Deliverable 4.1

Technical reports on results of verification analysis performed on preform

The preforms produced during the this last year of RePack Edoils Project, that are 31g preforms with 100% R-PET and 50% R-PET clear and colored, were submitted to dimensional, thermal, and chemical-physical investigation in order to verify their properties and compare their characteristics with correspondent pure virgin PET preforms.

100% V-PET	50% R-PET	100% R-PET

Figure 1: 31g PET preforms clear produced during the RE-PACK EDOILS Project.

In particular, this technical report focuses on the production of R-PET and pure V-PET preforms and on the evaluation of several analysis performed to qualify the produced preforms, that have consisted in:

- preform weight, determined with an analytical balance Shimadzu AUW220D;
- dimensional analysis, performed with caliper Borletti and with a Magna Mike 8500 by Olympus to measure the wall thickness;
- evaluation of intrinsic viscosity, using an Ubbelohde 1C capillary viscometer according to standard ASTM D4603;
- acetaldehyde determination, analyzed by a gas chromatograph GC-2014 by Shimadzu coupled with an head space tool HT200H by HTA, according to an internal method;
- thermal analysis in dynamic mode carried out with a Differential scanning calorimeter (DSC), DSC823 by Mettler Toledo, by setting the following thermal method:

I heating from 30 to 300°C at 10°C/min;
Isotherm at 300°C for 5 min;
Cooling from 300 to 30°C at 10°C/min;
II heating from 30 to 300°C at 10°C/min.

The percentage of crystallinity Xc was determined by using the following equation:

$Xc = (I\Delta HmI - I\Delta HcI)/\Delta H^0{}_{PET}$

where I∆HmI is the absolute value of the enthalpy of melting analyzed during the heating steps; I∆HcI is the absolute value of the enthalpy of crystallization analyzed during the heating/cooling steps;

$\Delta H^0{}_{PET}$ is the theoretical enthalpy of fusion of PET here considered as 140,1 J/g

- Moreover, rheological analyses (frequency sweep test) have been carried out on R-PET and V-PET raw material by mean of a rotational rheometer ARES (Rheometric Scientific) at 280°C; 25 mm plate-plate geometry; strain 20%; frequency range 0,1-100 rad/s; gap between plates: 1mm.

The above tests aim to verify if the R-PET food grade can affect the quality of the preforms that can be evaluate with the two main parameters: the Acetaldehyde (AA) content, since the AA is a well known by-product of thermo-mechanical degradation of PET (1), and the Intrinsic viscosity, that is directly related with the molecular weight of PET according to the empirical equation of Moore (2):

$IV_{(25°C)} = 7{,}50 * 10^{-4} * Mn^{0{,}68}$

While, the thermal analyses by DSC in dynamic mode are important to verify if the thermal characteristics of the preforms and of the material used for the preform productions show any difference due to process condition and R-PET presence.

Results and Discussions

The 31 g preforms have been produced with an industrial injection molding line and the process parameters have been set properly according to the polymer fed, in order to reduce the preform degradation and to obtain a high quality product.

The optimized parameters for the injection process of the different material used are reported in the following Table 1.

Table 1 Optimized process condition parameters set according the different PET materials used for RepackEdoils preforms.

Preform's Materials	100% V-PET	50% R-PET/V-PET	100% R-PET
Plasticization temperature [°C]	295-300	290-295	280
Hot runner temperature [°C]	288	285	280
Injection time [s]	5,4	5,5	5,7
Residence time [s]	5,2	5,2	5,3
Pressure [bar]	54	52	55
Cooling time [s]	18,0	19,3	19,0

It is important to underline that the addition of colorant during the colored preform production (white, green and red preforms) have not required a significant change in process parameter.
However, it is also possible to observe that the different temperature profiles set according to the different PET material is essentially due by a different melt viscosity of the materials. Rheological measures carried out in dynamic mode on the raw materials have shown that R-PET LP80 supplied by CIER, even if is characterized by an Intrinsic Viscosity similar of the V-PET used for preform production, shown a complex viscosity at 280°C significant lower than V-PET. Therefore, during the 100% R-PET preform production, it was possible to work with the plasticizing and injection temperatures much lower than those required to process the virgin PET.

