

Recycling of polymer blends

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ABSTRACT

The growing need of multifunctional materials with tailor made properties led in the last decades to the development of novel commercial polymer blends, possessing superior physical properties with respect to traditional matrices and showing economical advantages with respect to the synthesis of new plastics. Due to the progressive increase of the environmental concerns on the management of plastic wastes, the difficulties in the sorting technologies and the limited chemical compatibility between the greatest part of polymer pairs, the technical potential of polymer blends often remains unexploited when the recycling stage is considered. In some cases, also the addition of compatibilizers to recycled blends does not represent a satisfactory solution to retain and/or tailor their properties.

The aim of this review is that to perform a critical analysis of the potentialities of polymer blends recycling. After an introductory section on the problems and the definitions of plastics recycling, some basic concepts about the physical behaviour of polymer blends are reported. The third section of the review is focused on the analysis of the mechanical recycling of polymer blends, and a general distinction between recycling techniques applied to compatible and un-compatible polymer blends is performed. In this chapter, also the analysis of the recycling potential of commingled plastics deriving from unsorted wastes and of the effect of the thermal reprocessing on the morphological and thermo-mechanical behaviour of polymer blends is reported. Considering the increasing importance of bioplastics in the modern society, the fourth chapter of this review is focused on the mechanical and chemical recycling of blends containing bioplastics, with particular attention to polylactic acid (PLA) and thermoplastic starch (TPS) based blends. The key aspects of the recycling technologies applied to polymer blends and the future perspectives are summarized in the last section of the review.

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1. Recycling of plastics

Due to their chemical stability, versatility, lightness and limited cost with respect to other classes of materials (i.e. metals and ceramics), in the last decades polymers have found a widespread application in many technological fields, such as construction, electronics, packaging and health care. The worldwide plastics production in 2017 amounted to 354 million tons, and about 26% of the polymers have been produced in China [1]. The cumulative production of polymers from 1950 to 2015 was about 7800 million tons, and considering a recycling rate as low as 14%, in the near future we will probably have to co-exist with 26,000 million tons of plastics [2]. Because of the evident mismatch between the long time required for the degradation of traditional polymers and the short service life of plastic products, severe environmental

damages to ecosystem and human health could be easily expected [3]. The wide variety of organic substances and the elevated concentration of heavy metals within commercial polymer matrices will lead in the near future to an intense pollution of soil and water [4–7]. The development of standardized methodologies for the evaluation of the environmental impact of materials and processes, like the life cycle assessment (LCA), clearly evidences that the replacement of virgin plastics with recycled ones could be beneficial both from an economical and environmental point of view [8].

Basically, three different kinds of mixtures can be detected in plastics wastes, i.e. municipal solid waste (MSW), waste electric and electronic equipment (WEEE) and automobile shredder residue (ASR). It is thus clear that the composition of the mixed waste is characterized by an elevated variability, and that its complexity increases if a wider source is considered [9]. As shown in Fig. 1, mixed plastic waste is generally constituted by polyethylene (PE), polyvinylchloride (PVC), polypropylene (PP), polystyrene (PS),

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List of acronyms

ABS	Acrylonitrile butadiene styrene
ASR	Automobile shredder residue
DSC	Differential scanning calorimetry
EAA	Ethylene acrylic acid copolymer
E-GMA	Ethylene glycidyl methacrylate copolymer
EOC	Ethylene octene copolymer
EPDM	Ethylene propylene diene monomers
EPR	Ethylene propylene rubber
EVAc	Ethylene vinyl acetate copolymer
GMA	Glycidyl methacrylate
HRR	Heat release rate
HDPE	High density polyethylene
HIIPS	High impact polystyrene
LA	Lactic acid
LCA	Life cycle assessment
LS	Light scattering
LOI	Limiting oxygen index
LLDPE	Linear low density polyethylene
LDPE	Low density polyethylene
LCST	Lower critical solution temperature
MA	Maleic anhydride
HDPE-MA	Maleic anhydride grafted high density polyethylene
SEBS-MA	Maleic anhydride grafted styrene ethylene butylene styrene
MFI	Melt flow index
MSW	Municipal solid waste
PA6	Polyamide 6
PBAT	Polybutylene adipate terephthalate
PBS	Polybutylene succinate
PBT	Polybutylene terephthalate

PCL	Polycaprolactone
PC	Polycarbonate
PE	Polyethylene
PE-g-GMA	Polyethylene grafted with glycidyl methacrylate
PET	Polyethylene terephthalate
PHAs	Poly(hydroxyalkanoates)
PLA	Poly(lactic acid)
PLLA	Poly(L-lactic acid)
PMMA	Polymethylmethacrylate
PO	Polyolefins
POM	Polyoxymethylene
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinylchloride
PCW	Post consumed waste
RHF	Rice husk flour
SAN	Styrene acrylonitrile
SAG	Styrene acrylonitrile glycidyl methacrylate copolymer
SBR	Styrene butadiene rubber
SMA	Styrene maleic anhydride
SEM	Scanning electron microscopy
SANS	Small angle neutron scattering
SAXS	Small angle X-ray scattering
SBS	Styrene butadiene styrene
SEBS	Styrene ethylene butylene styrene
TPS	Thermoplastic starch
UCST	Upper critical solution temperature
VST	Vicat Softening Temperature
WEEE	Waste electric and electronic equipment
WAXS	Wide angle X-ray scattering

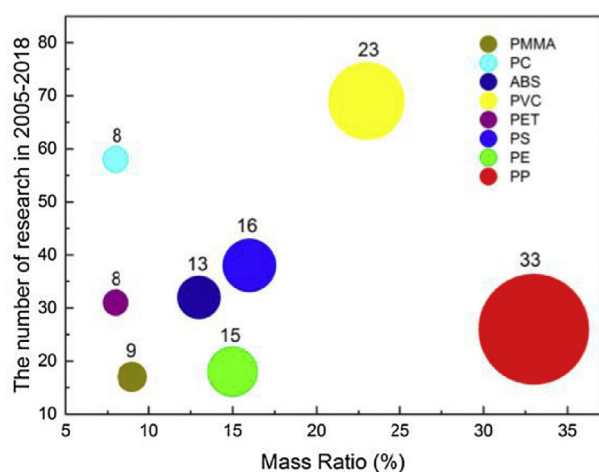


Fig. 1. Relative mass ratio of different polymer matrices in plastic waste and number of researches on these plastics in 2005–2018 (reprinted from Ref. [1] with the permission of Elsevier).

polymethylmethacrylate (PMMA), acrylonitrile butadiene styrene copolymer (ABS), polyethylene terephthalate (PET) and polycarbonate (PC). These polymer matrices have been largely investigated both by researchers and industries in the last decades.

Basically, there are two different methods to classify plastics recycling. According to the first methodology, it can be

distinguished between primary recycling (i.e. the recycled plastic has the same purpose of the virgin one), secondary recycling (i.e. the recycled plastic has a different purpose with respect to the virgin one), tertiary recycling (i.e. depolymerization of plastics to recover original monomers and/or chemicals) and quaternary recycling (energy recovery through incineration) [10]. Due to the wide variety of recycling and recovery techniques, the terminology adopted for plastics recycling is rather complex and confusing, and in Table 1 the definitions utilized in international standards are collected. In the second classification methodology, it can be distinguished between physical recycling (i.e. material recycling), chemical recycling and energy recycling [11]. In this review, physical and chemical recycling methods will be mainly considered.

For as concerns energy recycling technologies, thanks to the elevated calorific power of waste plastics (e.g. PE, 43 MJ/kg) it is possible to recover large amounts of thermal and electric power through their incineration. This technique could represent a valuable alternative to landfilling to dispose large amounts of mixed waste [12]. The main drawbacks related to an uncontrolled

Table 1

Terms used for plastics recycling and recovery (adapted from Ref. [10]).

ASTM D5033 definitions	equivalent ISO 15270 definitions	other equivalent terms
primary recycling	mechanical recycling	closed-loop recycling
secondary recycling	mechanical recycling	downgrading
tertiary recycling	chemical recycling	feedstock recycling
quaternary recycling	energy recovery	valorization

incineration and/or open burning operations are represented by dangerous emissions of greenhouse gases, heavy metals, dioxins, polychlorinated dibenzo-p-dioxins and dibenzofurans [13]. Moreover, energy recycling of plastics should be based on well consolidated separation technologies, as large fluctuations in the composition of the feedstock and wrong sorting operations could lead to variable heating output and to the risk of corrosion of the recycling plant [14].

Chemical recycling consists in the depolymerization of the polymer macromolecules in lower molecular weight fractions (i.e. oligomers and monomers). Thanks to different processes (i.e. hydrolysis, glycolysis, pyrolysis, gasification, ammonolysis and hydrogenation), it is possible to recover valuable chemicals and raw materials. Nevertheless, considering that the composition of the reaction products can change by using different plastic mixtures [15] and that every chemical conversion system is unique due to the complex composition of waste plastics [16–21], even for this technology the availability of a feedstock with constant formulation is a fundamental requirement to standardize operating conditions and to obtain monomers with elevated purity [16,22].

Physical recycling is probably the most diffused technology, and it consists in the mechanical reprocessing of waste plastics, without any chemical reaction. While this method can be potentially applied to all thermoplastic matrices (like PE, PP and PET), it can not be used to recover thermosetting polymers (like epoxy or unsaturated polyester resins), because of their crosslinked nature. The same limit is present also in the elastomers, and the EU Directive on Landfill of Waste (1999/31/EC), which banned the landfilling of waste tyres, led to a growing recycling activity of post consumed car tyres to re-manufacture other products [10]. In a close loop recycling process the recycled products have the same purpose and similar chemical composition with respect to the virgin ones. On the other hand, when an open loop recycling process is considered, the composition of plastics mixtures could be rather complex, and problems of chemical incompatibility and of physical inhomogeneity of different plastics may arise. As an example, PET becomes brittle and yellow when it is blended with a small concentration of PVC, as molten PVC, at the high temperature required to reprocess PET, will degrade the PET resin due to the evolution of hydrochloric acid gas. In another case, PE shows a brittle behaviour when it is contaminated by small amounts of PP [15,23]. For instance, PET in a reprocessed PVC will form solid lumps of undispersed crystalline PET, causing a strong deterioration of the technical and the economical value of the recycled products. In many cases (e.g. multi-layer plastic components) the addition of recovered plastics to the virgin ones will lead to a deterioration of some functional properties, like colour, optical clarity or mechanical strength [10].

