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► To cite this version:

Elise Mathouillot, Monica Francesca Pucci, Pierre-Jacques Liotier. New pet recycling method : manufacture of thermoplastic tape. ECCM 21 - 21st European Conference on Composites Materials, Jul 2024, Nantes, France. hal-04653739

HAL Id: hal-04653739

<https://imt-mines-ales.hal.science/hal-04653739v1>

Submitted on 22 Jul 2024

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NEW PET RECYCLING METHOD : MANUFACTURE OF THERMOPLASTIC TAPE

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Keywords: recycling, impregnation, oceans polymers, composite tapes, PET

Abstract

The aim of the present work is to manufacture thermoplastic tapes using recycled PET as matrix and use as little energy as possible to recycle PET, including drifted bottles. The first step in our process is to solubilize the polymer so that it can be impregnated into fibrous reinforcement. The idea is to create a colloid or a solution. To do this, it is required to find a solvent that is effective on PET. Next, a path to characterize the wetting of both polymer in solution and polymer alone, followed by the wicking in the fibrous reinforcement, will be developed. Characterizing these parameters will enable us to maximize impregnation and minimize porosity inside the tape which is an issue with actual processes.

1. Introduction

Polyethylene terephthalate (PET) is one of the world most widely used polymer [1]. Transparent, lightweight and endowed with very interesting mechanical and chemical properties, it is mainly used in the manufacture of plastic bottles, food packaging, games and credit cards. After a slowdown in production due to the 2019 health crisis, plastic production has restarted and continues to grow. This increase in production means that more waste ends up in the oceans and washes up unevenly on beaches around the world. The PET found in rivers, seas, oceans and even on beaches is a critical waste, not only for marine ecosystems but for all living creatures. A human being ingests an estimated five grams of microplastics a week, equivalent to the weight of a credit card [2].

Nevertheless, PET is the most widely recycled plastic in the world [3] and the most widely used recycling method for this type of polymer is mechanical recycling. The main drawback of this method are that it requires a great amount of energy, particularly for shredding, but also subsequently to create a new product, using high temperatures. This method also calls into question the viability of the circular approach applied to successive mechanical recycling. It has now been proven [4] that this type of recycling reduces polymer properties, after several cycles. It can thus be considered that it prolong the linear economy more than make polymers circular.

That is why the manufacture of thermoplastic tapes came up. This method will use less energy and will be able to recycle both PET and reinforcements several times. First, Hansen solubility parameters will be used to find the effective solvents [5] for the dissolution of PET. The resulting solution will then be used to impregnate fibrous reinforcements. To do this, a non-solvent will be used to precipitate the PET onto the fibrous reinforcement, creating the thermoplastic tape. As a result, porosities will be created during impregnation or precipitation. The morphology of these porosities will depend on the solvents and non-solvents used, as well as on several physical parameters such as the dissolution/precipitation

temperature and the surface tension of the solution as a function of the level of polymer dissolved in it. Scanning electron microscopy (SEM) will be used to see the diameters and the distribution of the porosities on the materials depending of the solvent/non-solvent used. Then, Differential Scanning Calorimeter (DSC) and Fourier Transform InfraRed spectroscopy (FTIR) will be used to check if the PET is not degraded by the solvent and to prove there is no more solvent inside the recycled PET. Figure 1 summarizes the approach used in this study.

