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Overview on Mechanical Recycling by Chain Extension of POSTC-PET Bottles

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1. Introduction

The post consumer poly(ethylene terephthalate) bottles (POSTC-PET) can be recycled by chemical or / and mechanical processes. The POSTC-PET chemical recycling is widespread in Europe and is based on depolycondensation of secondary polymers and usage of the resulted products for the purposes of the fibre and unwoven material industry. The POST - PC mechanical recycling requires a phase transformation (melting) and can be attained without or with polymer up-gradation (Mancini, 1999; Akovali, 1988; Belletti, 1997; Ehrig, 1992; Erema, 2002; Firas, 2005; Sandro & Mari, 1999; Scheirs, 1998; Awaja, 2005).

The well-known worldwide POSTC-PET mechanical and chemical recycling ways are:

1. **Resorption back into the bottles manufacture.** After getting flakes, POSTC-PET is mechanically and /or chemically recycled into bottles for non-food products (soap, cosmetics, and cleaning agents). In 2004, around 50 % of the PET recycled in this way was processed;
2. **Re-use in the fibre and un-woven materials industry** for obtaining insulation membranes for roofs, shoe soles, filters, covers for car inner compartments. This direction is the most popular in Europe (Monika, 2007; Morawiec, 2002);
3. **Processing into thin sheets for thermoforming** refer only to the flakes resulted from POSTC-PET selective collected by colour. It is appreciated that the sheets obtained from such material can undergo a high degree of stretching during thermoforming in order to shape packaging cases such as transport trays for tomatoes, eggs and strawberries etc.;
4. **Up-gradation by melt processing compounding.** Although PET has excellent usage properties, because of certain characteristics such as low glass transition, low crystallization speed (for certain types) and low impact resistance, in order to be

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mechanically recycled into performing products, it is compounded at melt processing. However the results are not spectacular.

5. **Chemical recycling** is related to the recovery of the chemical compounds based on following depolycondensation particular reactions glycolysis, methanolysis, hydrolysis, acidolysis, amynolysis, etc. (Carta, 2001; Karayannidis, 2003; Minoru, 2003;);

In spite of long lasting efforts, because of the low cost and low performance applications of the recycled material, at present, the widely accepted opinion is that the POSTC-PET mechanical recycling without a structural up - gradation is not an efficient procedure.

The chapter presents an overview on the structural up-grading of POSTC-PET by macromolecular chain extension during mechanical recycling (reactive processing), a procedure considered efficient for the enhancement of its properties.

2. Parameters controlling the POSTC – PET mechanical recycling

The main parameters controlling the POSTC-PET mechanical recycling are: the contamination level and the degradation degree.

2.1 POSTC – PET contamination

POSTC-PET contamination can be of the following three types: *macroscopic and microscopic physical contamination and chemical contamination.*

Macroscopic physical contamination of POSTC-PET is easy to clear off as it consists of dust, glass chops, stones, adhesives, product residues, plastics such as PVC and PE, earth impregnation due to improperly storage.

Microscopic physical contamination is more difficult to clear off especially because is partially attached to the bottle because it is about adhesive or other impregnated impurities resulted after abrasion or impact. These impurities break the thread either during granulation in the melt processing or during the spinning in the fibre industry. This leads to decrease the quality and productivity of the recycling.

Chemical contamination is the result of *adsorption* of flavouring, oil, pesticides, household chemicals, and fuel if the bottles were re-filled with such products in a secondary utilization. The proportion of POSTC-PET interaction with these compounds depends on the diffusion behaviour of contaminants and the sorption properties of the polymer. The removing of these contaminants implies *undergoing the reverse processes, namely desorption.* The adsorbed chemical impurities into the polymer *settle on the risk potential of POSTC-PET* mechanically recycled especially if the food packages are targeted. The recycling by desorption can not be considered because of its very low productivity, this process being an extremely slow one. For diminishing as much as possible the impurity content, the POSTC-PET melts are filtered during the mechanical recycling at extrusion, before passing through the nozzle, using particular filters (Yang Tang & Menachem, 2008).

POSTC - PET requests a severe control of the contamination level especially if it is recycled into food packaging. Currently, the impurity content limits are established and generally accepted for POSTC-PET recycling as food and non-food packaging (EGPMFC, 1999; Franz,

2004). The following limits of the POSTC-PET impurity residual content have been accepted for recycling as food packaging: 20 ppm or less metal, 10 ppm or less paper and 30 ppm or less polyolefins (Di Lorentzo et al., 2002; Hong Ju Zhou et al., 2007; Hong Jun Zhou et al., 2007). The framing into these limits depends on the technicality of the applied conditioning solution (sorting - washing etc), and by the legislative effort necessary for: the increasing of the population cooperation, the setting up of the infrastructure to analyze the impurity content down to the parts per million (ppm) level, the inspection on the law observance (Knit, 2002; David, 2001; Novis, 2003;).

2.2 PET degradability

During POSTC-PET conditioning and melt processing, the polymer is degraded by mechanical and thermal agents that act in the presence of water and oxygen. If during the first life the POSTC-PET is exposed to UV radiations rather than to thermo-mechanical and hydrolytic degradation, the photo-oxidation must be considered too (Cioffi et al., 2002; Chen et al., 2002; Raki et al., 2004).

The degradation occurs at the weakest thermodynamic links namely at the ester those between the terephthalic acid and diethylene glycol of POSTC-PET macromolecules (Sandi et al., 2005; Vasiliu et al., 2002). In figs. 1 - 5, the main reactions that characterize the PET thermo-hydrolytic degradation are exposed.

By thermal-oxidative degradation (fig.1, - Awaja & Pavel, 2005), the macromolecular chains break resulting in the formation of volatile products (i.e. acetaldehyde - fig. 5 Alexandru & Bosica, 1966), 1.8 - 3 % cyclic and linear oligomers (fig.4 - Awaja & Pavel, 2005) and shorter chains with acid carboxylic and vinyl ester end groups. In hydrolytic degradation (fig.2 - (Awaja & Pavel, 2005), the mechanism is similar, with the difference that the end groups of the short macromolecules resulted from degradation are carboxylic acid and hydroxyl ester.

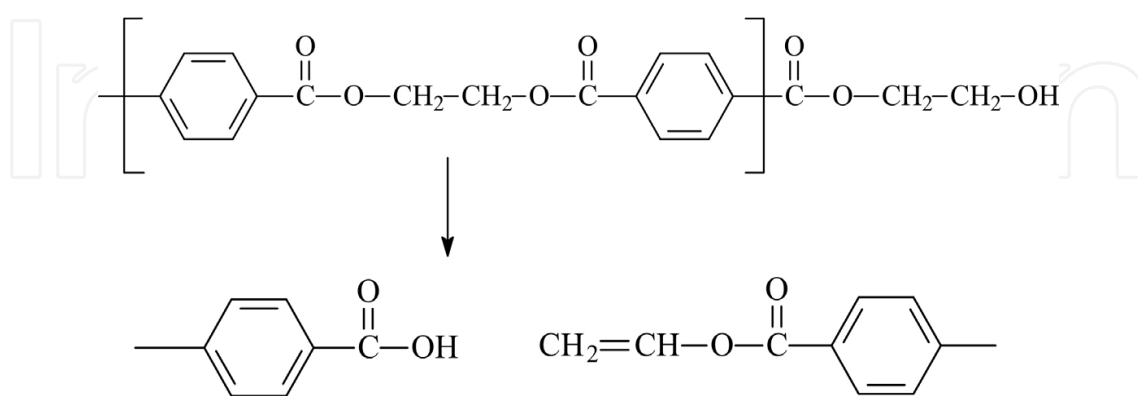


Fig. 1. PET thermal degradation mechanism with the formation of carboxyl acid and vinyl ester end group (Awaja & Pavel, 2005).

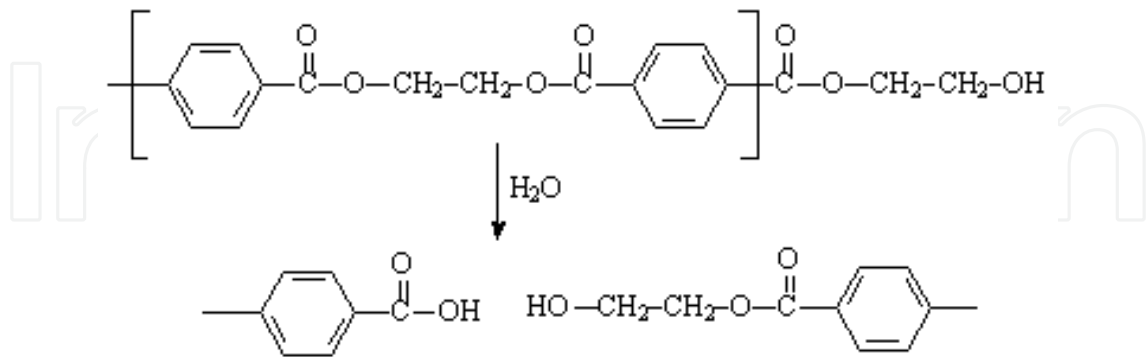


Fig. 2. PET Hydrolysis mechanism resulting in carboxyl acid and hydroxyl ester end group appearance (Awaja & Pavel, 2005).

