THERMAL DECOMPOSITION OF RADIO-OXIDIZED POLYMERS AND IMPACT ON RADIOACTIVE MATERIAL TRANSPORTATIONS

Nicolas GAMMELLA
CEA – France - Cadarache
Department of Radioactive
Materials Transportation (STMR)

Solène LEGAND
Den-Service d'Etude Du Comportement des
Radionucléides (SECR), CEA, Université
Paris-Saclay, Gif-sur-Yvette, France

Vincent DAUVOIS
Den-Service d'Etude Du Comportement des
Radionucléides (SECR), CEA, Université
Paris-Saclay, Gif-sur-Yvette, France

Stéphane ESNOUF
Den-Service d'Etude Du Comportement des
Radionucléides (SECR), CEA, Université
Paris-Saclay, Gif-sur-Yvette, France

ABSTRACT

Introduction
In case of accidental conditions of transportation, the temperature of packages can reach 150°C. The accumulation of the gases formed may affect the integrity of the package. Therefore, it is important to predict the gas quantity released by different organic materials and measure the kinetic of this decomposition. The purpose of this work is to present the results of a multi-year study performed on four polymers (polyethylene, cellulose, polyurethane, polyvinyl chloride). The effect of dose, atmosphere and degradation temperature on the quantity of gas release was investigated.

Experimental
The polymers were gamma-irradiated under air atmosphere at room temperature at different doses (from 0 to 4 MGy). After irradiation, the thermal degradation of polymers at different temperatures (from 60°C to 150°C) during 48 hours under two types of atmosphere (air or inert) was analyzed. For that purpose, a known amount of polymer was conditioned in a small hermetic chamber (made on stainless steel or glass) equipped with a pressure gauge. The pressure elevation during the thermal treatment was recorded. An identification and a quantification of the gas phase were also realized using high resolution mass spectrometry.

Results and discussion
In contrast to the non-irradiated polymers, which are mostly stable even at 150°C, a rapid increase of the pressure during the first hours after heating and a stabilization or a slow increase after is observed for radio-oxidized materials. The production of volatile species is almost proportional to the dose and is thermally activated. The main degradation products are water and carbon dioxide. The production of hydrogen and inflammable gases is rather limited. Under air atmosphere, the pressure increase is partially compensated by oxygen consumption.

Conclusions
The thermal decomposition of pre-oxidized polymers is rapid. The majority of the gases is released in the first hours. Water and carbon dioxide are the predominant species. Although irradiation reduces the thermal stability of the polymers, our results show that the risk of inflammation is not exacerbated.

INTRODUCTION

Many polymers are used in nuclear industries and are then stored in nuclear waste packages. During their transportation, for instance in case of fire, the temperature in the packages may increase and reach 150°C, and then remains above 80°C for several days. Radiation and thermal decomposition of polymers induce gas generation that can lead to overpressure or inflammable atmosphere, and then may affect the integrity of the transport cask.

Therefore, it is important to predict the gas quantity released by different organic materials and measure the kinetic of their decomposition. However, in the field of transport, the data from the literature are insufficient and generally not very representative of the regulatory conditions of transport.

The purpose of this work is to present the results of a multi-year study performed on four polymers (polyethylene, cellulose, polyurethane, polyvinyl chloride) which are the most present in nuclear waste. The effects of dose, atmosphere and degradation temperature on the quantity of gas release were investigated.

EXPERIMENTAL

Materials

The cellulose is in the form of cotton fibers. The fiber diameter is close to 15 µm. The materials was studied as received (raw) or after a drying in a desiccator (dry).

The polyethylene (PE) is a linear high-density polyethylene provided by Sigma-Aldrich in the form of granules. The average molecular weight is Mw = 120 000 g.mol^{-1}, the melting point is 130°C and the density is 0,95 g.cm^{-3}. The material was pressed into 50 µm thick films before irradiation to ensure a homogeneous radio-oxidation.

Plastunion ® provides the polyurethane (PUR). This is a translucent thermoplastic film with an ether base. The thickness is 200 µm. The melting point is 180°C and the density is 1,15 g.cm^{-3}.

Plastunion ® provides the polyvinyl chloride (PVC). The initial thickness is 300 µm and the density is 1,23 g.cm^{-3}. Except for the 1 MGy, the thickness is reduced to 100 µm by compressing the material under 5 tons for 30 seconds at 170 ° C.

Irradiation

Gamma irradiations were performed at LABRA (CEA Saclay, France), with a ^{60}Co source under air at room temperature and at a dose rate between 0,81 and 0,85 kGy.h^{-1} (UNIDOS PTW dosimeter equipped with a calibration chamber). No electronic correction was made to take into account the electronic density difference between water and polymers. Uncertainties on given doses are less than 6%.

