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Study on the Feasibility of Hazardous Waste Recycling: The Case of Pharmaceutical Packaging

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1. Introduction

Hazardous waste management should fulfil the following three main goals: (i) to protect human health and the environment, (ii) to reduce waste while conserving energy and natural resources and (iii) to reduce or eliminate the volume of waste to dispose of. The last two of these goals may derive from recycling, which aims at reducing raw materials and energy consumption and decreasing the volume of waste materials that must be treated and disposed of.

However, recycling must be conducted in a safe way, ensuring human health and environment protection. Recycling activities should be regulated at a different degree on the basis of the risk they cause to human health and the environment. A hazardous waste destined for recycling must be identified by type and recycling process in order to determine its level of regulation (Linninger & Chakraborty, 2001).

Pharmaceutical packaging represents a very small percentage of hazardous waste, but its management can cause problems for the environment, depending on the type of packaging waste is concerned (Sacha et al., 2010). Such waste may include:

- uncontaminated waste (assimilated to domestic waste: paper, cardboard, glass, plastic);
- contaminated waste (paper, cardboard, glass, plastic), e.g. waste that has been in contact with cytotoxic products, blood, blood-derived products or radioactive products.

Waste is created at all stages of the supply-chain: production, distribution and use of a pharmaceutical product. At each step, care therefore needs to be taken, either by the manufacturer or the end-user, to protect the environment (Biniecka et al., 2005; Dillon & Rubinstein, 2005).

In several European countries, pharmaceutical manufacturers must dispose of their waste, or by themselves or by external specialized companies, and are encouraged to recover packaging waste. In both cases, waste management represents a considerable cost for the manufacurers.

The use of environmental-friendly packaging (i.e. recyclable or degradable packaging) has to be considered. Valuable packaging materials, such as aluminium paper, glass and plastic materials, can been extensively recycled if they have not been in contact with toxic or dangerous substances (Bauer, E.J. , 2009).

This chapter is focused on a feasibility study for the management of packaging waste from a pharmaceutical plant, considering the following phases:

- waste materials characterization;
- preliminary tests on waste processing;
- set up of size reduction (comminution) operations.

Experimental tests have been executed on several typologies of packing, as listed:

- primary packaging:
  - bottles in high density polyethylene (HDPE), for suspension to be reconstituted;
  - bottles in poly(ethylene terephthalate) (PET), for syrup;
  - plastic bags and films of varying composition and thickness;
- pharmaceutical waste:
  - flexible multi-layered (plastic and aluminium) sachets containing granular medicine.

2. Experimental

In a first stage, the products under investigation were characterized as derived from the industrial process. The results of the characterization were utilized to set up preliminary tests on waste processing, in particular the comminution operations were evaluated. Finally, an experimental plan was carried out to assess the feasibility of waste recycling.

2.1 Methods for characterization

The following methods were adopted in the experimental set-up for the characterization of products under investigation:

- image analysis, to measure geometric and morphologic characteristics; the results were evaluated by statistical methods;
- dry sieve analysis, to classify the size distribution of particles;
- laser granulometry, to classify size distribution of particles in the interval between 0.1 e 1,000 μm;
- infrared spectroscopy, to recognize chemical composition of polymeric materials under investigation.

2.1.1 Image analysis

The images for characterization were acquired by the stereoscopic microscopy Leica Wild M8 and a by a digital camera Olympus C-5060 Wide Zoom. The image analysis was carried out by the software SigmaScan Pro© Version 5.0.0 (Systat Software Inc., 2007), which provides a complete set of tools to analyse structure and dimension of an object's image.

Firstly, calibration allowed to convert image unit from pixel to millimetre (Figure 1). After calibration, the image quality for data elaboration has been enhanced, increasing the distinction between particles and background, by varying contrast, brightness and colour of the image (Figure 2). In the measurement process, the software automatically recognizes objects on the image (Figure 3) and computes geometric and morphologic parameters, accordingly to operator's choice.

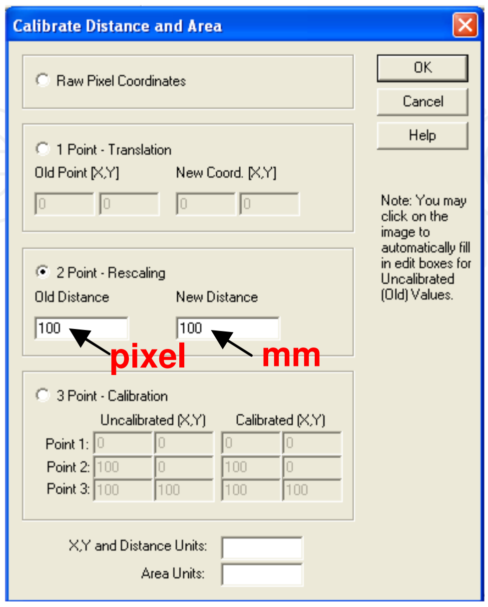


Fig. 1. Calibration process to convert image unit from pixel to millimetre.

Fig. 2. Variation of contrast, brightness and colour of an image.

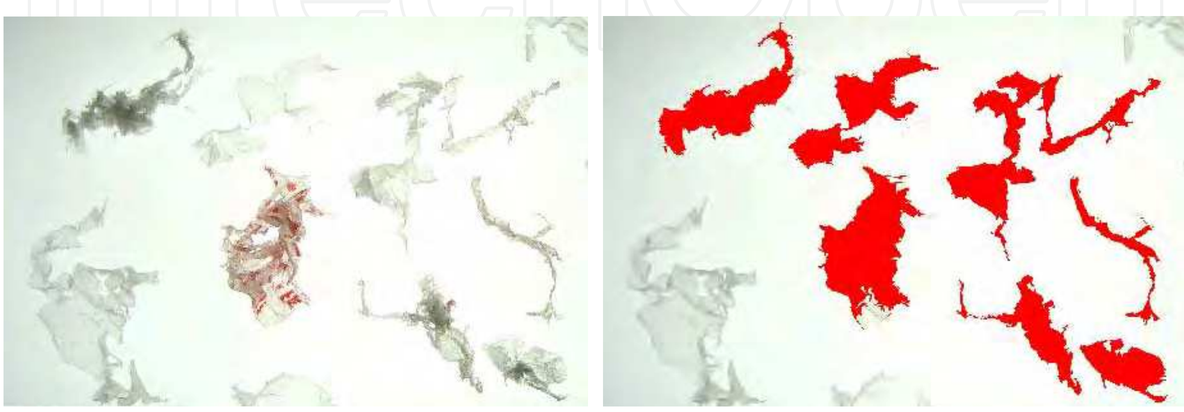


Fig. 3. Automatic recognition of objects on the image.

The following geometric and morphologic measurements were considered.

Area: reports the area in mm² for the selected object.

Compactness: reports a numeric non-dimensional measurement of the shape of an object. It is defined as the perimeter squared, divided by the area:

$$\text{Compactness} = \frac{\text{perimeter}^2}{\text{area}} \tag{1}$$

The minimum Compactness of a perfectly measured and digitized circle is 4π (about 12.57). As an object tends toward the shape of a line, the Compactness tends towards infinity.

Major Axis Length: calculates major axis of the object (defined by the two most distant points on the object) and reports the length in mm of the axis.

Minor Axis Length: calculates minor axis of the object (defined by the two most distant points on the object that creates a line perpendicular to the major axis) and reports the length in mm of the axis.

Perimeter: returns the perimeter in mm of an object.

Shape Factor: measures the shape (circularity) of a measured object. This non-dimensional measure is defined as 4π times the object's area divided by the perimeter squared:

$$Shape\ \ factor = \frac{4\pi \cdot area}{perimeter^2} \tag{2}$$

A perfect circle will have a Shape Factor of 1. A line's Shape Factor will approach zero.

Feret Diameter: describes the shape of an object. It gives the diameter of the equivalent circular object that has the same area as the current object. For each object, it calculates the theoretical diameter of the object if it were circular in shape. This measure is often compared with an object's major and minor axes lengths to create new shape parameters.

The results obtained from image analysis were evaluated by considering statistical parameters, as described in the following.

Number of objects: counts the numeric values in the considered set.

Mean: returns, as central tendency, the order of magnitude of the value for each considered measurement. The arithmetic mean $\bar{x}$ is calculated as the sum of all measurements divided by the number of observations in the data set:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \tag{3}$$

where x_i is the single measurement and N is the total number of measurements.

Minimum: returns the least value of the considered data set.

Maximum: returns the greatest value of the considered data set.

Standard deviation: shows how much variation or dispersion there is from the mean in the data set and it is measured in the same unit of the data. The standard deviation σ is directly derived from the variance (σ^2, which unit is the square unit of the considered data), as its square root:

$$\sigma_x = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})}{N}} \tag{4}$$

where $\bar{x}$ is the arithmetic mean.

Standard error: returns an estimation of the standard deviation σ_x of the estimator, giving a valuation of its imprecision. If the estimator is the arithmetic mean of N independent measurements with the same statistical distribution, the standard error is given via the equation:

$$se = \frac{\sigma_x}{N}. \tag{5}$$

Confidence interval: refers to the range of values preceding or following a mean value where it is expected an unknown population parameter (e.g. the true mean) is located. The width of the confidence interval gives an indication about uncertainty of the unknown parameter. If independent samples are taken repeatedly from the same population, and a confidence interval calculated for each sample, then a certain percentage (confidence level) of the intervals will include the unknown parameter. The confidence level is the probability value (1 – α) associated with a confidence interval. For example, say α = 0.05, then the confidence level is equal to 0.95, i.e. a 95% confidence level.

