Chapter 2
Case Study of Raw Materials Substitution: Natural Fillers Substitution in Plastic Composites

Elza Bontempi

Abstract In the frame of European problems of raw materials availability, this chapter describe a new technology (COSMOS) that allows to produce safe materials, starting from toxic ash waste (derived from municipal solid waste incineration). It is shown that this technology was evolved in the years to reduce its environmental costs and to use local available by-products for stabilization. The by-products and wastes that can be used in the COSMOS technology are coal fly ash, flue-gas desulfurization residues, rice husk ash, silica fume, and wood ash. The sustainability of the obtained COSMOS materials is demonstrated on the basis of their embodied energy and carbon footprint values. These parameters are reported and discussed also for several natural and engineered materials used as fillers, with great attention also to their cost. Results show that the new proposed material is comparable to calcium carbonate, in term of sustainability. A rapid analysis of the European plastic market and the results about mechanical performances of the obtained composites, highlights the possibility to reuse COSMOS filler as a substitute of calcite and talc, in polypropylene composites. Embodied energy and carbon footprint of the already available polypropylene composites and the new proposed ones are presented and discussed. In this context, Ashby plot is used to investigate possible substitution of polypropylene fillers that are unsustainable or very expensive, exploring the potential of one material to replace another. Finally, in view of its thermal properties the COSMOS filler is proposed as a substitute of antimony, one critical raw material, that urgently need alternative.

Keywords COSMOS · Fillers · Polypropylene composites · Fly ash · Sb · Biomass ash · Coal ash · Flue-gas desulfurization residues · Rice husk ash · Silica fume

E. Bontempi (✉)
INSTM and University of Brescia, Brescia, Italy
e-mail: elza.bontempi@unibs.it

© The Author(s) 2017

E. Bontempi, *Raw Materials Substitution Sustainability*, SpringerBriefs in Applied Sciences and Technology, DOI 10.1007/978-3-319-60831-0_2

2.1 A New Sustainable Filler from Waste: COSMOS Technologies

Every year about 11 billion tons of solid waste are collected worldwide and the European Union alone generates about 3 billion tons of waste (Eurostat). Highly dependent on imported raw materials, Europe must reduce the amount of waste generated by improving its resource efficiency through recycling, avoiding waste and using unavoidable waste as a resource, when possible. On the basis of developed policy on waste management, in Europe, from 1995 to 2013, the global amount of waste produced per capita (500 kg/year) results almost constant. Moreover the waste landfilling shows a negative trend, with a reduction at about one half of the waste designated to landfill in 2013, in comparison to data of 1995 (from about 300–130 kg/per capita). An opposite trend is found for waste incineration (with an increase from 67 to 127 kg/per capita, comparing data from 1995 to 2014). Waste incineration, that is acquiring a prominent role for domestic waste management in several EU countries, is at present exceeding the amount of waste that is landfilled.

Municipal solid waste incineration (MSWI) is now considered an efficient technique to recover energy and to manage waste. Indeed, it allows to widely reduce the total waste volume and mass to be disposed in landfill (Zacco et al. 2014).

During 2014, in Europe, 122 kg per capita of waste were incinerated (Eurostat), i.e. the 25% of the waste generated in the same year. Data about waste production and management in Europe show that, generally, where high incineration rate is reached (more than 35% of the total waste produced), as for example in Norway, Sweden, Germany, France, Austria, and Netherlands, the fraction of waste incinerated is constant considering the past years (some countries also exceed 50% waste incinerated, in respect to total waste generated). On the contrary, countries where the incineration rate is lower than 25%, the amount of waste incinerated, in respect to the waste generated, is continuously increasing with time (see Fig. 2.1). As a consequence, in the next years, the incineration of waste is expected to rise in several European countries.

MSWI technology induces environmental issues, mainly connected to the treatment and management of solid by-products generated by waste combustion. These residues include bottom ash, fly ash, and scrubber residue. Generally MSWI fly ash and air pollution control (APC) residue are not differentiated. Fly ash is the thinnest fraction of the particulate contained in combustion flue gas. After combustion, fly ash is caught by electrostatic precipitators without any other treatment of the gaseous stream (Zacco et al. 2014). APC residues are instead a product deriving from the injection of an alkaline material inside a scrubber system, in order to reduce the content of acid gases, particulates and flue gas reaction products. Fly ash can be incorporated inside the APC residue. Thus fly ash and APC residues are considered as an unique by-product of MSWI processes. This by-product is commonly called MSWI fly ash. MSWI fly ash is generally composed of sulphate and

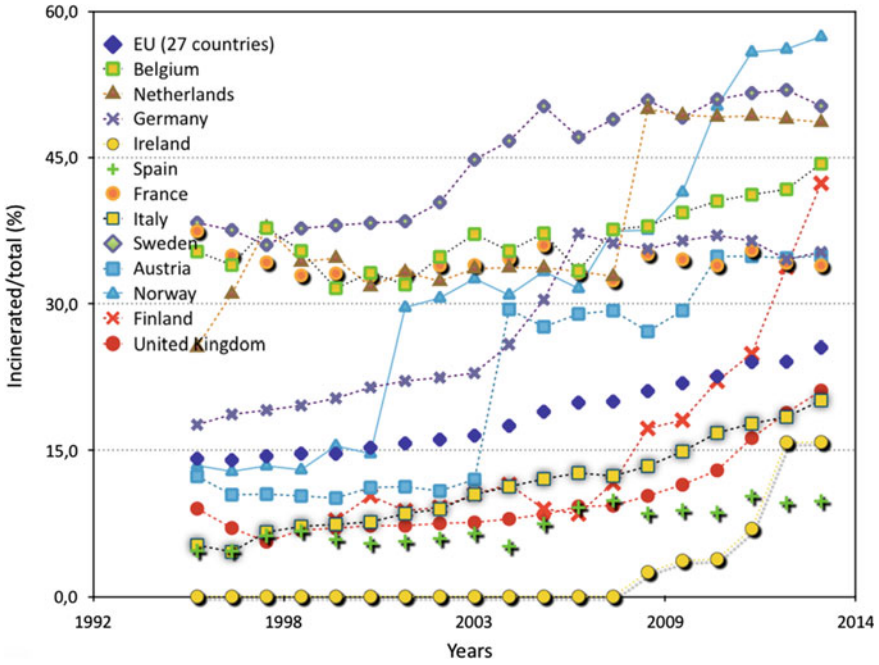


Fig. 2.1 Percent of waste incinerated, in respect to the waste generated, in Europe from 1995 to 2013 [data from (Eurostat)]