To get a homogeneous radio-oxidation, the films were hold on a glass stick with enough space between them, then placed in pillboxes covered with glass cristallizing dishes that allow air to circulate.

## *Pressure measurements and gas analysis*

For each experiment, about 40 mg of polymers were placed in a stainless steel cell equipped with a valve for conditioning and a pressure sensor. For the PVC, a glass cell was used.

Conditioning was realized at room temperature and atmospheric pressure. Argon was used for experiments under inert atmosphere. For air atmosphere, a mixture of gas with krypton tracer composed of 77.99% N_2, 20.00% O_2 and 2.01% Kr was used.

After conditioning the container was placed in an oven and the temperature increased from room temperature at a heating rate of 1°C.min^{-1} and hold at the set temperature for 48 hours. The rises of temperature and pressure in the cell were monitored all through the experiment. After 48 hours, the cell was cooled to room temperature and quantitative measurements of the gases formed during thermal decomposition were analyzed using a Thermo Electron Corporation MAT 271 mass spectrometer [1].

Pressure measurements were performed during 48 hours at 5 temperatures (60, 80, 100, 120 and 150°C), 4 irradiation doses (0, 1, 2 and 4 MGy) and 2 types of atmosphere (air or inert).
In the following, the measurements at 60°C are omitted because almost no evolution has been recorded after 48 hours at this temperature.
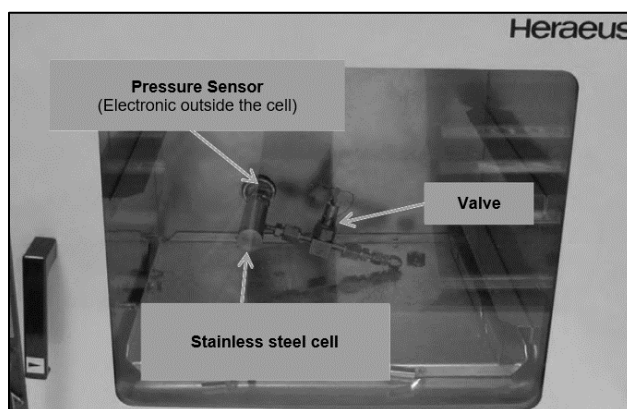
Figure 1. Picture of the pressure-measuring cell placed in an oven

Sealed glass ampoules measurements under vacuum

Aiming to identify and quantify by mass spectrometry all the volatile species evolved during heating of materials, material samples were placed in glass ampoules. After cooling down the bottom of the ampoules in order to ensure the trapping of volatile species, the air was evacuated and then the ampoules were sealed. Afterwards, each ampoule was heated at 150°C during a time ($\leq$ 48 hours) and finally all the volatile species in the hot glass vessel were introduced in a direct inlet magnetic mass spectrometer. The number of moles of all the gaseous products was then determined.

Thermogravimetric analysis

Thermal analyses were performed using a Netzsch STA Jupiter 449. Measurements were carried out under helium at a heating rate of 5°C.min^{-1} for a temperature range from 30°C to 1000°C.

Results and discussions

Effect of dose on thermal stability of radio-oxidized materials

Non-irradiated and pre-irradiated samples were characterized by thermal decomposition analysis under helium at 5°C.min^{-1}. Evolutions of weight loss as a function of temperature are shown in Figure 2 for non-irradiated and pre-irradiated polymers under air.