Let's be the true mean the considered unknown parameter; the confidence level is given by:

$$\bar{x} \pm A_{conf}\left(\frac{\sigma_x}{\sqrt{N}}\right) \tag{6}$$

where A_{conf} is area under the normal distribution curve that is equal to the chosen confidence level. In the case under investigation confidence levels of 95% and 99% have considered.

2.1.2 Dry sieve analysis

The dry sieve analysis is a mechanical method to assess the particle size distribution. A set of sieves with wire mesh cloth is stacked in column, so that each lower sieve has smaller openings than the one above; at the base of the column there is a round pan. A representative weighed sample is poured into the top sieve. The column is typically placed in a mechanical shaker, that shakes the column for a fixed amount of time. After the shaking is complete the material on each sieve is weighed and divided by the total weight to gain the percentage retained on each sieve. In this study, certified high-precision sieves Giuliani in stainless steel (ASTM series) were utilized.

2.1.3 Laser granulometry

The laser granulometry analyses of the effect of diffracted light produced by a laser beam passing through a dispersion of particles. The angle of diffraction increases as particle size decreases. After mixing in distilled water (or alcohol), the representative sample is introduced in the measuring cell. The laser beam (wavelength = 632.8 nm; power = 5 mW) passes through the suspension and is deviated by particles accordingly to their particle size. The deviation is then analyzed by detectors. This method can measure particle sizes between 0.1 and 1,000 µm.

The laser granulometer utilized in this investigation was SYMPATEC HELOS/KA.

2.1.4 FTIR spectroscopy

The Fourier transform infrared (FTIR) spectroscopy utilizes the infrared region of the electromagnetic spectrum (between 0.8 and 1,000 µm wavelength) to recognize chemical composition of materials. In the case of plastic materials it allows to identify the structural polymer. The infrared spectrum (by transmittance or absorbance) of a sample is recorded by passing a beam of infrared light through the sample. A data-processing technique called Fourier transform converts raw data into the sample's spectrum. Then the sample's spectrum is compared to reference spectra. The samples were cleaned with water and mild detergent, rinsed with deionized water and then dried in oven with air convection at 450 °C for 24 hours.

The characteristics of the instrument utilized in this study for FTIR spectroscopy are:

- FTIR Perkin-Elmer SpectrumOne;
- equipped with HATR, crystal ZnSe, 45°, (pressure 90) ;
- wavenumber range: 4000-630 cm^{-1};
- resolution: 4 cm^{-1};
- number of scanning: 4.

2.2 Methods for waste processing

Waste processing was carried out at laboratory scale to assess the feasibility of recycling. In particular, for the treatment of the different typologies of investigated pharmaceutical waste, comminution operations were evaluated. According to the composition of products (polymeric materials) cutting mills were employed, which apply shearing to reduce particle size. In this study a cutting mill Retsch – SM 2000 equipped with interchangeable sieves to control particle size in output product was utilized to carry out comminution tests.

2.3 Materials

The bottles in HDPE are utilized for suspension to be reconstituted. The analyzed samples are composed by waste bottles, collected at the end of the production line and manually emptied. The bottles are without labels and caps and may contain residual powder. A synthesis of HDPE bottles characteristics is reported in Table 1.

Material	HDPE
Longitudinal dimension (cm)	11.0
Transversal dimension (cm)	5.5
average weight (g)	17.4
average powder content (mg)	40.0
average powder content (%)	0.05

Table 1. Synthesis of the characteristics of HDPE bottles.

The bottles in PET are utilized for syrup packaging. The analyzed samples are composed by waste bottles, collected at the end of the production line and manually emptied. The bottles may have labels and aluminium caps and may contain varying amount of residual syrup. A synthesis of PET bottles characteristics is reported in Table 2.

Material	PET
Longitudinal dimension (cm)	14.2
Transversal dimension (cm)	5.2
average weight (g)	23.2
average syrup content (mg)	19.0
average syrup content (%)	8.99

Table 2. Synthesis of the characteristics of PET bottles.

Plastic bags and films derive from the packaging of raw materials utilized in production processes. The analyzed samples are of varying composition and thickness, and contain residual powders, whose composition is in relation to the production cycle. Four different typologies of plastic bags and films were identified:

- white and red bags, containing bicarbonate;
- thin-film;
- bags, with printed character "A" in black;
- bags, with printed character "A" in blue.

The samples were analysed by FTIR spectrometry to identify the polymeric composition (Figure 4).

As resulting from the comparison of acquired spectra with the reference one, all 4 types of materials are polyethylene (PE), in particular the recognized polymeric structure is low-density polyethylene (LDPE).

The residual powders were analysed by dry sieve analysis to identify size distribution, characterized by a mode of the distribution equal to 112 μm, while the top-size is lower than 1,000 μm.

The flexible multi-layered (plastic and aluminium) sachets containing granular medicine are wasted at the end of the production line because of incorrect filling. In this case, the sachets are collected and sent to disposal. The number of wasted sachet is $4{\cdot}10^6$ per year on average. Table 3 reports a synthesis of the sachets characteristics.

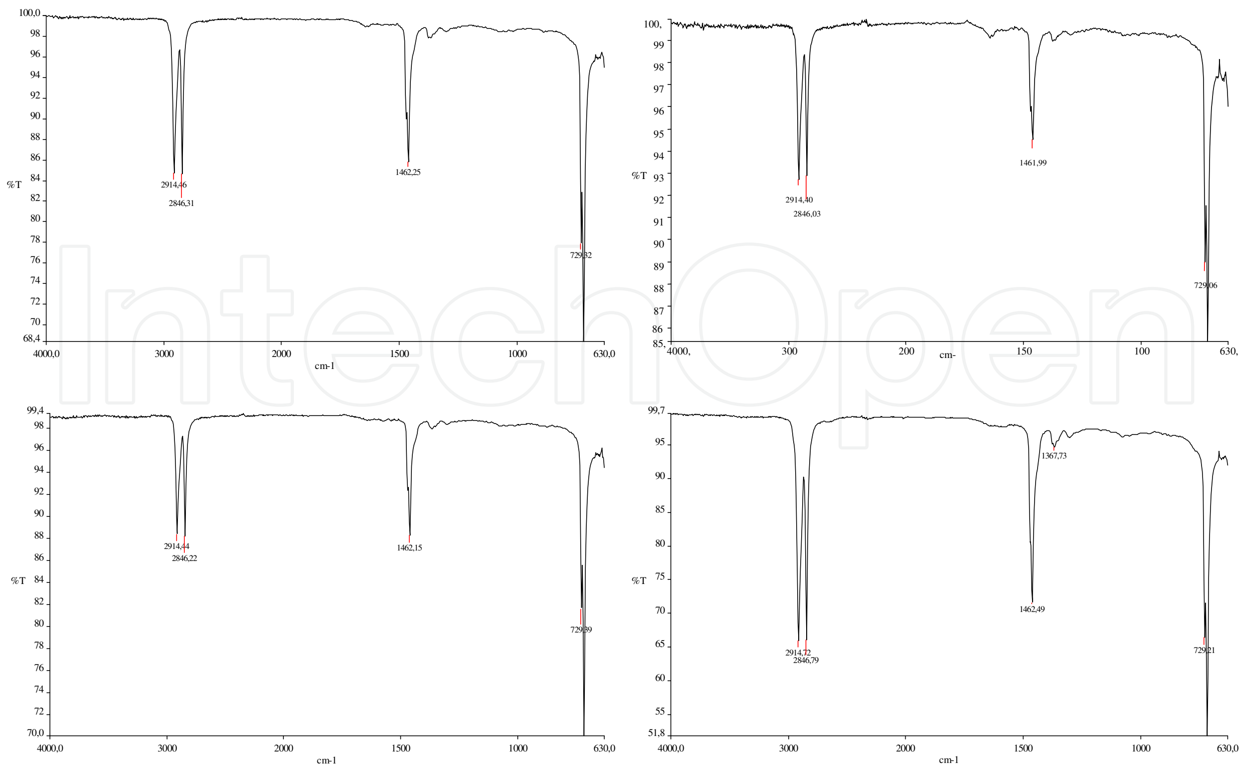


Fig. 4. FTIR spectra of plastic bags and films (y-axis: transmission %; x-axis: wavenumber cm^{-1}) : white and red bags, containing bicarbonate (above left), thin-film (above right), bags, with printed character "A" in black (below left), bags, with printed character "A" in blue (below right).

Material	plastic and aluminium
Longitudinal dimension (cm)	11.8
Transversal dimension (cm)	2.2
average weight of sachet(g)	7.4
average powder content (mg)	3.2
average powder content (%)	0.46

Table 3. Synthesis of the characteristics of flexible multi-layered (plastic and aluminium) sachets.

The granular medicine contained in sachets was analysed by dry sieve analysis and by laser granulometer to identify size distribution. Size distribution was analyzed by dry sieve analysis and laser granulometry (Figure 5), showing different mode and top-size. In particular, laser granulometry shows lower value of both (mode: 40 μm, top size: 100 μm) than dry sieve analysis (mode: 280 μm, top size: 1000 μm). This is probably due to the break-up of aggregated granules during mixing in water.