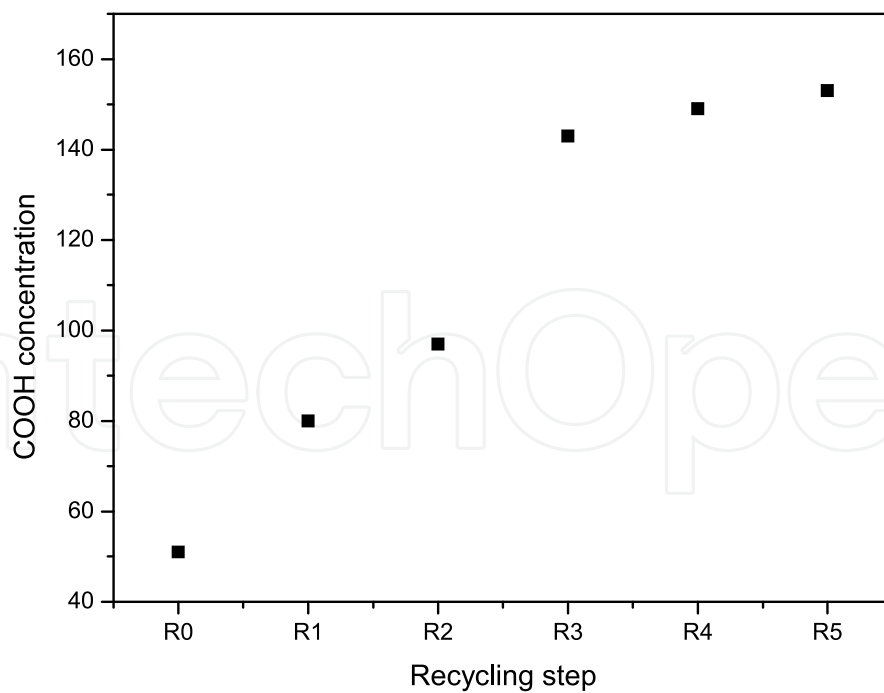


Fig. 3. The dependence of the carboxyl end group by the number of reprocessing of POSTC-PET (Spinace & De Paoli, 2001).

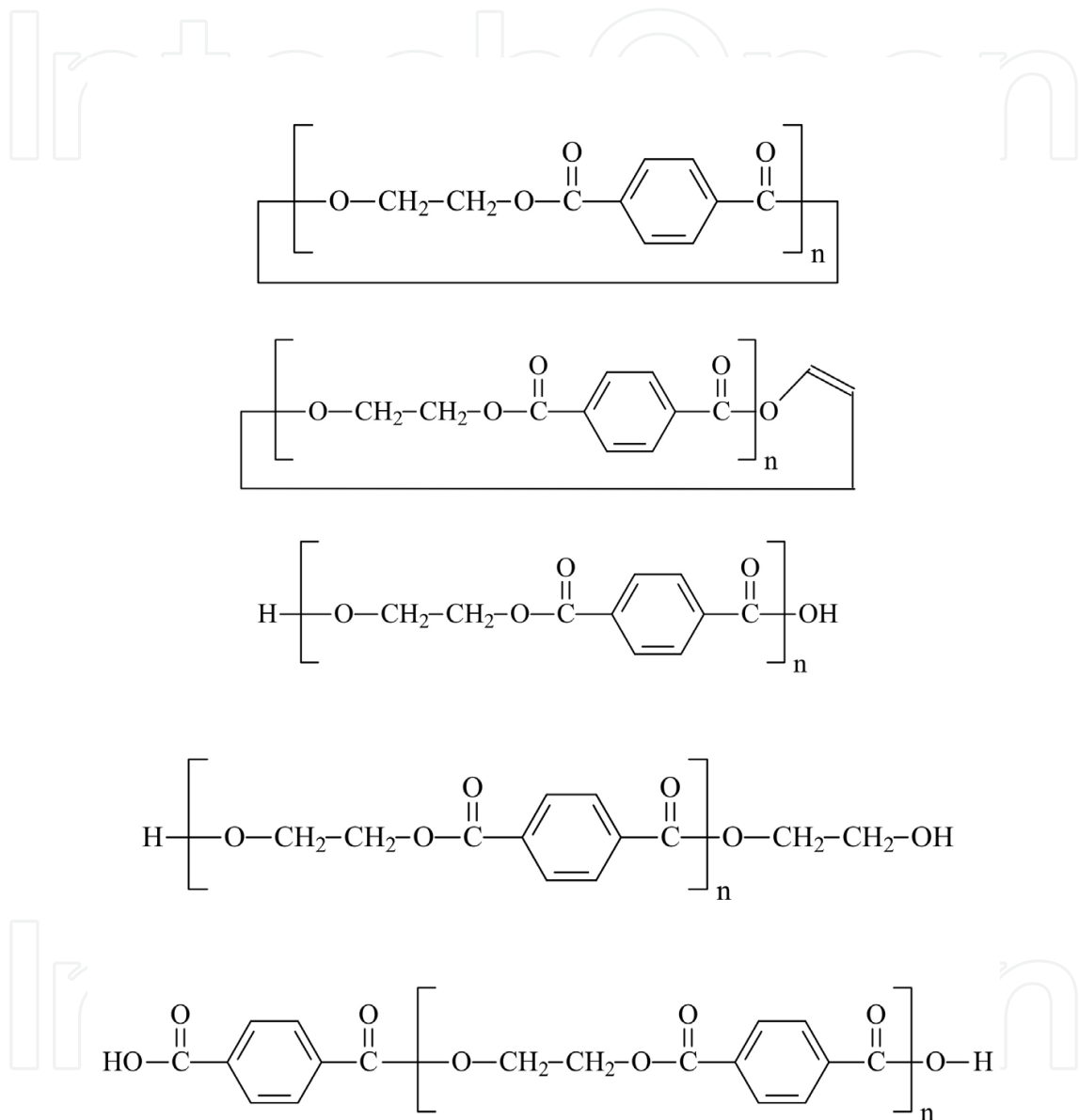


Fig. 4. Cyclic and linear oligomeric compounds resulted from PET degradation (Awaja & Pavel, 2005).

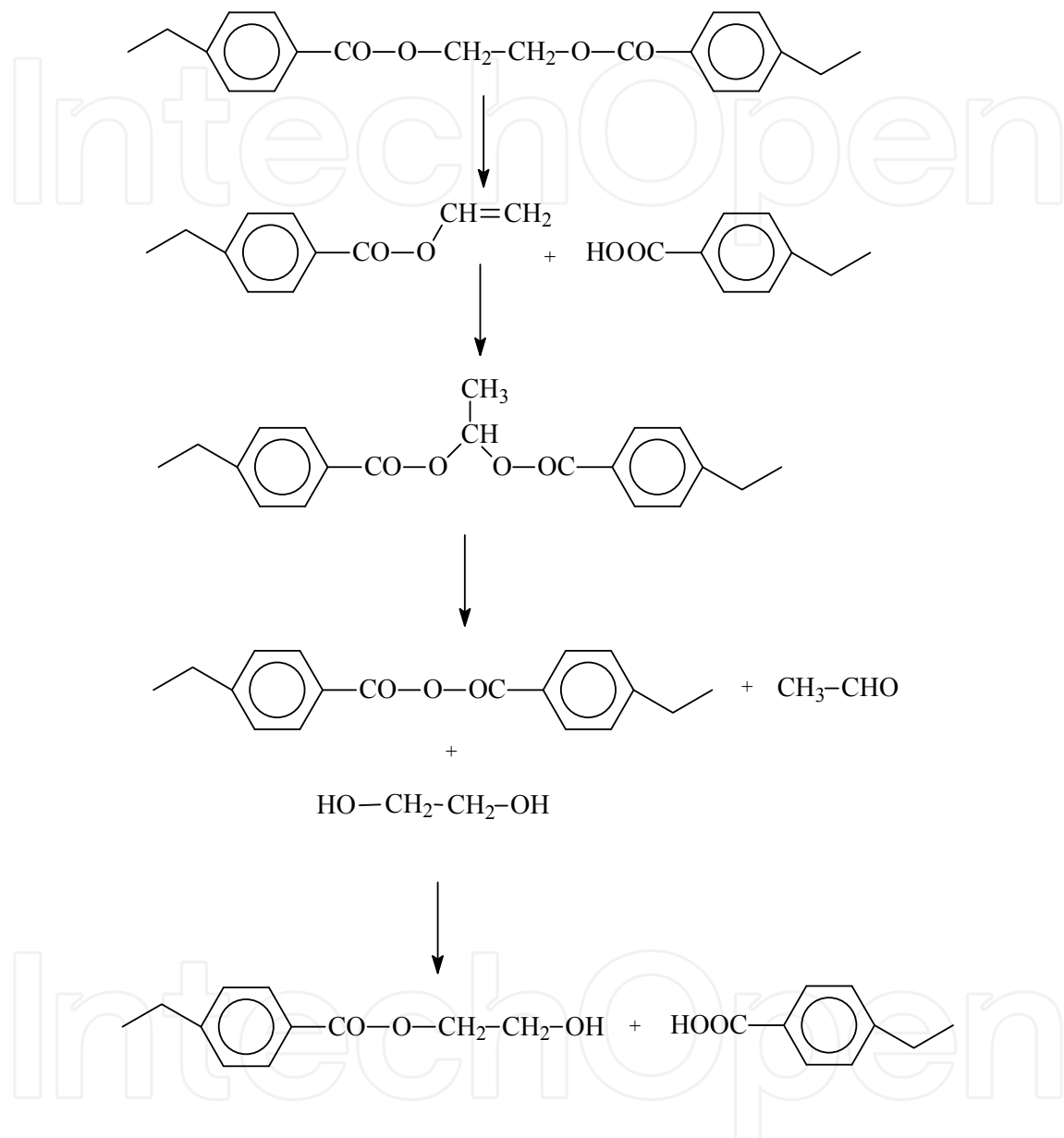


Fig. 5. The acetaldehyde formation during PET thermal degradation (Alexandru & Bosica, 1966).

