used and 796 000 tonnes was collected in Europe for recycling in 2005. The growing interest in PET recycling is due to the huge number of commercial applications such as textile fibres, films, bottles, food packaging materials. PET wastes can be melted and then reformed but products have lower properties. The degradation of the polymer by methanol at high temperature and pressure conditions (methanolysis) appears to be more promising for this task.[1–3] Methanolysis has been developed and patented by Lotz et al.[4] and Gruschke et al.[5]; all recycling processes and patents of PET have been reviewed recently.[6,7] Chemical recycling can be used to turn PET wastes into monomers, from which PET can be resynthesised using three methods (hydrolysis, glycolysis and methanolysis).[6,8] In hydrolysis, the polymer is decomposed into terephthalic acid and ethylene glycol.[9] Monomer, bis-2-hydroxyethyl terephthalate and oligomer are obtained if the glycolysis (with ethylene glycol) is applied to depolymerise the PET.[10] With the last chemical process, the methanolysis of PET generates mainly two products: dimethyl terephthalate and ethylene glycol which provides the advantage of easier purification than hydrolysis or glycolysis. Another advantage of the last process for PET recycling is the possibility of build an installation in the polymer production line. Waste PET coming up in the production cycle is employed and the monomers won back by methanolysis are restored back to the production process.

Vibrational spectroscopy can be used in situ to analyse at molecular level the structure of the polymer during the degradation. Thermal degradation of PET[11] and hydrolytic degradation of PET at 90 °C[12] have

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been studied by Fourier transform infrared spectroscopy to observe the crystallinity and the morphology of the polymer. Vibrational spectroscopy, Raman and IR (infrared) appear to be a good choice for studying the morphology and structure of PET.[12–18] Recently, ATR-FTIR (attenuated total reflection Fourier transform infrared) spectroscopy combined with a high-pressure cell has been utilized to study simultaneous sorption and swelling of polymers subjected to supercritical CO_2[19,20] and to study the decomposition of PET in superheated water.[18] The same apparatus can also be employed to measure the in situ evolutions of crystallinity and morphology of the polymer during methanolysis of a thin film of PET between 100 and 200 °C. Several studies have been published recently on the morphology and the structure of PET. Cole et al. have measured and analysed several samples thermally crystallized over a wide range of conditions, to study the crystallization and structure of PET.[21] X-ray diffraction has also been used recently on PET fibres to elucidate the effect of the microstructures of oriented chains on the thermal deformations.[22]

The overall aim of our studies is to understand how material is transformed during the recycling process. Infrared spectroscopy is able to measure the evolution of structure and the morphology of the polymer during this process. Our spectral analysis has been mainly concentrated on the evolution of the ratio between the gauche and trans conformation (Figure 1) and the change in the crystallinity of the PET film.

Experimental Part

A high-pressure cell was used to study in-situ interactions between liquid methanol and the PET film. The cell is fixed on the top-plate of a modified Golden Gate™ accessory (Specac, Ltd.) which utilises a diamond as the ATR crystal. The schema of the experimental setup has been given in Figure 2. Under total internal reflection the light is reflected and an evanescent field is developed at the interface. The depth of penetration is of the order of a micrometer and is dependent on the refractive index of the crystal and the sample, the incident angle of light, and the wavelength of the light. This phenomenon gives us the possibility to study the surface of a material at micrometric depth.

An Equinox 55 spectrometer (Bruker Optics) with a MCT detector was used to measure ATR-FTIR spectra with resolution of 2 cm^{-1}. All other technical details were fully presented in the previous paper.[18] To obtain a good contact between the PET film and ATR crystal, a thin film of PET was melted at 250 °C during half hour, the temperature was slowly decreased until ambient temperature was reached. Under these conditions, the PET film cast on the crystal is mainly in amorphous form. After that, the high pressure cell is attached to the top-plate of the accessory and the cell is completely filled by liquid methanol at

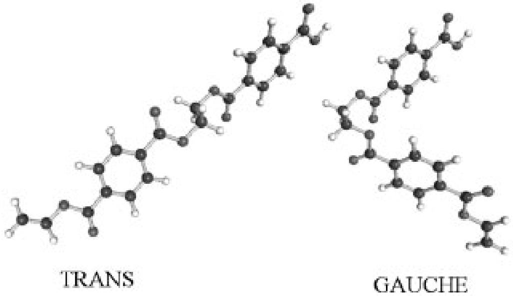

Figure 1.
Dimer of ethylene terephthalate in gauche and trans conformation.