It is therefore clear that the growing demand of polymer blends in the modern plastic market could represent an emerging problem in the physical recycling of post consumed recycled products, and only innovative and tailor made separation techniques will allow the attainment of plastic recyclates with suitable properties. Also the problem of the degradation of the properties upon multiple thermal re-processing of plastics waste should be taken into account [24,25], as its complexity depends on the polymer species and on the adopted processing parameters [26–30]. Therefore, separation represents one of the crucial steps in plastic recycling, as it can overcome the drawbacks related to the recycling of plastic mixtures, enhancing thus the economical value of the secondary products. There are different technologies to perform the selective separation of the different plastic families: manual sorting, density separation [31,32], dissolution sorting [33], biodegradation [34], spectroscopic separation [35], electrostatic sorting [36,37], supercritical separation [38] and selective flotation [39]. Nowadays,

manual sorting is often replaced by modern automated separation techniques [40]. In order to overcome the economic and environmental problems due to the need of separately compounding each plastic type, the possibility of directly recycling them seems to be the most attractive option [41]. In order to overcome the deterioration of the performances caused by the incompatibility of the different plastic types, the development of innovative compatibilizers is particularly interesting both from an industrial and academic point of view. In fact, it has to be considered that about the 85% by volume of the worldwide plastic production is constituted by only four kinds of thermoplastics, i.e. PE, PP, PVC and PS [42], and the interest is thus focused on the investigation of the role compatibilizers in polymer blends based on these matrices [43]. However, only few investigations have been devoted up to now to the systematic evaluation of the role of compatibilizers for recycled blends of these resins [44–46].

2. Polymer blends

Even if the interest on polymer blends is continuously increasing, the history of the polymer alloys is rather long and connected with the development of the different polymer matrices. In fact, the possibility to blend two or more matrices can lead to the development of novel polymers with tailor made properties, different from those of the constituents, overcoming thus the problems due to the synthesis of novel polymer species [47]. In other words, with polymer blends it is possible to obtain materials with different combinations of properties, with economical advantages over the development of new matrices [48,49]. As already seen in Chapter 1, a common drawback of this approach is represented by the fact that often immiscible and incompatible blends result. They are generally characterized by coarse particles of the minority component with inhomogeneous distribution and bad adhesion with the surrounding matrix. Compatibilization is thus necessary to tailor the interfacial interaction in such these blends, reducing the interfacial tension coefficient and obtaining thus the required microstructure [50,51].

When the mixture of two different amorphous polymer matrices is considered, a homogeneous mixture at the molecular level or a heterogeneous blend with two distinct phases can be formed. In literature, it is possible to find different terms to define the miscibility conditions of these blends. According to the terminology used by Utracki [52], a miscible polymer blend is constituted by a mixture of two or more amorphous matrices that present an homogeneity up to the molecular level, that satisfies the thermodynamic conditions of miscible multicomponent systems. On the contrary, an immiscible blend does not satisfy thermodynamic phase stability conditions. A compatible blend is relative to a polymer mixture that is optically homogeneous, with better properties with respect to their constituents, that could be commercially exploited. The conditions of the equilibrium phase behaviour of polymer blends, according to which a blend can be defined miscible, are reported in Equations (1) and (2) [53,54]:

$$\Delta G_{mix} = \Delta H_{mix} - T \cdot \Delta S_{mix} < 0 \quad (1)$$

$$\mu'_i = \mu''_i = 1, 2, \dots, n \quad (2)$$

where ΔG_{mix} , ΔH_{mix} , and ΔS_{mix} are respectively the Gibbs energy, enthalpy and entropy of mixing of a blend constituted by i components, while μ'_i and μ''_i represent the chemical potentials of the constituent i in the phase μ' and μ'' . In an incompressible polymer blend, the expression of the phase stability reported in Equation (3) can be derived:

$$\frac{1}{N_1 v_1} + \frac{1}{N_2 v_2} - 2\chi_{12} \geq 0 \quad (3)$$

where N_1, N_2 are the numbers of segments of polymer 1 or 2, v_1 and v_2 are the volume concentrations of polymer 1 and 2, and χ_{12} is the interaction parameter between the two constituents. The first and second terms on the left-hand side of Equation (3), that represent the entropy contribution supporting miscibility of polymers, tend to zero ($N_1, N_2 \gg 1$), and the miscibility is thus regulated by the enthalpy of mixing, represented by the interaction parameter χ_{12} . In other words, for non-polar polymers with elevated molecular weight, a positive value of χ_{12} is responsible of a very poor miscibility, while a negative value of χ_{12} leads to a homogeneous polymer blend. For non polar polymers, the values of the interaction parameter can be found in literature or determined through the expression reported in Equation (4), knowing the solubility parameters (δ_1 and δ_2) of the constituents [49]:

$$\chi_{12} \approx (\delta_1 - \delta_2)^2 \quad (4)$$

Considering that the values of χ_{12} strongly depend by the temperature, it is possible to determine the phase diagram of the blends and to define binodal and spinodal curves, reported in Fig. 2 [55]. Below the spinodal curve, it is possible to detect the area of instability of the blend, and in this case phase separation is controlled by a spinodal mechanism. The metastable region lies between spinodal and binodal curves, and in this situation phase separation is controlled by a nucleation mechanism. The tangent point of binodal and spinodal curves is defined as critical point and, as represented in Fig. 2, it is possible to detect the upper critical solution temperature (UCST) and the lower critical solution temperature (LCST). A detailed description of these curves can be found in the review of Horak et al. [49], but it is out of the main scope of this review.

On the basis of thermodynamic stability conditions, immiscible blends prepared through simple mixing are characterized by an evident separation tendency, leading to the formation of a microstructure characterized by coarse domains of the minority component having limited interfacial adhesion with the surrounding matrix. Consequently, the mechanical performances of the resulting material will be rather low. In order to improve the end-use properties of the resulting blend, it is necessary to stabilize the microstructure, obtaining thus a finer phase dispersion and a

higher adhesion between the polymer phases through a decrease of the interfacial tension. In this sense, compatibilization is the creation of physical or chemical bonds between the blend phases through the addition of a component, called compatibilizer [56]. Basically there are two methods, i.e. (i) insertion of block or graft copolymers and (ii) reactive compatibilization, that can be applied for the compatibilization of immiscible blends [49].

Block or graft copolymers are constituted by segments that are miscible with their respective blend constituents, and that are mainly localized in the interfacial region of the blends. In this way, these segments are able to stabilize the resulting morphology [57], avoiding the coalescence of the domains of the minority component and reducing the interfacial tension (see Figure 3(a-b)). This morphology stabilization is thus able to improve the physical properties of the resulting blend [58]. It is also clear that the morphological behaviour and the performances of the resulting blends will be strongly dependent by other factors, such as the adopted processing conditions, the relative concentration of the blend constituents and the copolymer structure [49].

In the reactive compatibilization method, graft or block copolymers used as compatibilizers are directly generated in situ during melt blending. The resulting copolymers can be synthesized at the blend interface through chemical reactions between properly functionalized polymers, linking thus immiscible constituents with covalent or ionic bonds. In this way, it is possible to decrease the size of the dispersed phase and enhance the interfacial adhesion. For instance, maleic anhydride-grafted PP, PE, ethylene propylene rubber (EPR), ethylene propylene diene monomers (EPDM), styrene ethylene butylene styrene (SEBS) or ABS are able to react with polymers with aminic functionalities, leading to an effective compatibilization effect [59,60].

At a general level five different techniques, i.e. melt mixing, solution blending, latex mixing, partial block or graft copolymerization and synthesis of interpenetrating polymer networks, can be identified for the processing of polymer blends. Practically speaking, melt mixing is the most diffused technology for the production (and the recycling) of polymer blends, and according to this technique the blend constituents are mixed at the molten state through extruders or melt compounders. This method is preferred over the other ones because of the use of well-defined components and of the versatility of the mixing devices, as the same equipment can be used to prepare a wide variety of polymer blends. On the other hand, this technology implies an elevated energy consumption, and it is generally unsuitable to perform the chemical modification of the blend constituents [61]. Solution blending is the preferred method at the laboratory scale, but this technique requires the identification of a common solvent for the blend components. Moreover, with this method it is necessary to recover big quantities of organic and harmful solvents. At the industrial level, this technique is mainly applied for the production of paints, surface layers and thin membranes [49].

A representative example of morphology evolution for a PLA/polybutylene adipate terephthalate (PBAT) blend at different relative contents is represented in Fig. 4 [62]. In immiscible polymers with a limited concentration of the second phase, particles of the minority component are dispersed within the matrix of the primary phase. Increasing the concentration of the second phase, a partially continuous structure of the secondary component is formed, and with a further increase of its volume fraction a co-continuous structure is generated. When the phase inversion occurs, the minority component becomes the matrix and the primary polymer the dispersed phase. In some cases, the co-continuous morphology could be replaced by a droplet-within-droplet (i.e. salami-like) microstructure [63] or by a ribbon like or stratified morphology [64].

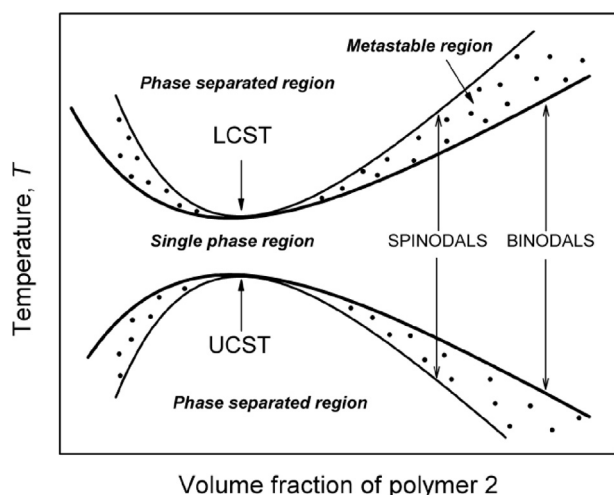


Fig. 2. An example of the typical phase diagram in a polymer blend (reprinted from Ref. [55] with the permission of John Wiley and Sons).

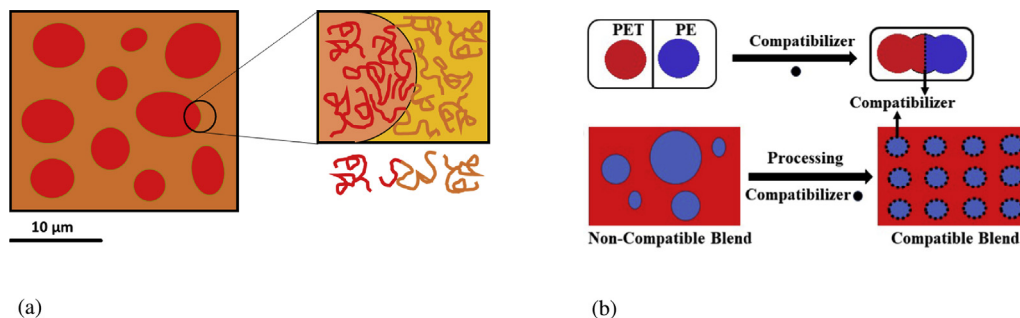


Fig. 3. (a) Position of a diblock copolymer at the interface of a polymer blend and (b) role of compatibilizer in a polymer blend (adapted from Ref. [58] with the permission of Elsevier).

