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Development of Recycled Blown Films Based on Post-Consumer Plastics Recovered from Seas And Rivers

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Post-consumer flexible packaging abandoned in seas and rivers represent an important environmental problem: their recovery is still a challenge and the management of the recovered material is equally difficult since, due to their heterogenicity and to their long-time permanence in seas or rivers, these plastics present various issues related to high incompatibility, hygroscopicity and presence of bad smells. All this translates into poor processability and mechanical performance and low organoleptic quality. The aim of this work is to characterize the seas and rivers plastic waste (SRPW) composition and to perform a preliminary investigation on the effectiveness of two different mineral fillers as reinforcing and compatibilizing agents for SRPW, in view of possible second-life applications of this waste. In particular, an organo-modified montmorillonite (Dellite 67G) and a natural sodium zeolite mineral (Zeolite 4A), loaded at 5 wt%, were considered for improving the processability and properties of SRPW blown films. The combined use of a polymeric compatibilizer (polyolefin block copolymer grafted with 0.4 wt% maleic anhydride was also considered, in order both to improve the filler dispersion within the polymer and to compatibilize the main constituents of SRPW. The results demonstrated that the addition of both fillers to SRPW leaves essentially unchanged the thermal stability, but gives interesting improvements mainly in terms of stiffness. The effects are more significant when the nanometric Dellite 67G is added, than for the micrometric Zeolite 4A, especially in compatibilized systems.

1. Introduction

Every year, 359 million tons of plastics are produced and, at the end of their life, that in some cases can be very brief, they became post-consumer plastic wastes (PlasticsEurope, 2019). When they are not collected in a properly way, they can be lost in the environment, in which they persist for long time because of their durability (Thompson et al., 2009). Food wrappers, beverage bottles, grocery bags, straws, and take-out containers principally compose plastics recovered from sea and rivers (Galgani et al., 2000, Riechers et al., 2021). Flexible films present a number of challenges due to multi-layer barrier materials (Apicella et al., 2021), difficulties in sorting it, high ink loadings and different types of inorganic and/or organic contaminants presence that affect the final recycled product colour and odour. Another major problem for producing recycled resins from flexible packaging stream is the presence of different plastic types, which are not easy to separate, due to the similarity of physical properties. They are often incompatible with each other and show differences in processing requirements at a macro-scale. As a consequence, the final properties of the products, obtained from these recycled materials, are very poor. One possible strategy for an effective mechanical recycling of mixed waste streams can be the upgrading of the polymeric blends through the inclusion of proper additives, able to improve the interfacial adhesion and the dispersion of the mixture components. Usually, they are used commercial compatibilizers, in form of graft or block copolymers composed by blocks chemically similar to the blend components to be compatibilized. So, the interfacial adhesion is improved by the physical miscibility of the copolymer segments in the different blend phases (Garofalo et al., 2015). However, traditional compatibilizers are specific, relatively expensive to engineer, and very difficult to produce for polymeric mixtures with more than two components. Recent literature studies show that an alternative can be represented by the use of fillers, particularly if nanosized (Salzano de Luna et al., 2016).

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Much of the researchers focus their efforts on investigating methods to collect plastic waste from seas and rivers rather than on the recovery techniques to be adopted once it has been recovered.

However, the authors of this paper have previously worked on the valorisation of small plastic waste from flexible packaging (Fil-s). As for the mechanical reinforcement of the matrices and the simultaneous compatibilizing action between the constituents of the polymer blend, Garofalo et al. (2015) investigated the effect of silicate nanoclays of different forms and with different organic modifiers (Dellite 67G, lamellar form, modified with dimethyl dehydrogenated tallow ammonium, and Sepiolite PM15 and UNISA1, acicular form, modified respectively with quaternary ammonium compounds , benzyl C14-18-alkyldimethyl, chlorides and trymetoxyvinylsilane), finding that the addition of nanometric reinforcements led to an increase in the mechanical properties, in terms of stiffness, more pronounced in the case of lamellar geometry, thus revealing a dependence on the increase obtained from the shape of the nanofill used. In this case, in fact, the best observed effects have been attributed to the ability of Dellite to exfoliate and allow the intercalation of the polymer chains between the layers of the silicate.

Further improvements of the polymer matrix were obtained by Garofalo et al. (2018) functionalizing the polymeric matrix with maleic anhydride in order to allow a better dispersion of the nanofiller (Dellite 67G and Sepiolite PM15) and, at the same time, improve the compatibility between the main polymeric phases making up the matrix.