Classically, the thermal degradation of polymers is characterized by the maximal degradation rate temperature T_{max} and $T_{1\%}$, which denotes the onset degradation temperature defined as the temperature belonging to 1% weight loss.
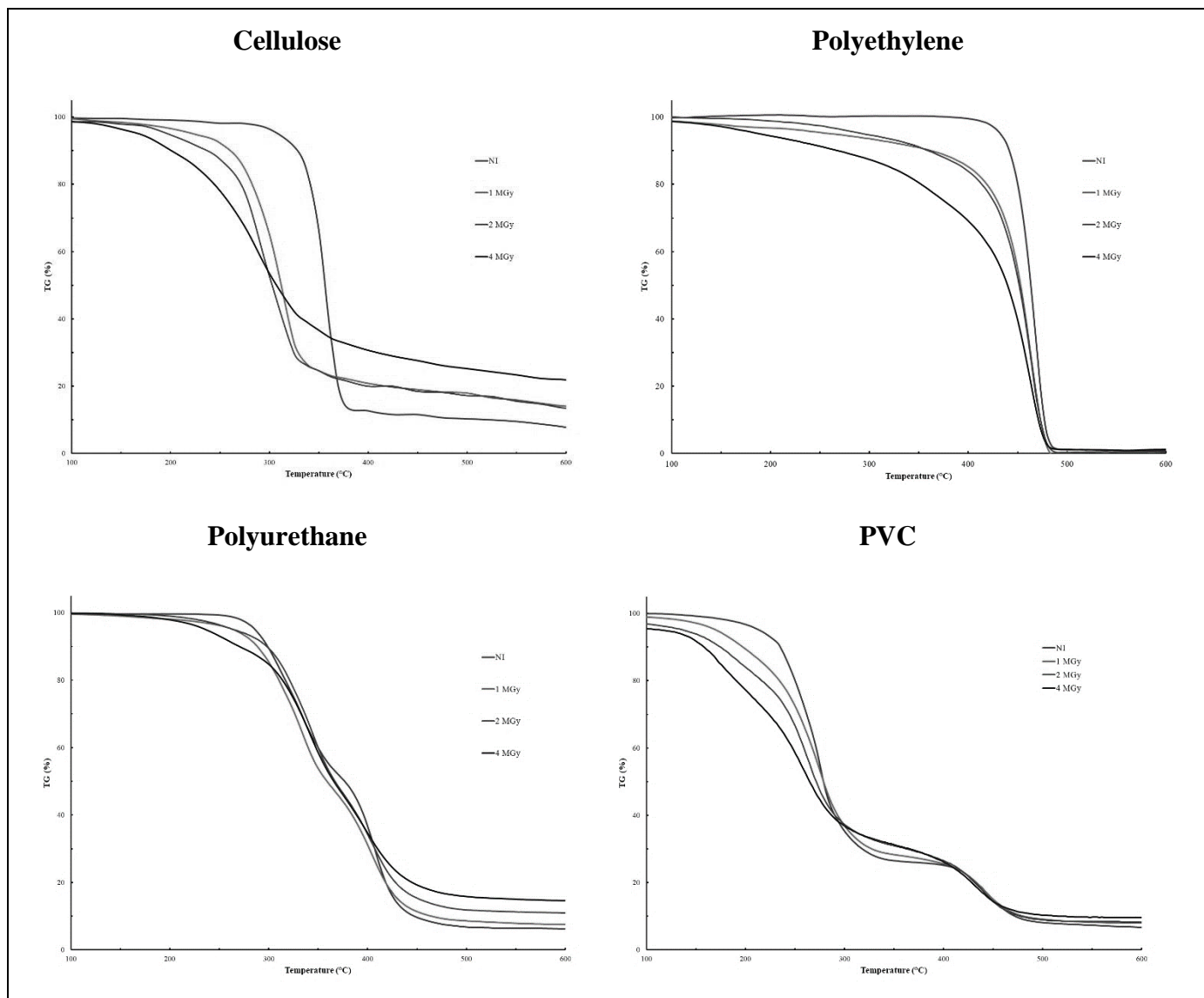
Figure 2. TGA curves for polymers pre-irradiated between 0 and 4 MGy - Heating rate: 5°C.min⁻¹

Cellulose is the polymer for which pre-irradiation has the major impact: a rapid decrease of T_{max} and $T_{1\%}$ is observed after irradiation.

For polyethylene, the results show that T_{max} remains almost constant as the dose increases. We conclude that radio-oxidation has a limited effect on the thermal decomposition of this polymer even at the highest dose (4 MGy).

The thermograms of PUR present two steps attributed to the degradation of hard segments (HS) (formed by an aromatic diisocyanate with a diol) and to soft segments (SS) (composed of polyether). Irradiation tends to reduce the decomposition temperature of the second step. It confirms that soft segments are less stable than hard segments.

The thermal degradation of plasticized PVC proceeds through two major stages, the first one corresponds to the dehydrochlorination (DHC) and loss of plasticizers, the second one is attributed to condensation.

Whatever the polymer, irradiation has an impact mainly on the onset temperature (cf. Table 1) which decreases with the dose.

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Table 1. $T_{1\%}$ and maximal degradation rate temperature T_{max} for non-irradiated and pre-irradiated polymers under air at room temperature

Temperatures	Cellulose (dry)		Polyethylene		Polyurethane		PVC	
	$T_{1\%}$	T_{max}	$T_{1\%}$	T_{max}	$T_{1\%}$	T_{max}	$T_{1\%}$	T_{max}
Non-irradiated	277	354	406	469	260	332	178	277
Pre-irradiated at 1 MGy	176	313	110	461	160	338	98	274
Pre-irradiated at 2 MGy	75	304	160	465	210	339	96	264
Pre-irradiated at 4 MGy	51	293	117	465	180	340	86	263

In addition, the above results show that all polymers are stable below 180 °C when they are non-irradiated and below 90°C/100°C when they are irradiated, except the cellulose.