2.4 Preliminary tests

For the recovery of the waste materials, in order to evaluate the possibility of adopting an industrial shredder installed in the production plant under investigation, preliminary comminution tests have been carried out on the following waste typologies:

- primary packaging:
  - bottles in high density polyethylene (HDPE), for suspension to be reconstituted;
  - bottles in poly(ethylene terephthalate) (PET), for syrup;
  - plastic bags and films of varying composition and thickness;
- pharmaceutical waste:
  - flexible multi-layered (plastic and aluminium) sachets containing granular medicine.

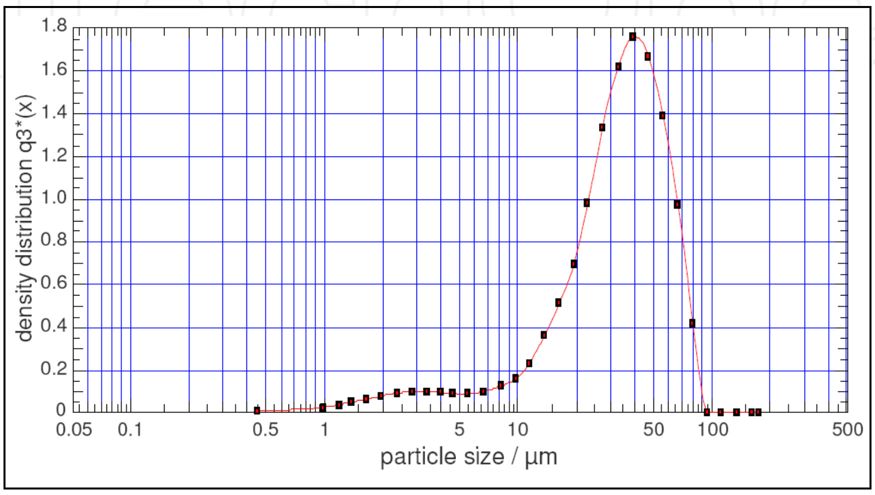


Fig. 5. Size distribution of granular medicine contained in sachets by laser granulometry.

The technical details of the industrial shredder are shown in the Table 4.

Producer	Satrind S.p.A.
Model	F615
Engine power	11 kW
n. shafts	2
Speed shafts	19/10-15/8 rpm
n. blades of 30 mm	19

Table 4. Technical characteristics of industrial shredder installed in the investigated plant.

On the two shafts of the shredder 19 blades are fixed that, thanks mainly to the application of cut stresses, are able to break the waste materials (Figure 6). Some of the material is broken by tear action due to the rotation of the blades. In the preliminary lab tests, the application of cut stresses have been obtained by mean of a blade mill RETSCH - SM 2000, that can be equipped or not with different grids that allow to control the size of the comminuted products. The comminution chamber of the mill is shown in Figure 6.

The preliminary laboratory tests have been conducted in dry conditions adopting two different operational configurations:

- without the grids for the control of the size of the comminuted products;
- with a 20 mm mesh grid.

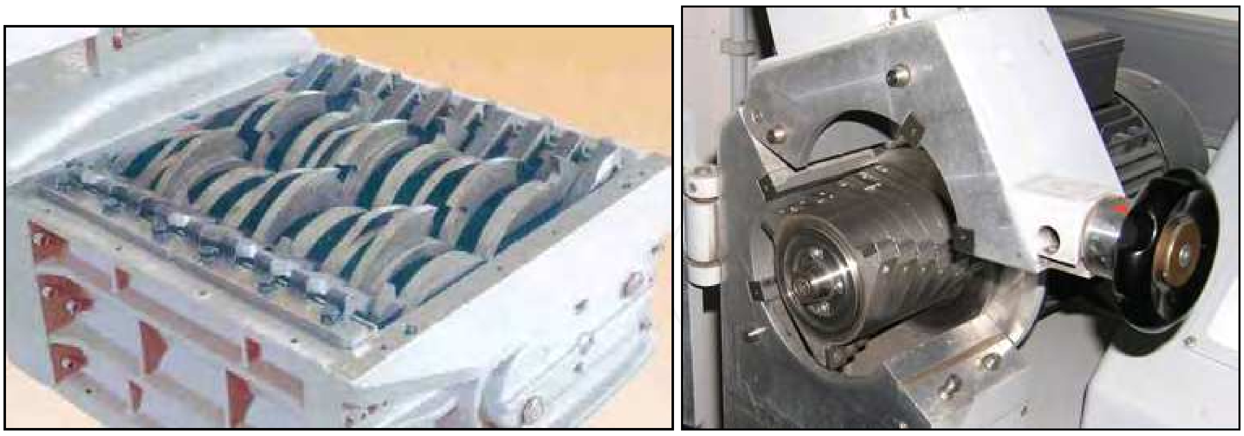


Fig. 6. Industrial shredder blades (left) and comminution chamber of the blade mill adopted in the preliminary tests (right).

2.4.1 Results of the preliminary laboratory tests

The preliminary lab tests have shown the effectiveness of the application of cut stresses to break the considered typologies of pharmaceutical waste materials. Moreover, the comminuted products obtained in the tests are characterised by an average lower size that is above the higher average size of the powder and granular medicine contained in the waste sachet (1.0 mm). The results obtained in the preliminary tests are reported for each considered waste typologies in the following.

- B*ottles in high density polyethylene (HDPE), for suspension to be reconstituted*

The bottles have been divided in two parts in order to reach dimensions suitable for the laboratory blade mill.

The tests carried out without the adoption of the control grids did not produce useful results, as no breakage were observed in the bottles collected in the output.

On the contrary, in the tests carried out with the adoption of a 20 mm mesh control grid it was possible to break the bottles in HDPE and reach comminuted products mainly belonging to the size class +1.0 mm. The comminuted products are shown in Figure 7.

- *Bottles in poly(ethylene terephthalate) (PET), for syrup*

The bottles have been divided in two parts in order to reach dimensions suitable for the laboratory blade mill. The bottles have been divided in two parts in order to reach dimensions suitable for the laboratory blade mill. The tap and aluminium ring have been kept in the sample. The bottles submitted to the tests did not contain syrup. The tests carried out without the adoption of the control grids did not produce useful results, as no breakage were observed in the bottles collected in the output. On the contrary, in the tests carried out with the adoption of a 20 mm mesh control grid it was possible to break the bottles in PET and reach comminuted products mainly belonging to the size class +1.0 mm. The comminuted products are shown in Figure 7.

Fig. 7. Comminuted bottles in HDPE (left) and PET (right) obtained in the preliminary tests with the adoption of a 20 mm mesh control grid.

- *Plastic bags and films of varying composition and thickness*

The preliminary comminuted tests have been carried out on samples of plastic bags containing bicarbonate and on samples of films. Both sample typologies are made of LDPE.

The plastic bags and films have been cut in samples of 50×50 mm and 100×100 mm in order to reach dimensions suitable for the laboratory blade mill. The tests carried out without the adoption of the control grids did not produce useful results, as no breakage were observed in the samples of 50×50 mm, and clogging and consequent stoppage of the mill for the samples 100×100 mm took place. On the contrary, in the tests carried out with the adoption of a 20 mm mesh control grid it was possible to break the plastic bags and films, both the 50×50 mm and 100×100 mm samples. The comminuted products of 100×100 mm samples of bags and films are shown in Figure 8. When submitted to sieving classification, the comminuted products presented average size generally above 1.0 mm and, therefore, higher than the higher average size of the powder medicine contained in the bags and films.

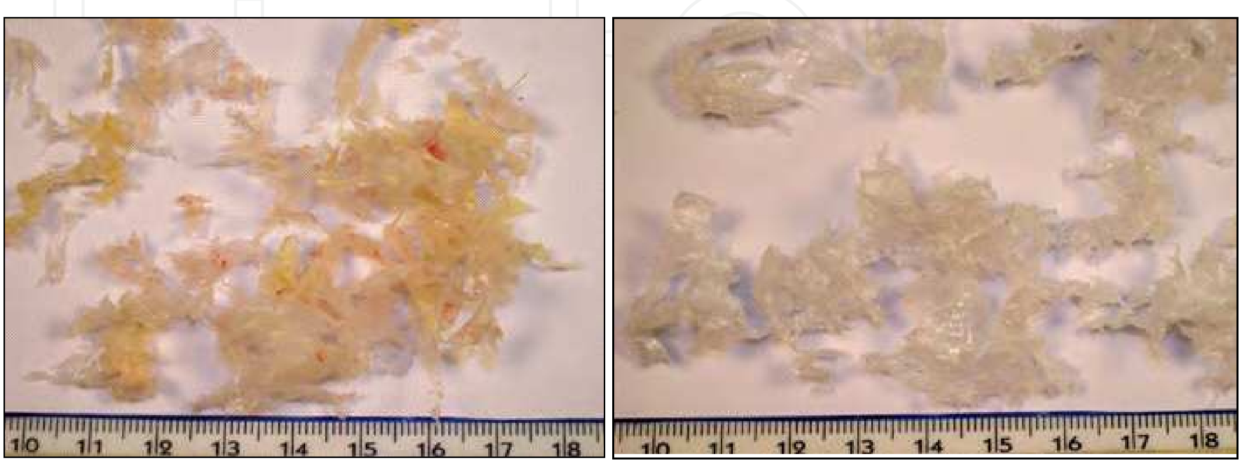


Fig. 8. Comminuted 100×100 mm samples of bags (left) and films (right) obtained in the preliminary tests with the adoption of a 20 mm mesh control grid.