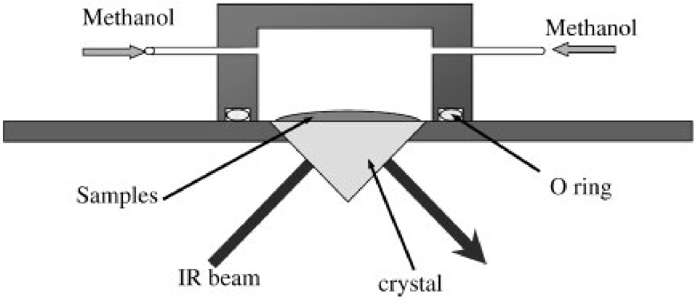

Figure 2.
Schematic presentation of a diamond ATR-IR accessory for studying polymeric materials subjected to high-pressure methanol.

ambient temperature. Finally, the system is heated up to the desired temperature, the pressure rises as expected with the increasing of the temperature. Experiments were done at four different temperatures: 125, 150, 175 or 200 °C and the pressure in the cell were between 1 and 10 MPa. All experiments have been done repeated twice.

Results and Discussion

The ATR-FTIR spectra of the PET film at 20 °C (more amorphous structure) and at 150 °C (more crystalline structure), spectra of methanol and seven different spectra of PET during methanolysis at 150 °C are displayed on Figure 3. Infrared spectra of a range of PET have been examined with minutiae by Cole et al.[23,24] They particularly drew attention to the structure of the polymer and compared several PET spectra corresponding to various states of order: highly amorphous, drawn at 80 °C to different draw ratios, and thermally crystallized under different conditions. Table 1 presents the proposed assignments of some of the main bands of PET, this indexation has also been previously examined in more detail by Holland et al.[25]

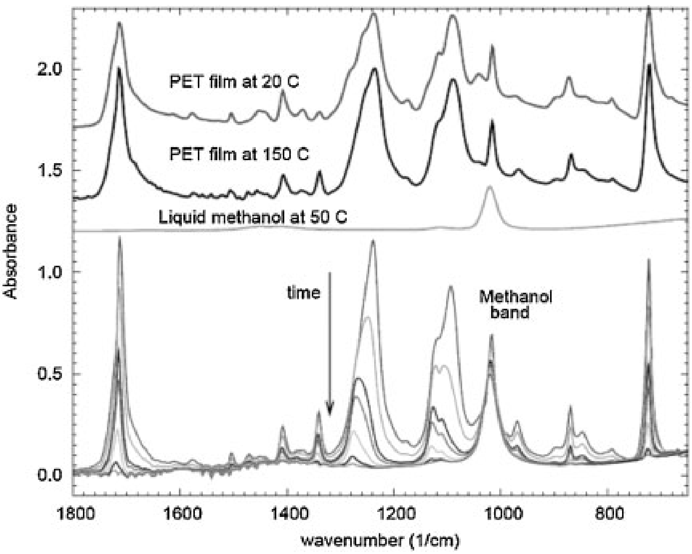

Figure 3.
ATR-FTIR spectra of PET, methanol and PET during methanolysis at 150 °C. Seven spectra of PET film have been measured at following time intervals: 0, 30, 60, 120, 240, 480 and 960 minutes.

Table 1.
Assignment of main vibrations of PET.