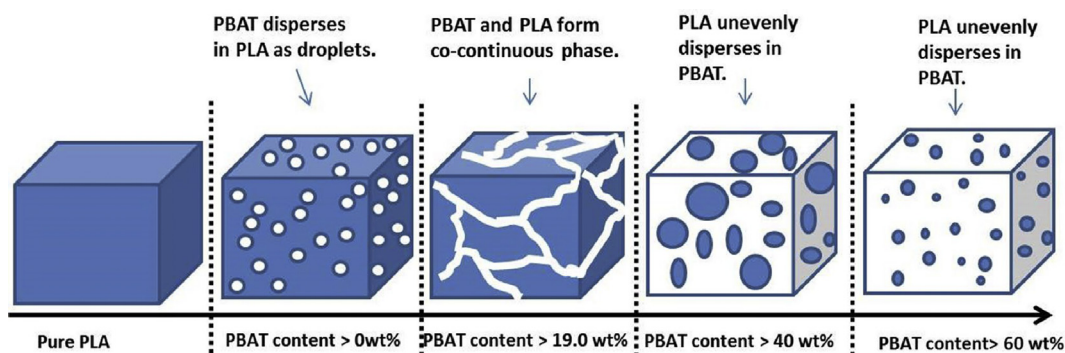


Fig. 4. Evolution of the phase structure as a function of the relative composition in a PLA/PBAT blend (reprinted from Ref. [62] with the permission of Springer Nature).

If the final performances of a blend are closely related to its morphology, also the crystallinity and the supermolecular structure of the components should be taken into account. The most widely utilized technique to investigate the morphological aspects of a blend is thus the electron microscopy. In particular, scanning electron microscopy (SEM) can be utilized for the determination of the size and the shape of the particles in the blend, to assess the adhesion conditions between the blend constituents, and to follow the evolution of the microstructure applying different processing parameters. However, the investigation of the properties of polymer blends is a very complex issue, and in many cases it is better to combine different techniques, like wide angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS), small angle neutron scattering (SANS), light scattering (LS) and differential scanning calorimetry (DSC) [49]. In many cases, the application of reliable models to predict the physical properties of a blend represents a desired option to save time and costs during the first phases of a blend development. Therefore, the application of theoretical models and simulations in the design and the structural analysis of blends has strongly increased in the last years, even if it cannot fully replace the experimental activity on these materials [48].

As previously reported in Chapter 1, polymer blending could be an attractive possibility in the future recycling technology, as it could allow to overcome the problems of sorting mixed plastics through the direct processing, with or without the addition of compatibilizers [65,66]. In fact, sorting of waste plastics could be expensive, but it can result in recyclates with good quality, while reprocessing of unsorted polymers is rather inexpensive, but the resulting products could have limited properties.

However, when the possibility of recycling polymer blends and/or mixed plastics waste is considered, the durability and environmental stability aspects of these materials should be

analyzed. In fact, recycling of polymer blends can lead to additional challenges, related to the fact that the “starting” blend could be degraded (i.e. photooxidized, thermally degraded, partially biodegraded, etc.). Moreover, the degradation behaviour of the blends constituents upon reprocessing is influenced by the presence of other components, like fillers [67]. This concern is even more important when biodegradable polymer blends are considered, with or without the addition of compatibilizers [68]. In particular, the photo-oxidation of polymer blends is a very challenging issue, since it is determined not only by the photo-oxidation kinetics of the two constituents, but also by the reactions between the degradation products of the two components, as well as the reactions between the degradation products of each polymer with the macromolecules of the other components [69,70]. Moreover, both blends and nanocomposites are often compatibilized with a third component, in order to improve the miscibility between the different phases [71–73]. In this case, the presence of this component can affect the photo-oxidative degradation of the uncompatibilized material [74–76]. For instance, in a recent paper of Mistretta et al. polymer blend nanocomposites made of low density polyethylene and polyamide 6 have been compatibilized with a maleic anhydride grafted SEBS copolymer and a glycidylmethacrylate-ethylene copolymer [77]. The blends were processed through film blowing, in order to investigate the influence of the orientation on the photo-oxidation of the resulting materials. Both compatibilizers significantly improved the photo-resistance of the blends, while the improvement in the nanocomposites was less evident, since the photo-oxidation rate was mainly dependent by the clay concentration. On the other hand, the mechanical performances of the resulting materials were marginally affected by the addition of the compatibilizers or by possible changes in the morphology.

3. Polymer blends recycling

In the previous chapters, it has been shown that the worldwide plastic wastes generation represents a heavy problem for the modern society both from a biological and environmental point of view, and that recycling could be an effective answer to this problem [1,2]. Polymer blends are generally characterized by good processability and versatile properties, therefore their recycling is advisable. However, recycled plastics should be often upgraded, and in the most cases this problem is considered in terms of chemistry, rather than in terms of the selection of the most suitable processing conditions [78]. The conversion of waste plastics in polymer blends could represent an interesting possibility to satisfy the technical requirements of specific industrial sectors. Generally, polymer alloys from waste polymers can be prepared following four different strategies [78]:

- use of synthetic commodity matrices like PE, PP, etc.
- modification of synthetic polymers through the introduction of suitable functionalities.
- use of biodegradable polymers, like PLA, TPS and poly(-hydroxyalkanoates) (PHAs), in combination with traditional plastics.
- preparation of blends through novel tailor-make hydrolyzable structures, like polyesters, polyanhydrides and polycarbonates.

In many cases, the recycling of polymer blends requires the regeneration of the pristine morphology and the general re-stabilization of the system. This could be obtained through adequate mixing operations and to a re-compatibilization of the blend. As in the preparation of the original polymer mixture, also in recycling operations it is important to prepare alloys with suitable, stable and reproducible performances. In this sense, re-compatibilization allows to obtain the original morphology of the blend and to provide a good interfacial adhesion between the constituents. In many cases, it is also necessary to modify the impact properties of the resulting alloy, in order to balance the negative effect played by the possible contamination by other polymers and by the degradation during processing of less stable compatibilizers and impact modifiers [79]. According to the classification of Utracki [79], four categories of recyclable polymeric mixtures can be distinguished:

- blends constituted by polymers belonging to the same chemical family and thus having similar chemical structure, like styrenics, polyolefins, polyesters, etc. For such these matrices, a limited compatibilization is generally adopted.
- blends constituted by commingled plastics belonging to different chemical families, like alloys of polyolefins (PO) with polyamides or polyesters, or mixtures comprising PO, PS, PVC and technopolymers. For these materials, compatibilization and impact modification are often required.
- recyclable polymer blends, in which it is important to regenerate the pristine morphology of the blends, also through re-compounding, re-compatibilization and re-stabilization.
- blends in which an extensive re-compatibilization is needed.

In the next paragraphs, these four groups of recyclable polymer blends will be analyzed, providing also some examples taken from literature. In this review, only the mechanical recycling of polymer blends will be considered, as it is the most established recycling technology for alloys constituted by petrochemical polymers. In the case of polymer blends in which bioplastics are involved, also chemical recycling methods will be considered (see Chapter 4.2).

3.1. Recycling of blends with limited compatibilization

Recycled polymer blends with suitable physical properties can be obtained without compatibilization in the following cases [79]:

- recycling polymer constituents that have a good miscibility, like PP with limited quantities of linear low density polyethylene (LLDPE), PS with styrenic copolymers, etc.
- recycling commingled plastics having similar chemical structure, like recycled resins with virgin ones, LLDPE with low density polyethylene (LDPE), metallocene PO with Ziegler-Natta PO, etc.
- recycling blends in which the concentration of the dispersed phase is below 10 vol%.
- recycling blends with co-continuous morphology.
- recycling blends to develop materials to be utilized only for aesthetic (and not structural) purposes.

Considering that large part of the plastic waste is constituted by polyolefins, particular attention should be given to recycled blends constituted by PE and PP.

In a paper of Taufiq et al. [80], the effect of the processing temperature on the mechanical performances and the morphology of a recycled PP/PE blend deriving from rejected-unused disposable diapers was studied. At this aim, a PP/PE (70/30 wt%) mixture was compounded through an internal mixer at 180 °C, the compounds were then crushed and compression moulded at three different temperatures (i.e. 180 °C, 190 °C and 200 °C). In this work, also virgin PP and LLDPE were considered for comparison. The stress at break of the recycled blend (r-PP/PE) was reduced from 9.4 MPa to 8.3 MPa increasing the processing temperature from 180 °C to 200 °C, and the same effect was also detected in the virgin blend. The observed decrease was attributed to the degradation of polymer chains caused by the higher moulding temperature. In the same way, also the elastic modulus of r-PP/PE decreased from 285 MPa to 226 MPa increasing the processing temperature. In Fig. 5a the strain at maximum load for r-PP/PE and virgin (v-PP/PE) blends is reported, and it can be noticed an increase from 3.3% to 17.2% passing from 180 °C to 200 °C, and a similar trend was also detected in v-PP/PE blend. This improvement was attributed to the better microstructural homogeneity that can be reached at higher compounding temperatures, as it can be observed in SEM micrographs reported in Fig. 5(b-c).

In another example, PP recovered from automotive interior parts (clips, buttons, seat-belt buckles, etc.) was blended with polyoxymethylene (POM) at concentrations up to 15 wt%. It was shown that the addition of POM improved the processability of the material and also the elastic modulus (up to 12%), without negatively affecting the stress at break [81].