Production of degradation molecules after thermal degradation of radio-oxidized polymers

Degradation molecules formed after thermal degradation are of two types:
- Condensable molecules (CM) that condense at room temperature (e.g.: water, organic molecules…),
- Non-condensable molecules (NC) that remain as gas at room temperature (e.g.: H_2, CO_2, CO, CH_4…).

Kinetics of formation of degradation molecules (CM and NC) during the thermal decomposition of polymers were determined using pressure measurements. A schematic evolution of the pressure as a function of time and temperature is presented in Figure 3. In inert atmosphere, the difference between the initial pressure and final pressure is used to determine the total amount of degradation molecules ΔN_{CC+NC}.

After return at room temperature, the pressure decreases, the remaining difference with the initial pressure corresponds to the amount of non-condensable molecules ΔN_{NC}.
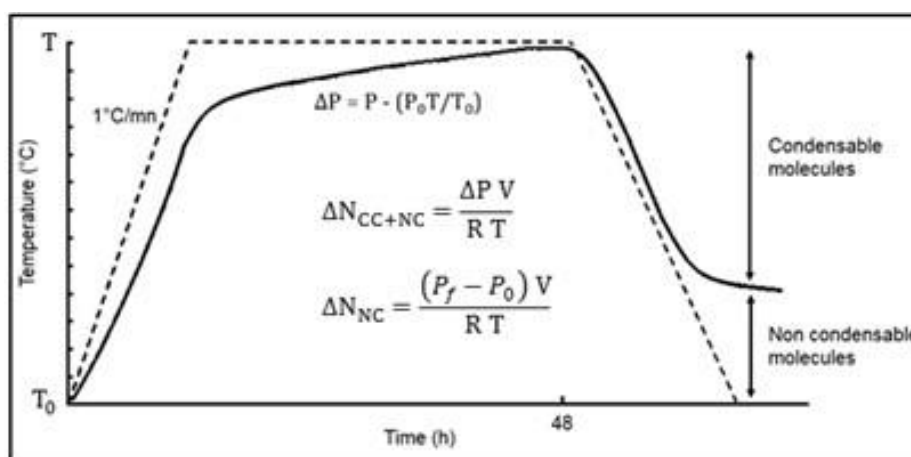

Figure 3. Schematic build-up pressure in a closed container containing thermal degradable polymer

In air, oxygen consumption should considered to evaluate the production of CM and NC molecules.

Thermal decomposition of radio-oxidized polymers was studied for four pre-irradiation doses (0, 1, 2 and 4 MGy) and five temperatures (60, 80, 100, 120 and 150°C). Figure 4 shows the pressure evolution measured at 150°C under argon for cellulose.

The evolution is qualitatively the same whatever the polymer, the dose and temperature: the pressure increases rapidly in the first hours, overtakes the thermal expansion pressure of conditioning gas (1.44 bar for 150°C), then slows down. The long time evolution is almost linear with time.
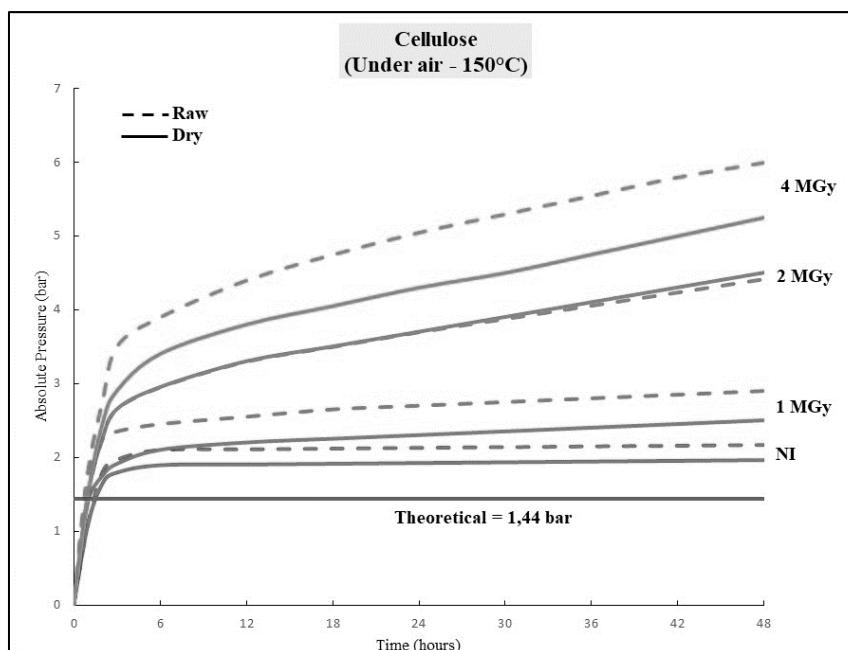
Figure 4. Evolution of pressures as a function of time at 150°C for non-irradiated (NI) and pre-irradiated polymers

The initial pressure rise can be explained by two phenomena: the release of physisorbed water in the polymer (each studied polymer are hydrophilic and this tendency is increased under the effect of the irradiation) and the impact of the radio-oxidation. The second phase, slower and linear, can be explained by the decomposition of oxidized functions of polymers.