Wavenumber (cm^{-1})	Assignment
722	Out of plane of benzene group
845	CH_2 rocking of glycol
870	Out of plane of benzene group
897	CH_2 rocking of glycol
970	C-O stretching of glycol
1017	In-plane vibration of benzene
Broad band ca. 1090	Mainly due to ester C=O stretching
Broad band ca. 1230	Mainly due to ester C=O stretching
1340	CH_2 wagging of glycol
1370	CH_2 wagging of glycol

Several simple observations can be achieved using Figure 3. In this wavenumber range, the C-O stretching of methanol at circa 1015 cm^{-1} is the only intense band of methanol and all others bands disappear in less than ten hours. The methanol band appears in the spectra from the beginning of the experiments. In this case, the diffusion of methanol inside the PET film is much faster than the depolymerisation process. These experiments have been repeated several times and the presence of methanol from the beginning of the experiment is not due to presence of methanol in the interfacial area between the diamond and the PET film, but rather to methanol inside the PET film. At the end of the process, after 15 hours, the only band observable is the methanol band. Under these conditions it is not possible to comment on the product of the methanolysis but only on reactants.

Most visible differences between the spectra of the crystalline and amorphous structures are the shapes of large bands around 1100 and 1250 cm^{-1} which are too complex to be simply decomposed by a single Gaussian or Lorentzian function. The intensities of some of the smaller bands are also changing substantially between the crystalline and amorphous form. More comment will be added on this point afterward. The last observation using Figure 3 is on drastic change in the shape of the broad band at 1100 cm^{-1} between 0 and 30 minutes. To see the progression of the shape of both broad bands at 1250 and 1100 cm^{-1} the evolution of spectra have been shown in more detail in Figure 4. Vibrations involved in the broad band at 1100 cm^{-1} are mainly attributed to the deformation of the benzyl group. A strong change in the spectra could be due to an evolution in the structure and/or morphology of the polymer at molecular level.

The two bands of CH_2 wagging at 1340 and 1370 cm^{-1} correspond respectively to the trans and gauche conformations. Atkinson et al. have investigated the glass form of PET with both wagging bands, a structural alteration occurs on cooling and the change from trans to gauche conformations of the ethylene units in PET.[26] Another interesting band to examine is the aromatic skeletal stretching band at 1410 cm^{-1} which is not influenced by the crystallinity rate or the morphology of PET.[23] In fact, Cole et al. have shown a small sensitivity of this band to the environment but they have explained why it was the best choice to have as an internal reference anyway.[21] Ideally, a reference band should not show any sensitivity and in the case of PET the band at 1410 cm^{-1}, which is associated with the ring in-plane deformation, is generally used to normalize spectra of the polymer.[27] As often for quantitative analysis using ATR-FTIR spectroscopy, the contact between the sample and the crystal is a crucial because the results depend on the absorbance of bands which are directly correlated to the quality of the contact between the sample and the crystal. As presented in the Figure 4, spectra have been recorded regularly with the time and the absorbance shows a homogenous and continuous evolution. This result and the

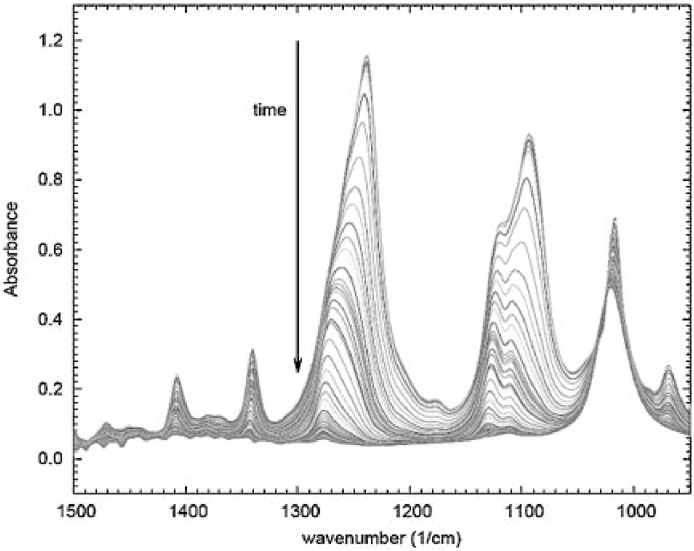

Figure 4.
Evolution with time (15 hours) of PET/methanol ATR-FTIR spectra at 150 °C.