It has to be taken into account that also the mixture of two different PE resins obtained from different sources could be intended as a polymer blend, and in some cases polyethylenes synthesized with different catalysts or containing different comonomers could be immiscible. Considering that also miscible blends of PE matrices differing for the molecular weight could have problems of homogeneity, virgin PE is often added to recycled ones to improve the physical properties of the resulting materials [79]. The elastic modulus (E) and yield stress (σ_y) of miscible or well-compatibilized blends can be predicted through the rule of mixture (see Equation (5)), while the elongation at break (ϵ_b) can be determined through the inverse additivity rule, as reported in Equation (6):

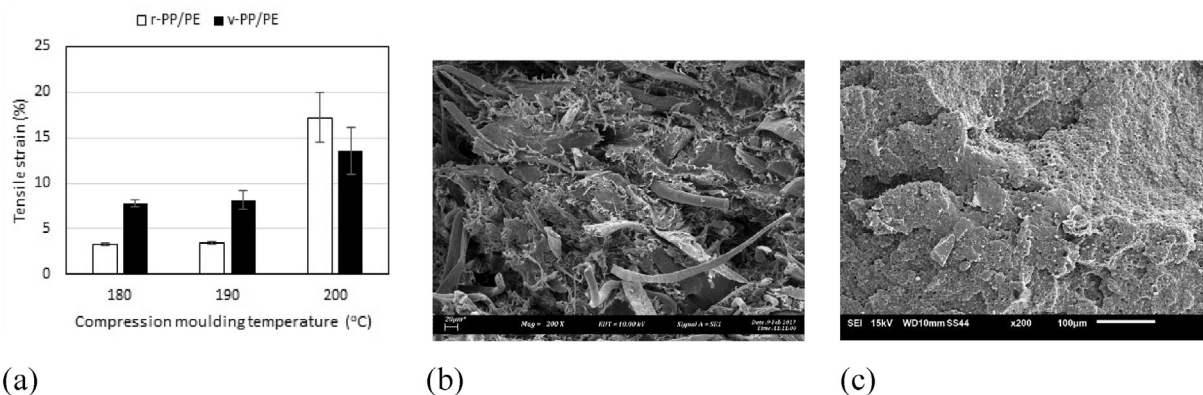


Fig. 5. (a) Tensile strain of r-PP/PE and v-PP/PE blends at different moulding temperatures. SEM micrographs of r-PP/PE blend moulded at (b) 180 °C and (c) 200 °C (reprinted from Ref. [80]).

$$Y = \varphi_1 Y_1 + \varphi_2 Y_2 \quad (5)$$

$$\frac{1}{\varepsilon_b} = \frac{\varphi_1}{\varepsilon_{b1}} + \frac{\varphi_2}{\varepsilon_{b2}} \quad (6)$$

where $Y = E, \sigma_y$ and φ_i is the volume fraction of polymer $i = 1, 2$. In literature it is possible to find several examples in which important deviations from these theoretical predictions are highlighted. For instance, when two semi-crystalline matrices (e.g. PE/PP) are blended, it has been often observed that heterogeneous nucleation phenomena, leading to a higher crystallinity and crystals with smaller size, could increase the stiffness and the strength of the resulting blends, with a positive deviation from the additivity rule. Lee et al. blended LDPE with recycled high density polyethylene (HDPE) up to a concentration of 60 wt%, adding also 0.1–1.5 wt% of zinc oxide and 0.1–2.0 wt% of glycerol mono-stearate. Thanks to heterogeneous nucleation effects, the resulting blends showed a strength increase of 50%–90% with respect to the neat LDPE [82]. On the other hand, the lack of adhesion between the phases of the blends was responsible of a strong deterioration of the strain at break. In some examples of recycled PE/PP blends, low molecular weight fractions generated by the partial degradation of the resin upon reprocessing could be localized at the interphase between PP and PE, lowering the interfacial adhesion and the failure properties of the resulting material.

Also the recycling of styrenic polymers based blends is very important from a technological point of view, as a large amount of expanded polystyrene (EPS) is actually recycled. The recycling can be performed in a close loop process, i.e. from EPS to EPS, or in an open cycle. In the latter case, recycled EPS can be upgraded through the addition of SEBS.

In a paper of Adam et al. [83], the mechanical properties of blends obtained by mixing the most important polymers present in recovered printers were investigated. Therefore, high impact polystyrene (HIPS)-90%/PS-10%, HIPS-90%/ABS-10% and HIPS-100% samples were prepared through extrusion and injection moulding, and then characterized. HIPS-90%/ABS-10% blends showed the best properties, with a yield strength of 39.0 MPa and strain at break of 46.2%, followed by HIPS-90%/PS-10%, having a σ_y value of 37.5 MPa and an ε_b of 39.1%. For the HIPS-100% sample a yield strength of 45.1 MPa and an elongation at break of 14.9% were determined, as shown in Table 2. Strain at break values were remarkably higher in the blends with PS rather than in the formulation with HIPS, with an enhancement of 24.2% of the first with respect to the latter. In the blends with HIPS σ_y was 45.1 MPa, with a difference of 3.7 MPa,

Table 2

Tensile properties of polymer blends recovered from printers (adapted from Ref. [83]).

sample	yield strength (MPa)	strain at break (%)
HIPS-90%/ABS-10%	39.0	46.2
HIPS-90%/PS-10%	37.5	39.1
HIPS-100%	45.1	14.9

due to the presence of an elastomeric part in the HIPS of the printers.

Blends of PE and PP with 30–40 wt% of recycled PS were successfully developed [79], thanks to the attainment of a stable, co-continuous morphology and to a decrease of the crystallinity degree of the PO. Regardless to the presence of contaminants (like pigments, additives and other plastics) in the PO formulation, the addition of the PS phase was responsible of a noticeable increase of the stiffness and of the yield resistance of the material. With a PS concentration of 50 wt%, a 2.5-fold increase of the modulus and a 2-fold enhancement of the stress at yield were obtained.

Garcia et al. [84] investigated the performances of polymer blends constituted by polyvinyl chloride (PVC) recovered from credit card waste and two different styrenic polymers, i.e. styrene acrylonitrile (SAN) and ABS. Both virgin and recycled styrenic matrices were considered, and the samples were prepared through melt blending and hot pressing. As reported in Fig. 6a, Vicat Softening Temperature (VST) linearly increased with the styrene copolymer concentration, and the higher increase could be obtained with the addition of SAN, probably because of its better thermal stability. For as concerns the trends of the stress at break with the relative composition of the blends, reported in Fig. 6b, it can be noticed that the introduction of virgin SAN produced a noticeable increase of the tensile strength, while the addition of the other polymers was responsible of a slight drop of this property. However, the observed decrease was not dramatic and did not limit the applicability of these blends in most industrial applications. This drop was attributed to the lack of interfacial adhesion between the different blend components. Interestingly, the elastic modulus increased with the addition of SAN, especially in the case of virgin polymers, while the introduction of recycled ABS determined an important stiffness reduction (see Fig. 6c).

Also some examples of recycling of polymer blends with other polymer matrices can be found in literature. In a paper of Zicans et al. recycled PC was compounded at the molten state with an ethylene vinyl acetate copolymer (EVAc) at different relative concentrations, in order to limit its brittleness [85]. As reported in Fig. 7, tensile strength was increased by 14% with an EVAc amount of 5 wt%, while the impact strength was enhanced by 450% through

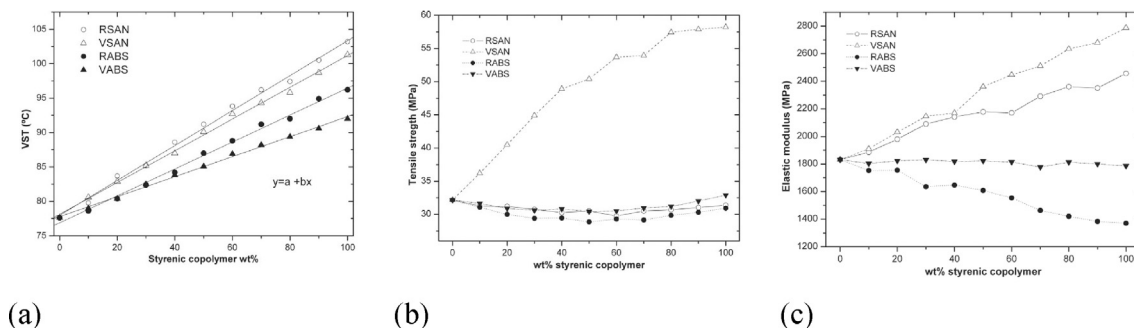


Fig. 6. Trends of (a) VST temperature, (b) tensile strength and (c) elastic modulus versus styrenic polymers concentration in recycled PVC based blends (reprinted from Ref. [84] with the permission of John Wiley and Sons).

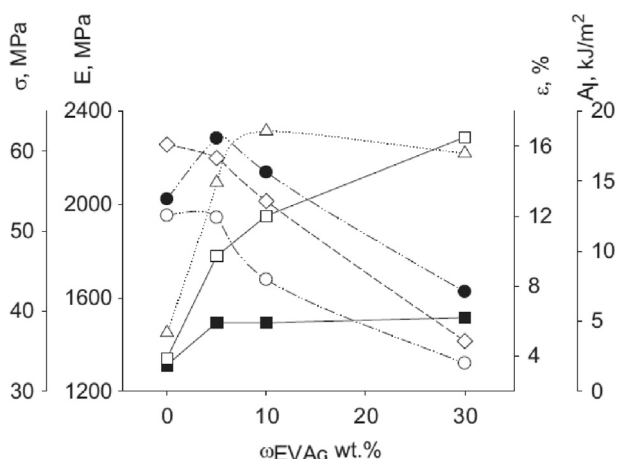


Fig. 7. Elastic modulus E (\diamond), tensile strength σ_M (\bullet), elongation at tensile strength ϵ_M (\square), tensile stress at break σ_B (\circ), elongation at break ϵ_B (\square) and Charpy impact strength A_I (\triangle) as a function of EVAc concentration in recycled PC based blends (reprinted from Ref. [85] with the permission of John Wiley and Sons).

an EVAc addition of 10 wt%. Moreover, it was noticed that the addition of nanoclay in the blend with 10 wt% of EVAc determined a further improvement of the elastic modulus, of the strength and of the creep resistance of the material.

3.2. Recycling of blends from commingled plastics

Basically speaking, the main problem in the recycling of blends constituted by commingled polymers is the presence of multiple interfaces in immiscible polymer mixtures. In a paper of Le Coroller et al. [86], thermodynamically driven polymer segregation and phase encapsulation were applied to concentrate minority phase within one of the two major phases. As reported in SEM micrograph of Fig. 8, encapsulated PS/PMMA/PC droplets located within the PP matrix could be detected in a co-continuous blend of HDPE and PP, if the HDPE/PP interface was properly compatibilized. By using the most suitable processing parameters, it was thus possible to improve the stiffness, the tensile strength and also the ductility of the resulting materials.