aluminosilicate glass and it is quite rich in terms of soluble salts. The most abundant crystalline compounds generally detected in MSWI fly ash are CaClOH, NaCl, KCl, $CaCO_3$ and $CaSO_4$. Moreover, also amorphous phases are always present (Zacco et al. 2014). The typology and concentration of the contaminants found in this waste are quite various, depending on the solid waste original composition, the plant operational conditions, the incinerator typology and the air pollution system design. MSWI fly ash may contain high concentrations of leachable heavy metals such as As, Cd, Hg, Pb and Zn (Le Forestier and Libourel 1998) and can contain organic micro-pollutants (PCDD and PCDF) (Zacco et al. 2014).

Because of the dangerous effects produced on humans and environment, MSWI fly ash is generally landfilled, after a partial stabilization with cement. On the other hand, because Europe faces issues with raw materials depletion, there is an increasing need to encourage resource conservation. As a consequence, the materials recycling represents a large and significant contribution to protect the environment (Brunner and Rechberger 2015) and a way to reach the objectives established in the framework of COP21 meeting (COP21).

The need to reuse valuable materials contained in toxic fly ash has been reported and discussed in the literature (Funari et al. 2015). However, the papers on this subject are mainly dedicated to the recovery of precious metals and earth elements that represent only a limited content in these wastes.

In this frame, the COSMOS project (it was realized in 2011–2013), financed by European Commission, developed a new method for MSWI fly ash stabilization and explored the stabilized material recovery possibilities. The stabilization technology was based on the use of colloidal silica and other fly ashes (i.e. coal fly ash and flue-gas desulfurization (FGD) residues).

In the following the required ingredients for the COSMOS process, which are mixed to obtain the MSWI fly ash stabilization, are briefly analyzed; they are: colloidal silica, coal fly ash, and flue gas desulphurisation (FGD) residues.

Colloidal silica is a concentrated stable dispersion of dense particles of amorphous silicas, generally monodispersed with size ranging from about 5 to about 1500 nm. Colloidal silica is composed of discrete particles, thus it is different from silica glass, because despite both are amorphous, the structure of the glass is macroscopically continuous (Bergna 1994). Colloidal silica is used in the form of a gel, made of a network of interconnected pores with a silicon dioxide core where water is entrapped. The silica surface can be covered by silanol groups (Iler 1979). The surface silanol groups are responsible for physically adsorbing water molecules and holding them in place by hydrogen bonding. The silanol hydroxyl groups, the water entrapped in the core, and the physically adsorbed water together represent the moisture content in the dispersed silica gel particles (Kamath and Proctor 1998).

The high dispersion of its particles makes colloidal silica very reactive. In the COSMOS process the commercial colloidal silica that was used has a particles dimension less than 10 nm.

Coal fly ash is a by-product originated from the flue gases of furnaces at pulverized coal power plants. It is predominantly an inorganic residue; however, its characteristics can be different, depending on several factors, such as on the coal source, the temperature and the method of combustion of power plants, the technology of emission control devices, and the ash storage and handling (Zacco et al. 2014). Therefore, coal fly ash shows a wide variation in its physicochemical and mineralogical properties. This material is generally composed of crystalline and amorphous phases. Crystalline phases are mullite, quartz, magnetite, hematite and anhydrite. Glass is found as amorphous constituent. Coal fly ash is sometimes reused in building application, to produce concrete (as reported in Chap. 1). Coal fly ash can be reused in other applications (that will be discussed in Chap. 3), to increase the sustainability of the obtained material (see also Chap. 4).

Coal fly ash is used in the COSMOS stabilization technology to mainly improve the mechanical characteristics of the obtained filler (Bontempi et al. 2010).

Flue gas desulphurisation (FGD) residues are a by-product generated by the air pollution control equipment in coal-fired power plants. They are formed as a consequence of the required pretreatment made on coal, in combustion plant, to reduce sulphur amount. Indeed, coal contains large quantities of natural sulphur and its burning produce severe air pollution problems, because sulphur-bearing impurities are transformed into gaseous SO_2, that is an atmospheric pollutant and a precursor to acid rains. For this reason, in Europe, coal power plants are forced to remove sulphur oxides from the flue gases, before releasing them to the atmosphere (Zacco et al. 2014). FGD residues generally contain calcium sulfite and calcium

hydroxide. As a consequence, flue gas desulphurisation residues are used, as an inexpensive calcium hydroxide source, in the COSMOS stabilization technology. FGD were chosen to promote the carbonation reaction, which naturally takes place with atmospheric carbon dioxide.