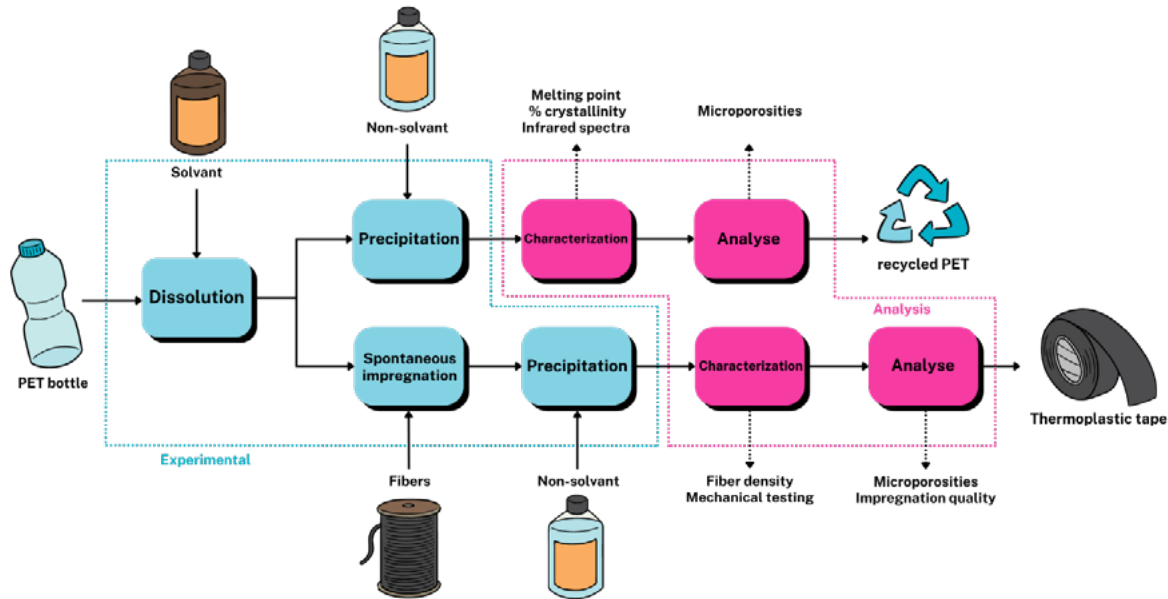


Figure 1. General diagram of the thermoplastic tape production process

2. Solubilization and precipitation

To solubilize PET, it is necessary to find a solvent that is effective on the polymer. Hansen's solubility principle was applied. The solubility of polymers in solvents can be predicted by Hansen solubility theory [5]. It is based on three solubility parameters: δ_D , δ_P , δ_H which are the dispersion, polar and hydrogen-bonding component of the solubility parameter δ (according to eq 1).

$$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \quad (1)$$

Solvents with similar components are more likely to dissolve the polymer. The distance and the relative energy difference (RED) allow us to find out how compatible the solvent and the polymer are. R_a (eq 2) is the distance between the polymer and the solvent in the Hansen space with R_0 , the radius of the sphere associated with the polymer under study. Theoretically, if the RED (eq 3) is under 1, the polymer will be dissolved by the solvent.

$$Ra^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 \quad (2)$$

$$RED = \frac{Ra}{R_0} \quad (3)$$

Several solvents were therefore tested. The PET sphere (figure 2) was modeled to identify "good solvents" and "bad solvents". All solvents were then tested to verify the results obtained using Hansen's principle.

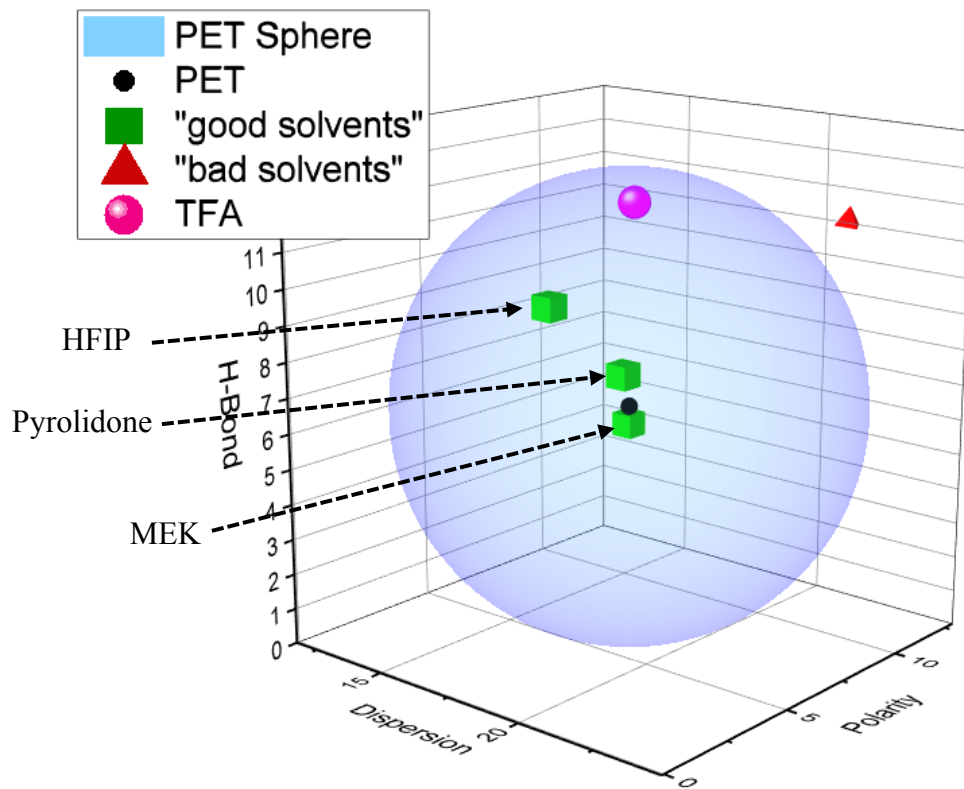


Figure 2. PET Sphere and some tested solvents

Once the effective solvents have been found, the polymer is precipitated. For this purpose, two non-solvents were selected based on the literature [6], [7]. Water and ethanol are used to precipitate PET.

3. Characterization

Different analyses were performed in order to characterize manufactured polymer samples. Firstly, DSC analyses were carried out to check whether our material had been degraded or not. Melting temperature and crystallinity were measured.

FTIR analyses were then conducted to verify the composition of the polymer obtained after precipitation. We also searched for any traces of solvent to check that there was no solvent left in our samples.

Finally, SEM analysis was carried out to check for the presence of microporosities and to determine their size and homogeneity in the material.

4. Tape

To manufacture tapes, there are several steps as shown in figure 1: (1) solubilize the PET with the selected solvent, (2) impregnate the fibers with the solution created, and then (3) precipitate the polymer so that it binds to the fibers.