It was also seen that blends with polar matrices, like PVC, PC, PMMA, thermoplastic polyurethane (TPU), polyamides, polyesters, SAN, or ABS could be compatibilized through the addition of two copolymers, i.e. vinyl alcohol and anhydride. For instance, it has been observed that blends of TPU with EVAc, modified cellulose and/or polyalkylene oxide were characterized by good physical, optical and barrier properties, and they could be processed at the molten state without degradation.

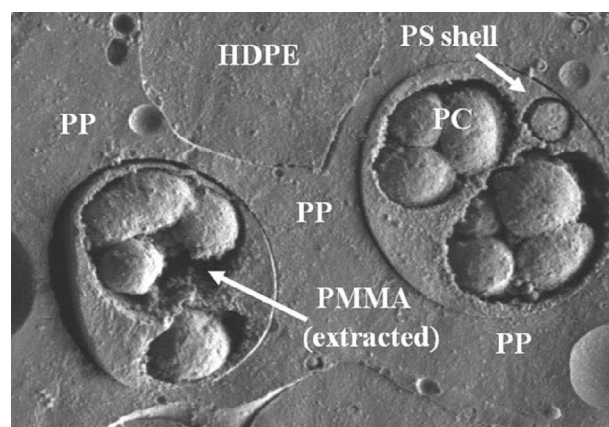


Fig. 8. SEM micrograph of HDPE/PP/PS/PMMA/PC blends after 30 min annealing with 20% EPDM. PMMA was selectively etched (reprinted from Ref. [86] with the permission of John Wiley and Sons).

In another paper, blends of recycled thermoplastics recovered from domestic and commercial waste, constituted by PE and/or PP, PS, PVC and less than 10 wt% of other thermoplastics, were compatibilized and impact modified though the addition of styrene butadiene styrene (SBS) up to 20 wt%. In order to recover the pristine light and thermo-oxidative degradation resistance, pentaerythritol ester and phosphite were added [79]. In a work of Xanthos et al. [87], commingled simulated post consumed waste (PCW), constituted by PE, PP, PVC, PET, and PS was compatibilized through the addition of maleic anhydride grafted HDPE (HDPE-MA) or styrene ethylene butylene styrene (SEBS-MA), and also glass fibers or vitrified fly ash were used as reinforcement.

The paper of Matko et al. [88] was focused on the flame retardant effect of an ammonium polyphosphate/polyurethane (APP/PU) intumescent additive in a LDPE/EVAc blend containing also rubber waste, and on the analysis of the gas evolution during the combustion of the prepared alloys. In Fig. 9(a-b) the heat release rate (HRR) and the mass loss curves of the prepared blends at different APP/PU and rubber contents are represented. Through a comparison between the flame behaviour of the neat EVAc/LDPE compound and sample 1, it could be concluded that a phosphorus amount of 1.6 wt% did not improve the UL 94 grade, the limiting oxygen index or the time to ignition. On the other hand, the maximum HRR was decreased by about 50%, the mass loss rate of the 20%, and also the time associated to the maximum HRR was enhanced by 70 s. An increase of phosphorus concentration (sample 3) was responsible of an increase in both UL 94 grade (up to V-0) and the LOI values (up to 30%), and also the time to ignition and

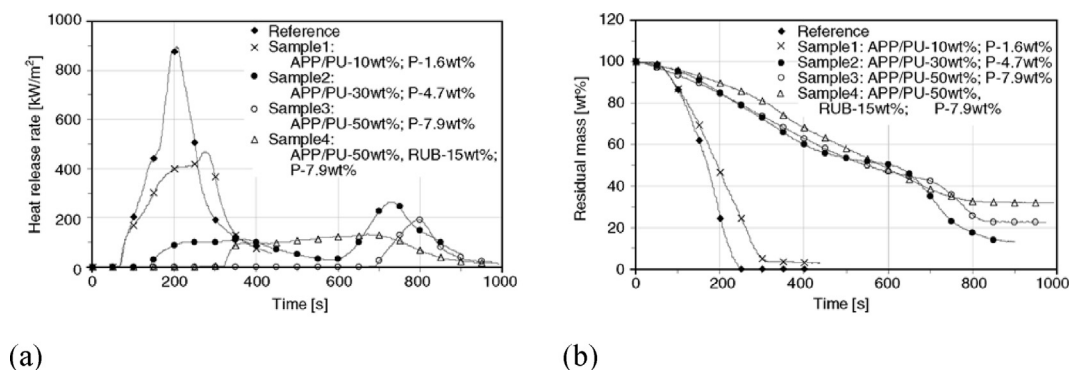


Fig. 9. (a) Heat release rate (HRR) vs. time and (b) residual mass vs. time in mass loss calorimetric measurements on LDPE/EVAc/rubber (RUB) compounds at different phosphorous (P) contents (reprinted from Ref. [88]).

mass residue were enhanced. It is also important to underline the evident reduction of the maximum HRR and of the mass loss rate values. Moreover, the introduction of waste rubber in the blends (sample 4) did not lead to a substantial variation of the LOI and UL94 values, while the maximum HRR decreased by about 30%. The evaluation of the environmental impact of the prepared blends through IR analysis of the evolved gas during the calorimetric measurements revealed that the amount of CO₂ and CO decreased with the APP/PU concentration, and that also the blend with rubber powder showed considerably reduced CO₂ and CO emissions with respect to the neat EVAc/LDPE compound.

3.3. Recyclable blends

Considering that in the plastics industry a strong need of polymer blends able to retain the desired performances upon reprocessing has been recently arisen, the evaluation of the effect of the reprocessing on the microstructural and thermo-mechanical properties of polymer mixtures is of utmost importance [79].

In order to investigate the reprocessability of virgin/recycled HDPE blends, these materials were reprocessed up to three times by extrusion moulding [89], and the performances of these materials were evaluated in terms of tensile properties and melt flow index (MFI) values. The mechanical performances of the prepared blends decreased with the recycle amount and after each reprocessing stage, even if the most sensible drop was detected after the first recycling step. The elastic modulus of virgin HDPE was noticeably affected by the introduction of recycled HDPE at concentration above 50%, because of its lower starting molecular weight and of the drop of the crystallization rate induced by the microstructural heterogeneity. For the same reasons, also the stress at break decreased up to 40% increasing the recycled HDPE amount.

In a paper of Wang et al. [90] the effect of reprocessing on the performances of polypropylene/ethylene octene copolymer (EOC) blends was studied. In this work, the EOC concentration varied up to 20 wt%, while up to 6 recycling steps (by extrusion) were applied. As shown in Fig. 10, in the PP/EOC 80/20 blend six recycling steps produced a narrower inclusions size distribution and a decrease of their size from 0.27 μ m to 0.22 μ m, associated also to a drop of their aspect ratio from 1.42 to 1.27. The observed decrease of the aspect ratio was attributed to the repeated shear and elongational flow to which EOC particles were subjected during thermal reprocessing. After six extrusion stages, an enhancement of the melt flow index (MFI), associated to a slight increase of the crystallinity, was detected. Even if the onset degradation temperature was decreased, no significant oxidation phenomena were noticed. It was thus concluded that the thermo-mechanical reprocessing of these blends caused a thermo-mechanical degradation by chain scission,

without oxidation. An increase in the concentration of EOC determined an enhancement of the MFI and of the onset degradation temperature, while applying repeated reprocessing steps both the stiffness and the yield resistance of the blend decreased. The observed decrease of the EOC domains size upon thermal reprocessing was able to stabilize the strain at break values after 3 recycling steps, while ϵ_b of neat PP continuously decreased with the reprocessing stages.

In another work [118], DSC tests were utilized to investigate the non-isothermal crystallization of polypropylene in PP/polyamide 6 (PA6) blends prepared through a single-screw extruder and with a PA6 content of 20 wt%. The resulting blends were then reprocessed under the same conditions up to ten times. As reported in Fig. 11a, the crystallization temperature (T_c) of PP was not substantially affected up to 8 extrusion steps, while a further reprocessing was responsible of a noticeable T_c increase. Interestingly, an evident increase of the crystallization rate of PP was detected upon thermal reprocessing (see Fig. 11b). The total crystallinity increased and the half-time of crystallization decreased with the processing stages applied. These effects were explained considering the thermo-oxidation or thermo-mechanical degradation phenomena that could occur on PP matrix after repeated reprocessing steps.

In a paper of Scaffaro et al. [91] virgin/post-consumed ABS blends were reprocessed and re-formed up to three times. The influence of the recycle concentration and of the reprocessing steps on the thermo-mechanical and rheological properties of the blends was investigated. The processability of the prepared mixtures did not differ to that of the virgin ABS up to two recycling stages, while in the third step a viscosity decrease, especially at elevated ABS amounts, was observed. Both the thermal and mechanical performances of the blends were decreased by the progressive addition of ABS recycle and also by increasing the number of reprocessing steps, even if the most sensitive drop was evidenced after the first recycling stage.

Considering that PC/ABS blend (CS) is one of the most popular engineering plastics, recycling and reprocessing potential of CS blend was investigated by Chiu et al. through thermal, rheological and mechanical tests on samples reprocessed up to 20 times by using a real industrial equipment [92]. The thermal degradation stability and the glass transition temperature were not substantially affected by the number of reprocessing steps, confirming the elevated stability of this blend. On the other hand, the observed increase of the stress at break (from 46.1 to 51.0 MPa) and of MFI (from 40 to 66 g/(10 min)), associated to a drop of the strain at break (from 27.2 to 11.7%) and of the impact strength (from 87.7 to 14.2 J/m), indicated that a partial chain breakage occurred during reprocessing. In order to recover the original properties, 30 wt% of virgin PC and ABS, 1.5 wt% of chain extender and 2 wt% of styrene

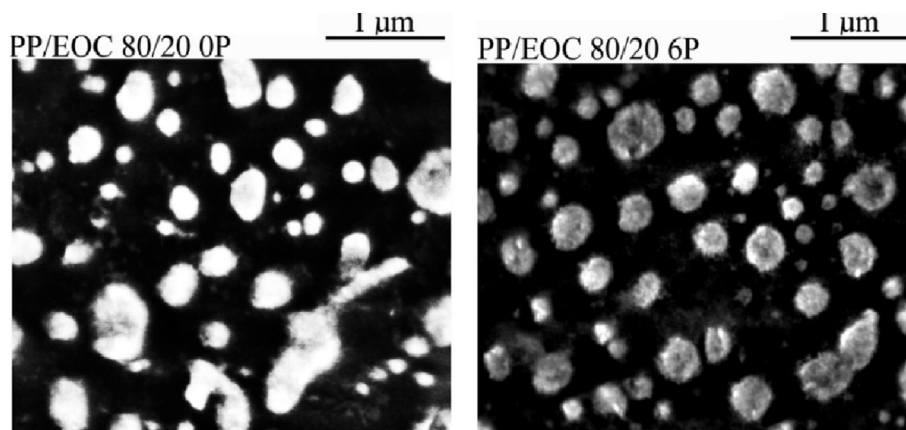


Fig. 10. SEM micrographs of non-recycled (0P) and six-times recycled (6P) PP/EOC 80/20 blends (adapted from Ref. [90] with the permission of Elsevier).