The reaction mechanism occurring during the stabilization, is due to the amorphous colloidal silica reactivity. The adsorption of metal ions seems take place on the silica surface, and can be explained on the basis of the surface complex formation model. The hydrolysis of silicon dioxide produces hydrous oxide surface groups –SiOH (the silanol groups). When colloidal silica is added to a solution containing leachable metals, the sorption of metal ions on silica can occur by the cation exchange reaction through the substitution of protons from silanol groups on the surface by the metal ions contained in the solution (Srivastava et al. 2006). This reaction mechanism can be represented as:

$$\mathrm{m}(-\mathrm{SiOH}) \; <-> \; \mathrm{m}(-\mathrm{SiO}^{-}) + \mathrm{mH}^{+}$$

$$\mathrm{A}^{\mathrm{n}+} + \mathrm{m}(-\mathrm{SiO}^{-}) \; <-> \; \mathrm{A}(\mathrm{OSi}-)_{\mathrm{m}}^{(\mathrm{n}-\mathrm{m})+}$$

and the overall reaction can be written as:

$$\mathrm{A}^{\mathrm{n}+} + \mathrm{m}(-\mathrm{SiOH}) \; <-> \; \mathrm{A}(\mathrm{OSi}-)_{\mathrm{m}}^{(\mathrm{n}-\mathrm{m})+} + \mathrm{mH}^{+}$$

where A^{n+} is the metal ion with n^{+} charge, *SiOH* is the silanol group on SiO_2 surface, and mH^{+} is the number of protons released (Bosio et al. 2014a).

To verify the efficacy of the stabilization procedure, leaching solution of MSWI fly ash and stabilized samples are prepared and analyzed.

Leaching tests consist in the realization of an aqueous leaching of the material which must be analyzed, to verify the presence of soluble heavy metals. The tests are generally realized following the European Committee for Standardization normative (EN 2002).

Some results of leaching tests, made on a MSWI fly ash sample and corresponding stabilized material, are shown in Table 2.1. Analysis were made by means of inductively coupled plasma (ICP) spectroscopy. Data show that the main soluble heavy metals, present in MSWI fly ash are Pb and Zn. Generally Hg, Cd, Co, Mn, Se and V are below instrument detection limits. Data reported in Table 2.1 also show that the stabilization treatment reduces the amount of soluble Pb ad Zn. The amount of leachable Si, in the stabilized material, is increased due to the use of amorphous silica as stabilizing agent.

Figure 2.2 shows Pb and Zn concentrations in the leaching solutions of stabilized samples, as a function of added silica gel amount. The zero point of the silica corresponds to concentration of metals in the MSWI fly ash leaching solution, i.e. in the leaching solution of fly ash, before stabilization (Bosio et al. 2013). Data of Fig. 2.2 are presented in logarithmic scale, due to the change of about two orders of magnitude in the metals' leaching, as a function of the quantity of employed silica gel. These data show that the quantity of leachable metals depends on the content of

Table 2.1 Concentration of elements detected in the leaching solutions of MSWI fly ash sample and corresponding stabilized material. Analysis were made by means of inductively coupled plasma (ICP) spectroscopy

Element	MSWI fly ash (mg/l)	Stabilized material (mg/l)
As	<0.02	<0.02
Ba	2.42	0.81
Be	<0.02	<0.02
Bi	<0.02	<0.02
Ca	6672.69	1741.22
Cd	<0.02	<0.02
Co	<0.02	<0.02
Cu	0.06	<0.02
Fe	<0.02	<0.02
Hg	<0.02	<0.02
K	17,966.00	3150.00
Li	2.69	0.99
Mn	<0.02	<0.02
Mo	0.51	0.25
Ni	<0.02	<0.02
P	<0.1	<0.1
Pb	77.34	<0.02
S	1583.78	283.66
Sb	<0.02	<0.02
Se	<0.02	<0.02
Si	0.11	8.68
Sn	<0.02	<0.02
Ti	<0.02	<0.02
TI	<0.02	<0.02
V	<0.02	<0.02
Zn	11.93	<0.02
Zr	<0.02	<0.02

silica used in the stabilization process. The leachability of heavy metals into solution decreases because of the increase in the efficacy of the stabilization technology.

Despite the fundamental role of amorphous silica in the stabilization of MSWI fly ash, the reaction mechanism of the COSMOS technology involves also carbonation reactions.

Carbonation of MSWI fly ash can naturally occur as a result of weathering processes upon contact with atmospheric carbon dioxide, during temporary storage, and is commonly associated to a pH decrease (Belevi et al. 1992) from 12 to 13 (strongly alkaline) to lower values (generally 8–10).

The main crystalline phase in MSWI fly ash responsible of carbonation is CaClOH, and the reaction can be written as:

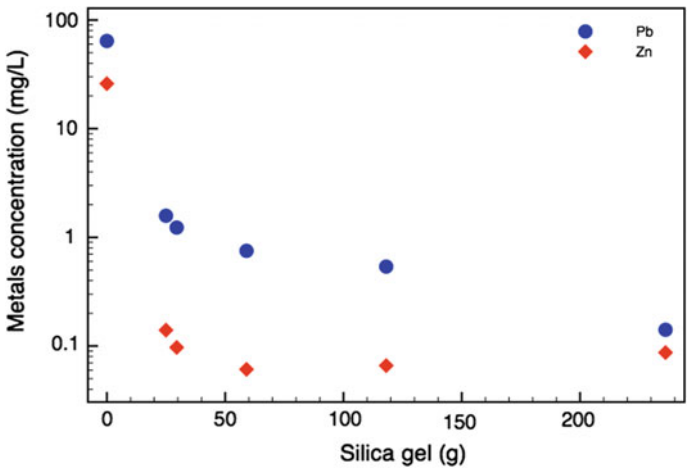


Fig. 2.2 Pb and Zn concentrations in the leaching solutions of stabilized samples, as a function of added silica gel quantity (Bosio et al. 2013)

$$2CaClOH + CO_2 \rightarrow CaCl_2 + CaCO_3 + H_2O$$

Unfortunately, the natural carbonation process of MSWI fly ash is generally quite slow and becomes significant only over horizons of several years. As a consequence, accelerated carbonation of MSWI fly ash has been proposed as a possible carbon dioxide capture and storage technology (Fernández Bertos et al. 2004), with the advantage of heavy metals mobility reduction. In the COSMOS stabilization technology, the carbonation of the stabilized material, due to the reactions promoted by the new technology, has been detected and quantified. The carbonation reactions typically occur during the samples drying, and they are more effective if samples are naturally aged in air. Depending on temperature and humidity conditions, generally these reactions naturally occur in one-two months. However, it is possible to accelerate them by treating the samples in a oven, at temperatures of about 100 °C for few hours (generally less than 4 h).