The increasing of the carboxylic end group with the number of the reprocessing of the POSTC-PET is presented in fig. 3 (Spinace & De Paoli, 2001, Silva Spinace, 2001). The end groups content puts on view the POSTC-PET degradation degree, the carboxyl end groups being correlated with the thermal and hydrolytic degradation and the hydroxylic end groups with hydrolytic ones.

The result of the degradation reactions is a severe drop in the molecular weight which leads to the failing of intrinsic viscosity, melt strength and melt processability and finally, to poor usage properties and a low quality of the products obtained from reprocessed polymers. Because of the severe molecular weight diminishing during POSTC-PET reprocessing, the intrinsic viscosity may decrease from 0.72 dl g⁻¹, the virgin polymer specific value, down to 0,04 - 0,26 dl g⁻¹ (Raki et al., 2004; Zong Zhang et al., 2004; Seo et al., 2006; Cuberes et al., 2000).

Because of the formation of shorter macromolecules as a result of the hydro-thermal degradation, the crystallization capacity of the POSTC-PET increases and its degradability becomes more pronounced. This process known as chemi-crystallization is a complex one because at the beginning it is a chemical one (diminishing the macromolecules length due to degradation) and in the end it is a physical phenomenon (crystallization of the shorter macromolecular chains) (Pralay, 2002;). As a result of an increased crystallinity, the glass transition (T_g), melting temperature (T_m), melting heat and density of the POSTC-PET are greater. Also because of the dependence of the crystallinity on the degradation degree, the colour of POSTC-PET can differ from transparent (un-degraded or poorly degraded), to translucent (small degraded) and opaque (great degraded).

The strong degrading tendency during the melt processing is specific for all polycondensation polymers, not only for PET, and is observed in case of primary polymer melt processing too. The higher the molecular weight of the primary polymer the greater the melt processing degradation.

The structural changes resulted from degradation can be so dramatic that the melt processing of POSTC-PET may become not viable. It is therefore easy to understand why the mechanically recycling of POSTC-PET can consider only applications which do not require high performance properties.

3. The chain extension up-gradation of POSTC-PET

Considering the general opinion according to which POSTC-PET can be mechanically recycled only into low-property goods, it becomes clear the interest to find new economic solutions for the reprocessing of these materials into products with practical importance. In the last 20 years the researchers have been concerned in the up-gradation of POSTC-PET by increasing the macromolecular weight based on chain extension reactions (Cavalcanti et al., 2007, Awaja & Pavel, 2005, Villalobos et al., 2002, Karaianidis, 1993).

The efficiency of these reactions is controlled by many factors. Their presentation begins with emphasis the importance to eliminate humidity by drying before melt processing and to stabilize the POSTC-PET at melt processing.

3.1 Drying /degassing

Before the chain extension, the POSTC-PET is dried to remove the humidity. It was observed that drying before chain extension and degassing and /or operation under vacuum during chain extension are able to decrease the degradation of POSTC-PET during

melt processing. The drying of POSTC - PET restrains the hydrolysis during the melt processing but it is not a simple action (Buxton et al., 2002;). The POSTC-PET drying method should be the same as the ones used for primary polymers that means 3 - 7 hours at 140 - 180 °C, in desiccators or standard drying equipments (Xanthos et al., 2000). According to other opinions, the drying at temperatures greater than 160 °C can not be done because at this temperature the polymer hydrolysis becomes active. These opinions argue that the efficient drying temperatures should range between 110 - 140 °C, and the drying time should be greater than 12 hours. The final accepted water level is no more than 50 ppm - 0,01 %. If the POSTC-PET water content is smaller than 100 ppm, then the loss in the intrinsic viscosity during reprocessing shall be less than 0,04 dl g⁻¹ (Denisyuk et al., 2003; Awaja & Pavel, 2005).

3.2 POSTC-PET stabilization

The POST - PET stabilization has the aim to block the polymer's thermo-hydrolytic degradation, to remove the formation of acetaldehyde as a result of degradation and to reduce the influence of the residual PVC. The free radicals resulted from the splitting of the macromolecular chain during degradation and those appeared after the decomposition of hydroperoxides can be captured with phosphorous compounds. Avoiding the degradation, these stabilizers hinder the formation of acetaldehyde (Karayannidis et al., 2003; Swoboda et al., 2008). For the capture of the existing acetaldehyde, compounds such as amino-benzoic acid, diphenylamine, 4,5 dihydroxy benzoic acid are very practical. The PVC traces are inhibited by tin mercaptide, antimony mercaptide and lead phthalate. The only disadvantage in using the stabilizers is the rise in the cost of the POSTC- PET mechanic recycled (Awaja & Pavel, 2005).

3.3 Methods for POSTC-PET up-gradation by chain extension

The macromolecular chain extension is a result of particular post condensation reactions between the degraded polymer and selected chain extenders. Theoretically, these coupling reactions annihilate the effect of degradation as they determine the growth of molecular weight by extension, branching, reticulation. Expertise has shown that it is very difficult to separate these reactions from the degradation that occurs in the same time. The intensity of the degradation is greater or smaller depending on the way the extension reaction is conducted. The reaction of molecular weight increase has to be performed in such a way as to diminish or avoid the degradation. As the high gel content is a disadvantage for the melt processing and for the control of reprocessed POSTC-PET usage properties, the reticulation near degradation should be avoided (Raki et al., 2004;torres et al., 2001; Yilmazer et al., 2000; Inata et al., 1987; Bikiaris & Karayannidis, 1993).

The chain extension reaction is rendered schematically in figure 6 (Villalobos et al., 2006) The most suggestive presentation of the way in which the chain extension reaction can develop depending on the reaction conditions (i.e. concentration of the extender) and how the same material can yield both chain extension and reticulation was accomplished by (Villalobos et al., 2006;) (fig.7). The same figure shows that the chain extension can result in intrinsic viscosity values, proper for various targeted applications.

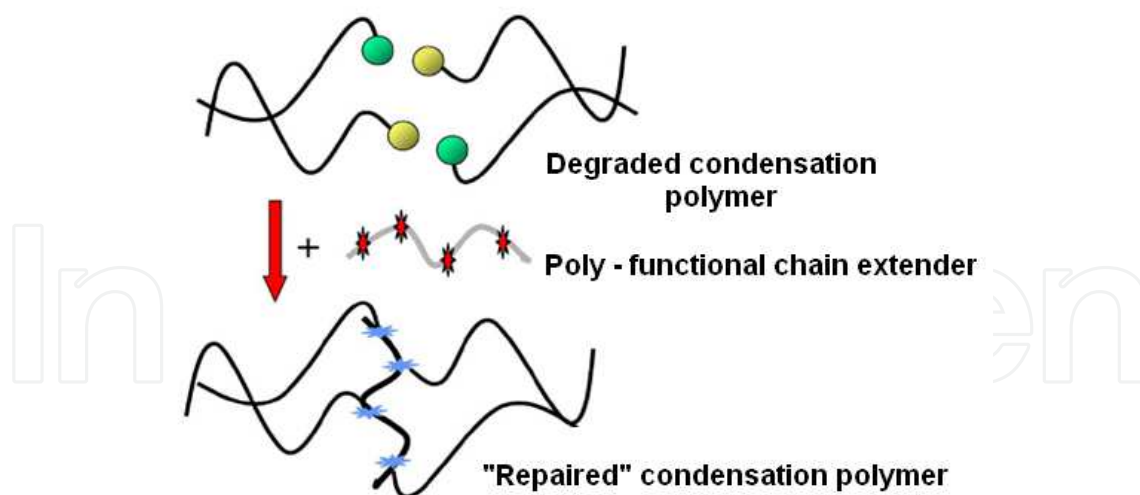


Fig. 6. Schematically presentation of the chain extension reaction (Villalobos et al., 2006).

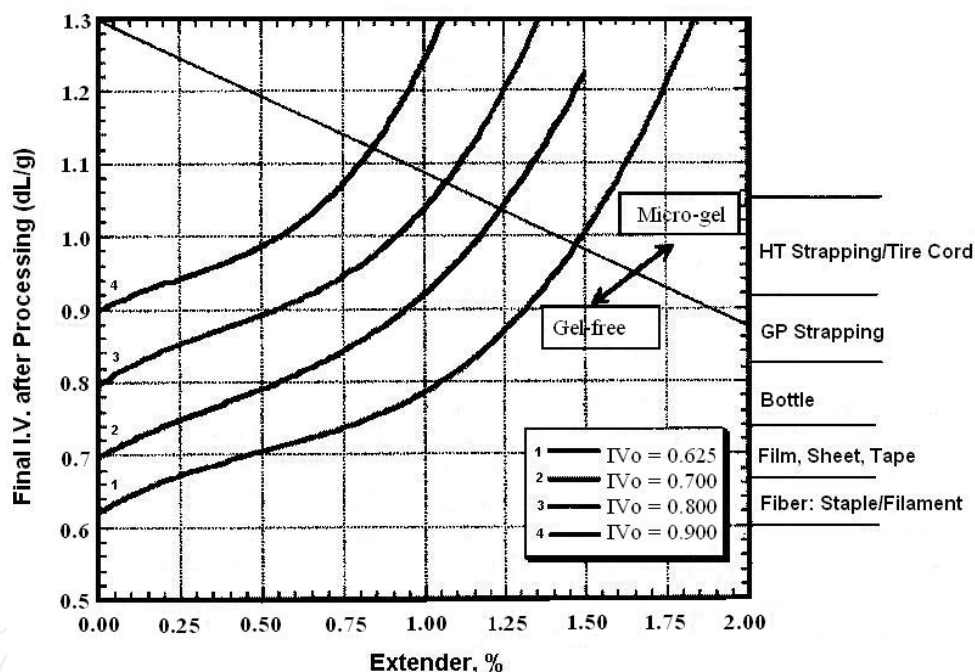


Fig. 7. The dependence of the nature of the reactions in chain extension and the possible applications depending on the accomplished intrinsic viscosity (Villalobos et al., 2006).