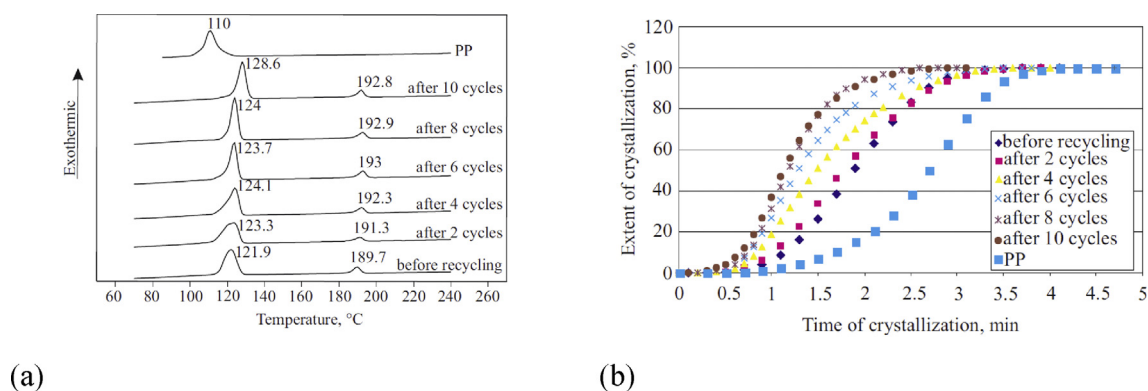


Fig. 11. (a) DSC thermograms of non-isothermal crystallization of neat PP and PP/PA6 blends and (b) extent of PP crystallization in neat PP and in PP/PA6 blends (reprinted from Ref. [118]).

maleic anhydride (SMA) were added to the CS blend reprocessed 20 times.

Ramesh et al. investigated the recyclability potential of blends constituted by PC, ABS, HIPS, recovered from waste electronic equipment plastics products, trying to improve their performances by adding virgin PC and an impact modifier [93]. After an optimization of the formulation of the blends, five reprocessing cycles at temperatures between 220 and 240 °C were performed, while the environmental stability of the recycled alloys was assessed through accelerated weathering up to 700 h. Rheological, thermal and mechanical tests on the prepared materials evidenced that both tensile and impact strength were considerably decreased upon both thermo-mechanical reprocessing and accelerated weathering, and this drop was probably due to the decrease of the molecular weight, as evidenced by rheological measurements.

In order to evaluate the retention of the properties upon recycling, blends of syndiotactic PS were prepared by adding copolymers of styrene with either maleic anhydride (MA) or glycidyl methacrylate (GMA), and elastomeric phases like SEBS, styrene butadiene rubber (SBR), SBS and EPDM. The resulting materials highlighted noticeable impact resistance and strain at break, and also the other physical properties were retained upon recycling. Moreover, also the possibility to recycle blends of poly(*p*-phenylene oxide) (PPE) with SBS was examined, by adding an antioxidant/metal deactivator. If recycled at temperatures between 250 and 350 °C, the prepared blends maintained most of their impact strength [79].

3.4. Recycling where re-compatibilization is needed

In order to reproduce the original properties of the blends, the current tendency in the recycling technology is based on the use of the same compatibilization and re-compatibilization method. In order to achieve this objective, it is clear that a complete knowledge of the composition of the recovered blends is necessary. It is well known that outside the interval of high dilution and of phase co-continuity, the greatest part of PO/PS blends are immiscible, and thus a suitable compatibilization process is required. In this sense, compatibilizers can be applied to improve the dispersion of the minority component, to retain the original morphology upon thermal reprocessing and thus to achieve the desired final properties. Among the different compatibilization systems for these blends, the most widely utilized are based on the addition of hydrogenated styrene-butadiene copolymers (like SEBS) and on the reactive radical co-grafting. Even if SEBS was successfully utilized to homogenize several PS/PO mixtures, its rather elevated cost could limit its application in many recycling processes. For this reason, a cheaper compatibilizer (like SBR) is often utilized. Other compatibilizers that could be successfully applied for PO/PS systems are styrene butadiene block copolymers, polybutylene-1 and its copolymers with ethylene, isotactic polybutene, etc. For instance, good results in terms of compatibilization were obtained on PS/PP blends by adding SEBS or PP grafted with 4 wt% styrene [79].

Considering the relevant amount of PS and PE matrices in the mixed plastics waste, Ha et al. compared the effectiveness of both SEBS and SEBS-MA in HDPE/PS blends [41]. In Fig. 12(a-c) SEM

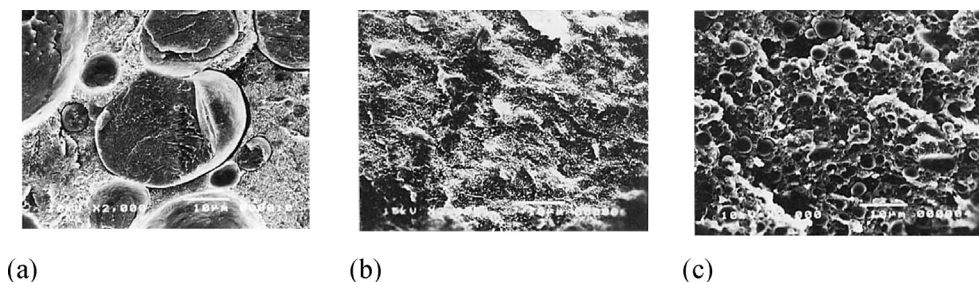


Fig. 12. SEM micrographs of (a) HDPE/PS, (b) HDPE/PS/SEBS (40/40/20), (c) HDPE/PS/SEBS-MA (40/40/20) blends (reprinted from Ref. [41] with the permission of John Wiley and Sons).

micrographs of the fracture surface of HDPE/PS blends and of the blends compatibilized with 20 wt% of SEBS and SEBS-MA are reported. It can be easily noticed that PS domains size within the HDPE matrix was considerably reduced upon the introduction of SEBS and these domains could not be easily detected, meaning that an effective compatibilization occurred. Interestingly, also the addition of maleated SEBS was able to reduce the dimension of PS domains, but not at the same extent observed for the SEBS, probably because both HDPE and PS do not possess functional groups that can specifically react with maleic anhydride.

For as concerns reactive compatibilization technique, a LLDPE matrix was recycled by adding rubber recovered from scrap tires and by using an ethylene acrylic acid copolymer (EAA). Moreover, an amine-terminated butadiene nitrile liquid rubber with a diperoxide initiator was introduced. After melt compounding and injection moulding operations, compatibilized samples highlighted a 50% increase of the tensile and impact strength [94].

The compatibilization is also important when recycled blends constituted by tecnopolymers are considered. In a paper of Tsademir et al. [95], blends of PC and ABS were extruded and compatibilized by adding two kinds of styrene isoprene styrene copolymer (SIS) at concentration up to 20 wt%. Regardless to the SIS typology, the stiffness, the hardness and the strength of the materials decreased with the SIS content, while the strain at yield and the Izod impact strength were improved. SEM images demonstrated that the presence of the compatibilizer improved the interfacial adhesion and the distribution of the dispersed phase within the matrix, explaining thus the toughening effect produced by SIS introduction in the blend. In a paper of He et al. [96], different styrene-acrylonitrile-glycidyl methacrylate (SAG) copolymers were utilized to compatibilize recycled ABS/polybutylene terephthalate (PBT) blends, produced through melt blending and batch feeding. The influence of SAG chemical composition and concentration on the microstructural, rheological and mechanical properties of the prepared mixtures was studied. It was demonstrated that through a proper selection of the processing parameters and of the blends composition it was possible to obtain recycled products with good performances, that could be applied as 3D printing feeding material.

In some cases, also fillers can be added to recycled polymer blends, in order to retain their pristine physical properties. In the papers of Chen et al. [97,98], rice husk flour (RHF) at various concentrations (from 40 up to 80 wt%) was utilized as filler of recycled HDPE/PET blends, compatibilized with an ethylene glycidyl methacrylate (E-GMA) copolymer. It was noticed that the presence of the compatibilizer improved the tensile properties (i.e. elastic modulus and stress at break) of the resulting blends, regardless to the RHF addition, thanks to a better adhesion between HDPE and PET. RHF addition led to an improvement of the tensile strength, but not for the uncompatibilized blends (see Fig. 13a). Considering that the

tensile modulus is affected by the interfacial adhesion conditions, it is evident that the presence of a stiff filler like RHF was responsible of an increase of the elastic modulus, also in not compatibilized samples (Fig. 13b). In Fig. 13c, it is evident that elongation at break of HDPE matrix was negatively affected by the presence of PET, that had an intrinsically low elongation at break. The introduction of RHF produced a further drop of ϵ_b , with an evident decrease in the ductility of the material. Even in this case, the presence of the compatibilizer helped to partially retain the elongation at break, even if this effect was less evident at elevated RHF amounts.

4. Recycling of bioplastics based blends

As in the case of pure bioplastics, also the recycling of bioplastic blends has been studied through both mechanical and chemical recycling methods. It is generally believed that blends of bio based and petro-based polymers are more sustainable than pure synthetic polymers, because part of the petro-based matrix is replaced by plastics with renewable origin [99]. Moreover, in these hybrid blends it is possible to overcome the limitations derived by the use of neat bioplastics [100].

4.1. Mechanical recycling of blends containing bioplastics

Generally speaking, PLA is characterized by some drawbacks, like a limited elongation at break and impact resistance, and a slow crystallization tendency. Moreover, it shows a low thermal degradation stability when it is processed at the molten state, especially at elevated temperature and in the presence of moisture. All these aspects limit its application in the packaging field, and impairs its recyclability [101]. In order to solve these problems, it is possible to blend PLA with traditional plastics [100]. Also thermoplastic starch has some serious drawbacks, mainly related to its limited moisture and temperature resistance. Moreover, it tends to recrystallize, producing thus a strong embrittlement of the material. Therefore, also TPS blending with non biodegradable matrices could represent an interesting solution [102]. Also blends with poly(hydroxyalkanoates) could be an attractive option to develop novel materials with a well balanced cost/performance ratio. It is possible to prepare miscible PHAs based blends through hydrogen bonding and/or donor-acceptor interactions, or immiscible blends, characterized by a better biodegradability with respect to the miscible ones. In some cases, it could be also possible to successfully prepare blends of PHAs with other biodegradable polymers, showing a better biodegradability than the neat PHAs [103]. Beside man-made bioplastic blends, it has to be considered that the increasing presence of biopolymers in the plastics waste stream renders the recyclability of bioplastics based blends particularly important both for the academia and for the plastic industry.