XRD spectra collected on stabilized samples, obtained by using amorphous silica and FGD residues, suggest that the following additional carbonation reactions occur:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

On the basis of this reaction, it is evident that flue gas desulphurisation residues, which contains calcium hydroxide, is a fundamental ingredient in the proposed COSMOS technology, not only because it promotes carbon dioxide sequestration, with high environmental advantages, in terms of CO_2 footprint, but also because carbonation reaction seems to promote metal entrapment (Bosio et al. 2014b), with synergic effects with amorphous silica action. As a consequence of these reactions,

the carbon dioxide sequestration quantity, in respect to the MSWI fly ash, results about 100 g/kg for the proposed COSMOS technology. This is about double in respect to data reported in literature on similar MSWI fly ash (Bosio et al. 2014b). The carbonation of alkaline fly ash, with the consequent formation of calcite (calcium carbonate), reduces the pH value of the mixture from 12-13 to 8-9. For this reason, carbonate is often measured as total alkalinity of the ash (Chandler et al. 1997).

It was reported that the MSWI fly ash is a pollutant dangerous for humans and the environment. Recently biotoxicity tests have also demonstrated that the stabilization of MSWI fly ash with classical methods (i.e. using concrete matrices) allows to obtain a material, that is not biologically safe (Guarienti et al. 2014, 2016).

The experiments were based on the evaluation of the mortality rate and assessment of morphological developmental hallmarks and teratogenic defects in zebrafish embryos exposed to increasing concentrations of the investigated substance ranging between 1.25×10^4 and 1×10^5 mg/L. The same experiments were made of stabilized MSWI fly ash obtained by the COSMOS technology.

In the last case, no significant mortality and defects on development stages were observed in embryos exposed to solutions of stabilized MSWI fly ash. This allows to deduce that the developed stabilization technology provides a biologically safe inert.

Because of the cost and the sustainability of the COSMOS process resulted highly dependent on the colloidal silica quotation, the technology was improved by the substitution of commercial colloidal silica with rice husk ash (RHA), an agricultural by product of the rice cultivation (Bontempi et al. 2015).

Rice husk (RH) is the outer shell enclosing the rice grain. It is a by-product deriving from the processing of rice and represents an interesting material for composition, availability and cost. Indeed, RH contains about 20% of amorphous silica and, when it is burn for thermal recovery, the percentage of silica passes from 20% in RH to 80% (even 90% in case of proper combustion) in RHA. Rice husk ash is then considered as an excellent source of silica suitable for reuse as raw material. The project, which employ RHA as a silica source, was named COSMOS-RICE (it was realized in 2013-2015). Initially the silica gel employed for the stabilization process was extracted from RHA. Then, RHA was directly added to other ashes, because the alkaline conditions established by all used fly ashes promoted the silicates availability directly in the solution (Bosio et al. 2014b).

COSMOS-RICE project demonstrated the capability to produce new fillers, by using stabilized wastes, and to obtain attractive and sustainable products that can compete with the market of natural raw materials on the global stage.

The obtained material has been employed to realize several composites, such as bitumen, tiles, and objects in polypropylene and resins (COSMOS-RICE) (see Fig. 2.3) (Benassi et al. 2015). The zebrafish embryos tests, made on samples stabilized by the use of RHA, confirmed that the obtained material is safe (Guarienti et al. 2016), in respect to starting MSWI fly ash, that, as expected, is very toxic for zebrafish embryos.



Fig. 2.3 Picture of some composites made in resin and polyamide containing stabilized fly ash (COSMOS) (Benassi et al. 2015)

The environmental and economic sustainability of the new proposed COSMOS-RICE technology is based on the fact that all the materials employed in the stabilization reactions are wastes and by-products, with a consequent very low embodied energy of resulting final material.

As already diffusely discussed in Chap. 1, the critical raw material initiative (EC 2011) has pushed the European policy to pay major attention to the fundamental role of raw materials to guarantee the European living standards. The capability to develop new materials, by optimizing the resources and minimizing the wastes, coupled with the technological innovation and new design concept, is a fundamental aspect for competitiveness and growth. COSMOS-RICE technology is a virtuous example of this: the obtained filler can be used to realize new sustainable composites. The European need of raw materials must force the research policy towards development of innovative solution for raw materials substitution.

The COSMOS-RICE technology was proposed and optimized by using the ashes available in north Italy, where the technology was born and assessed. Moreover MSWI fly ash is present in all European countries (and practically in all the world) and its quantity is continuously increasing (see Fig. 2.1). As a consequence, to guarantee the possibility to apply the same stabilization process in all countries, where for example the availability of RHA and other fly ashes is not guaranteed, adequate substitutes of some raw materials used in the process were also proposed.

Because of silica fume can be considered one cheap amorphous silica source, and it is available almost in all the Europe, the technology was optimized also by using this by-product as amorphous silica source (in substitution of RHA and colloidal silica).

Additionally, the technology was assessed to be applied also in countries where the availability of FGD residues and/or coal fly ash is not guaranteed.

Amorphous silica source is necessary to promote heavy metals entrapment, as already reported and discussed (Bontempi et al. 2010). COSMOS-RICE project demonstrated the possibility to employ RHA as a source of silica, to substitute commercial colloidal silica use. However, in principle, also other by-products, containing amorphous reactive silica, can be employed instead of colloidal silica. In particular, the stabilization material that contains amorphous silica is chosen as a function of its sustainability and local availability. Very recently it was also showed

that silica fume can be considered a low-cost valid alternative silica source (Rodella et al. 2014).