Otherwise, in practice, the obtained results demonstrate that the chain extension can be controlled in such a way to ensure the best melt processing properties and the most convenient usage properties for up-graded recycled POSTC-PET. The process can be controlled by monitoring the value of the intrinsic viscosity (ASTM D 4603 -91) and of the carboxyl and hydroxyl end group. An increased carboxyl end group content is associated with a very degraded polymer and the decreasing of the hydroxyl end groups means in progress chain extension reactions (Changli et al., 2006; Bizzaria et al., 2007). The process can be also monitored in terms of melt flow behavior, die swell degree and viscoelastic properties (Yilmazer et al., 2000).

In most cases, chain extension leads to thermal, mechanical and rheological performances equal or even higher than the performances of the primary polymers (Bikiaris et al., 1998). It is appreciated that chain extension is an important way to add value to POSTC-PET and to manufacture products with high technical and economic added value.

The following two alternatives are known for macromolecular chain extension, which are applied to all polycondensation polymers: solid state polymerization (SSP) and reactive processing (RP).

4. Solid State Polymerization (SSP)

Solid state polymerization (SSP) is a coupling reaction between POSTC-PET and extender that takes place in steel reactors, under high vacuum, at temperature above glass transition (T_g) and under melting temperature (T_m), in the catalysts presence (Karayannidis et al., 1991, 2003; Baldi et al., 2006; Flieger et al., 2003; Mano et al., 2004; Cangli et al., 2008; Bikiaris et al., 2003; Gantillon et al., 1990, 2004; Rosu et al., 1999; Karayannidis et al., 1991; 1993, 2003). Usually the reaction occurs at temperatures ranging between 200 – 240 °C. These temperatures favour the SSP chain extension in detriment of the degrading ones. In SSP, the temperature control is essential because if the temperature is too low the extension lasts too long, and if the temperature is too high then the POSTC-PET flakes agglomerate and the extension can no longer happen evenly (Lee & Lichtenhan, 1999). In SSP the reaction time is too long (hours) because the reaction speed is controlled by the diffusion of the reaction by-product and the diffusion of the end-groups into the reaction mass (Gantillon et al., 2004; Apoorva, 2002; Yong et al., 2008). A convenient growth of molecular weight is obtained after 8 hours at 230 °C (Karayannidis et al., 2003). The reactions speed can be increased by the presence of nanomaterials probably because of their nucleation effect (Huimin et al., 2004; Tannenbaum et al., 2002;) The volatiles are constantly removed from the reactor that must operate under vacuum or under an inert gas blanket (Awaja & Pavel, 2005).

To eliminate the negative influence of the residual impurities there exists an alternative solution according to which the POSTC-PET is dissolved first in a selected solvent, then the polymer is recovered by precipitation with methanol and finally the polymer is chain extended according to SSP methods (Karayannidis et al. 2003). SSP can be a proper method to prepare POSTC-PET nanocomposites (Bikiaris et al., 2006; Apoorva, 2002).

Although, apparently SSP can be considered a good “bottle to bottle” recycling method, due to the longer reaction time and the high cost of the equipments and of the control devices, the procedure is considered unsuitable for industrial level (Martinez et al., 2008; Cavalcanti et al., 2007; Awaja & Pavel, 2005).

5. Reactive processing

The reactive processing (RP) of POSTC-PET for the extension of the macromolecular chains, takes place in the equipment generally used for primary polymer melt processing, at temperatures ranging between the polymer melting temperature and the degradation those, under particular working conditions to each pair POSTC-PET – chain extender (Akkapeddi, 1988;). The reaction is also used for obtaining those melt properties which make possible the PET melt processing by extrusion –blowing and thermoformation (Lacoste et al., 2005).

Usually for RP the following equipment, that operate as reaction reactors, is used: one or twin screw extruders, Brabender plastographe, capillary rheometers, rheomixers, injection machines s.o, (Ganzeveld, 1993; Torres et al., 2000; Dhavalikar & Xanthos, 2002). In laboratory experiments or at industrial level, the twin screw extruders are preferred because of their effectiveness in achieving a better dispersion of small compounds into the polymeric matrix (Janssen, 1998; Akkapeddi et al., 1988; Rober et al., 2006).

Depending on the chemical structure of the extender and the concrete reaction conditions, the chain extension is more or less accompanied by ramification and reticulation, with gel formation or / and by degradation (Paci & La Mantia, 1998). Nevertheless it is considered that the extender chemical structures can be so conceived and the operating conditions can be found in such a way that, the prevalent reaction during the POSTC-PET reactive processing to be the chain extension those. The “reconstruction” of the macromolecular chains by reactive processing is a simple procedure that takes minutes, and has been performed at industrial level by extrusion and injection (Chem et al., 2002; Cavalcanti et al., 2007; Xanthos et al., 2001).

The obtained experimental results show that based on reactive processing, it is possible to reach an intrinsic viscosity higher than 0,6 dl_g-1, the basic quality condition needed for reprocessing POSTC-PET in products for high performing applications. (table 1). It was also reported an intrinsic viscosity higher than 1 dl_g-1 (Fumio Asaba, 2002).

Application	Intrinsic Viscosity, dl _g -1
Recording tapes	0,60
Fibres	0,65
Bottles for drinks	0,73 - 0,8
Cord for industrial tyres	0,85
Micro and nano foam for multi-layer panels	0,7 - 1,1
Fields with outstanding mechanical properties	> 1

Table 1. Values of PET intrinsic viscosity, specific for different applications.

In most cases, by reactive processing, one can obtain mechanical and rheological performances equal or higher than those of virgin polymers. This is the reason for which the reactive processing of POSTC-PET is seen as an important possibility to add value to the post consumer condensation polymers and to create products with added technical and economical value. The “repaired” POSTC-PET can be used without physically modification in main applications as bottles and foam sheets or after physically modification as compounds, composites and nanocomposites applications that will be detailed in the following.

5.1 Chain extenders / reticulants

The chain extenders (“recycling aids” (Rossi et al., 2002)) are mono, di or polyfunctional (fn) organic liquid or solid compounds, with low molecular weight ($M_n < 3000$) and controlled polydispersity. The typical extender functional group are hydroxyl, carboxyl, anhydride, amine, epoxy, etc (table 2) (Inata, 1985; Inata, 1986;). Oligomeric or multifunctional polymeric extenders are more and more used (Volker et al., 2008).

Extender functional group	Main representatives, reference
Epoxy	Diepoxides (Haralabakopoulos, 1999;), Epoxy/styrene Oligomers which can be used as master - batch (Zammarano et al., 2006) , Epoxy functionalized compounds (Ren et al., 2003; (Dhavalikar, 2002); Polyepoxides (Dhavalikar, 2002;) Di and tri epoxy, glycidil reactive (Dhalikar & Xanthos, 2001; Hambir et al., 2002;Shanti et al.,2002;), Glycidil multifunctional compounds (Bras et al., 2001); Bis(glycidil ester(pyrorellitimides) (Bikiaris et al.,1995;)
Anhydride	Maleic anhydride, Phtalic anhydride (Shivalingappa et al., 2005;), Pyromellitic dianhydride (Kamal et al., 2002; Giusca et al., 2002; Shah et al., 2002; Shanti et al., 2002; Denisyuk et al., 2003; Lacoste et al., 2005;)
Phosphites/phosphates	Triphenyl phosphate(Cavalcanti et al. 2007;), Lactamyl phosphite (Pham Hoai nam et al., 2002; Bikiaris et al., 2006; Aromatic phosphates (Aharoni, 1986)
Oxazoline	2,2 - (1, 4 phenilen) bis 2 oxazoline (Hongyang et al., 2002; Karim et al., 2002; Shyalingappa et al., 2005; Warburton et al., 1990;)
phosphazene	Ciclo-phosphazene , bis-5,6-dihydro-4h-1,3-oxazolines,
lactame	Polyacyllactams (Bureau et al., 2002;
Isocyanate	Isocyanate triglycidil (Knite et al., 2002) 0,9 % Hexamethylene diisocyanate (Teh et al., 2004;)
Alcohol / polyol	Polyol having 3 -6 hydroxyl groups: Glycerol, Trimethylolpropane, Pentaerytritol, Sorbital ; Polyfunctional Alcohol, 0.1 - 2 % pentaerythritol (Denysiuk et al., 2003;)
Hydroxy -acid	Citric acid, Tartric acid, Trihydroxyglutaric acid. (Tang & Menachem, 2007)
Carboxyl / polycarboxylic acids	Trimellitic or Himimellitic acid, Pyromellitic acid (Tang & Menachem, 2007)

Table 2. The possible chain extender for POSTC-PET reactive processing.