For the PVC, above 80°C the thermal degradation is very fast and increases under the effect of the dose. This degradation results in the rapid achievement of a pressure level and is due to the low temperature resistance of the material, as shown in Figure 2.

It appears that, the higher the pre-irradiation dose the higher the pressure increase and final pressure.

Figure 5 represents for polyethylene the total production of degradation molecules and the production of NC molecules depending on pre-irradiation dose and on temperature after 48 hours of heating under inert atmosphere.

As can be seen, the production of degradation molecules under inert atmosphere and air increases linearly with increasing dose. A saturation at 4 MGy is observed at high temperatures. It appears also that, the higher the temperature the higher the production of degradation molecules.

Condensable molecules are clearly predominant over non-condensable molecules (except for PVC for which the quantities are similar). Mass spectrometry analyses of the samples after heating show that carbon dioxide is predominant (except for PVC).

As condensable molecules cannot be identified from pressure measurements, additional sealed glass ampoules measurements under vacuum were performed and heated at 150°C in order to identify all the degradation products.
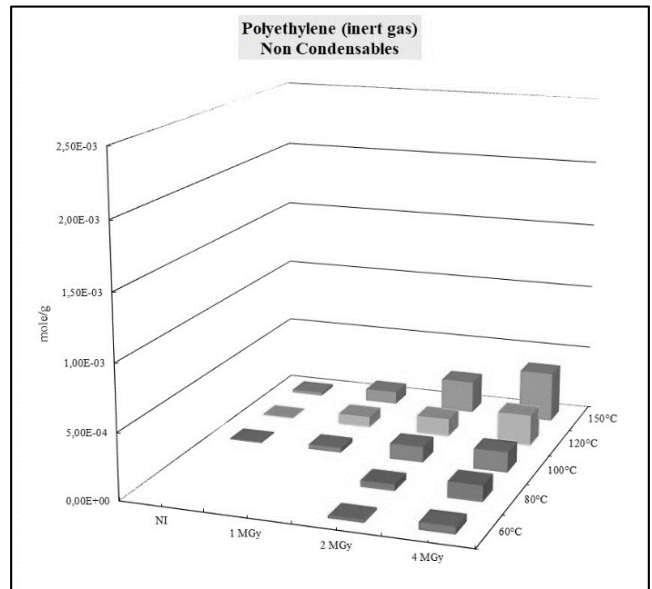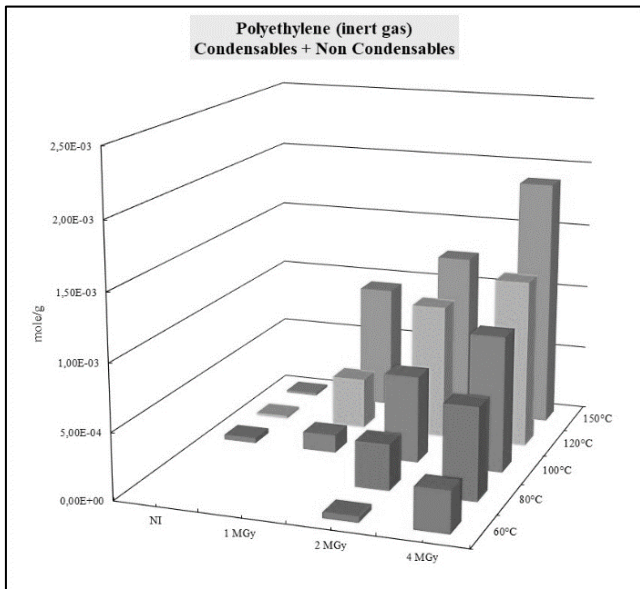
Figure 5. Quantity (mole.g^{-1}) of degradation molecules as a function of pre-irradiation dose and temperature after 48 hours of heating of radio-oxidized polyethylene under inert atmosphere