- *Flexible multi-layered (plastic and aluminium) sachets containing granular medicine*

Preliminary tests were conducted on flexible multi-layered sachets containing granular medicine. The comminution tests resulted effective both without and with the adoption of the 20 mm mesh control grid. Notably, due to the lower resident time, the milling operations conducted without the control grid produced particles belonging to size classes greater than 1.0, i.e. greater than the maximum size of the granulate medicine contained in the sachet. Figure 9 shows the comminuted products classified in the size class +1.0 mm, while Figure 10 and Figure 11 show the comminuted products classified in the size classes obtained -1.0 +0.5 mm and -0.5 mm.

Fig. 9. Comminuted flexible multi-layered sachets containing granular medicine, belonging to the size class +1.0 mm, obtained in the preliminary tests without control grid (left) and with 20 mm mesh control grid (right).

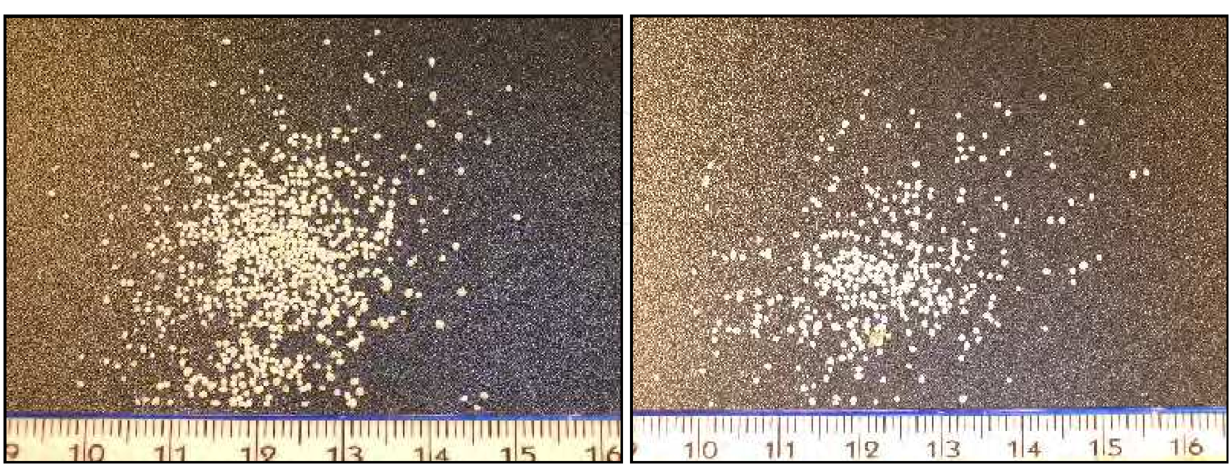


Fig. 10. Comminuted flexible multi-layered sachets containing granular medicine, belonging to the size class -1.0 +0.5 mm, obtained in the preliminary tests without control grid (left) and with 20 mm mesh control grid (right).

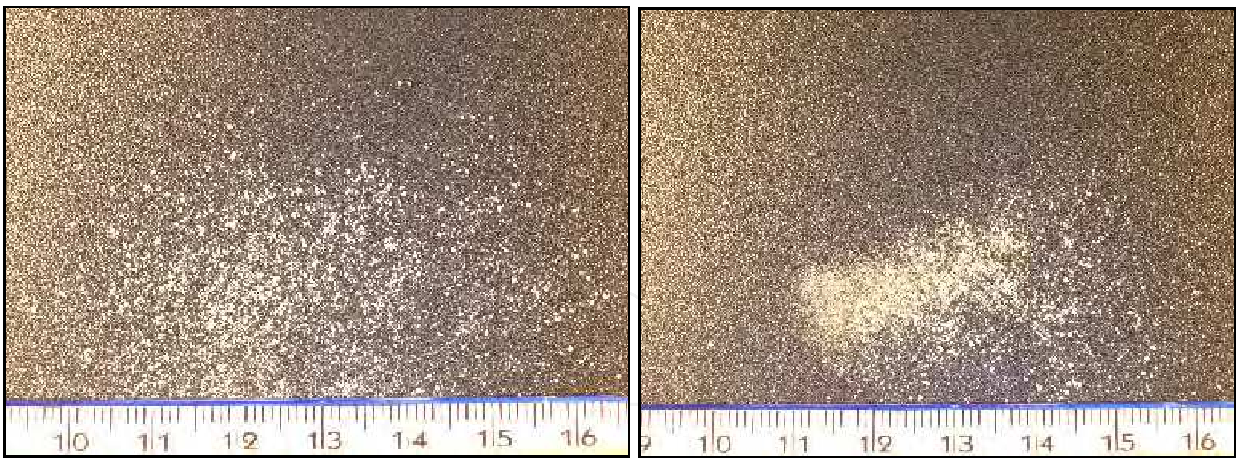


Fig. 11. Comminuted flexible multi-layered sachets containing granular medicine, belonging to the size class -0.5 mm, obtained in the preliminary tests without control grid (left) and with 20 mm mesh control grid (right).

2.5 Waste processing (comminution) tests

On the basis of the results of the preliminary tests, the comminution processes in laboratory scale have been set up. Notably, the tests have been carried out adopting the blade mill Retsch - SM 2000 under two operational conditions:

- dry milling, with 2 cm mesh control grid;
- wet milling, with 2 cm mesh control grid.

Wet drying has been realised feeding the mill with the waste materials together with little quantities of water. In such a way, the operational conditions that could be achieved with the shredder installed in the considered industrial plant have been simulated. For the Flexible multi-layered (plastic and aluminium) sachets, tests have been conducted with the blade mill and with a mini-shredder, in order to evaluate the possibility of recovering the granular medicine they contain. The comminuted products have been analysed by mean of:

- dry sieving;
- laser granulometry;
- imagine analysis.

The comminution processes are described in the following paragraphs, for each considered waste typology.

- *Bottles in high density polyethylene (HDPE), for suspension to be reconstituted*

The HDPE bottles have been cut in their longitudinal axes before feeding them to the blade mill.

In the dry comminution tests, samples made of 5 bottles in HDPE have been adopted. The products of the dry and wet comminution tests have been submitted to dry sieving and image analysis. The sieving tests have been conducted adopting sieves of ASTM series with 2.0 and 1.0 mm mesh. The results of the sieving tests are reported in Figure 12 in terms of cumulative passing for dry and wet comminution tests.

Comparing the results of sieving tests (Figure 13), the dry and wet comminution tests do not show substantial differences in the size distribution of their products.

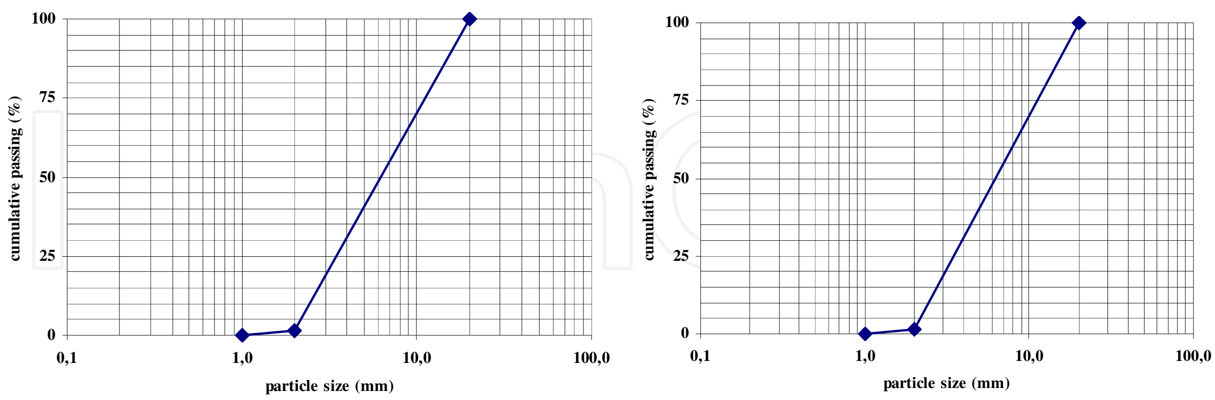


Fig. 12. Bottles in HDPE, 20 mm grid, cumulative passing, dry (left) and wet (right) comminution.