fact that experiments have been reproducible show that the kinetic measure is not spurious and is not due to the penetration of methanol between the film and the crystal which should be a random process. Moreover, a first attempt was done by compression of a PET film on the diamond and not by casting it, in this case, the methanol can diffuse more easily between the PET film and the crystal, and the results obtained were random and the evolution of the absorbance of the spectral bands was not continuous.

To observe more clearly the shape evolution of the spectral region, subtraction spectra are presented in Figure 5. Spectra

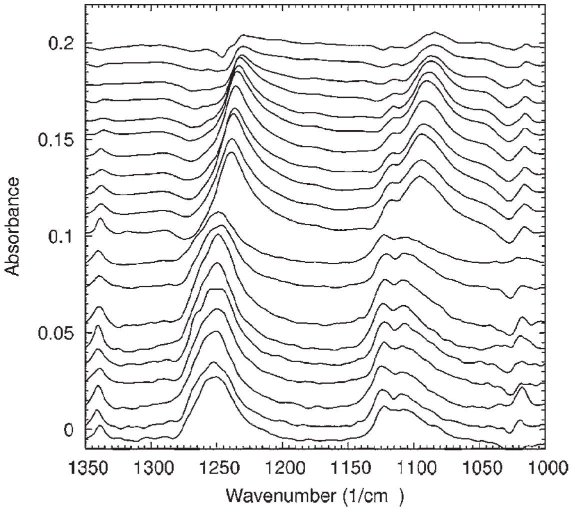

Figure 5.
Difference ATR-FTIR spectra of PET/methanol at 150 °C obtained during the first 2 hours of the depolymerisation (from top to bottom).

presented in the figure have been calculated by the systematic subtraction of the earlier one. The 10 spectra on the top correspond to the subtraction obtained in the first 100 minutes of depolymerisation at 150 °C and the other 10 spectra represent the evolution in next 2 hours. The beginning of the depolymerisation process shows a decrease of the band at 1180 cm^{-1} and 1235 cm^{-1}, both bands have been attributed to a ring mode or CH_2 twist and ring-ester in plane mode respectively. After that, the bands at 1260, 1240, 1125 and 1110 cm^{-1} are decreasing during the methanolysis. All these bands also result from some ring mode.

Decomposition of spectra by mathematical function can give additional information about the evolution of the PET during the process. An integration of each band has been calculated for each measured spectra to achieve a quantitative analysis of average morphology and of the structure of PET during methanolysis. Using the same approach, Pardal et al. have published very recently the evolution of trans and gauche conformations during glycolys of PET by ATR-FTIR spectroscopy.[28] They has measured an increase of the trans form in proportion with the comparison of band at 1340 cm^{-1} (trans) and 1370 cm^{-1} (gauche). In our experiments the signal is too low (sample with high rate of crystallinity) to extract any quantitative information from the band at 1370 cm^{-1}. But as discussed previously the deformation in plan of benzyl ring at 1410 cm^{-1} can be used as an internal reference. Under this condition the evolution of absorbance of CH_2 wagging in trans conformation at 1340 cm^{-1} and of the internal reference (band at 1410 cm^{-1}) has been reported on Figure 6. The evolution of the absorbance of the C=O stretching band, circa 1720 cm^{-1} and the absorbance of Gaussian at 1245 cm^{-1} has been also illustrate in the same figure. The broad band at 1250 cm^{-1} has been decomposed by two Gaussian functions centred around 1245 and 1265 cm^{-1}.