Figure 6 gives for each polymer the composition of the atmosphere after 48 hours at 150°C under vacuum.
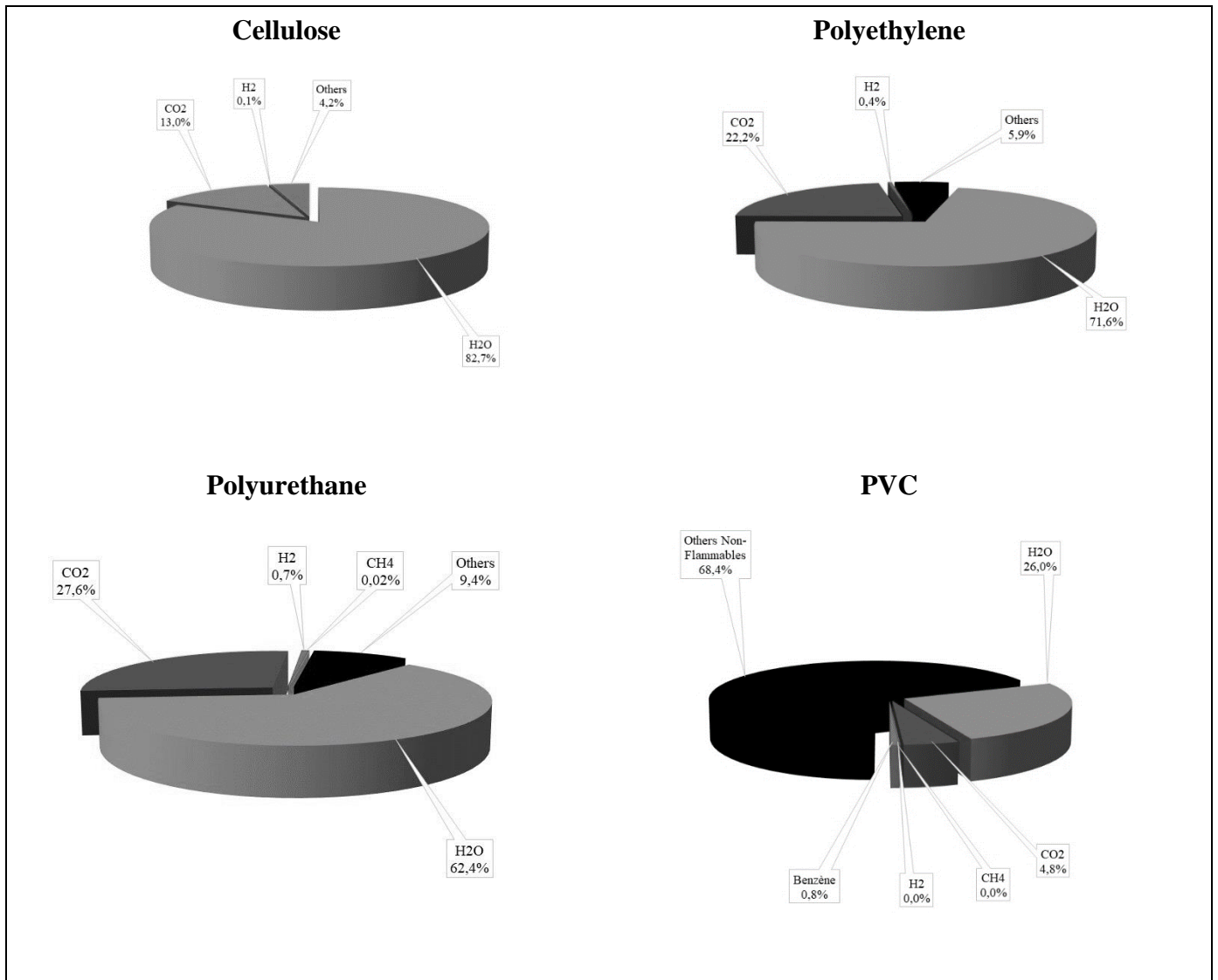
Figure 6. Volume distribution of gaseous compounds after heating of pre-irradiated polymers 4 MGy under air and heating at 150°C under vacuum during 48 hours

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These results confirm that water is the most abundant degradation product, followed by carbon dioxide (except for PVC). Other volatile compounds such as H_2, non-flammables and organic compounds are produced in very small quantity.

Moreover, the quantity of H_2 and flammable gas remains constant and very low during heating.

Gas release prediction: Temperature effect

The common way of treating data as a function of dose (or time) and temperature is by means of superposition principle.

We suppose that the degradation mechanism is the same in the investigated range of temperature and the different curves obtained at various temperatures can be superimposed by shifting along the dose axis.

Normalisation of the data at a reference temperature of 150°C under air is plotted in Figure 7 for polyurethane and CM and NC molecules.