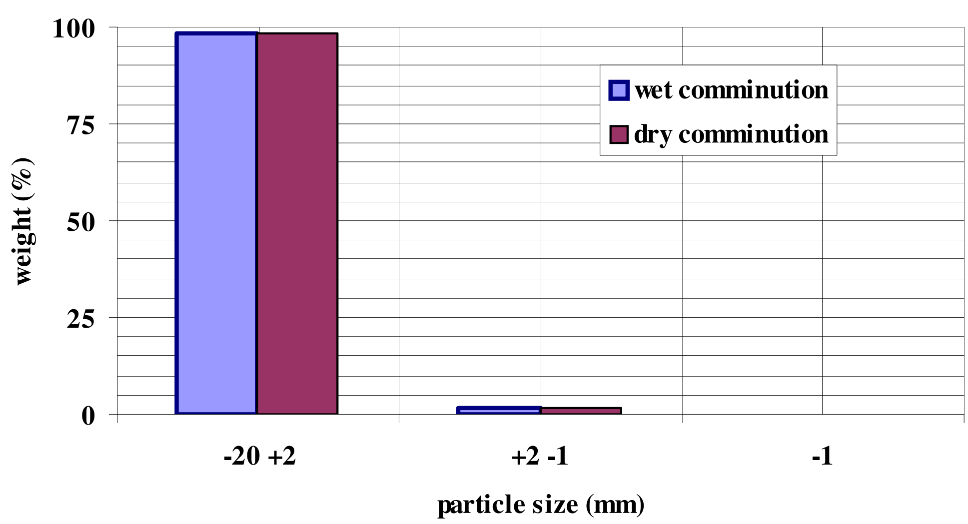


Fig. 13. Bottles in HDPE, comparison of the products of dry and wet comminution tests in terms of size distribution.

After the classification of particles in the size classes +2 mm, -2 mm +1 mm, and -1 mm obtained by sieving, image analysis has been conducted on the products of dry and wet comminution tests.

The results of image analysis for the bottles in HDPE are given in Tables 5-10.

Examples of images of the dry and wet comminution products are shown in Figure 14 and Figure 15 respectively.

Comparing the results of the image analysis for the considered size classes, no major differences can be observed in the particles size of the products obtained in the dry and wet comminution tests in terms of the values of the parameters *Area, Major Axis Length, Minor Axis Length and Feret Diameter*.

+2.0 mm -2.0 mm +1.0 mm -1.0 mm

Fig. 14. Bottles in HDPE, images of the products of dry comminution tests.

+2.0 mm -2.0 mm +1.0 mm -1.0 mm

Fig. 15. Bottles in HDPE, images of the products of wet comminution tests.

The high values of the parameter *Compactness*, measured in the products of both dry and wet comminution products, are in relation with the irregular morphology of particles, reasonably due to the cut stresses applied by the blades of the mill.

The values of the parameter Shape Factor describe a shape of elongated particles.

The statistic parameters, notably the standard deviation, show a high variability in the analysed particles, with standard error and confidence intervals substantially constant for both dry and wet comminution products.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	120	120	120	120	120	120	120
Mean	205.066	188.244	24.942	13.659	173.927	0.124	15.124
Min	7.272	34.974	6.584	2.208	27.283	0.009	3.043
Max	961.603	1437.503	73.747	24.068	753.578	0.359	34.991
Std Dev	152.176	232.241	10.375	5.290	129.450	0.077	5.712
Std Err	13.892	21.201	0.947	0.483	11.817	0.007	0.521
95% Conf	37.879	57.808	2.583	1.317	32.222	0.019	1.422
99% Conf	49.781	75.973	3.394	1.730	42.347	0.025	1.869

Table 5. Bottles in HDPE, dry comminution, size class: +2.0 mm.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	42	42	42	42	42	42	42
Mean	5.917	107.792	5.397	2.067	22.963	0.194	2.649
Min	0.909	22.001	2.209	0.863	9.138	0.018	1.076
Max	15.461	684.613	11.824	3.209	92.040	0.571	4.437
Std Dev	3.175	110.433	2.439	0.589	14.100	0.122	0.727
Std Err	0.490	17.040	0.376	0.091	2.176	0.019	0.112
95% Conf	0.790	27.488	0.607	0.147	3.510	0.030	0.181
99% Conf	1.039	36.126	0.798	0.193	4.612	0.040	0.238

Table 6. Bottles in HDPE, dry comminution, size class: -2.0 +1.0 mm.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	48	48	48	48	48	48	48
Mean	1.040	67.968	2.205	0.768	7.582	0.263	1.023
Min	0.011	19.554	0.185	0.054	0.514	0.055	0.118
Max	3.614	227.840	6.093	2.334	21.682	0.643	2.145
Std Dev	0.930	45.895	1.494	0.433	5.192	0.148	0.532
Std Err	0.134	6.624	0.216	0.062	0.749	0.021	0.077
95% Conf	0.232	11.424	0.372	0.108	1.292	0.037	0.132
99% Conf	0.304	15.014	0.489	0.142	1.698	0.048	0.174

Table 7. Bottles in HDPE, dry comminution, size class: -1.0 mm.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	70	70	70	70	70	70	70
Mean	178.616	286.454	25.949	13.569	203.690	0.084	14.500
Min	22.718	38.559	10.575	3.509	42.665	0.009	5.378
Max	349.484	1430.789	41.267	22.467	558.069	0.326	21.094
Std Dev	94.828	263.140	7.478	4.529	112.930	0.066	4.175
Std Err	11.334	31.451	0.894	0.541	13.498	0.008	0.499
95% Conf	23.604	65.500	1.861	1.127	28.110	0.016	1.039
99% Conf	31.021	86.081	2.446	1.482	36.943	0.022	1.366

Table 8. Bottles in HDPE, wet comminution, size class: +1 mm.

- *Bottles in poly(ethylene terephthalate) (PET), for syrup*

The PET bottles have been fed to the blade mill without any pre-treatment, therefore including the aluminium cap and relative ring, and in some cases also the paper labels. The comminuted tests have been carried out only in dry conditions, as in the wet tests the

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	29	29	29	29	29	29	29
Mean	5.231	91.432	4.927	1.874	20.587	0.176	2.517
Min	0.885	26.783	1.890	0.700	8.621	0.051	1.062
Max	9.565	245.852	10.922	3.359	34.566	0.469	3.490
Std Dev	2.190	45.358	1.892	0.656	6.504	0.100	0.580
Std Err	0.407	8.423	0.351	0.122	1.208	0.018	0.108
95% Conf	0.545	11.290	0.471	0.163	1.619	0.025	0.144
99% Conf	0.717	14.838	0.619	0.215	2.128	0.033	0.190

Table 9. Bottles in HDPE, wet comminution, size class: -2 +1 mm.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	61	61	61	61	61	61	61
Mean	1.279	71.463	2.384	0.911	8.827	0.223	1.178
Min	0.115	20.377	0.529	0.255	1.529	0.077	0.382
Max	7.051	164.213	7.085	3.252	28.419	0.617	2.996
Std Dev	1.151	34.111	1.293	0.481	4.833	0.115	0.495
Std Err	0.147	4.367	0.166	0.062	0.619	0.015	0.063
95% Conf	0.287	8.491	0.322	0.120	1.203	0.029	0.123
99% Conf	0.377	11.159	0.423	0.157	1.581	0.038	0.162

Table 10. Bottles in HDPE, wet comminution, size class: -1 mm.

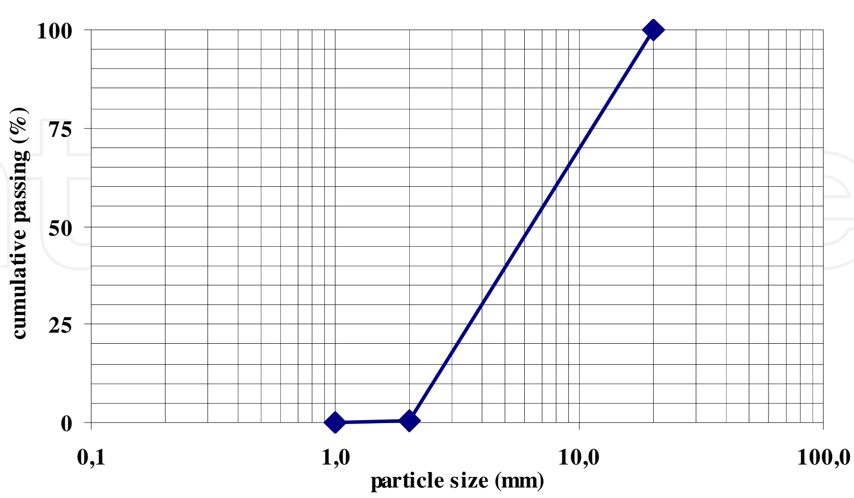


Fig. 16. Bottles in PET, 20 mm grid, cumulative passing, dry comminution.

products of comminution could not be easily extracted from the mill due to the presence of the syrup acting as a bonding agent for the PET particles and the mill surface. The dry comminution tests have been carried out on samples composed of 5 PET bottles. The products of the dry comminution tests have been submitted to dry sieving, laser granulometry and image analysis. The sieving tests have been conducted adopting sieves of ASTM series with 2.0, 1.0 mm and 38 µm mesh. Results of sieving tests and of laser granulometry analysis are reported in Figure 16 and Figure 17, respectively, both as cumulative passing for the dry comminution tests. The size class -38 µm has not been analyzed due to the presence of paper fibres of the labels including fine plastic particles.

After the classification in the particle size classes +2 mm, -2 mm +1 mm, and -1 mm +38 µm obtained by sieving, image analysis have been conducted on the products of dry comminution tests. The results of image analysis for the bottles in PET are given in Tables 11-13. Examples of images of the dry comminution products are shown in Figure 18.