In a recent study, Garofalo et al. (2021) dedicated their efforts to the removal of moisture from Fil-s, caused by the presence of hygroscopic contaminants, directly during the extrusion process. To this end, two micrometric zeolites (4A, with pores of 3.8 Å size, and 13X, with pores of 8.1 Å size) and a conventional CaO-based desiccant were added to the polymeric matrix. The best results, from the point of view of mechanical performance, were observed through the addition of 2% of the molecular sieve with pores characterized by the smaller diameter.

Based on the experiences gained by the authors of this paper, in this work we investigated the effectiveness of two different fillers in improving the processability and the performances of mixed post-consumer polyolefin plastic packaging collected from seas and rivers (SRPW). As fillers, an organo-modified montmorillonite nanoclay (Dellite 67G, d001 = 3.6 nm) and a natural sodium zeolite mineral (Zeolite 4A; particle D = 4-5 μm) were used at 5wt% loading. A polyolefin compatibilizer (AUS), mainly made up of polyethylene and polypropylene and functionalized with 0.4 wt% of maleic anhydride, was added at 5 wt% to the different batches of SRPW, with and without fillers, in order both to improve the filler dispersion within the polymer matrix and to compatibilize the main SRPW polymeric fractions.

2. Experimental

2.1 Materials

The study was carried out on post-consumer plastic wastes recovered from sea and rivers (SRPW), supplied by Sky Plastic Group AG as pellets.

The supplied pellets were additivated with two mineral fillers: an organo-modified mortmorillonite, named Dellite 67G (D67G), supplied by Laviosa Chimica Mineraria in Italy, and a Zeolite 4A, supplied Honeywell Fluka in USA, whose characteristics are reported in Table 1 and Table 2, respectively.

Table 1: Characteristics of Dellite 67G.

Morphology	Organic modifier	Moisture [%]	Particle size (dry) [μm]	Specific weight [g/cm^3]	Bulk density [g/cm^3]
Lamellar	Dimethyl dehydrogenated tallow (C14-C18) ammonium	3	7-9	1.7	0.45

Table 2: Characteristics of Zeolite 4A.

Type	Cation	Si/Al ratio	Particle dimension [μm]	Pore dimension [Å]	Pore volume [cm^3/g]	M_∞ [%]	K
4A	Na^+	1.23	4	3.8	0.28	27.5	47.6

The zeolite was regenerated in the muffle before use, subjecting it to drying at 300 °C for 16 hours. As compatibilizer, it was used a block polyolefin copolymer supplied by COREPLA (the Italian National Consortium for the Collection and Recycling of Plastic Packaging) and named Auser (AUS), constituted by polyethylene and polypropylene, grafted with 0.4 wt% of maleic anhydride, added at 5 wt%.

2.2 Sample production: melt compounding and blow molding

SRPW-based films were produced after melt compounding of SRPW with mineral fillers (at 5 wt%) and compatibilizer (at 5 wt%) in a twin-screw extruder (Dr. Collin GmbH – model ZK 25-48D, Germany) equipped with co-rotating intermeshing screws (D_{screw} = 25 mm, L/D = 42). Before melt compounding of SRPW with D67G and/or AUS, all materials were dried overnight at 70 °C in the vacuum oven. Instead, in order to evaluate the effect of zeolite as water remover, SRPW wasn't dried before compounding with zeolite 4A. The melt compounding A screw speed of 100 rpm and a temperature profile of 190-205-195-190-190-190-200-135 °C, from hopper to die, were used. The collected extruded mixtures were cooled in air using coils and then pelletized.

Then, SRPW-based films were obtained from the melt compounded pellets, using a laboratory-scale film blowing plant. The plant consists of a GIMAC single-screw extruder with a ratio of L/D = 40, screw diameter equal to D = 12 mm and the filming head is characterized by an external diameter equal to D_{est} = 32 mm and D_{int} = 30 mm. The temperature profile from the hopper to the head was: 220-220-210-190 °C, with an extrusion speed of 85 rpm and a collection speed of 1.6 m/min. Subsequently the films were characterized from a mechanical, physical and chemical point of view.