Each extender, depending by its own chemical structure, yields typical extension reactions. It seems that di-functional chain extenders like bisepoxy compounds or bis (cyclic carboxylic anhydride or diisocyanate), do not form by-products and lead to strong reticulated POSTC-PET. Polyfunctional extenders having in their molecule at least three functional groups ($f_n > 3$) involving a combination of at least one group selected from those presented in table 1 (Arif et al., 2007;) are extremely efficient in case of highly deteriorated macromolecules or when a high level of intrinsic viscosity is targeted. These type of extenders are used in order to avoid combinations among extenders (i.e. pyromellitic dianhydride and pentaerytriol (Forsythe et.al, 2006)). The chain extenders with a higher than 3 functionality (f_n), leads to branched molecules. As a rule, the average functionality of the chain extenders is $f_n > 4$.

The chain extenders can be classified considering the POSTC-PET end functional group with which react to extend the macromolecular chains. It is known that there are chain extenders which react with carboxyl end groups and chain extenders which react with hydroxyl end groups. The chain extenders which react to *carboxyl* end groups yield chain extension reactions in a higher proportion than the branching reactions. The chain extenders which react with POSTC-PET hydroxyl end groups are more efficient in the case of PET with low molecular weight, and the hydroxyl content is higher than the carboxyl one (Cavalcante et al., 2007; Inata et al.1986).

In the following it is presenting a few chain extension mechanisms proper to the most known chain extenders.

Pyromellitic Dianhydride (PMDA) is a tetra functional chain extender ($fn = 4$), available on the market, thermally stable, which does not lead to secondary products. It is efficient in proportion of 0.2 - 0.3 % and grows the intrinsic viscosity based on the reaction with the POSTC-PET *hydroxide end groups* (fig.8 -(Xantos et al., 2000; Awaja & Turcu, 2005). Depending on the PMDA concentration and the way the reaction is conducted, extremely branched or even reticulated structures can result. PMDA has been used also for primary PET for increasing the melt strength (Inata et al., 1985).

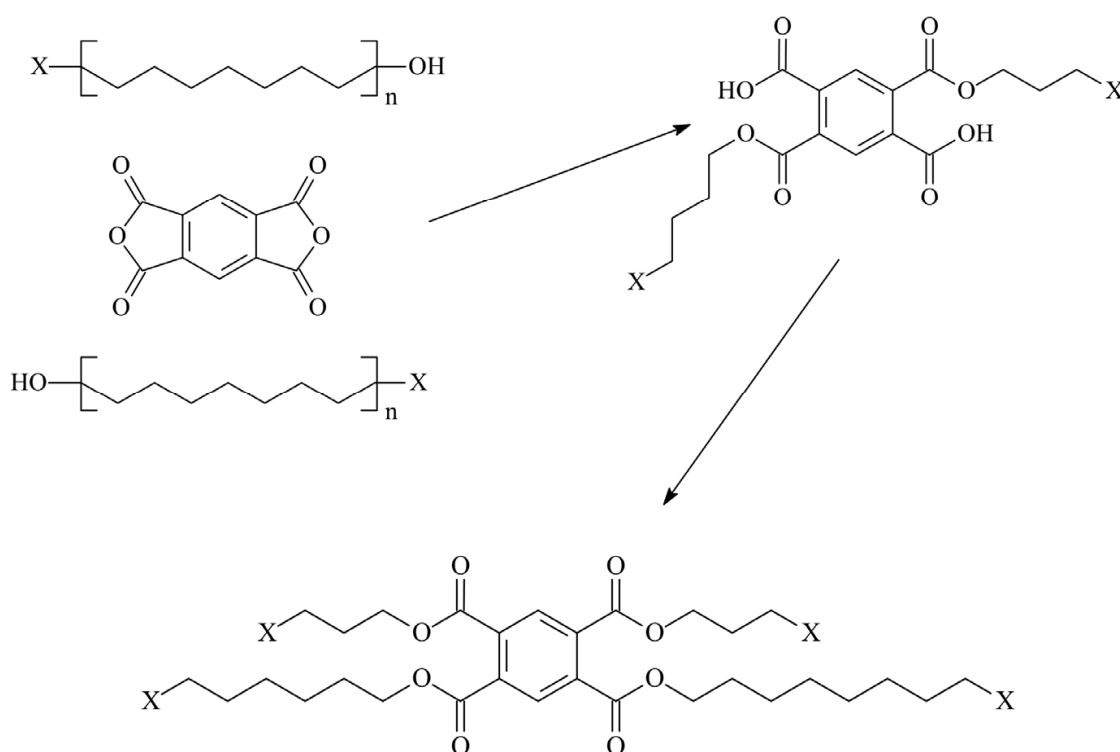


Fig. 8. POSTC-PET chain extension with pyromellitic dianhydride (Xantos et al., 2000; Awaja & Turcu, 2005).

Tri-phenyl phosphit (TPP). The increasing of the intrinsic viscosity is a result of the reaction between the non-participating electrons from phosphorus with the end *carboxyl and hydroxyl* groups of the POSTC-PET (figs 9, 10 Cavalcanti et.al, 2007). The good results are obtained with 1-3%, preferably 1% TPP, at 260 °C. (Cavalcanti et.al, 2005). The main reactions is

accompanied by the by - products development. The competition between the chain extension and the formation of by-products is obvious at temperatures ranging from 280 - to 300 °C.

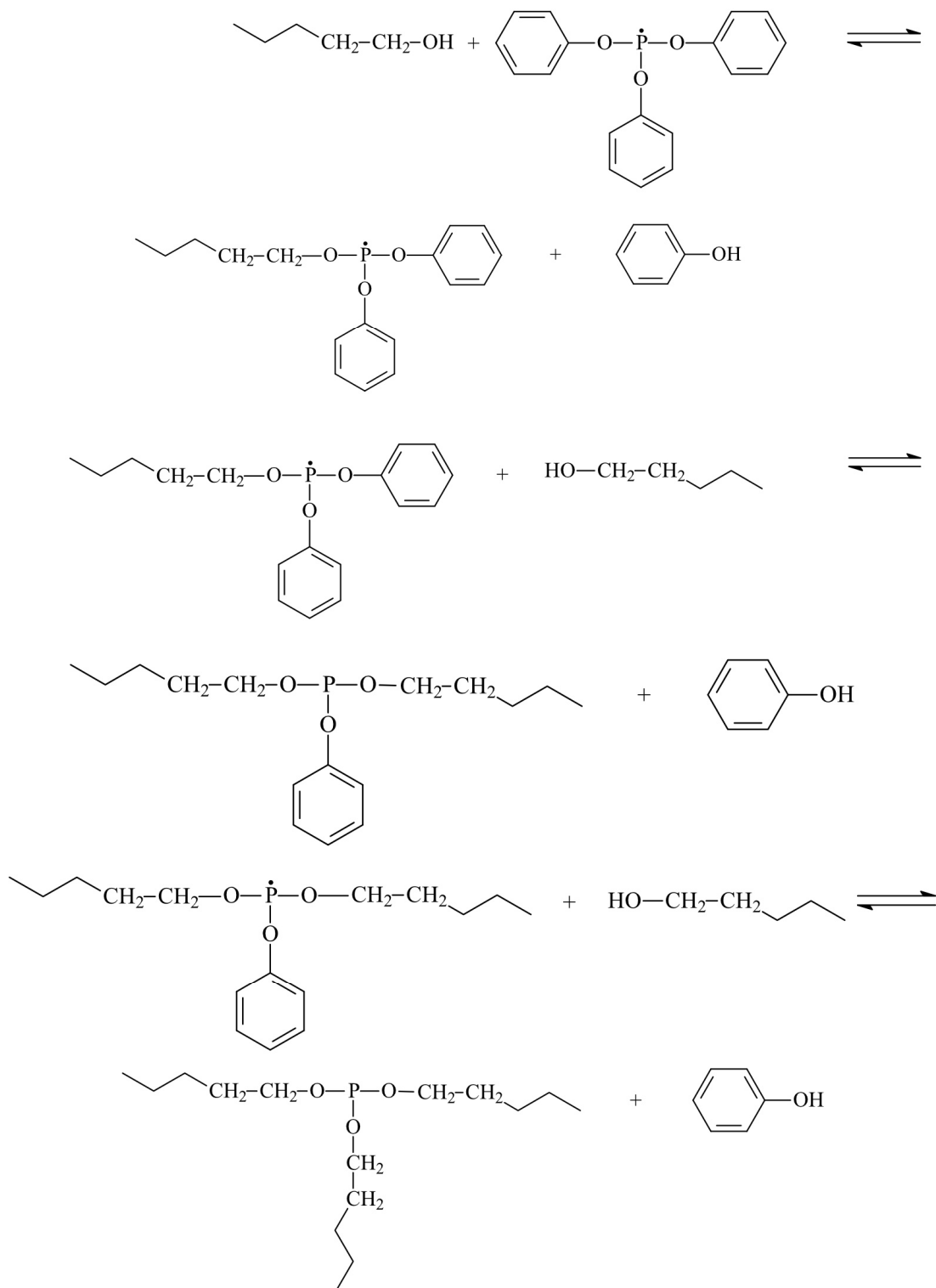


Fig. 9. Chain extension of PET with TPP. Chemical reaction between phosphate and hydroxyl group (Cavalcanti et.al, 2007).