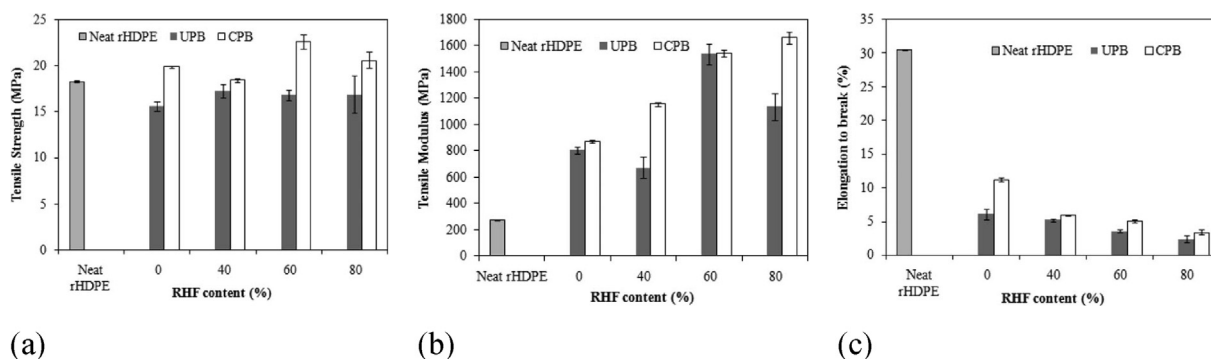


Fig. 13. (a) Tensile strength, (b) tensile modulus and (c) elongation to break of uncompatibilized (UPB) and compatibilized (CPB) HDPE/PET blends at different RHF amounts (reprinted from Ref. [97] with the permission of John Wiley and Sons).

PLA/PS blends are interesting from a commercial point of view, as they are cost-competitive and their properties are intermediate between those of PLA and PS. For this reason, they can find application in biomedical and in packaging sector. Moreover, the degradability of PS is increased by the presence of PLA [104]. Therefore, the investigation of the recyclability of these products and of the influence of multiple reprocessing steps in PLA/PS alloys is a key issue to evaluate the possibility of reusing post consumed PLA/PS waste.

Hamad et al. [105] tried to characterize the reprocessability conditions in PLA/PS blends. Due to the reduction of the molecular weight of the blend constituents with the processing steps, the melt viscosity of PLA/PS blends decreased in a uniform and continuous way (see Fig. 14(a-b)). While tensile modulus was not significantly influenced by the thermal reprocessing, multiple extrusion in the 50/50 wt% PLA/PS blend determined an evident decrease of the failure properties of the material. After four processing steps, an elastic modulus drop of 26% was detected, while a larger decrease was observed both for the stress at break (79%) and for the strain at break (73%).

Scaffaro et al. investigated the possibility to recycle PLA by adding two different organic elastomers as impact modifiers [63]. The addition of small amounts of elastomers (up to 15 wt%) determined a general improvement of the mechanical properties. Even if most of the performances were retained after three recycling steps, multiple reprocessing was responsible of a noticeable decrease of the impact strength (60%). The decrease of the molecular weight promoted by the recycling stages determined a change in the crystallinity degree, leading thus to stiffer materials.

A recently paper published by La Mantia et al. [106] demonstrated that the addition of limited amounts of PLA (less than 5 wt

%) in PET waste could strongly influence its rheological properties in non-isothermal elongational flow conditions (i.e. in spinning and blow moulding processing). The mechanical performances of the resulting blends were influenced only in some circumstances, while their thermal stability was not substantially affected.

Yarahmadi et al. [107] investigated the durability of reprocessed PLA based blends. At this aim, commercial PLA/PC and PLA/PE blends were considered, and post-processing and accelerated weathering conditions were simulated. The stiffness of the prepared materials was not influenced by multiple processing, while the strain at break was significantly affected. PLA/HDPE blends showed increased ϵ_b with the number of extrusions, while the opposite trend was detected in reprocessed PLA/PC samples. If the thermo-mechanical degradation due to the reprocessing could lead to chain scission and to a decrease of the strain at break, it could also happen that multiple recycling steps improve the homogeneity of the dispersed phase, leading thus to the formation of smaller domains size, to a lower interfacial tension and to an enhancement of the elongation at break. Fig. 15 compares the fracture surfaces of PLA/HDPE blends after one and after six extrusion steps. It can be seen that in the blend extruded once the mean dimension of the domains was between 1.0 and 1.4 μm , while after six extrusion steps a substantial size reduction in the range 0.5–0.9 μm could be observed. This means that thermal reprocessing in PLA/HDPE blend was responsible of a better homogeneity of the dispersed phase and thus to higher failure properties, while in PLA/PC blends thermal degradation upon reprocessing and the consequent chain scission determined a decrease in the elongation at break.

Also blends with TPS and petro-based polymers are interesting both for an environmental, mechanical and economical point of view. In fact, it was demonstrated that in LLDPE/TPS blends the

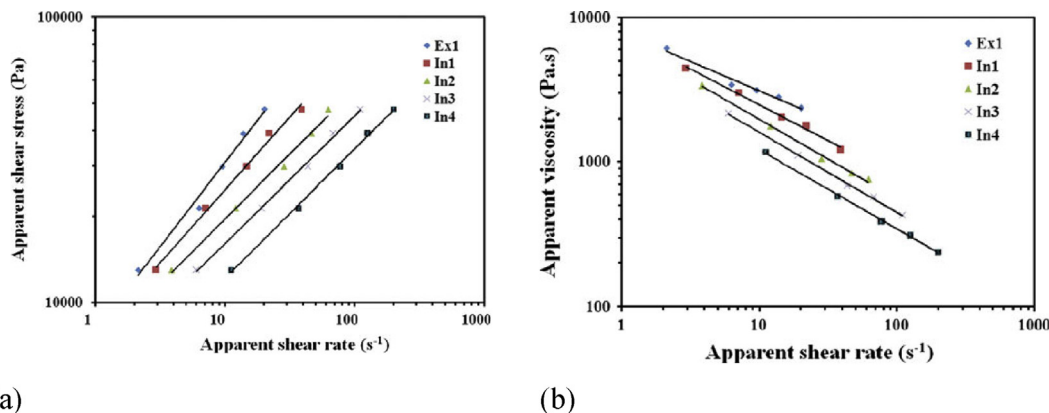


Fig. 14. (a) Flow curves and (b) apparent viscosity curves of the PLA/PS melts at 165 °C (reprinted from Ref. [105] with the permission of Springer Nature).

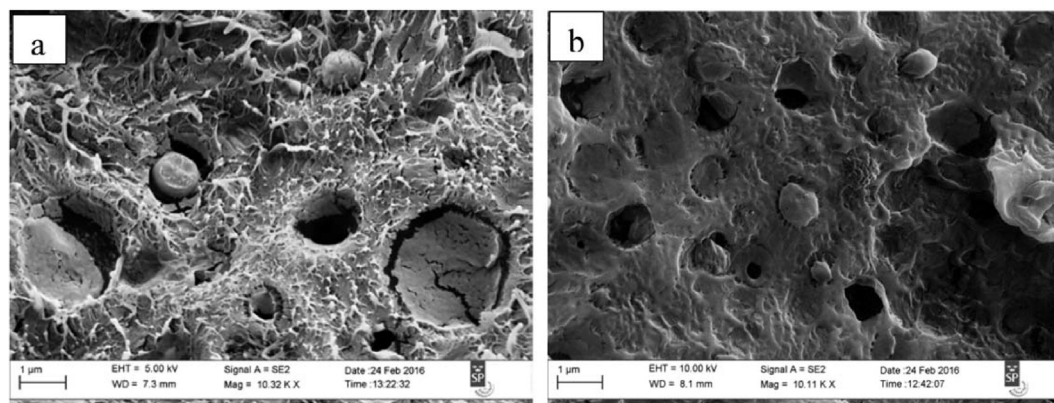


Fig. 15. Representative SEM images of cryofractured surfaces of (a) PLA/HDPE extruded once and (b) PLA/HDPE extruded six times (reprinted from Ref. [107] with the permission of John Wiley and Sons).

material could be easily bio-degraded, if the PE constituent was properly modified to facilitate its disintegration [100]. Therefore, also the analysis of the recyclability conditions in these blends could be of utmost importance [108]. Rosa and Pedroso investigated the properties of LDPE (both virgin and reprocessed) blended with corn starch through extrusion. In these blends, polyethylene grafted with glycidyl methacrylate (PE-g-GMA) was considered as compatibilizer [109]. The introduction of starch in LDPE determined a reduction of the MFI and an increase of the elastic modulus, while the properties at break were decreased, especially when a TPS concentration of 40–50 wt% was utilized. Interestingly, the introduction of the compatibilizer at a concentration of 3 wt% was responsible of an increase of both MFI and tensile strength.

Peres et al. investigated the influence of reprocessing (i.e. repeated extrusions) on the morphological and mechanical properties of LDPE/TPS blends, in comparison with those of the neat LDPE matrix [110]. It was highlighted that the thermal reprocessing of the prepared blends led to a reduction of the TPS domains within the LDPE matrix, without affecting the processability and the mechanical properties of the material (see Table 3).

In the paper of Oliveira et al. the influence of the thermo-mechanical reprocessing in PP/PBAT/TPS blends was studied. At this aim, the prepared materials were subjected up to seven recycling steps through a single-screw extruder [111,112]. As reported in Fig. 16, the morphology of the prepared blends was characterized by PBAT/TPS spheroids within the PP matrix, and the presence of voids indicated a weak interfacial interaction between the blend components. Increasing the number of extrusion cycles, a drop in the number and the size of PBAT/TPS domains and an improvement of the interfacial interaction could be detected, meaning that the shear stress associated to the thermo-mechanical recycling was able to improve the miscibility between the phases. The tensile properties of the reprocessed blends (i.e. elastic modulus and yield resistance) were thus improved.

La Mantia et al. analyzed the recyclability of a starch/polycaprolactone (PCL) blends, reprocessed several times upon

extrusion [113]. Rheological and mechanical tests on these blends revealed that the properties of the material were retained, and only a slight drop could be detected after five extrusions. This result was explained as a balance between two concurring effects arising during the reprocessing, i.e. the decrease of the molecular weight due to the thermomechanical degradation (especially in the PCL phase) and the formation of some crosslinked structures in the starch component.