During the precipitation step, microporosities are homogeneously created within the tape. Microporosities can be linked both to the solvent used and to the non-solvent. These porosities are inevitably created, with a significant size and distribution. They are the result of solvent "migration" out of the polymer during precipitation, i.e. the solvent diffusion in the non-solvent.

5. Results and conclusion

After calculating the Hansen solubility sphere for PET (figure 2) and conducting solvent tests, two solvents were found to be effective for the polymer: trifluoroacetic acid (TFA) and Hexafluoroisopropanol (HFIP). After consideration of both solvents, TFA was chosen as the main solvent. The carcinogenic nature of HFIP led to the choice of TFA, even though it is a Per- and polyfluoroalkyl substance (PFAS).

The melting temperatures measured using DSC analysis (Table 1) prove that there is no degradation of our polymer and that TFA does not degrade our polymer but only solubilizes it. In Table 1, we can also see that even when using ethanol as a non-solvent, there is no polymer degradation. Moreover, the infrared spectra of the samples (Figure 3) proved that there is no degradation of our samples, as the characteristic PET peaks are present in the spectra.

Table 1. Melting temperatures of PET samples

Specimen Type	<i>Solvent</i>	<i>Non Solvent</i>	<i>T_f</i> (°C)
Virgin PET Bottle	X	X	248.11
PET Bottle	TFA	Water	259.15
PET Bottle Precipitated twice	TFA	Water	255.39
PET Bottle	TFA	Ethanol	249.63

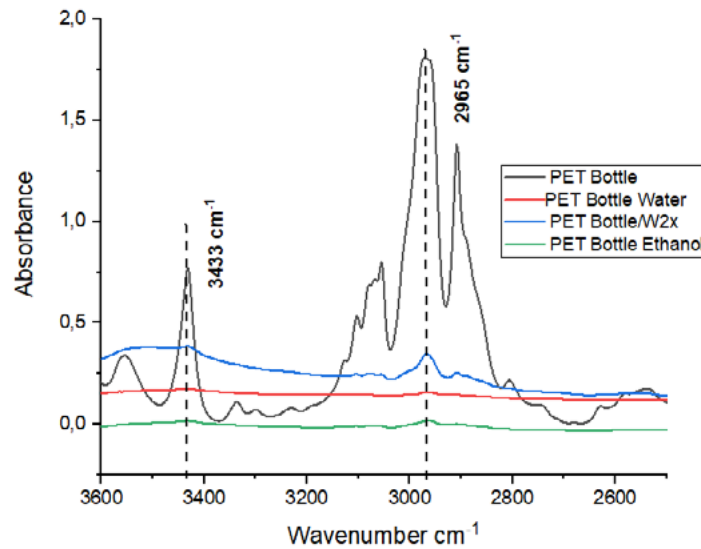


Figure 3. Infrared spectras of PET samples - PET region

It is also important to search for the presence of TFA in our precipitated PET samples, since TFA is a PFAS. After analyzing the infrared spectra of our samples and focusing on the areas where the characteristic TFA peaks should be found (Figure 4), we can say that there is no longer any TFA in our samples. This conclusion is particularly promising for the final tape manufacturing process, as it will be possible to recover the TFA by distillation and have a complete circular process.

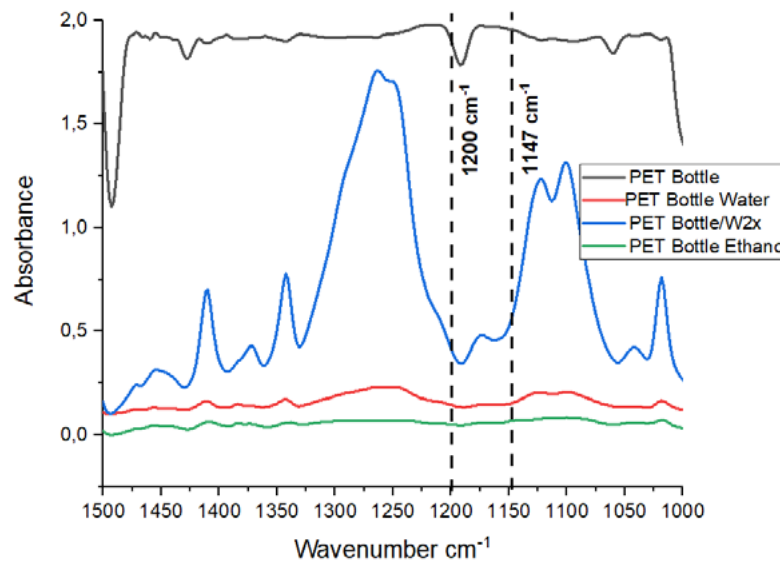


Figure 4. Infrared spectras of PET samples - TFA region

Finally, manufactured tapes have porosities evenly distributed along the fibers. Porosities vary accordingly to the non-solvents used. It would be interesting to see whether different solvents also create different porosities and perhaps find a combination to minimize the creation of these porosities, and in any case to understand the precipitation of the polymer versus diffusion of the solvent in the non-solvent phenomenon.

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