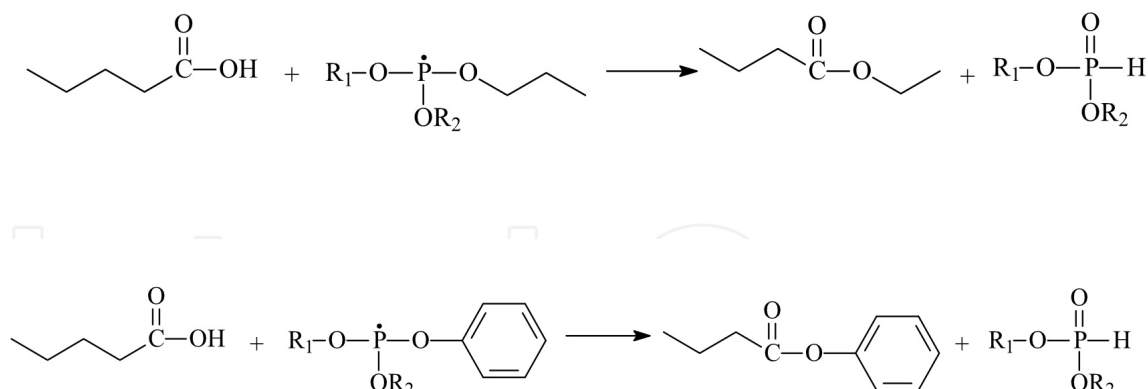


Fig. 10. Extension of PET with TPP. Reaction of phosphite with hydroxyl group (Cavalcanti et.al, 2007).

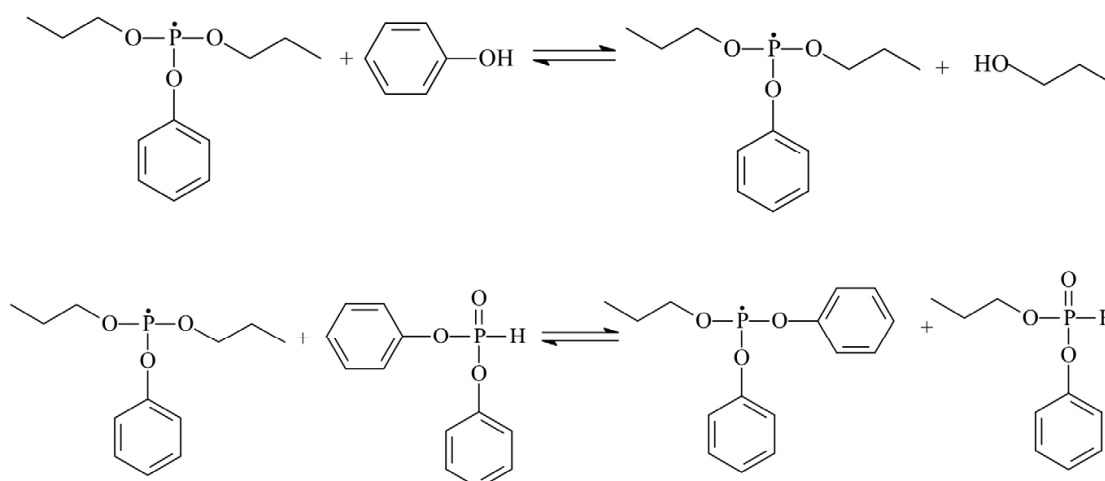


Fig. 11. By-products formation during the chain extension of PET with TPP (Cavalcanti, 2007).

The by-products are dangerous for the reason that, during storage, they act as degrading agent diminishing in this way the stability of “repaired” POSTC-PET. It is demonstrated that if these by-products are extracted with acetone, the degrading during storage is avoided (Cavalcanti et al.,2005).

Epoxy compounds give the esterification of end carboxyl groups (fig.12, (Xanthos et.al, 2000)) and etherification of the end hydroxyl groups (fig.13, (Xanthos et.al, 2000)) from the POSTC-PET macromolecules. In both cases, secondary hydroxyls are formed that can react later with the carboxyl or epoxy groups leading to the formation of branched or reticulate structures (Bikiaris et al., 1995).

Oxazoline compounds such as 2,2'-bis(2-oxazoline) give, with POSTC-PET, the following 3 types of interactions: *blocking reactions* (the molecule of chain extender reacts with the end carboxyl group from a POSTC-PET chain), *coupling reactions* (an extender molecule reacts with 2 polymer chains) and the *absence of any reactions* (Inata, 1987;). (BO) yields secondary

reactions because the oxazoline ring is sensitive to acids. 2,2 - (1,4 - phenylene) bis(2 - oxazoline) (PBO) is a very reactive compound considering only the carboxyl groups within the macromolecular chains. PBO can be used together with a chain extender which reacts with hydroxyl end group i.e. phthalic anhydride.

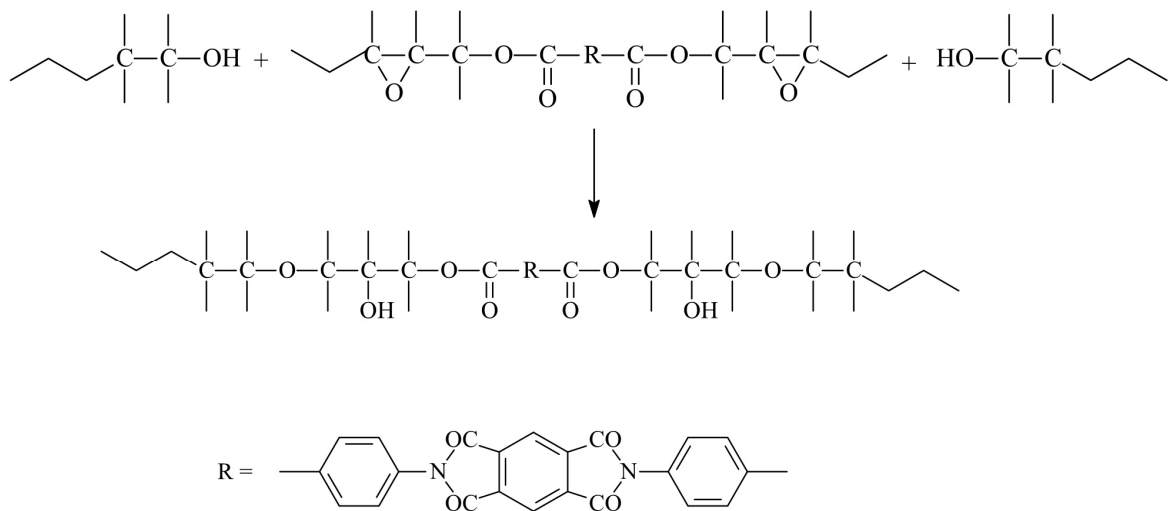


Fig. 12. Initial esterification step in PET chain extension with diepoxide (Xanthos et.al, 2000).

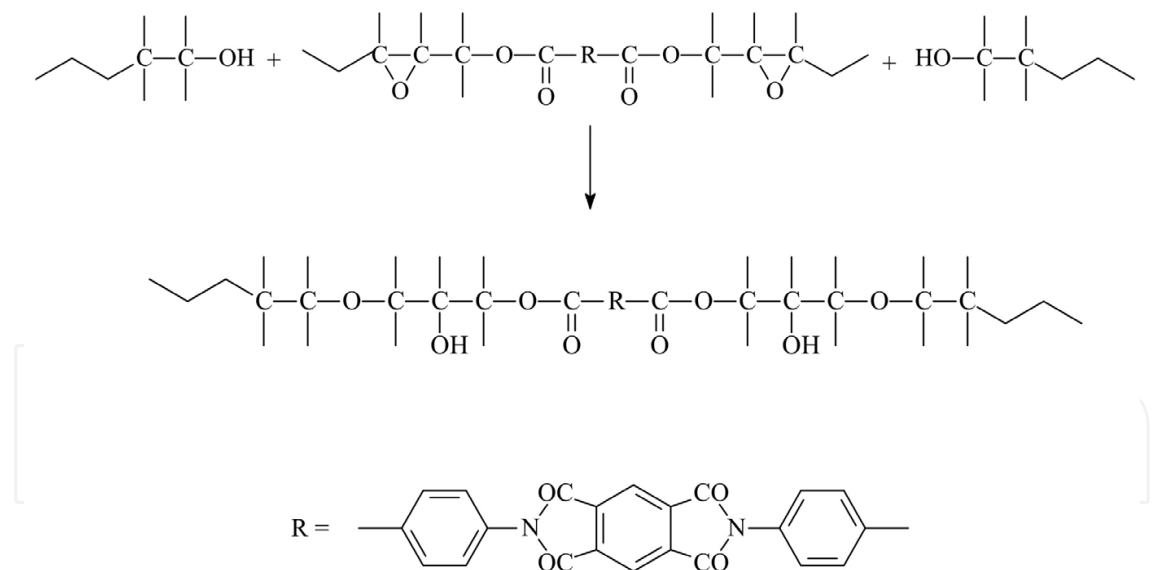


Fig. 13. Initial esterification in the chain extension of PET with diepoxide (Xanthos et.al, 2000).

5.2 Conditions for the chain extension reactions

5.2.1 Reaction parameters - Reaction control

In POSC-PET reactive processing, the chain extension reactions are controlled by the extender concentration, reaction temperature and time and parameters proper to the equipment in

which the reactions occur. *The extender concentration is calculated in relation with the stoichiometry of the extension reaction, considering the measured content of hydroxyl and carboxyl end groups (Nair et al., 2002;)* In theory, a larger quantity than that resulted from stoichiometry leads to strongly reticulated structures, that means a high gel content. *Reaction time can be up to 10 min.* The measuring of the stationary time in the equipment is important because it controls the development of the chemical reactions (Janssen, 1998). Usually the reaction temperature ranges between 260 °C and 310 °C (Bras et al., 2001)

In the case of a Brabender plastometer, the extension is monitored based on the dependence between the motor torque and reaction temperature and time, while in the case of a capillary rheometer, it is recorded the correlation between the nozzle pressure and the swelling extrudate or on the relationship between the melt flow index and the melt strength (Nair et al., 2002;)

In modern industrial systems the monitoring of the intrinsic viscosity is automatic. Obviously, the evolution of the chain extension reaction is rounded up with gel measurements and other properties that characterize the “repaired” POSTC-PET in the melt and solid state.