2.3 Characterization techniques

First, the raw material, supplied in form of pellet, was analysed by several techniques (Differential Scanner Calorimetry, DSC, Thermal Gravimetric Analysis, TGA, Fourier Transform Infrared Spectroscopy, FT-IR, Rheological Analysis) in order to establish its composition, its processability and the amount of its water content.

Differential scanning calorimetry (DSC) analyses were carried out on pellets using a Mettler DSC30 apparatus (Mettler-Toledo International Inc., USA). Thermal behavior of samples was investigated performing a thermal cycle composed by: a first heating step from 25 °C to 250 °C, an isotherm step for 5 min to melt the residual crystals and remove the thermo-mechanical history; a cooling step from 250 °C to 25 °C and a second heating step from 25 °C to 250 °C. All the steps were carried out with a scan rate of 10 °C/min. Fourier-Transform Infrared Spectroscopy (FT-IR) measurements were carried out on both raw material and films in the range of 4000-650 nm^{-1}, using a Nexus ThermoNicolet spectrometer (Thermo Fischer Scientific, USA) equipped with a SmartPerformer accessory for ATR analysis. The spectra were collected at 2 cm^{-1} spectral resolution and 64 scans were co-added. Thermal stability was evaluated by thermogravimetric analyses (TGA), which was carried out with a TGAQ500 (TA Instruments) from 25 °C to 800 °C at a thermal scan rate of 10 °C/min, in nitrogen atmosphere, according to ASTM E1131-03. Rheological tests in oscillatory mode were performed using a rotational rheometer ARES (Rheometric Scientific, USA) under a nitrogen atmosphere on pellets. The measurements were performed at 190 °C in an angular frequency range from 0.1 to 100 rad/s, using 25 mm diameter parallel plates. The deformation of 5 % of strain amplitude was proven to ensure linear viscoelasticity during the dynamic tests. The moisture content of pellets was measured by the Brabender Messtechnik AQUATRAC®-3E moisture analyzer. Density (ρ) measurements were carried out on raw material and films by using a balance equipped with a device to measure the weight of a solid in air and immersed in a liquid of known density. The principle of operation of this technique is based on Archimedes' thrust. Mechanical tensile tests on films were carried out according to ASTM standard D682 by a CMT4000 series dynamometer (SANS, Shenzhen China), using a load cell of 1 KN, with a grip distance of 50 mm. The tests were performed at a crosshead speed of 5 mm/min to evaluate elastic modulus (E_t), stress and strain at yield (σ_y and ε_y), and of 500 mm/min, to measure stress and elongation at break (σ_b and ε_b).

3. Results

3.1 SRPW characterization

In order to obtain information on the material composition, the SRPW pellets were submitted to DSC and FT-IR analyses. Figure 1a,b reports the DSC thermograms (a) and the FT-IR curve (b) of the sample. The DSC heating traces show the typical melting peaks of the polyethylene at 111 °C and 124 °C, corresponding to the LLDPE and LDPE form, respectively, and a low peak at 162 °C that can be related to a small amount of polypropylene.

The relative weight amount of PE/PP in the SRPW pellets was ca. 95/5, as estimated according to a procedure reported in our previous paper (Garofalo et al., 2018). The intense PE transitions are clearly visible in the cooling scan trace, too, that also reveals the presence of low molecular weight compounds as it can be inferred by the low temperature (<100 °C) endothermic features. According to DSC, the FT-IR spectrum (Figure 1b) clearly shows the characteristic peaks of polyethylene and polypropylene at 2915 and 2848 cm^{-1} and at 1375 cm^{-1}, a broad signal at about 3400 cm^{-1} due to water, and some small peaks probably related to –

NH stretching and bending vibration respectively, at 1577 cm^{-1} and between 874 and 718 cm^{-1}. Moreover, a weak C=O signal at ca. 1720, indicative of the presence of polar compounds (coming from contaminants, additives, degradation phenomena, etc.), is observable.

Other non-polymeric contaminations in SRPW can be detected by thermogravimetric analysis (TGA). To this purpose, TGA measurements under inert atmosphere were performed on pellets and reported in Figure 2. The maximum decomposition temperature, T_{dmax}, turned out to be equal to 476°C while no unburned residues at 800 °C can be observed.