Silica fume is a by-product of the silicon and ferro-silicon industry. It is formed by condensation from the vapor phase of SiO_2. In this material, generally, 85-95% of the contained silica fume is in the form of amorphous silica (Bonen and Khayat 1995), with sizes ranging between about 0.3-1 um (Diamond and Sahu 2003). Silica fume is generally supplied for use in building applications because it is a pozzolanic admixture that is effective in enhancing the mechanical properties of concrete to a great extent (Siddique and Khan 2011).

For a better handling of this by-product, and to decrease its cost of transport, silica fume is also produced in a more compacted form, i.e. densified silica fume. The compact form of silica fume is generally obtained by air flotation of starting material within silos. The end products of this process consist in amorphous silica agglomerates of various shapes and of sizes much larger than the original clusters. This agglomerates range in size from about 10 microns to as much as several thousand of microns (Diamond et al. 2004).

To preserve the amorphous silica reactivity, for the building application (and for COSMOS technologies), the densification process is made at temperatures lower than the melting point of silica. Thus, it is expected that the agglomerations formed during the densification are formed avoiding any additional permanent bonding between individual spheres (Diamond et al. 2004).

Calcium hydroxide, $Ca(OH)_2$, was proposed as possible substitute of FGD residues, where by-products of coal desulfurization are not available. Indeed, calcium hydroxide is an abundant and low-cost material, which has been used for approximately 2000 years in building applications, as for example in mortar, external render, flooring, internal plaster, foundations, decorative applications and so on (Carran et al. 2012). Calcium hydroxide naturally reacts with the carbon dioxide contained in the air, to produce calcium carbonate (the already discussed carbonation reaction). This must be considered when calcium hydroxide is employed in the stabilization procedure.

To take into account the local availability of raw materials used in the stabilization process, some innovations to the traditional COSMOS technology have been proposed (Rodella et al. 2016). In particular, coal fly ash was not considered in the procedure. Fly ash from coal fired power plants is generally used as milling additive to Portland cement (see Chap. 1). This makes this material sometimes not available in some countries. This material was used, in the COSMOS technology, to improve the mechanical characteristics of the obtained filler. As a consequence the possibility to realize the stabilization process removing coal fly ash is considered. This was done, because the coal fly ash can have a commercial value, that generally is considered higher in respect to other residues.

A mixture of MSWI fly ash (130 g), FGD residues (70 g), and silica fume (20 g) was incorporated to 200 mL of milliQ water, and then stirred for 30 min in a laboratory mixer at room temperature. This sample is the reference sample (SF + FGD) (Rodella et al. 2016). Other stabilized samples were obtained by using densified silica fume (dSF) instead of silica fume (SF) as amorphous silica source.

FGD residues were also substituted with calcium hydroxide (Ca(hd)) powders in some samples. The quantity of materials which substitute some ashes in the described procedure was taken equal to original substituted materials.

The pH value of the leaching solutions was also measured. This allowed to evaluate the occurrence of carbonation in the final obtained materials. Indeed, carbonation reaction decreases the pH of the MSWI fly ash (generally 12-13) to values of about 8-9.

To check the efficacy of the stabilization process, leaching tests on all samples were performed according to the European Committee for Standardization normative (EN 2002), in order to quantify the leachability of heavy metals in water. Leaching solutions were realized by tacking the solid-to-liquid ratio equal to 1/10.

The concentration of Pb and Zn in the leaching solution of all stabilized samples, obtained by using different raw materials, are shown in Fig. 2.4 (Rodella et al. 2016).

The y-axis in Fig. 2.4 is limited at the concentration of 3 mg/L, to compare the residual quantities of heavy metals that can be found in the stabilized samples. As a consequence, the concentrations of Pb (104 mg/L) and Zn (8 mg/L) in the leaching solution of the starting MSWI fly ash result out of the scale.

To properly understand and discuss the data reported in Fig. 2.4, it is important to highlight that better stabilized samples exhibit lower soluble heavy metals (mainly Pb and Zn) concentrations in their leaching solutions, in respect to samples that have high amount of soluble metals. By analyzing these data it appears that sample SF + FGD, i.e. using silica fume and FGD residues in the procedure, results to be the best (Pb is undetectable and the Zn concentration is about 0.25 mg/L). As a consequence, it is confirmed that the already established stabilization procedure

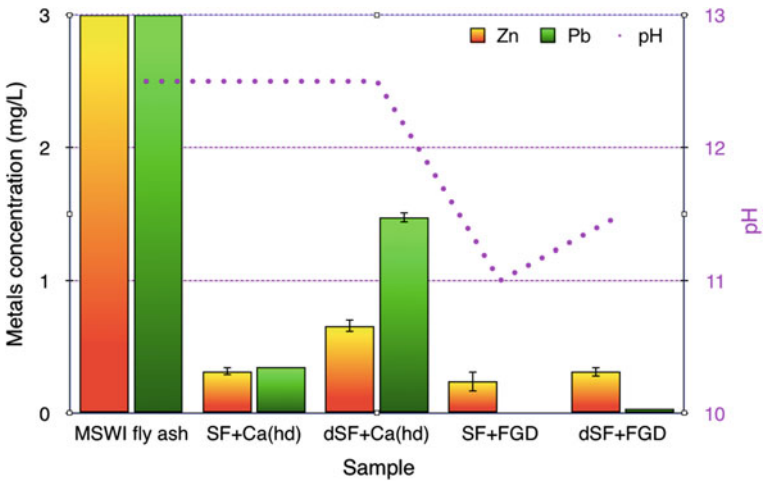


Fig. 2.4 The concentration of Pb and Zn in the leaching solution of MSWI fly ash and stabilized samples, obtained by using different raw materials. *SF* silica fume; *dSF* densified silica fume; *Ca(hd)* calcium hydroxide; *FDG* FGD residues (Rodella et al. 2016)

(Rodella et al. 2014) for heavy metals stabilization, based on the use of amorphous silica source (SF), with the addition of FGD residues, results extremely effective in Pb and Zn stabilization. Moreover, also sample dSF + FGD shows comparable results, with slight high concentrations of Pb and Zn in the leaching solution; this sample was obtained by applying the stabilization procedure, with only one difference: silica fume was substituted by densified silica fume. This leads to the conclusion that, despite that also dSF can be employed as silica source, the reactivity of condensed silica fume seems to be less than corresponding non-condensed silica. The decreased reactivity of silica fume, due to the densification procedure, was already reported in literature (Mitchell et al. 1998). In particular, during the cement production, it was found that the densified silica cannot be easily dispersed during the mixing procedure, due to the impossibility in the complete breaking of silica agglomerates. Although the reduced reactivity of condensed silica fume, the stabilization procedure can be optimized, probably by increasing the quantity of used dSF in respect to the MSWI fly ash amount.