Pardal et al.[28] have shown the same evolution of trans/gauche proportion: an increase in the ratio of trans/gauche during the beginning the alcoholysis by diethylene glycol. In our case, the PET film has been melted before the alcoholysis, and the film has been largely crystallized in trans conformation. As Schmidt et al. have

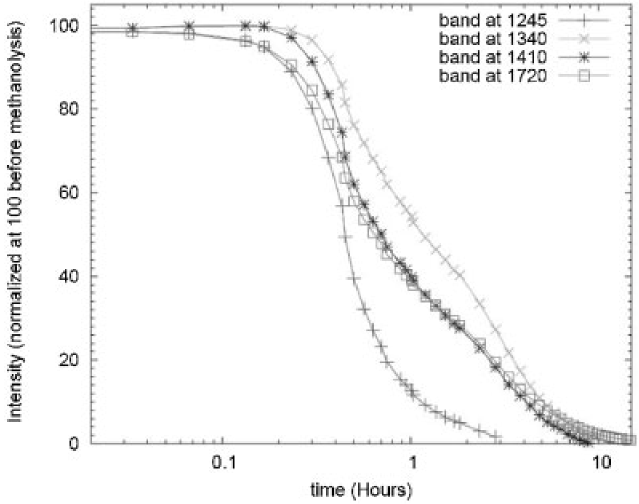

Figure 6.
Normalized absorbance of PET bands during degradation of PET by methanol at 150 °C: band at 1245 cm^{-1} shows the evolution of crystallinity of PET, band at 1340 cm^{-1} represents the evolution of trans conformation of PET, band at 1410 cm^{-1} is used as an internal reference for the quantity of PET; band at 1710 cm^{-1} is the C=O stretching mode.

demonstrated by two dimensional NMR, in crystalline PET the trans content is 100 percent and in the amorphous PET it is 14 percent (±5 percent).[29] The PET film used in the depolymerisation is mainly in crystalline form. To quantify the evolution of the gauche conformer, the CH_2 rocking can also be used. In fact, Cole et al. have shown for this vibration the frequency is around 900 cm^{-1} for the gauche conformer and 850 cm^{-1} for trans conformer. With Figure 6, the comparison between the absorbance of band at 1245 cm^{-1} and the reference band (at 1410 cm^{-1}) shows a heterogeneous evolution of the structure during the decomposition of the polymer by methanol. For clarity reason, the evolution have not been added to the Figure 6, but the evolution of the absorbance of this band is similar to the band at 1245 cm^{-1}. As the band at 1410 cm^{-1} is considered as the internal reference, we can observe that the percentage of the trans conformation is increasing during the process and at the same time the amount of gauche conformation is decreasing.

We have carried out calculations of quantum chemistry using density functional theory for the two conformations of di-ethylene terephthalate at the B3-LYP/6-31G(d) level using the PC GAMESS program.[30,31] Full structure optimizations were performed and used to evaluate harmonic frequencies and infrared intensities of the both conformation. The optimized structures of the two conformer trans and gauche are shown on Figure 1. As it has been explained previously,[32] the absorbance calculated by these methods are altered by large uncertainties. However, these methods are very useful for comparison of positions and/or absorbance the bands of molecular vibrations of different conformers or isomers.

On Figure 7, corrected frequencies and intensities are represented for both trans and gauche conformer of di-ethylene terephthale. The most intense band in infrared for both conformer is around 1250 cm^{-1} and it corresponds to an in plane benzyl vibration. This vibration is more important in trans than in gauche conformation. We have already measured the evolution of the percentage of trans conformation in PET film with the band at 1340 cm^{-1}, and evolutions of intensities bands at 1340 cm^{-1}