SRPW processability was evaluated by carrying out rheological tests at 190 °C using a rotational rheometer in dynamic mode. The tests revealed that the complex viscosity curve of SRPW (Figure 3a) has a pronounced shear thinning behavior in the whole frequency range investigated (0.1-100 rad/s), with viscosity values typical of other post-consumer mixed plastic wastes from different sources (Garofalo et al., 2018). It is also possible to observe from Figure 3b that both the elastic modulus G’ and the viscous modulus G” increase with frequency. At low frequencies the viscous modulus G” is greater than the elastic modulus G', a liquid-like behavior typical of polyolefinic matrices, up to the crossover point in the high-frequency zone.

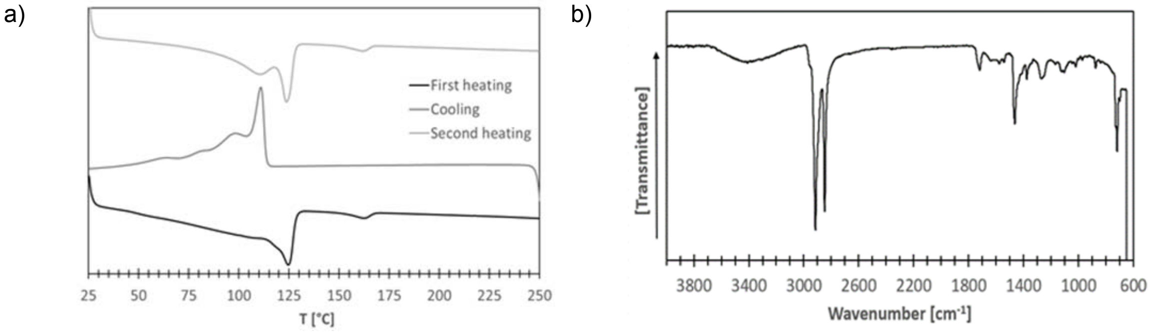

Figure 1: a) Differential scanning calorimetry curves and b) FT-IR spectrum obtained on plastics recovered from seas and rivers recycled in form of pellets.

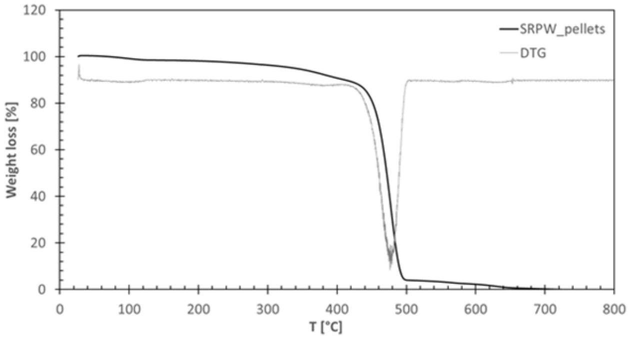

Figure 2: Thermogravimetric plot of SRPW in form of pellets.

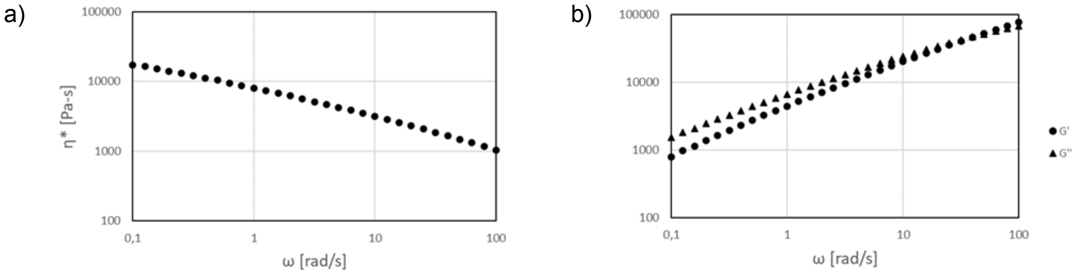

Figure 3: Rheological characterization of SRPW pellets: a) complex viscosity; b) elastic G’ and viscous G” modulus.

SRPW are also characterized by a huge amount of water (about 13000 ppm), but after a drying process (conducted in a vacuum oven at 70 °C for 16 h) a one order magnitude reduction can be observed.

3.2 Film characterization

In order to evaluate the effectiveness of mineral fillers and compatibilizers in upgrading SRPW mixed plastics, by making them processable by blown film extrusion and improving their performances, recycled blown films were produced from SRPW pellets melt blended with different fillers and/or compatibilizers: a lamellar organoclay (D67G), a zeolite (4A) and a blocky copolymer grafted with maleic anhydride (AUS). The obtained samples were characterized from a mechanical point of view by means of tensile tests and their mechanical property values are summarized in Table 3.