Samples SF + Ca(hd) and dSF + Ca(hd) generate the leaching solutions with the higher quantities of leachable Pb and Zn. These two samples were obtained by employing calcium hydroxide powder instead of FGD residues. Then it is possible to conclude that the efficacy of FGD residues in heavy metals stabilization seems higher than that of low-cost calcium hydroxide powder. However, even with the use of this powder, optimization of the stabilization procedure is possible, for example by increasing the amount of the added silica fume.

Figure 2.4 also reports the pH of the leaching solution of original MSWI fly ash (12.5) and the pH of the leaching solution of the COSMOS samples obtained after the stabilization reactions.

Comparing the pH values of leaching solutions, it is evident that sample SF + FGD and dSF + FGD that exhibit the better results in terms of heavy metals stabilization, show a lower pH, in respect to other samples. It is possible to conclude that, as already shown for samples stabilized by using RHA, also for these COSMOS samples carbonation reactions causes a pH decrease. It contributes to increase the efficiency of stabilization, because the pH lowering causes the reduction of the heavy metals mobility. This is more effective for samples realized with FGD.

Very recently (Benassi et al. 2017) it was finally shown that FGD residues can be also substituted by wood ash, the waste obtained from domestic biomass combustion. In particular, the presence of CaO in these ashes supported the decision to use wood biomass ash as a source of calcium hydroxide in the process.

2.2 Plastic Industry in Europe

In the previous paragraph it was introduced the possibility to reuse COSMOS inert as a filler in plastics (some examples of already realized composites are reported in Fig. 2.3).

Due to their many and different applications, plastic composites are now fundamental for global world economy. Indeed, the use of an inert, in partial substitution of a polymer, allows obtaining several advantages, as for example concerning the reduced cost of the final obtained composite. In addition, the replacement of part of polymer with a low-energy material (i.e. with a material with low embodied energy), involves an increase of the final product sustainability (with a decrease of its environmental cost). The other main reason to produce composites is related to the possibility to modify the properties of the obtained material, in respect to the starting virgin polymer. For example, mechanical properties of a composite can be very different from those of the corresponding matrix.

The reuse of materials produced from wastes as filler for plastics can be an opportunity for Europe, where the plastics market is very active and productive.

Despite the economic crisis the world plastics request is continuously increasing, starting from 2009. The world plastics production was about 311 Mtonnes in 2014 (PlasticsEurope). Figure 2.5 shows that in Europe the plastics production is quite stable: Europe has an annual production of about 59 Mtonnes of plastics (PlasticsEurope). On the contrary the world production is increasing from 2010, due to the increased request of developing countries.

China is the largest producer of plastics (thermoplastics and polyurethanes) materials (26% of the market). Europe is the second plastics world producers (about 20% of the market) (PlasticsEurope). The EU plastics demand was about 47.8 Mtonnes in Europe in 2014. This highlights that the EU production of plastics exceed the internal request, with a resulting export market which is higher than import.

Europe has a positive trade balance in plastics manufacturing and processing (PlasticsEurope). Indeed, the exports in both these two sectors are higher than the imports. The EU positive trade balances in plastics manufacturing and processing are shown in Fig. 2.6. It is evident that the trend of both trade balances is also increasing starting from 2009, consolidating the EU world market on plastics.

About 40 years ago the increasing of oil prices made necessary the replacement of some expensive polymers with more economic fillers. The term "filler" is too

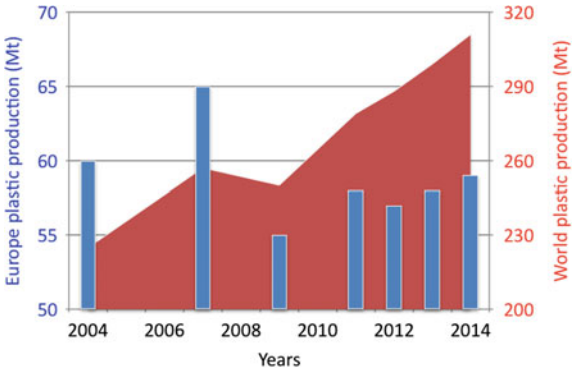


Fig. 2.5 Europe and world plastics production from 2004 to 2014 (PlasticsEurope)

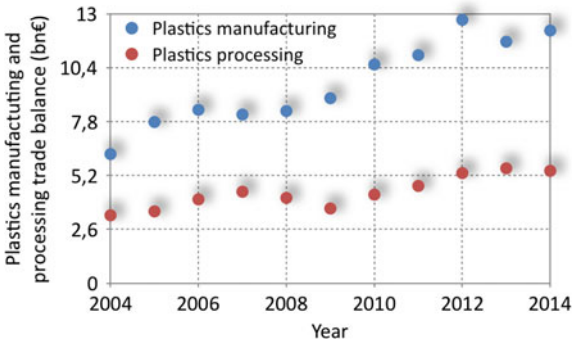


Fig. 2.6 Plastics manufacturing and processing trade balance (PlasticsEurope)

generic, because several typologies of materials, other than polymers, can be used as additive, to obtain a composite. Moreover, in this book the interest is mainly devoted to natural resources. Then the fillers considered in this work are natural inorganic solid particulates that are used, in most cases, in reasonably large amount in plastics.