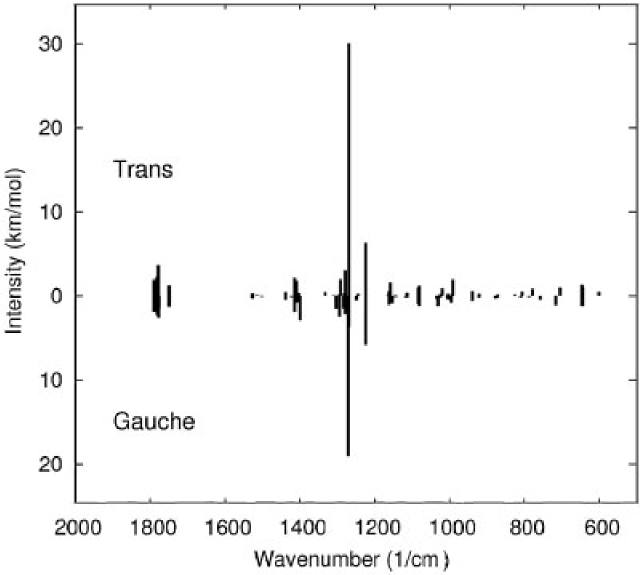

Figure 7.
Scaled harmonic frequencies and infrared intensities of trans and gauche di-ethylene terephthate. Each frequency has been corrected using the scaling factor calculated by Scott and Radom (0.9614 for B3-LYP/6-31G(d)).[33]

(sensitive to trans conformation) and 1250 cm^{-1} are obviously dissimilar. The evolution of the absorbance of the band around 1250 cm^{-1} cannot be explained by the difference of intensities between trans and gauche conformers. Nevertheless, the intensities of the crystalline and amorphous forms are probably also relatively different.

Not only can the absorbance of one band be used to observe the evolution of molecular interactions but the wavenumber of the band can also be very informative. The shift of the C=O stretching band has been employed to detect the variation of crystallinity in the system. Jang et al. exploited this shift to observe the progression of the crystallinity in the polymer blend.[34] For PET, the wavenumber of the ν(C=O) band can be used to distinguish between the crystal (lower frequency) and amorphous (higher frequency) form. As we have shown previously in the paper, the absorbance of the C=O stretching band has the same evolution as the reference band, it's possible to observe the evolution of the shift of the band with the change of absorbance. The position of the band shifts to the higher wavenumber region much slower than the evolution of the absorbance of the same band. It should indicate that during the process the PET film is transformed to a less crystalline form and probably this evolution of the crystallinity ratio is slower than the evolution of trans/gauche conformation. This analysis is in good agreement with the observation that can be achieved if it is assumed that the band at 1245 cm^{-1} is reflecting the crystallinity of the system.

As Huang et al.[35] have shown by solid-state nuclear magnetic resonance (NMR) and differential scanning calorimetry techniques there exists three-domain models containing crystalline (all *trans*), constrained noncrystalline (*trans* rich), and amorphous phase (*gauche* rich), they clearly showed that it is not possible to connect directly an evolution of trans conformation with an increasing of crystallinity. It is not possible to link directly the evolution of the ratio of trans/gauche conformation with the amount of crystallinity. In previous studies on hydrolytic degradation of PET,[12,36–39] authors have explained a 'chemicrystallisation' process to describe the variation of the density due to variation of trans conforma-

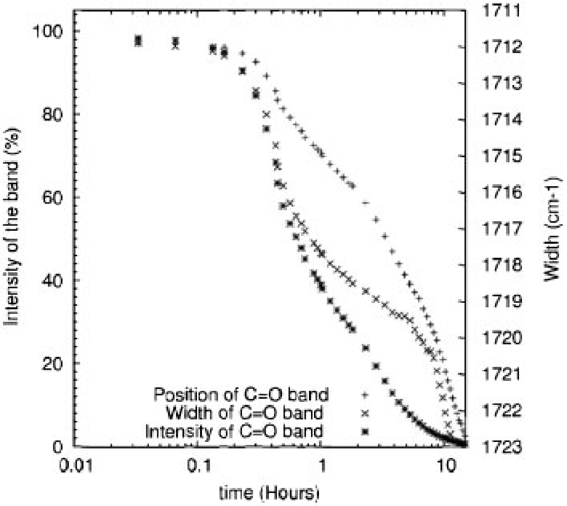

Figure 8.

Evolution of the 3 parameters position, width and intensity (absorbance) of the Gaussian function used to analyse the band of the carboxyl group's stretching vibration during the decomposition process of the PET film. (The width is decreasing from 10.3 to 3.5 cm^{-1}).