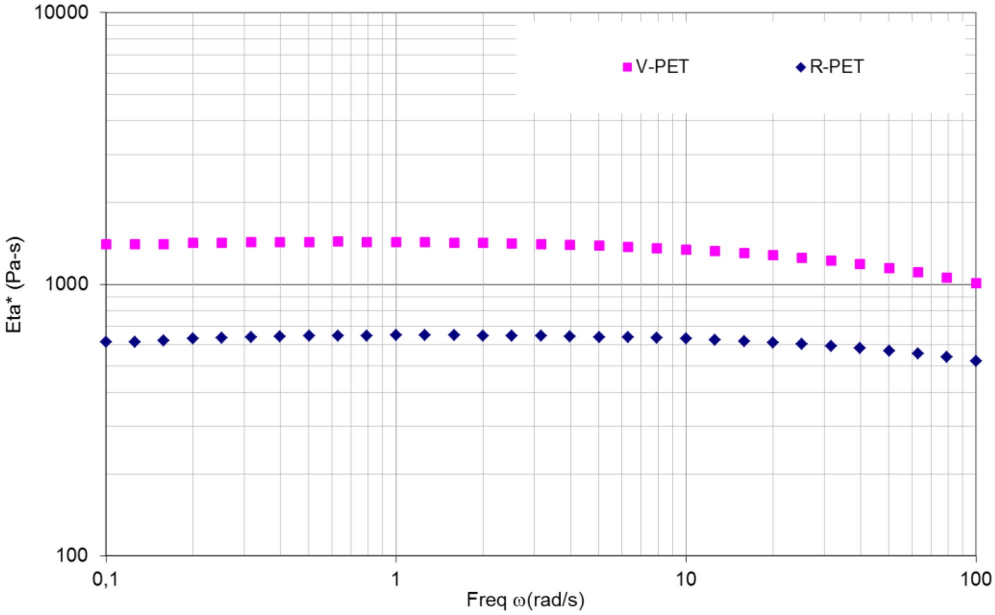

Figure 2. Complex viscosity curve in function of frequency for V-PET and R-PET used for preform production evaluated at 280°C and 20% strain.

Moreover, the production of 50% R-PET-50% V-PET preforms (here reported as 50% R-PET) requires higher temperature profile compared to 100% R-PET preform process, due to the presence of high percentage of virgin PET that is characterized by an higher melt viscosity, as shown in Fig 1.
After the production a visual and dimensional check of the preforms have been performed. All dimensional data are in accordance with the technical drawing, reported in Figure 3; while the visual inspection let to verify the absence of macroscopic defects.

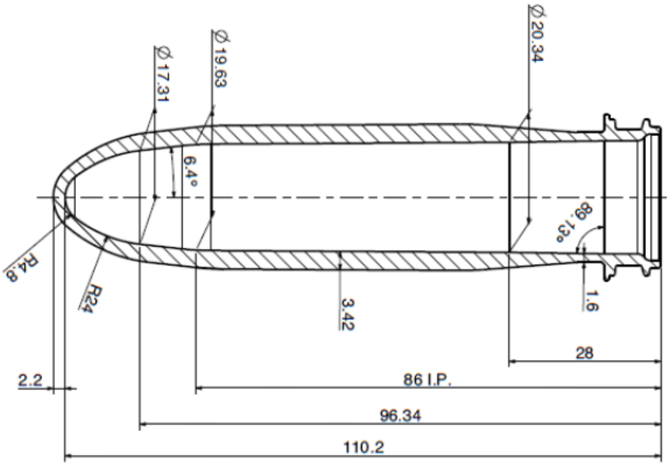

Figure 3. Technical drawing of 31g preform, designed by SIAPI for RE-PACKEDOILS Project**.**

The injection molding process was verified by analyzing the Intrinsic viscosity of the produced preforms and the free acetaldehyde. The intrinsic viscosity is one of the most important characteristics of PET. In fact, as previously said, the intrinsic viscosity (IV) is dependent upon the length of the polymer chains and then it let to point out the effect of process condition on the degradation of material and on the quality of the preforms. In Table 2 are reported the measured values of IV of raw material before the process and of produced preforms. The presence of colors has not affected the process condition and the preform characteristics.