5.2.2 Operation under vacuum or nitrogen blanket

POSTC-PET has always a residual content of humidity. It was underlined that the chain extension reaction is favoured, and the thermal and hydrolytic degradation is diminished if the humidity content and the reaction time are reduced (Haralabakopoulos et al., 1999). If the chain extending reactions take place under vacuum or a nitrogen blanket then the thermal and hydrolytic degradation can be very much diminished or even eliminated. For these reasons the extruders must be equipped with high vacuum degassing areas for volatiles removal. Also the Brabender plastometers must work under a nitrogen blanket. This condition near the procedure price limit the industrial applicability of chain extension on elderly equipments. It is difficult to have industrial devices that work under such conditions (Paci & La Mantia, 1998). Nevertheless the modern POSTC-PET extrusion systems have high vacuum lines for volatiles removal.

5.2.3 The engineering of reactive processing

The POSTC-PET extending chain reactions that take place in an extruder are controlled by the reaction parameters presented in fig.14 (Awaja & Pavel, 2005). For controlling the reactions that occur in such conditions first of all the system has to be stable (Janssen, 1998;). The stability of the twin screw extruders depends on their designing concept (Bulters, 2001; Potente & Flecke, 1997; Shen et al., 2005;).

The fluctuation of the parameters presented in fig.14 is the major cause determining the *thermal, hydrodynamic and chemical instability*, and consequently the fluctuation in the operation of the reactive extruder. All these types of instability were described in detail in (Awaja & Pavel, 2005) where the bi-univocal relations between the parameters presented in fig.14 and the way in which they influence each other were explained.

The concentration of the extender / reticulant and the stationary time within the extruder are two parameters which control the efficiency of the procedure. A longer waiting time in the extruder is the main reasons of the system instability because the longer the waiting time the bigger the thermo - mechanically degradation (Giusca et al., 2002; Hongyang et al., 2002;)

Kamal et al., 2002). The system instability can result in various situations. The presence of the branched chains within the polymer structure has a great influence on the crystallization induced by shearing (Hanley, 2007; Rosu et al., 1999; Van Meerveld et al., 2002). The resulted morphology will be heterogeneous if the chemical reactions have fluctuations in their evolution (Rosu et al.1999). The orientation of the macromolecules within a shearing field is directly linked to the increase in viscosity. The orientation degree will be irregular in the case of a random viscosity increase (Soares et al., 2004).

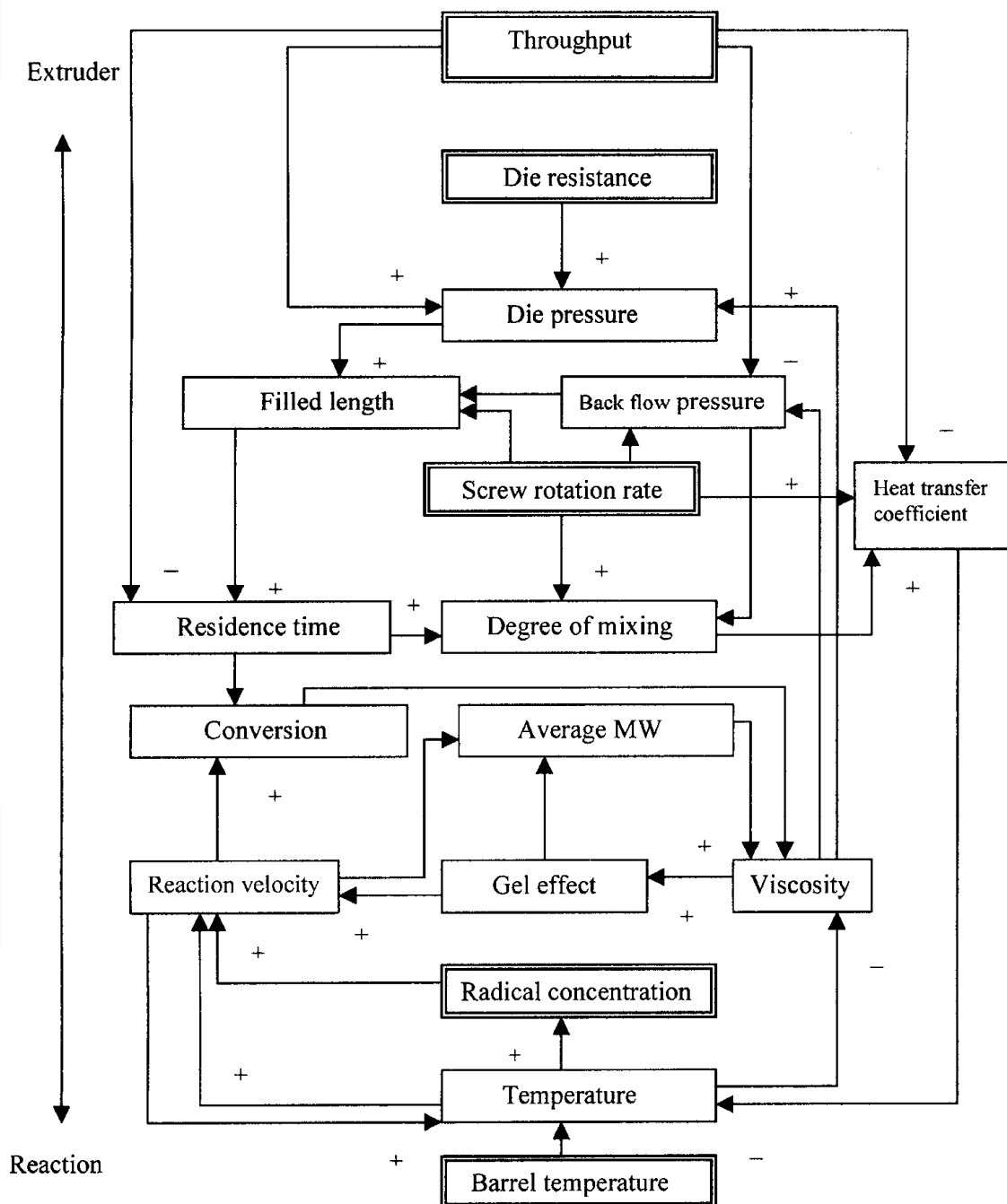


Fig. 14. The factors influencing the stability of an extruder system used for chain extension (+ positive influence; - negative influence) (Awaja & Pavel, 2005).

The counter-pressure and the pressure fluctuation are the most frequent instability described by most of the researchers (Kamal, 2002). Fluctuation can as well occur in the high vacuum degassing system. The pressure in the vacuum system also needs a severe control and a minimal variation (Cavalcanti, 2007).

It is considered that the reaction system specific to the reactive processing is constant if the defining parameters vary within a minimally accepted controllable level. Actually it is considered that the reactive processed is constant when the nozzle pressure, the cylinder temperature and the flow speed are constant.

5.3 SSP and PR comparative economical analyse

A correct approaching of comparative economical analysis for SSP and PR needs details for both procedures and the reaction devices, details about the cost of energy, nitrogen, cooling water, additives and specific labour. In [Vilabados, 2006] it is demonstrated that the chain extension with Joncryl-ADR-4368 (Epoxy/styrene oligomeric extender) by reactive processing in a single screw extruder results in a competitive PR of POSTC-PET. As the reaction uses smaller quantities of energy, water and nitrogen, the reactive processing is more cost-efficient than SSP, which needs catalysts and other special reaction conditions..

5.4 POSTC-PET chain extended applications

The main applications of the “repaired” mechanically recycled POSTC-PET, valuable in practice, are manufacture of: bottles, expanded sheets, multi-layer sheets and foamed panels for constructions and /or compounds composites and nanocomposites for different uses obtained by physical modification.

5.4.1 Bottles

In chap.1 it was underlined that only the colour selected POSTC-PET can be mechanically or thermally recycled into bottles. The chain extension reactions offer a new perspective on this subject. Currently “closing the loop” has become an actual possibility as the bottles and containers can be recycled back as bottles and containers. So, considering the chain extension possibilities it seems that the bottle-to-bottle recycling system is a feasible approach. These bottles can be used for packaging of non-food or food contact products. The re-use of POSTC-PET into food area depends on the potential of the reprocessed material to provide as much safety as the primary polymers do. POSTC-PET can be reprocessed also in multilayer bottles that do not require special safety measures as their inner layer, which comes into contact with the food, is made of primary polymer (Chaiko et al., 2002; kamal et al., 2002; Tannenbaum et al., 2002; Liane et al., 2002; Tjong et al., 2002; Kim et al., 2001; Hu et al., 2002; Lochhead, 2006;)

5.4.2 Sheets and foamed panels

The “repaired” POST-PET can be used for obtaining sheets or multi-layer structures in which at least one layer consists of POSTC-PET (Hong et al., 2007; Yan & Zao, 1988). Sandwich panels (Banosz et al., 1996) and /or high strength uniaxially drawn tapes (Morawiec et al., 2002) can be also attained from “repaired” POST-PET or “repaired” POST-PET foams.