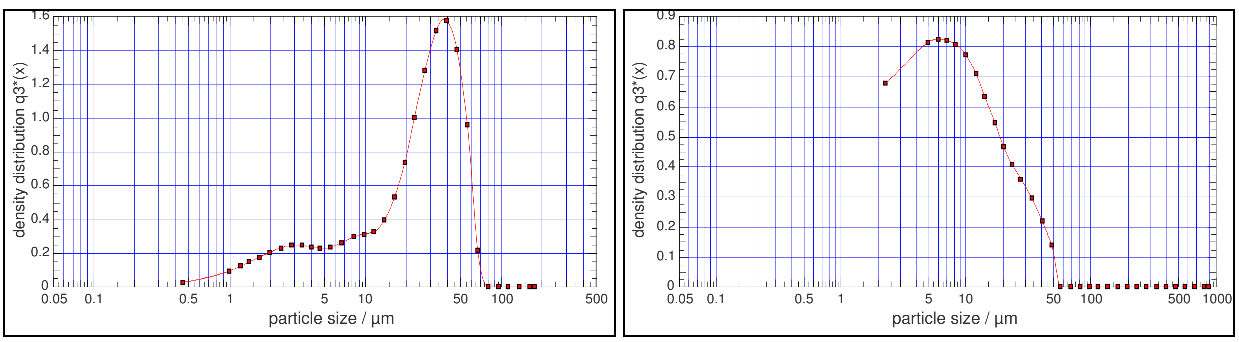


Fig. 17. Bottles in PET, 20 mm grid, size distribution, dry comminution, size class +2.0 – 1.0 mm (left) and -1 mm +38 µm (right), laser granulometry.

+2.0 mm *-2.0 mm +1.0 mm* *-1.0 mm +38.0 µm*

Fig. 18. Bottles in PET, images of the products of dry comminution tests.

The high values of the parameter *Compactness*, measured in the products of both dry comminution products, are in relation with the irregular morphology of particles, reasonably due to the cut stresses applied by the blades of the mill. The values of the parameter Shape Factor describe a shape of elongated particles. The statistic parameters, notably the standard deviation, show a high variability in the analysed particles, in particular for the higher size class (+2 mm), while the intermediate size class (-2 +1 mm) presents more homogeneous values of the morphologic and dimensional parameters.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	183	183	183	183	183	183	183
Mean	164.865	44.458	21.181	11.656	77.378	0.334	13.151
Min	0.563	16.702	1.171	0.805	4.024	0.083	0.847
Max	571.600	152.309	50.237	27.126	264.501	0.752	26.977
Std Dev	140.469	20.766	9.826	5.912	42.869	0.132	6.097
Std Err	10.384	1.535	0.726	0.437	3.169	0.010	0.451
95% Conf	34.965	5.169	2.446	1.472	10.671	0.033	1.518
99% Conf	45.952	6.793	3.214	1.934	14.024	0.043	1.995

Table 11. Bottles in PET, dry comminution, size class: +2 mm.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	46	46	46	46	46	46	46
Mean	5.681	47.475	4.676	2.072	15.530	0.327	2.587
Min	0.463	19.162	1.763	0.560	4.587	0.105	0.768
Max	17.147	119.185	11.921	3.325	38.087	0.656	4.672
Std Dev	3.379	24.258	2.045	0.559	7.238	0.142	0.744
Std Err	0.498	3.577	0.302	0.082	1.067	0.021	0.110
95% Conf	0.841	6.038	0.509	0.139	1.802	0.035	0.185
99% Conf	1.106	7.936	0.669	0.183	2.368	0.046	0.243

Table 12. Bottles in PET, dry comminution, size class: -2 +1 mm.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	8	8	8	8	8	8	8
Mean	4.690	72.620	3.232	1.592	18.006	0.320	2.002
Min	0.111	28.067	0.595	0.334	1.764	0.038	0.376
Max	22.233	330.335	7.219	4.877	85.700	0.448	5.321
Std Dev	7.236	104.285	2.024	1.471	27.651	0.127	1.498
Std Err	2.558	36.870	0.716	0.520	9.776	0.045	0.530
95% Conf	1.801	25.958	0.504	0.366	6.883	0.032	0.373
99% Conf	2.367	34.115	0.662	0.481	9.046	0.042	0.490

Table 13. Bottles in PET, dry comminution, size class: -1 mm +38 µm.

- *Plastic bags and films of varying composition and thickness*

The composition of the samples that contain the 4 typologies of plastic bags and films used in the dry and wet comminution tests are reported in Table 14.

Material typology	Polymer	Weigh (%)	
		dry comminution	wet comminution
white and red bags containing bicarbonate	LDPE	23	23
thin film	LDPE	23	20
bags, with printed character "A" in black	LDPE	24	27
bags, with printed character "A" in blue	LDPE	30	30

Table 14. Composition of the samples of plastic bags and films used in the dry and wet comminution tests.

The plastic bags and films have been cut in samples of 50×50 mm in order to reach dimensions suitable for the laboratory blade mill. Moreover, the samples maintained their content of bulk powder.

The products of the dry and wet comminution tests have been submitted to dry sieving, laser granulometry and image analysis.

The sieving tests have been conducted adopting sieves of ASTM series with 2.0 and 1.0 mm mesh. The results of the sieving tests are reported in Figure 19 in terms of cumulative passing for dry and wet comminution tests.

Comparing the results obtained in the sieving tests (Figure 20), the wet comminution shows less particles belonging to the +2 mm size class than the dry comminution.

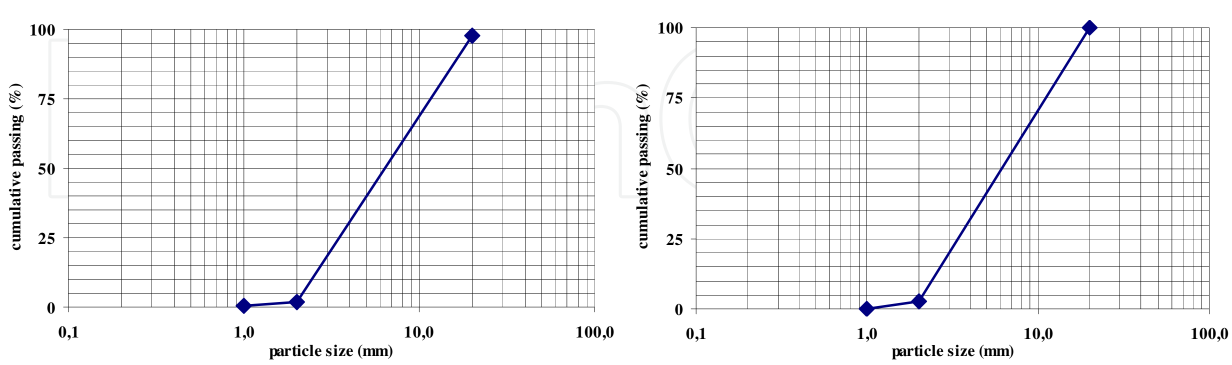


Fig. 19. Plastic bags and films, 20 mm grid, cumulative passing, dry (left) and wet (right) comminution.

The results of laser granulometric analysis are shown in Figure 21 in terms of size distribution for products of dry and wet comminution tests belonging to the -1 mm size class.

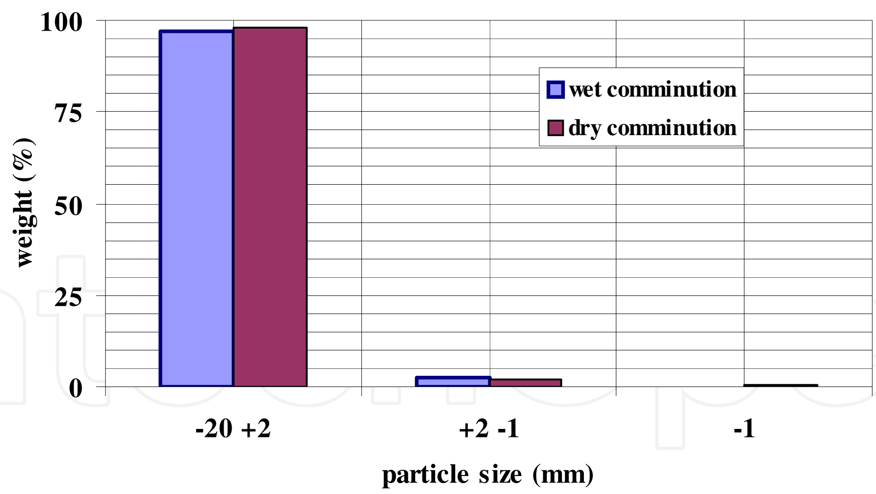


Fig. 20. Plastic bags and films, comparison of the products of dry and wet comminution tests in terms of size distribution.

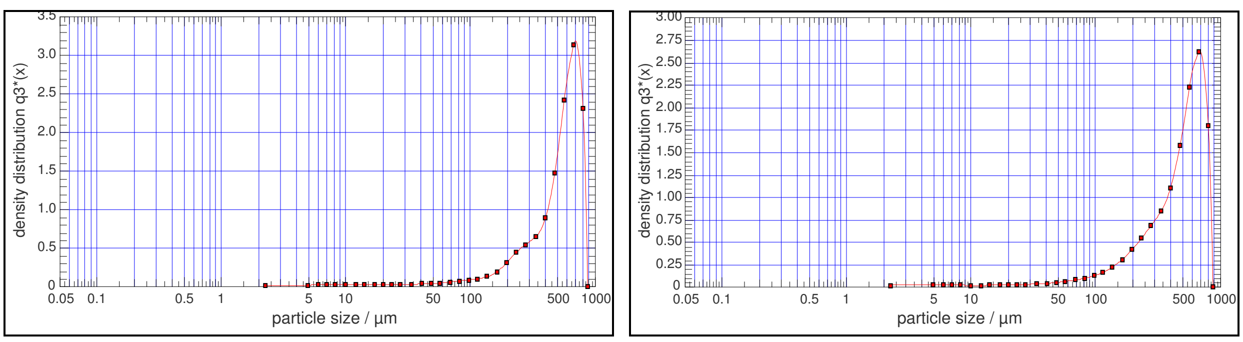


Fig. 21. Plastic bags and films, 20 mm grid, size distribution, size class – 1.0 mm, dry comminution (left) and wet comminution (right), laser granulometry.