Table 2. Intrinsic viscosity of raw material used and of 31g produced preforms.

Pellets	**IV [dl/g]**	**Std Dev**
V-PET	0,81	0,02
R-PET	0,79	0,01
Preforms		
100% V-PET	0,78	0,01
100% R-PET	0,77	0,01
50% R-PET/V-PET	0,75	0,02

It is interesting to observe that the measured intrinsic viscosity of 100% R-PET preforms is comparable with the one of 100% V-PET preforms and it was slightly higher than the IV of 50% R-PET/V-PET preforms. This behavior is essentially due to degradative phenomena of recycled material contained in the 50% R-PET/V-PET preforms occurring during the injection process performed at process temperature similar to pure V-PET preforms. Because of the presence of 50% of virgin PET it is in fact necessary to set a temperature profile during the injection process higher than that used when 100% recycled PET (R-PET) is used as raw material. The higher temperature let to reduce the injection time and to limit the mechanical shear stress. Nevertheless, the R-PET is very sensitive to thermo degradation and even 5-10 °C degrees can affect the molecular weight of the produced preforms.

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However, the measured IV values for all the preform produced is within the optimal range for bottle blowing production.

Another index of polymer degradation is represented by acetaldehyde content. Acetaldehyde (AA) is a degradation product of PET and it is usually generated during preform production. In Table 3 are reported the values in ppm of acetaldehyde in all the different preforms produced, and it is possible to verify that in all the cases the values analyzed are lower than 6 ppm. Looking at the table 3 it is possible to point out that the AA analyzed in the 100% R-PET bottle is not higher than pure virgin PET manufacts and that the presence of acetaldehyde in 50% R-PET/V-PET is increased probably because the process temperature condition set induce the degradation of recycled material contained in the preforms.

Table 3. Acetaldehyde content in the produced preforms**.**

Preforms	Acetaldehyde [ppm]	Std Dev
100% V-PET	4,3	0,4
100% R-PET	3,3	0,9
50% R-PET/V-PET	5,4	0,6

Finally thermal analysis was carried out by Differential Scanning Calorimetry (DSC) to determine all thermal parameters of the preform (analyzing the I heating run) and of the materials (analyzing the cooling and II heating steps), such as glass transition temperature (Tg), crystallization temperature peak (Tc), melting temperature peak (Tm) and degree of crystallinity (Xc). In table 4 are resumed the main thermal characteristics of the preforms produced with different materials, determined during the first heating step by DSC technique. It is possible to observe in Table 4 that all the preforms produced are characterized by an amorphous morphology as expected and required.

Table 4. Thermal Characteristics of the produced preforms determined by DSC technique in dynamic mode.

Preforms	Tg °C	Tc °C	Tm °C	Xc %
100% V-PET	75	127	250	5
100% R-PET	76	134	248	6
50% R-PET/V-PET	75	136	250	7