It was reported that thermoplastics, filled with several inorganic fillers, such as talc, calcite, clay, mica, and carbon black can successfully bridge the gap in performances between near commodity plastics, engineering resins, and short fibers reinforced thermoplastics (Jancar et al. 1999).

The European plastics demand is higher than 45 Mtonnes per year, with polypropylene, which is the most required polymer (about 10 Mtonnes per year). Figure 2.7 shows the EU plastics demand by polymer from 2012 to 2014 (PlasticsEurope). These data are in accord with those reported in Chap. 1, showing

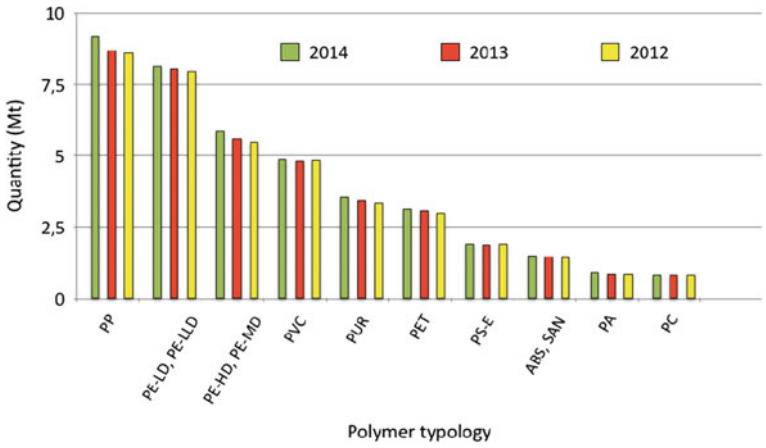


Fig. 2.7 EU plastics demand by polymer (data for 2014, 2013, and 2012) (PlasticsEurope)

the world annual materials production (data from (GRANTA). It is evident that the most requested and produced polymers (PP, PE, and PVC) result the most interesting materials to be tested as a matrix for composites production, with the addition of COSMOS.

The inorganic fillers family contains oxides (glass, MgO, ZnO, Sb_2O_3, Al_2O_3, and SiO_2), hydroxides (mainly Al and Mg hydroxides), salts (carbonates, sulphates, phosphates, and hydrotalcite), silicates, and metals (Xanthos 2010). Antimony trioxide (Sb_2O_3) is often used as a synergic component in combination with halogenated fire retardants. Unfortunately Sb is a critical raw material, then the necessity of its recovery and/or substitution is urgent. This will be diffusely discussed in the next paragraph.

In general, the main parameters affecting the properties of polymer composites are the following:

- the filler properties (size, and shape);
- the filler and matrix composition;
- the surface adhesion between the components;
- the synthesis method (Xanthos 2010).

The plastics filler market cannot be quantified, due to different amounts and types of fillers used. Moreover, literature reports that about 30% of polymers made worldwide it is used for composites production (Jancar et al. 1999). This makes the possibility to substitute the natural filler employed in composites with materials obtained from waste a very promising approach to increase the sustainability of plastic sector.

2.3 Alternative Plastic Composites: Increased Sustainability by Substitution of Natural Fillers

As reported in Sect. 2.1, stabilized fly ash material results chemically stable due to silica network formed by added silica and to carbonation reactions. In particular carbonation reactions are quite slow, then the stabilized sample aging promotes its chemical stability. Samples stability was verified and confirmed by leaching tests made on COSMOS samples, two years after stabilization. One advantage of the produced material is its physical form: it is a powder, then it can be used as a filler in a composite, realized by mixing a matrix with a powder. As a consequence, in principle this material may be used with all matrices requiring inorganic filler.

To evaluate the environmental sustainability of the proposed new filler embodied energy (EE) and carbon footprint (CF) of the synthesis procedure were evaluated. On the basis of the reported stabilization procedure (described in Sect. 2.1) it results that COSMOS material generally has an EE ranging between 0.779 and 0.859 MJ/Kg and a CF ranging between 0.016 and 0.028 kg/Kg. These values have been calculated in accord with the principle to use local raw materials for MSWI fly

ash stabilization. Indeed, as explained in Sect. 2.1, the COSMOS technology requires an amorphous silica source, for heavy metal stabilization. This was originally obtained by using a colloidal silica solution. However, due to the low sustainability of this commercial product, the technology was assessed by the substitution of colloidal silica with rice husk ash (RHA) or silica fume. The second fundamental ingredient is FGD residues. The possibility to use inexpensive calcium hydroxide (or calcium oxide, available in wood biomass ash), instead of FGD residues, when these by-products are not locally accessible, was also investigated. When the basic materials for stabilization are not locally available, EE and CF must be calculated taking into account also materials transport. For example, in the eventual stabilization of MSWI fly ash in Russia, using RHA as silica source, where RHA is transported for several kilometres (for example from Italy) because it is not locally available, the CF contribution must be reconsidered to take into account also carbon footprint due to the RHA transport.

Figure 2.8 shows the EE and CF of the obtained COSMOS inert (represented as green stars), as a function of their price (Bontempi 2017). For comparison also some other ceramic materials, which are used as a filler, for example in the building applications, are also considered. They are all natural resources, generally available in many locations around the world. Data are obtained from CES selector (GRANTA). The natural resources used for construction, mainly calcite and sand, are not expensive, and often can be found locally, saving transport costs and CO_2 emissions. These materials are also minimally processed (they are often used as well). This, coupled with minimal transport, results in relatively low embodied energy and carbon footprint figures. Other materials are reported for comparison, as for example glasses, silicates, titanium dioxide, and halite (sodium chloride). EE and CF of engineering bricks, mainly used in building applications, are also shown. Figure 2.8 indicates that, among the reported materials, the most sustainable are halite, dolomite and wollastonite. Bricks are made primarily from clay and shale. Both materials are abundant nontoxic natural resources, and can be found in many locations around the world. Bricks are used in building for their durability (hundreds of years) and low maintenance. Then, despite bricks have a relatively high EE and CF, this can be offset by their durability (Calkins 2009). From a rapid analysis of Fig. 2.8 it appears that the new proposed inert can be compared to calcium carbonate, in terms of energy and environmental parameters, which are chosen to quantify the sustainability of a material. The price, which is used to evaluate the commercial applications of a material, is a fundamental criterion, that is also considered, because it can be related to the market possibilities of the considered material. The price of stabilized material was tentatively calculated on the basis of LCA evaluations (COSMOS-RICE) made on the technology and considering different final uses.