The addition of both the mineral fillers to the system improves the elastic modulus, even if the D67G seems to be more performing than zeolite. The better behaviour of D67G with respect to zeolite 4A can be related both to its higher surface area, due to its lamellar shape, and to its higher compatibility with the polymer phases, being it organomodified. Even improved performances are obtained by adding compatibilizer to the systems. The most performing system is the SRPW+D67G+AUS, showing an increment of the Young modulus of about 30 % with respect to the original SRPW. In terms of stress at yield and at break, small benefits arise from the addition of the AUS compatibilizer with respect to the corresponding uncompatibilized systems, whereas no significant improvements are given by the mineral fillers. Finally, no relevant differences among the samples were detected in terms of deformation at yield and at break. Moreover, density slightly increase for compatibilized systems, while more significant improvements are attributable to the addition of D67G and even more so of zeolite 4A.

Table 3: Tensile mechanical properties (elastic modulus - Et, stress and strain at yield - σy and Ɛy, stress and elongation at break - σb and Ɛb) and density values (ρ) of SRPW, SRPW+D67G and SRPW+4A, with and without compatibilizer, extruded as ribbons.

Ribbons	E_t [MPa]	σ_y [MPa]	ε_y [%]	σ_b [MPa]	ε_b [%]	ρ [g/cm^3]
SRPW	311 ± 21	8.11 ± 0.16	10.4 ± 0.67	13.6 ± 0.75	330 ± 40	0.954 ± 0.011
SRPW + AUS	319 ± 22	8.40 ± 0.20	10.4 ± 1.20	13.8 ± 0.93	308 ± 32	0.965 ± 0.040
SRPW + D67G	363 ± 19	7.93 ± 0.44	9.88 ± 0.55	12.6 ± 0.94	351 ± 30	0.972 ± 0.005
SRPW + D67G + AUS	401 ± 16	9.13 ± 0.32	10.5 ± 0.90	14.2 ± 0.76	356 ± 31	0.976 ± 0.001
SRPW + 4A	333 ± 25	7.67 ± 0.32	9.78 ± 0.49	12.7 ± 0.66	310 ± 38	1.007 ± 0.014
SRPW + 4A + AUS	375 ± 27	8.92 ± 0.48	9.24 ± 0.88	12.2 ± 0.63	302 ± 30	0.993 ± 0.008

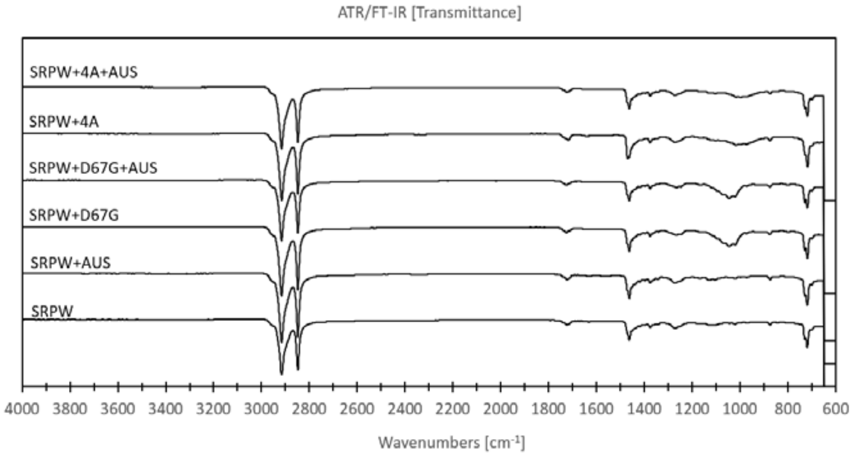

Figure 4: ATR/FT-IR spectrum of SRPW-based mixtures additivated with D67G and zeolite 4A, with and without compatibilizer addition.

The spectrograms of SRPW-based mixtures additivated with D67G and zeolite 4A, with and without compatibilizer addition, were reported in Figure 4. As can be seen, the appearance of a huge, rather large peak, between 962 and 1162 cm^{-1} for the samples reinforced with D67G and of a less evident and more flattened one, between 879 and 1070 cm^{-1}, is quite evident, in samples reinforced with 4A zeolite. These peaks are nothing more than evidence of the presence of nanofillers in the polymer matrix.