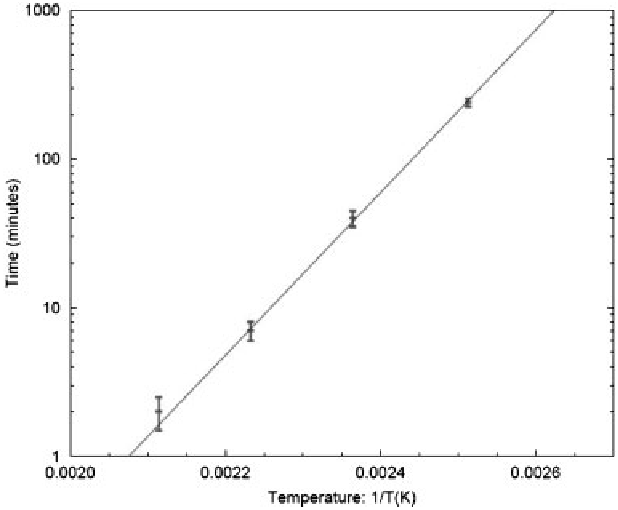

Figure 9.
Degradation rate of PET film under methanol between 100 and 200 °C.

tion in the polymer during the degradation. It appears in fact with a third "phase" that hydrolysis and methanolysis used the same way for the depolymerisation of PET. All efforts to understand both the evolutions of structure and morphology have clearly demonstrated a non correlation between the evolution of crystalline/amorphous phase and trans/gauche conformation. The quantity of the trans form is decreasing rapidly during the process opposing the amount of amorphous form which is increasing. Nevertheless, it is important to notice also that the evolution of the molecular weight during the methanolysis has not been taken into account in this analysis. As the evolution of the crystallinity and the conformation of the PET, this phenomenon might also affect the evolution of the spectra during the depolymerisation process.

Methanolitic degradations have been also studied and analysed at three other temperatures (125, 175 and 200 °C) and similar evolutions have been found. The half life time of PET (using an internal reference band at 1410 cm^{-1}) under methanol pressure are presented in Figure 9. The time of degradation depends exponentially on the inverse of temperature as expected by using a simple Arrhenius law. The process is 100 time faster at 200 °C than at 125 °C.

$$\mathrm{K} = \mathrm{A}\ \exp(-E_a/\mathrm{R}T(\mathrm{K}))$$

Arrhenius equation

Where K is the rate constant of the chemical process, T the temperature (in Kelvin) and E_a the activation energy.

As discussed recently by Mishra[40] to the methanolysis of depolymerization of PET waste using zinc acetate in the presence of lead acetate as the catalyst at 120–140 °C in a closed batch reactor, the methanolysis can be modelled by an Arrhenius equation as a simple reaction. In our case, we have found low activation energy of 5.8 $\mathrm{kJ{\cdot}mol^{-1}}$.

Conclusions

ATR-FTIR spectroscopy has been applied in situ during the degradation of PET by methanol at 125, 150, 175 and 200 °C. Infrared spectroscopy is able to observe interactions at molecular level. These experiments gave us the possibility to observe in situ the evolution of morphology of the polymer. The opportunity to observe in situ a complex phenomenon like the degradation of polymer (which is directly related to the polymer recycling process) has been demonstrated with the possibility to observe at same time the proportion of trans/gauche conformer using an internal reference. The evolution of the degree of crystallinity has not been quantified. During the degradation the trans conformations have been destroyed more slowly than the average PET and at the same time the proportion of crystalline form was decreasing. The evolution of the degradation time depends exponentially on the inverse of temperature.

In summary, the in situ spectroscopic approach developed here shows good promise in evaluating of degradation processes of polymers subjected to high-temperature methanol. We hope that this approach can contribute to the optimisation of existing polymer recycling processes under these conditions and could also be used for the design of new processes using high-pressure gases and supercritical fluids.

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