Remark : For each temperature, the contribution of the non-irradiated polymer has been subtracted.
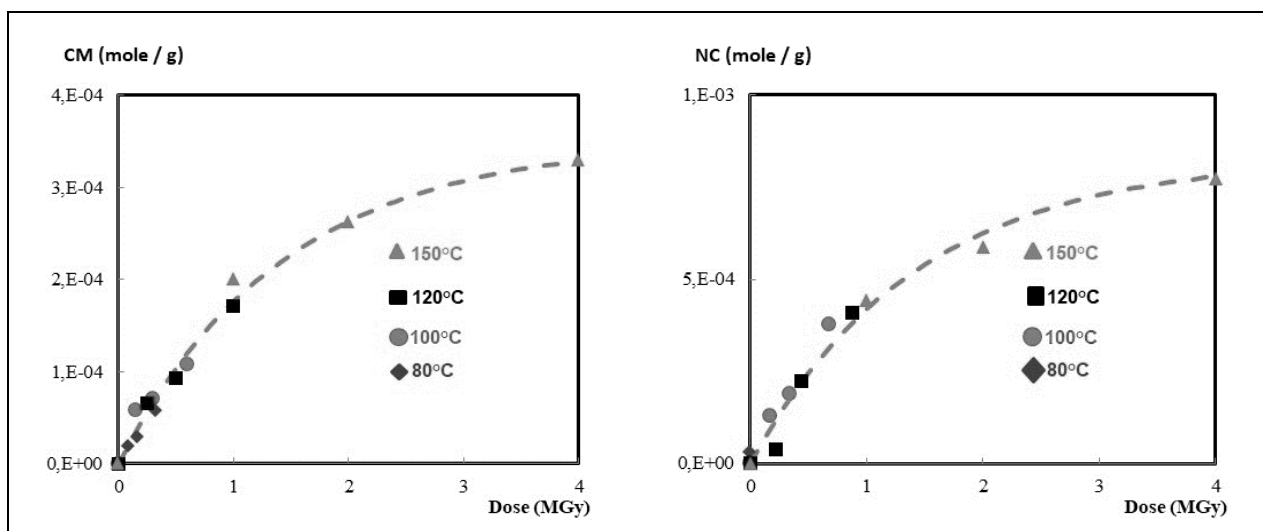
Figure 7. Normalisation at 150°C of the quantity of CM and NC produced during the heating under air during 48 hours of polyurethane pre-irradiated under air

In Figure 8, for each polymer (except PVC) and heating atmosphere, the log of the thermal shift factors a_T determined for CM and NC molecules are plotted versus $1/T$.

The points are rather aligned suggesting that the degradation mechanism is dominated only by one process.

The activation energies can be determined from the various slope.

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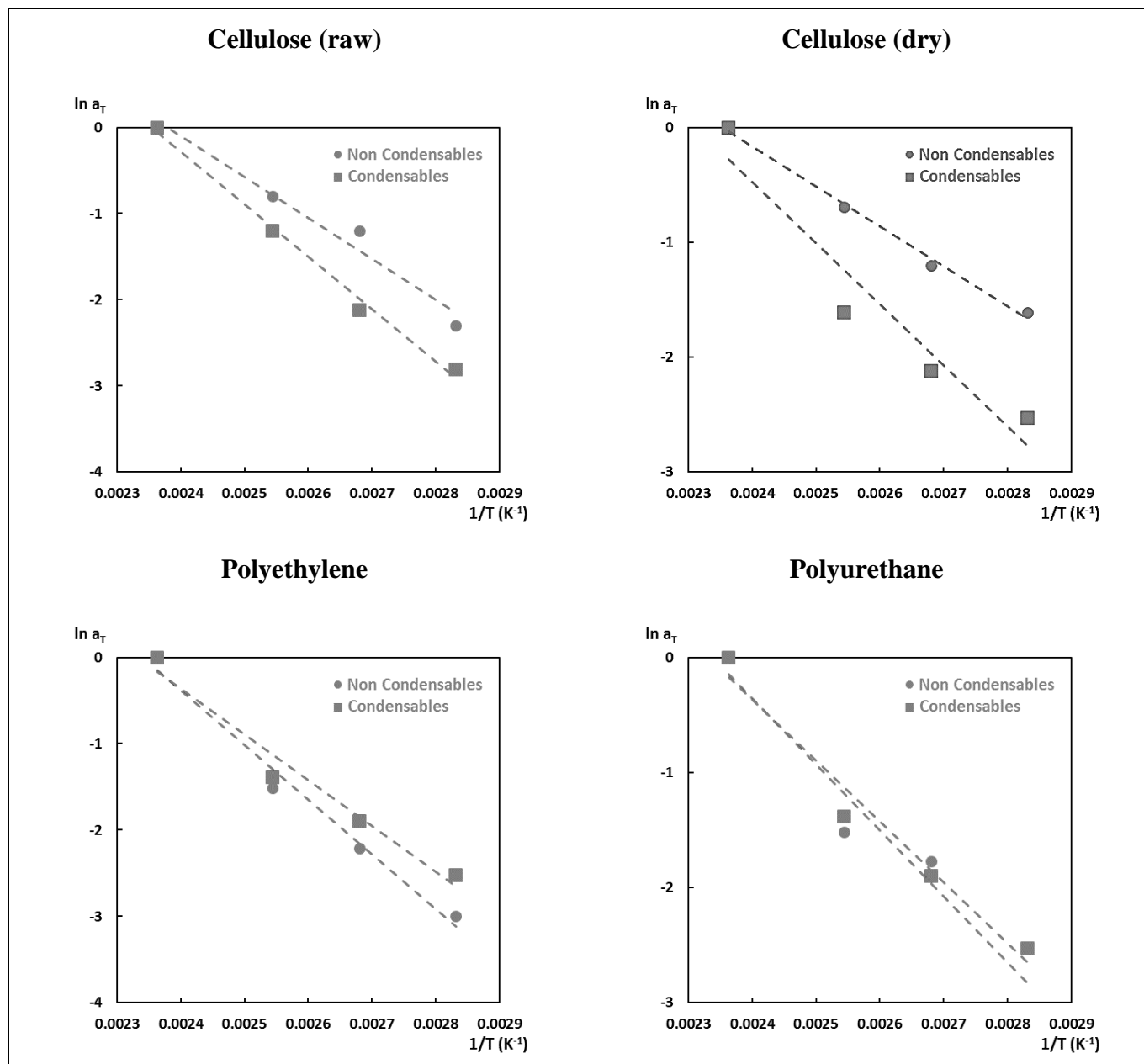
Figure 7. Arrhenius plot for thermal shift factor a_T againt temperature for cellulose, polyethylene and polyurethane