4. Conclusions

In this work a preliminary investigation was carried out aimed both to perform a chemical-physical characterization of SRPW and to evaluate the effectiveness of mineral fillers and/or compatibilizer addition in upgrading the recycled SRPW for possible second-life applications.

The thermal (DSC and TGA) and chemical (FT-IR) analyses performed on SRPW allowed to establish the matrix composition, which resulted largely composed of PE (92-96 wt%) and containing PP in a low percentage (4-8 wt%) and traces of hydrophilic contaminants. The intrinsic incompatibility between the PE and PP constituents of SRPW results in poor mechanical properties of the recycled materials. Moreover, as a consequence of the presence of polar contaminants, the SRPW showed a high hydrophilic nature, resulting in a high amount of equilibrium moisture content (13000 ppm) that makes necessary to dehumidify the recycled material before processing it. Thus, to overcome these issues, as an upgrading strategy, mineral fillers (a lamellar silicate and a zeolite) that could operate at the same time as reinforcement, compatibilizing medium (in the case of Dellite 67G) and moisture absorber (in the case of zeolite), was tested. A block compatibilizer functionalized with maleic anhydride was also used. Blown films were successfully produced from SRPW-based melt compounded systems at different compositions and then characterized in terms of mechanical and thermal properties. The results demonstrated that the addition of both mineral fillers to SRPW increases slightly the thermal stability of the recycled materials even if no difference is observed between the two types of additives used. Moreover, fillers addition gives interesting improvements of their mechanical response, mainly in terms of stiffness. The effects are more significant for the nanometric Dellite 67G than for the micrometric Zeolite 4A, so highlighting the importance of the filler size on its reinforcing ability. Additional relevant benefits arise from the combined use of fillers and compatibilizer: in fact, compatibilized recycled blends show an improvement of both elastic modulus and elongation at break values, in the range of 20 % to 30 %, depending on whether Zeolite 4A or Dellite 67G was used as filler, respectively.

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References

Apicella, A., Scarfato, P., Di Maio, L., Incarnato, L., 2018, Transport properties of multilayer active PET films with different layers configuration, Reactive and Functional Polymers, 127, 29-37.

Galgani F., Leaute J.P., Moguedet P., Souplet A., Verin Y., Carpentier A., Goraguer H., Latrouite D., Andral B., Cadiou Y., Poulard J.C., Nerisson P., 2000, Litter on the Sea Floor Along European Coasts, Marine Pollution Bulletin, 40, 516–527.

Garofalo E., Claro M., Scarfato P., Di Maio L., Incarnato L., 2015, Upgrading of recycled plastics obtained from flexible packaging waste by adding nanosilicates, AIP Conference Proceedings 1695, 020053.

Garofalo, E., Di Maio L., Scarfato P., Di Gregorio, F., Incarnato L., 2018, Reactive compatibilization and melt compounding with nanosilicates of post-consumer flexible plastic packagings, Polymer Degradation and Stability, 152, 52–63.

Garofalo, E., Scarfato P., Di Maio L., Protopapa, A., Incarnato L., 2021, Technological and environmental advantages of using zeolites as desiccant during processing of recycled post-consumer plastic film fractions, Journal of Cleaner Production, 295, 126379.

PlasticsEurope. Plastics – the Facts, 2019, An analysis of European latest plastics production, demand and waste data, Plastics Europe. PlasticsEurope. <https://www.plasticseurope.org/it/resources/publications/1804-plastics-facts-2019> accessed 25.10.2020.

Riechers, M., Fanini, L., Apicella, A., Batista Galván, C., Blondel, E., Espiña, B., Kefer, S., Keroullé, T., Klun, K., Pereira, T.R., Ronchi, F., Rodríguez, P.R., Sardon, H., Silva, A.V., Stulgis, M., Ibarra-González, N., 2021, Plastics in our ocean as transdisciplinary challenge, Marine Pollution Bulletin, 164, 112051.

Salzano De Luna, M. and Filippone, G. 2016, Effects of nanoparticles on the morphology of immiscible polymer blends – Challenges and opportunities, European Polymer Journal, 79, 198–218.

Thompson R.C., Moore C.J., vom Saal F.S., Swan S.H., 2009, Plastics, the environment and human health: current consensus and future trends, Philosophical Transactions of the Royal Society B, 364, 2153–2166.