Comparing the results obtained in the laser granulometry analysis, the dry and wet comminution tests do not show substantial differences in the size distribution of their products.

After the division in the particle size classes in +2 mm, -2 mm +1 mm, and -1 mm obtained by sieving, image analysis have been conducted on the products of dry and wet comminution tests. The results of image analysis for the plastic bags and films are given in Tables 15-20. Examples of images taken of the dry and wet comminution products are shown in Figure 22 and Figure 23 respectively.

The results of image analysis are reported in the following for all the considered size classes.

Comparing the results of the image analysis for the considered size classes, the difference between dry and wet comminution tests can be observed in the dimensions of the collected particles, measured by the values of *Area, Major Axis Length, Minor Axis Length e Feret Diameter*: the analysed particles generally belong to smaller size classes.

The high values of the parameter *Compactness*, measured in the products of both dry and wet comminution products, are in relation with the irregular morphology of particles, reasonably due to the cut stresses applied by the blades of the mill to very thin material (LDPE).

+2.0 mm *-2.0 mm +1.0 mm* *-1.0 mm*

Fig. 22. Plastic bags and films, images of the products of dry comminution tests.

+2.0 mm *-2.0 mm +1.0 mm* *-1.0 mm*

Fig. 23. Plastic bags and films, images of the products of wet comminution tests.

The values of the parameter Shape Factor describe a shape of elongated particles.

The statistic parameters, notably the standard deviation, show a high variability in the analysed particles, with standard error and confidence intervals substantially constant for both dry and wet comminution products.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	84	84	84	84	84	84	84
Mean	110.169	858.617	22.404	11.392	276.048	0.033	10.525
Min	0.353	45.314	0.943	0.691	3.999	0.003	0.670
Max	460.604	4994.348	54.142	28.985	1175.889	0.277	24.217
Std Dev	101.475	828.363	12.335	6.681	232.520	0.038	5.464
Std Err	11.072	90.382	1.346	0.729	25.370	0.004	0.596
95% Conf	21.700	177.145	2.638	1.429	49.724	0.008	1.168
99% Conf	33.195	270.983	4.035	2.186	76.065	0.012	1.787

Table 15. Plastic bags and films, dry comminution, size class: +2 mm.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	67	67	67	67	67	67	67
Mean	4.586	147.115	4.563	2.075	23.798	0.151	2.325
Min	0.349	31.033	2.480	0.474	8.716	0.016	0.666
Max	15.881	765.458	13.879	3.402	110.257	0.405	4.497
Std Dev	2.654	143.863	1.931	0.627	17.288	0.101	0.665
Std Err	0.324	17.576	0.236	0.077	2.112	0.012	0.081
95% Conf	0.636	34.448	0.462	0.150	4.140	0.024	0.159
99% Conf	0.868	47.062	0.632	0.205	5.655	0.033	0.218

Table 16. Plastic bags and films, dry comminution, size class: -2 +1 mm.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	62	62	62	62	62	62	62
Mean	0.886	103.529	2.157	0.847	8.870	0.169	0.974
Min	0.070	23.744	0.483	0.173	1.579	0.052	0.300
Max	3.647	242.053	5.013	2.413	21.939	0.529	2.155
Std Dev	0.725	59.113	1.078	0.479	5.028	0.100	0.428
Std Err	0.092	7.507	0.137	0.061	0.639	0.013	0.054
95% Conf	0.181	14.714	0.268	0.119	1.251	0.025	0.107
99% Conf	0.237	19.338	0.353	0.157	1.645	0.033	0.140

Table 17. Plastic bags and films, dry comminution, size class: -1 mm.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	55	55	55	55	55	55	55
Mean	55.820	777.032	16.333	8.129	189.172	0.034	7.174
Min	4.040	73.678	4.976	1.902	22.982	0.002	2.268
Max	418.924	6791.312	56.129	31.755	1686.727	0.171	23.095
Std Dev	81.603	939.346	10.465	5.434	250.611	0.033	4.469
Std Err	11.003	126.661	1.411	0.733	33.792	0.004	0.603
95% Conf	20.312	233.818	2.605	1.353	62.381	0.008	1.112
99% Conf	26.695	307.289	3.423	1.778	81.983	0.011	1.462

Table 18. Plastic bags and films, wet comminution, size class: +2 mm.

- *Flexible multi-layered (plastic and aluminium) sachets containing granular medicine.*

The flexible multi-layered sachets have been fed to the blade mill without any pre-treatment, including the granular medicine they contained. For the dry and wet comminution tests, samples made of 25 sachets (equal to 184.87 g) and of 10 sachets (equal to 73.70 g) have been respectively used.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	55	55	55	55	55	55	55
Mean	3.638	319.329	4.975	1.915	32.679	0.051	2.039
Min	0.354	113.617	1.577	0.451	7.857	0.016	0.671
Max	9.377	776.877	10.951	3.989	83.139	0.111	3.455
Std Dev	2.309	172.573	2.079	0.847	17.157	0.026	0.695
Std Err	0.311	23.270	0.280	0.114	2.313	0.003	0.094
95% Conf	0.575	42.956	0.517	0.211	4.271	0.006	0.173
99% Conf	0.755	56.454	0.680	0.277	5.613	0.008	0.227

Table 19. Plastic bags and films, dry comminution, size class: -2 +1 mm.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	75	75	75	75	75	75	75
Mean	0.679	123.913	2.000	0.809	8.781	0.163	0.851
Min	0.049	16.139	0.463	0.136	1.124	0.027	0.249
Max	3.544	463.666	5.469	2.341	38.710	0.779	2.124
Std Dev	0.606	86.252	1.026	0.527	6.619	0.127	0.377
Std Err	0.070	9.960	0.118	0.061	0.764	0.015	0.044
95% Conf	0.151	21.470	0.255	0.131	1.648	0.032	0.094
99% Conf	0.198	28.216	0.336	0.172	2.165	0.041	0.123

Table 20. Plastic bags and films, dry comminution, size class: -1 mm.

The products of the dry comminution tests have been submitted to dry sieving, laser granulometry and image analysis.

The sieving tests have been conducted adopting sieves of ASTM series with 1.0 mm, 0.85 mm and 0.50 mm mesh.

The results of the sieving tests are reported in Figure 24 in terms of cumulative passing for the dry comminution tests.

The wet comminution tests have been carried out in order to verify the effect of the use of water on the granular medicine. The results of the tests have been analysed in qualitative terms. In the Figure 25 are shown the images of the products of the comminution test in which 0.4 l of water have been fed to the mill together with the sachets. From the images it can be observed that the sparkling granular medicine has not relevant effects. Moreover, the presence of water allowed reducing the dispersion of powder in the environment during the comminution.

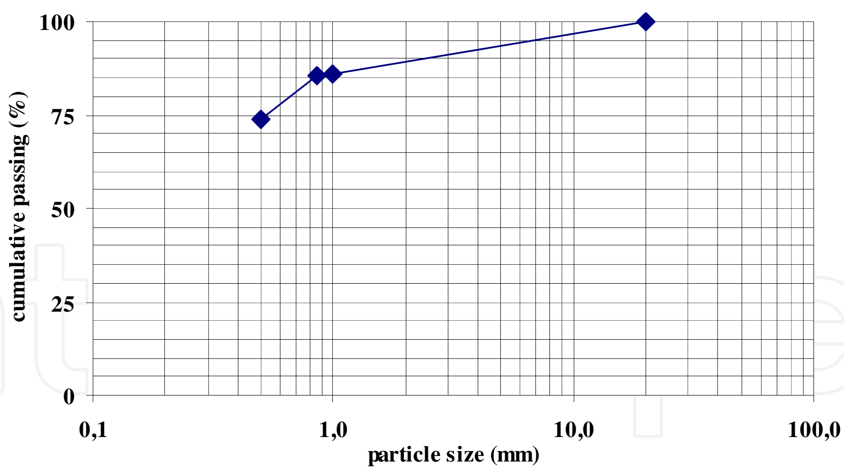


Fig. 24. Flexible multi-layered sachets, 20 mm grid, cumulative passing, dry comminution.

Fig. 25. Flexible multi-layered sachets, 20 mm grid, cumulative passing, wet comminution.

The results of laser granulometry analysis are shown in Figure 26 and Figure 27 in terms of size distribution for products of dry comminution tests belonging to the -1 mm +0.85 mm, -0.85 mm +0.5 mm and -0.5 mm size classes.