The foaming of the thermoplastic semi-crystalline materials is efficient if at a certain working temperature their melt has high elongation viscosity, elevated strength and enhanced elasticity. The melt of the polymer with low molecular weight and narrow molecular distribution has low viscosity, small strength and reduced elasticity and because of these, the formation and stabilization of the cells cannot be controlled. The increase in molecular weight and polydispersity of POSTC-PET by reactive processing is a way to obtain high property foamed products (Quintans et al., 2004; Forshythe et al., 2006; Fujimoto, 2003; Japon et al., 2004; Kumar et al., 2001; Place et al., 2003; Warburton et al., 1992).

It was found that the “repaired” recycled RPOSC-PET can be foamed if its apparent viscosity is 0.9 dl g^{-1} (Nair et al., 2002) that was realised by means of extenders with a molecular weight of 50 - 5000 and a functionality of 3 - 6. (Tang & Menachem, 2007). In this way, it is possible to produce structures with closed pores which have the right density, pore size, pore distribution, mechanical and thermal properties proper for insulating panels or microcellular foams (Kiatkamjornwong et al., 2001; Xanthos et al., 2004; Chem & Curliss, 2003; Carotenuto et al., 2000). The “repaired” POST-PET can be modified in order to make of cheap composites for expanded panels (Deng et al., 1996).

5.4.3 Compounds, composites and nanocomposites realised by physical modification

In order to improve the melt processability and the utilization properties to POSTC-PET qualify for the desired application, the polymer can be physically modified with: *melt processing agents, agents for improving the mechanical, barrier and optical properties, toughening agents, crystallization and coefficient of friction modifying agent, thermo-oxidative antioxidants and ultraviolet stabilizers* (Smiidt et al., 1999; Salgueiro et al., 2004; Kalpana et al., 2006; debashis et al., 2006; Unnikrishnan & Sabu, 1998; zammarano et al., 2006; Zhang et al., 2001; Zhong et al., 2004;).

Several examples of such modifiers are: *primary* PET (Utraki & Kamal, 2002;), glass fiber (Unnikrishnan & Sabu, 1998; longzhen et al., 2006; Aghlan, 2003; Gersappe, 2002), maleic anhydride grafted styrene - ethylene/butylene - styrene triblock copolymer (SEBS - g-MA) (Javaid, 2006), poly (ϵ - caprolactone) (Guo, 2002), copolymer having at least one block comprising a vinyl aromatic polymer and at least one block comprising a conjugated diene polymer (Kiatkamjornwong et al., 2002; Shanti, 2002;), polyolefins, recycled polyolefins with proper compatibilization agents (Tortora, 2002; Chen et al., 2002; Chabert et al., 2004; Leszezynska et al., 2007; Glasel et al., 1999; Chrissopoulou et al., 2005; Qing-ming et al., 2006; Hadal et al., 2004; Conde et al., 2003; Place et al., 2003; Fujimoti et al., 2003;). Clear blends must be tailored based on branched slow crystallizing PET and faster crystallizing PET (Shriroth et al., 2006; Swoboda et al., 2008; Aghlara, 2003). To improve the brittleness, “repaired” PET is modified with an epoxy group containing styrene thermoplastic elastomer and polycaprolactone (Sikdar et al., 2006). To obtain the side material for cooling towers, “repaired” PET is modified with styrenic thermoplastic elastomer (Arif et al., 2007; Zilg et al., 1998;). Nanocomposites can be achieved with non-modified natural montmorillonite or with ion-exchanged clay modified with quaternary ammonium salt (Pegoretti et al., 2004; Lee & Lichtenhan, 1999; Sharma, 1999; Schmidt et al., 1999; Carotenuto et al., 2000; Aravind, 2007; Bandosz, 1996; Bartholome, 2005; Buxton, 2002; Chrissopoulou, 2005; Feng, 2002; Utraki & Kamal, 2002). Nanocomposites can be

also obtained with CaCO₃ (Di Lorenzo, 2007). Experimental models were conceived for understanding the interaction between the polymer and the ranforsant (Kalpana, 2006; lingaiah, 2005; Tortora et al., 2002). Also, researches are known about the possibility to increase the exfoliation degree of the multilayered silicate, the order degree of the resulted lamellae (Gilmer, 2004; Ren et al., 2003; Rossi, 2002;), the influence of the ranforsant, possible compatibilizer (Giselle, 2005; Hambir, 2002; Pegoretti et al., 2004; Schimidt et al., 1999; The et al., 2004;) The parameters of the reactive processing have a critical role on the obtained results (Hong Jun, 2007).

6. Conclusions

1. The chapter presents an overview on the up-gradation of POSTC-PET by increasing the macromolecular weight based on chain extension reactions, as the most efficient method for adding value to the secondary polymers and for the creation of products with added technical and economical value, for applications within the economy.
2. The post consumer poly(ethylene therephtalate) bottles (PET-PC) can be recycled by chemical or / and mechanical procedures. The PET - PC chemical recycling is based on the depolymerisation of secondary polymers and the use of the depolymerisation products within the fibre and unwoven material industry. The PET - PC mechanical recycling is based on a phase transformation (melting) and can be performed without or with polymer up - grading.
3. The mechanical recycling is controlled by the impurities content and by the reprocessed polymer degradation. The mechanical recycling of PET - PC without up - gradation takes into account the melt processing of the recycled polymer into packages for non - food goods and into thermoformable sheets with a resulted shape adjusted to the transported packed products (eggs, tomatoes, strawberries, apples, so.).
4. In spite of the long efforts performed during the years, because of the low cost and low performance applications of the obtained products, the widely accepted opinion is that the mechanical recycling of PET - PC without up - gradation is not an efficient procedure.
5. The chain extension reaction is favoured, and the thermal and hydrolytic degradation is diminished if the POSTC-PET humidity content is reduced by drying.
6. The POSTC-PET drying is performed as in the case of primary polymers: drying for 3 -12 hours at a temperature of 120 - 180 °C in desiccators or standard drying equipments. The drying of POSTC - PET restrains the hydrolysis during melt processing.
7. The POSTC-PET stabilization during melt processing is needed to block the polymer thermo-hydrolytical degradation, to remove the formation of acetaldehyde as a result of degradation and to reduce the influence of the residual PVC.
8. The macromolecular chain extension is a result of particular post condensation reactions between the degraded polymer and selected chain extenders. The following two alternatives are known for POSTC-PET macromolecular chain extension, which are applied to all polycondensation polymers: solid state polymerization (SSP) and reactive processing (RP).

9. Although, apparently SSP can be considered a good “bottle to bottle” recycling method, due to the longer reaction times and the high cost of the equipment and of the control devices, the procedure is considered unsuitable for industrial level.
10. Solid state polymerization (SPP) is based on the reaction between the POSTC-PET and the extender that takes place in steel reactors, under high vacuum, at temperature above glass transition (T_g) and under melting temperature (T_m), in the presence of catalysts.
11. The reactive processing (RP) of POSTC-PET, takes place in equipment usually used for primary polymer melt processing, at temperatures ranging between the melting temperature and the degradation those, in working conditions suitable to each pair POSTC-PET - chain extender.
12. The chain extenders (“recycling aids”) are mono, di or polyfunctional organic liquid or solid compounds, with low molecular weight ($M_n < 3000$) and controlled polydispersity ($PDI > 3$). The typical extender functional group are hydroxyl, carboxyl, anhydride, amine, epoxy etc.
13. In POSC-PET reactive processing the chain extension reactions are controlled by the extender concentration, reaction temperature and time and parameters proper to the equipment in which the reactions take place.
14. The extruders used in the reactive processing must be equipped with high vacuum degassing areas for the volatiles removal. These condition limits the industrial applicability of the reaction. The modern POSTC-PET extrusion systems have high vacuum lines for removal of volatiles.
15. It is considered that an extrusion system used for the reactive processing is stable if the defining parameters vary within a minimally accepted controllable interval. Actually it is considered that an extruder system is constant when the nozzle pressure, the cylinder temperature and the flow speed are constant. The pressure in the vacuum system, also needs a severe control and a minimal variation
16. Due to reactive processing, it is possible to reach an intrinsic viscosity higher than 0.6 dl/g, which is a basic quality condition for the reprocessing of POSTC-PET into products designed for high performance applications. In most cases, by reactive processing to get properties in melt and solid state equal or higher than the ones of the virgin polymers;
17. As the reaction uses smaller quantities of energy, water and nitrogen, the reactive processing is more cost-efficient than SSP, which needs catalyzers and other special reaction conditions.
18. The main applications of the “repaired” mechanically recycled POSTC-PET are: bottles, expanded sheets, multi-layer sheets and foamed panels and compounds, composites and nanocomposites obtained by physical modification used in important applications.

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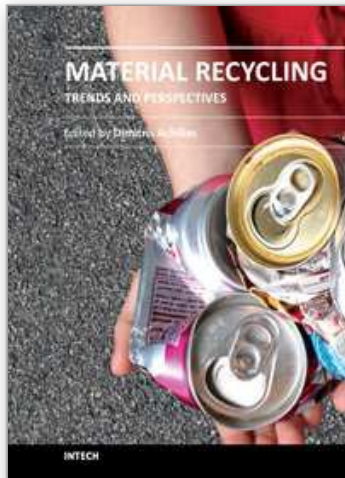
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The presently common practice of wastes' land-filling is undesirable due to legislation pressures, rising costs and the poor biodegradability of commonly used materials. Therefore, recycling seems to be the best solution. The purpose of this book is 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.

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