The data for the production of CM and NC under air are summarized in Table 2.

Table 2. Activation energies (kJ.mol^{-1}) for the production of CM and NC molecules after 48 hours of thermal degradation of radio-oxidized polymers under air

	E_a (kJ/mol)	
	CM	**NC**
Cellulose (dry)	50.5	39.4
Cellulose (raw)	44.3	28.9
Polyethylene	44.0	52.6
Polyurethane	44.0	47.8

In order to predict the quantities of gas release by a polymer subjected to a rise of temperature, it is possible to use the activation energy presented in Table 2 and the data recorded at 150°C as a master curve.

Conclusion

Thermal decomposition of gamma-oxidized polymers has been studied under representative conditions of nuclear waste's transportation.

Different techniques under different conditions of irradiation doses, temperatures and atmospheres were used for this study, which made it possible to identify and quantify the compounds formed during the thermal decomposition, to study the influence of various parameters and to evaluate the speed of production of these compounds.

For all the polymers studied, it was observed that:
- All the polymers, except cellulose, are stable below 180 °C when they are not irradiated and below 90/100°C when they are irradiated;
- The thermal decomposition increases with the temperature and the dose;
- The thermal decomposition of polymers is divided into two phases:
  - a rapid rise in pressure due to two phenomena: the release of physisorbed water in the polymer and the impact of the radio-oxidation;
  - slower and linear rise in pressure due to the decomposition of oxidized functions of polymers;
- Degradation molecules formed after thermal decomposition are of two types: Condensable molecules (CM) that condense at room temperature (e.g.: water, organic molecules…) and non-condensable molecules (NC) that remain as gas at room temperature (e.g.: H_2, CO_2, CO, CH_4…);
- Condensable compounds are in the majority (except for the PVC);
- Water is the major condensable compound;
- Carbon dioxide is the major non-condensable compound (except for the PVC);
- Hydrogen and flammables compound are presents in very low quantities;
- The thermal decomposition is thermally activated and the activation energies are around 30-50 $kJ.mol^{-1}$.

These studies will be continued to analyze the thermal degradation of the polymers over long periods between one month and one year.

Acknowledgement

References

[1]   M. Ferry, A. Dannoux-Papin, N. Dely, S. Legand, D. Durand, J.L. Roujou, et al., Chemical composition effects of methylene containing polymers on gas emission under g-irradiation, Nucl. Instrum. Methods Phys. Res., Sect. B 334
(2014) 69-76.

[2]   Boughattas, I., Ferry, M., Dauvois, V., Lamouroux, C., Dannoux-Papin, A., Leoni, E., Balanzat, E., Esnouf, S., Thermal degradation of γ-irradiated PVC: I-dynamical experiments, POLYMER DEGRADATION AND STABILITY 126: 219-226 (2016)