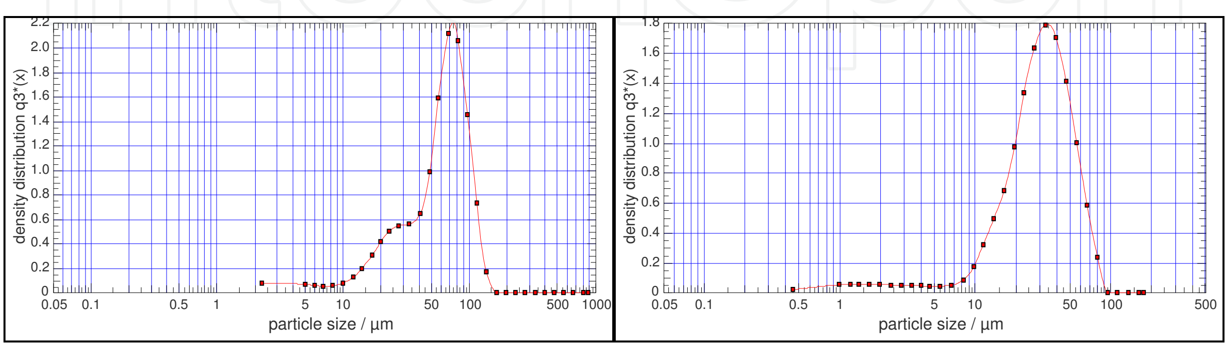


Fig. 26. Flexible multi-layered sachets, 20 mm grid, size distribution, size classes -1 +0.85 mm (left) and -0.85 +0.5 mm (right), dry comminution, laser granulometry.

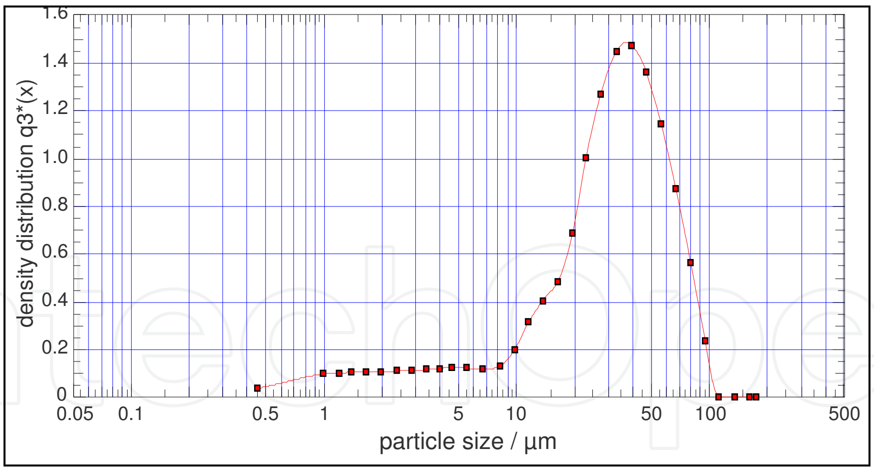
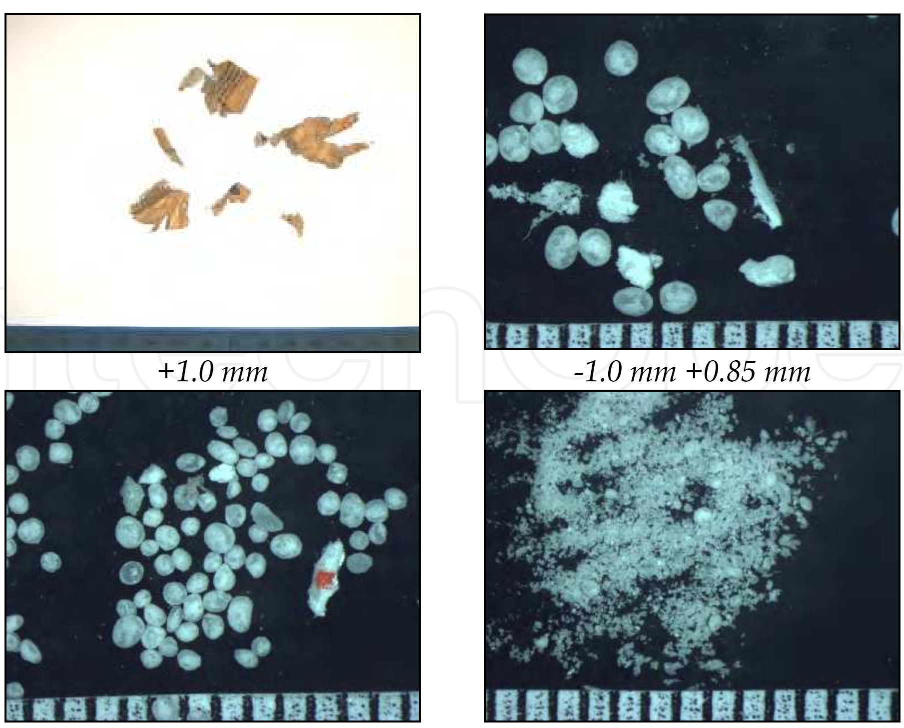


Fig. 27. Flexible multi-layered sachets, 20 mm grid, size distribution, size class -0.5 mm, dry comminution, laser granulometry.

The results of the sieving tests show that the comminuted dry sachets are mostly found in the +1.0 mm and -0.5 mm size classes. In fact, in these classes are respectively collected the multi-layered materials and the granular medicine particles. In the size class –1.0 mm +0.85 mm, the results of laser granulometer analyses show two principal modes, reasonably due to the presence of both multi-layered materials and granular medicine.

After the division in the particle size classes in -1 mm +0.85 mm obtained by sieving, image analysis have been conducted on the products of dry comminution tests. The results of image analysis for the multi-layered sachets are given in Table 21. Examples of images taken of the dry comminution products are shown in Figure 28.



+1.0 mm *-1.0 mm +0.85 mm*

-0.85 mm +0.50 mm *-0.50 mm*

Fig. 28. Flexible multi-layered sachets, images of the products of dry comminution tests.

The high values of the parameter *Compactness*, measured in the products of dry comminution products, are in relation with the irregular morphology of multi-layered particles, reasonably due to the cut stresses applied by the blades of the mill.

The values of the parameter Shape Factor describe a shape of elongated particles.

The statistic parameters, notably the standard deviation, show a high variability in the analysed particles, due to the simultaneous presence of multi-layered and granular particles.

	Area	Compact	Maj Len	Min Len	Perim	S Factor	Feret D
# Obj	11	11	11	11	11	11	11
Mean	253.133	73.910	27.032	15.394	131.359	0.193	16.894
Min	32.653	38.744	10.198	3.748	35.569	0.092	6.448
Max	495.707	136.919	41.900	26.437	227.952	0.324	25.123
Std Dev	154.107	27.727	9.990	7.452	63.551	0.072	6.371
Std Err	46.465	8.360	3.012	2.247	19.161	0.022	1.921
95% Conf	38.360	6.902	2.487	1.855	15.819	0.018	1.586
99% Conf	50.413	9.070	3.268	2.438	20.789	0.024	2.084

Table 21. Flexible multi-layered sachets, dry comminution, size class: -1.0 mm.

3. Conclusions

The results of experimental tests demonstrate the effectiveness of shear stress to comminute primary packaging and waste pharmaceutical product under investigation.

The comminution tests by blade mill RETSCH – SM 2000 show the following outcomes:

- shear stresses on plastic materials determined an irregular and elongated shape on output particles;
- wet and dry conditions are irrelevant on geometric and morphological characteristics of output particles;
- statistical analysis on image analysis data evidenced a high variability in geometric and morphological parameters: this is probably due to plasticity property of materials under investigation and to applied shear stresses;
- size distribution of the plastic particles after comminution is always greater than 1.0 mm and, therefore, greater than powder eventually contained inside packaging (e.g. in pharmaceutical waste).

Considering the outlined results, the comminution process seems to be a feasible treatment for pharmaceutical waste, in order to reduce particle size and to separate packaging materials (mainly plastics) and powder eventually contained.

The wet comminution, even if not influential on geometric and morphological characteristics of output particles, can be adopted to avoid powder dispersion in air.

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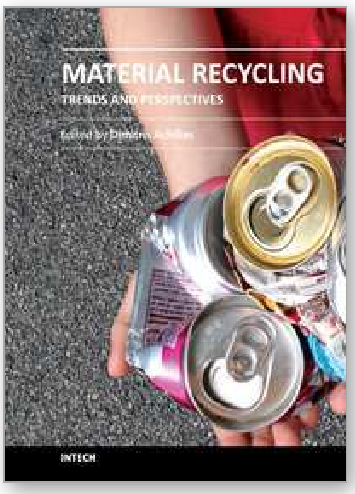

Material Recycling - Trends and Perspectives
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The presently common practice of wastes' land-filling is undesirable due to legislation pressures, rising costs and the poor biodegradability of commonly used materials. Therefore, recycling seems to be the best solution. The purpose of this book is to present the state-of-the-art for the recycling methods of several materials, as well as to propose potential uses of the recycled products. It targets professionals, recycling companies, researchers, academics and graduate students in the fields of waste management and polymer recycling in addition to chemical engineering, mechanical engineering, chemistry and physics. This book comprises 16 chapters covering areas such as, polymer recycling using chemical, thermo-chemical (pyrolysis) or mechanical methods, recycling of waste tires, pharmaceutical packaging and hardwood kraft pulp and potential uses of recycled wastes.