However, a complete comprehension of the potential of bioplastic blends and of the recyclability conditions of these materials is not yet achieved, and the importance of these materials will continue to grow, due to the increasing concentration of biopolymers in the waste stream.

4.2. Chemical recycling of blends containing bioplastics

Chemical recycling of bioplastics is a very important alternative to common mechanical recycling, as it can allow to overcome some limitations of the thermal reprocessing, like the need of a fine sorting and the degradation of polymer matrices at elevated temperatures. For instance, PLA and PET can not be easily separated by traditional physical methods based on density, because of their similar specific weight [114]. Moreover, it was shown that even a limited concentration of PLA in the PET recovered stream (i.e. around 0.1 wt%) could represent a contamination able to impair the final properties of PET. In order to be able to effectively separate PLA from PET, near infrared technology associated to other expensive techniques should be utilized, increasing thus the cost of the recycling operations. In this case, alternative methods like selective chemical recycling could represent a valuable solution [100].

Tsuneizumi et al. developed two techniques for the chemical recycling of poly (L-lactic acid) (PLLA)/PE and PLLA/polybutylene succinate (PBS) blends [115]. In particular, PLLA/PE blend was dissolved in toluene, a clay catalyst (MK5) was then added and the resulting mixture was stirred. Upon the completion of the reaction, acetonitrile was poured and the precipitated PE and insoluble MK5 were collected. The solvent was then removed by the filtrate and the resulting lactic acid (LA) oligomer was then utilized in the repolymerization process, carried out using SnCl_2/p -toluene sulfonic acid. In Fig. 17a the relationship between MK5 concentration and the numeric molecular weight (M_n) of the LA oligomer after 1 h degradation at 100 °C is shown. It can be noticed that the M_n of the LA oligomer slightly decreased with the MK5 content. The trend of the M_n of the LA oligomer as a function of the PLLA concentration is shown in Fig. 17b. It can be seen that the M_n of the LA oligomer was rather constant at about 250 g/mol (for the pure PLLA), meaning that no significant influence of PLLA concentration on the M_n of the

Table 3

Results of tensile tests on LDPE and LDPE/TPS blends after 5 (5ext) and 10 (10ext) extrusion cycles (adapted from Ref. [110]).

Sample	E (MPa)	UTS (MPa)	ϵ_b (%)
LDPE	66 ± 2	8.4 ± 0.1	170 ± 4
LDPE-5 ext	68 ± 1	8.3 ± 0.1	167 ± 3
LDPE-10 ext	67 ± 2	8.1 ± 0.1	168 ± 2
Blend	48 ± 5	6.2 ± 0.1	236 ± 5
Blend-5 ext	48 ± 3	6.3 ± 0.1	219 ± 4
Blend-10 ext	53 ± 5	6.5 ± 0.2	214 ± 2

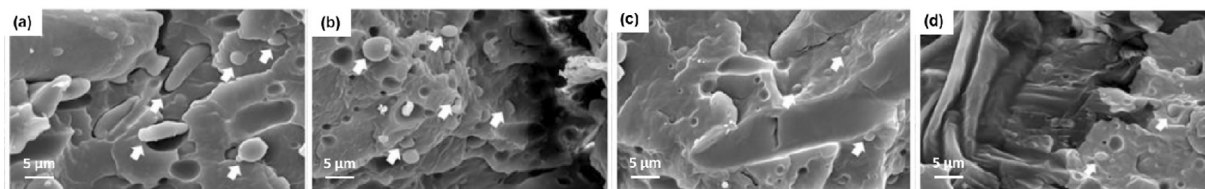


Fig. 16. SEM micrographs of PP/PBAT/TPS blend with (a) 1 reprocessing cycle, (b) 3 reprocessing cycles, (c) 5 reprocessing cycles and (d) 7 reprocessing cycles. The white arrows indicate the distribution of PBAT/TPS domains in PP (adapted from Ref. [111] with the permission of Elsevier).

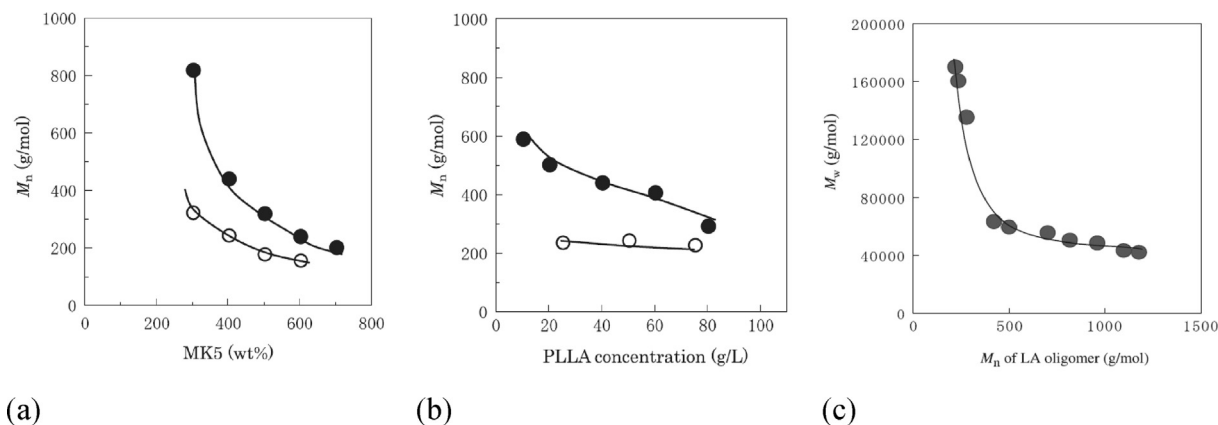


Fig. 17. Chemical recycling of PLLA/PE blends. (a) Effect of MK5 concentration (relative value to PLLA) in toluene on M_n of LA, at a PLLA concentration of 40 g/l at 100 °C for 1 h. PLLA/PE (1:2 wt/wt) blend (closed circle) and pure PLLA (open circle). (b) Effect of PLLA concentration in toluene on M_n of LA after degradation by MK5 (400 wt% relative value to PLLA) at 100 °C for 1 h. PLLA/PE (1:2 wt/wt) blend (closed circle) and pure PLLA (open circle). (c) M_n of LA oligomer versus M_w of the repolymerized PLLA (reprinted from Ref. [115] with the permission of Elsevier).

LA oligomer degradation products could be detected. It could be also important to determine the relationship between M_n of the LA oligomer and the ponderal molecular weight (M_w) of the produced PLLA. As reported in Fig. 17c, the M_w of the PLLA was strongly dependent on the M_n of the LA oligomer, and the M_w of the repolymerized PLLA increased with the decreasing M_n of the LA oligomer from 1200 to around 400 g/mol, probably because of the solubility of SnCl_2 catalyst in the LA oligomer. Therefore, a M_n of LA smaller than about 300 g/mol was necessary to synthesize PLLA having a M_w higher than 100,000 g/mol.

Jararat et al. [116] reported an innovative and economically competitive way of biological recycling for polylactic acid. A PLLA degrading enzyme was developed through the addition of 0.1% (w/v) silk fibroin powder into a liquid culture medium of an Actinomyces (i.e. *amycolatopsis orientalis*). It was demonstrated that the developed enzyme possessed a very interesting degrading capability, and 2000 mg/l of PLA powder was fully degraded within 8 h at 40 °C by using this enzyme at a concentration of 20 mg/l. Moreover, a L-lactic acid oligomer was obtained as degradation product of PLA, without undesirable racemization.

Sanchez and Collinson [117] investigated a selective recycling strategy for mixed PLA and PET, based on the depolymerization of PLA into a liquid and the recovery of unreacted solid PET by filtration. Among different catalysts that could be utilized for the glycolysis of post-consumer PET waste, zinc acetate was the most suitable one. For as concerns the alcoholysis of PLA, zinc acetate could effectively depolymerize waste PLA (in methanol or ethanol) producing lactate esters, while PET remained as an unreacted solid in the same reaction conditions. This technique could be very promising for the chemical recycling of both neat PLA and mixed PLA/PET, as the separation was facilitated through the conversion of PLA in a liquid monomer and the subsequent filtration of the solid PET.

5. Conclusions and future perspectives

This review clearly showed that recycling of polymer blends has a great importance not only for environmental reasons but also for the economical aspects. It was highlighted that the most logical and petrochemical way for recycling polymer mixtures deriving from petrochemical resources is the mechanical reprocessing. In fact, it was shown that blending is essential for the homogenization of in-house generated plastics scraps, especially for complex mixtures. Commingled plastics scraps coming from processing plants or from post consumed waste (PCW) can be successfully recycled when the most suitable practices of polymer blending are followed. In this sense, the use of compatibilizers plays a key role in the homogenization of the mixtures and in the achievement of the desired properties, and in this review many examples of recycling without any degradation of performance have been reported. Considering that multiple recycling steps should be applied to plastics blends, it is of utmost importance to consider the effect of the thermal reprocessing on the morphology of the resulting blends, as it greatly influences the final properties of the products.

With this review it was highlighted that blending technology is flexible, capable to provide tailored performance to any mixture, and that the difficulties in blends recycling are not only technical, but also related to the stability of the plastic supply, of the blend formulation and of the market situation. Considering the limited profit margins of the plastics industry, it is clear that also the recycling technologies applied to polymer blends will be in the future very sensitive to these socio-political conditions.

The increasing quantity of synthetic plastics discarded inappropriately in the environment is nowadays forcing the search for biodegradable polymers. This review showed that blends between synthetic matrices and biodegradable polymers (like PLA and TPS) can be an effective solution to different environmental issues, as

they combine good processability with biodegradation and the use of renewable raw materials. However, traditional polymers usually present high levels of recyclability, also thanks to the use of the well-established recycling infrastructures, and the introduction of bioplastics in the traditional waste stream could impair the recycling efficiency of these plants. In the future, it will be necessary to develop specific recycling technologies for blends containing bioplastics, in order to overcome these limitations. The problems of the compatibility between conventional and biodegradable plastics and of the thermal degradation stability of bioplastics during thermal reprocessing, especially in the presence of absorbed moisture, should be solved to permit a general scale up of the recycling technologies applied to bio-based blends. In some cases, also the application of specific chemical recycling processes could be helpful to sort plastic wastes and to recover valuable chemicals to be applied both in close loop and open loop recycling processes.

Declaration of competing interest

The author declares no conflicts of interest.

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