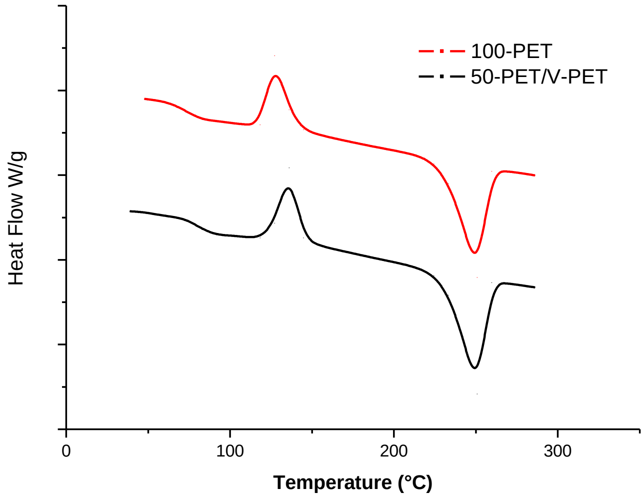

Figure 4. First Heating thermograms of 100% V-PET and 50% R-PET/V-PET preforms

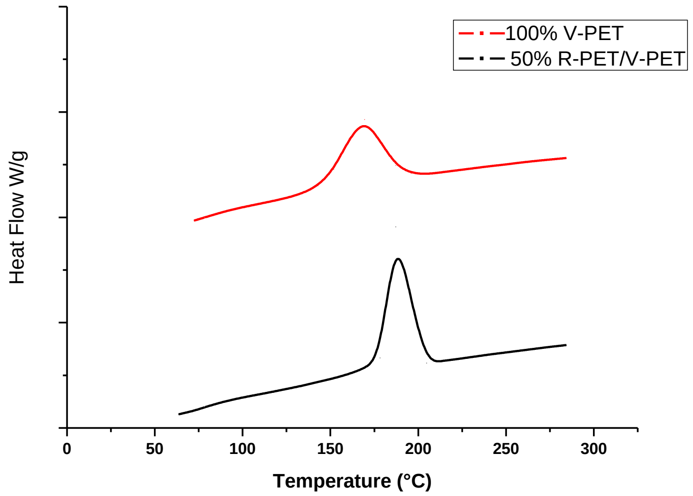

Figure 5. Cooling thermograms of 100% V-PET and 50% R-PET/V-PET preforms

The thermal analysis performed have pointed out that the preforms with R-PET material show higher tendency to crystallize during the cooling. In fact, as shown in figure 5, the crystallization peak of 50% R-PET/V-PET preforms is anticipated and its shape is narrow compared to the correspondent peak of pure virgin PET preforms. Therefore, it is suggestible to slightly increase the cooling time of the injection molding process when R-PET material is used for preform production.

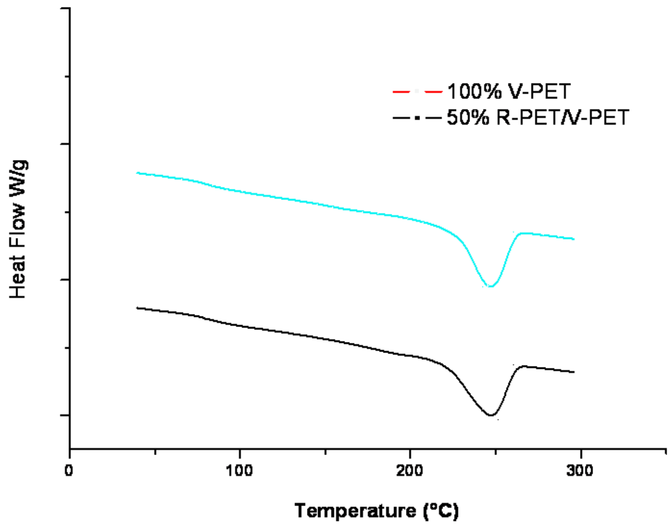

Figure 6. Second Heating thermograms of 100% V-PET and 50% R-PET/V-PET preforms

Conclusions

In conclusion, the physical chemical, thermal analysis performed on the produced preforms have pointed out that:

- the 100% R-PET and 50% R-PET/V-PET preforms are as performant as pure V-PET preforms;
- all preforms produced using R-PET are comply with the expected characteristics and can be considered suitable for the production of bottles for edible oil;
- the colorants do not affect the characteristics of the preforms produced and their main characteristics are essentially dependent by the raw material used and by process condition set.

References

1) F. Samperi, C. Puglisi, R. Alicata, G. Montaudo *"Thermal degradation of poly(ethylene terephthalate) at the processing temperature"* Polymer Degradation and Stability Volume 83, Issue 1, Pages 3–10 (2004).

2) F. Bueche "*A Derivation of Moore's Equation Relating Melt and Intrinsic Viscosities*" Journal of Polymer Science, Volume XII, Issue 138, Pages 551-552 (1959)