From data shown in Fig. 2.8 it is evident that the new proposed inert is more sustainable if compared to some other natural resources, as for example talc, marble, and sandstone. Then its market applicability is potentially very promising.

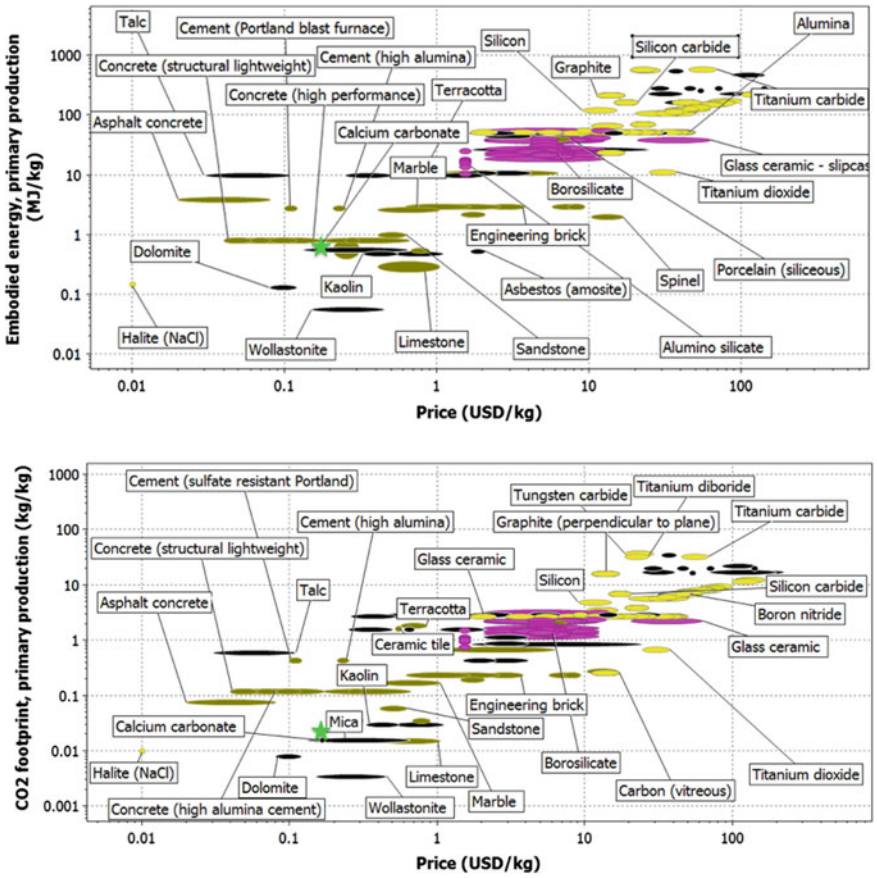


Fig. 2.8 Embodied energy and carbon footprint of some ceramic materials that are used as a filler (Bontempi 2017). Other materials are reported for comparison, as for example glasses, silicates, titanium dioxide, halite (sodium chloride), and bricks. The values of EE and CF of COSMOS inert are represented as green stars

As already discussed, one of the main advantage of the new proposed material is related to its physical form: the COSMOS material is a powder, that it can be applied as a filler.

To choose the most suitable application, the particle size analysis of the obtained inert was also considered. Figure 2.9 reports an example of particles size distribution for two obtained COSMOS materials, by using colloidal silica and RHA as stabilizing agents. It appears that the particles dimensions distributions are quite similar, with 80–90% of the particles having dimensions lower than 50 microns. The maximum particles sizes are of the order of about 70–80 microns. The absence of any coarse aggregate is fundamental to guarantee the filler uniform distribution in the matrix. Indeed the particles distribution in a matrix influences functional and

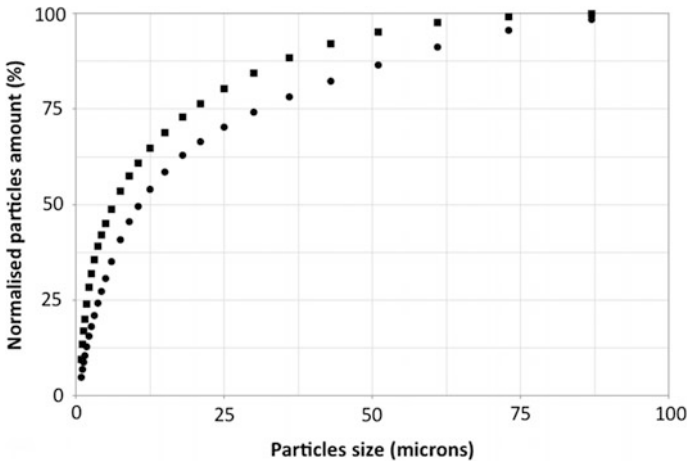


Fig. 2.9 Particles size distribution for two obtained COSMOS inert materials, by using colloidal silica and RHA as stabilizing agents. The two size distributions are quite similar

mechanical properties of the final obtained composite. The size distribution curve is extremely important also to have an idea about the opportunity of inert injection, for example for plastic composites realization.

The possibility to reuse the new filler in building industry was considered and some obtained results were very promising (Zacco et al. 2012). Indeed, as already reported, this filler is mainly composed of calcium carbonates and silicates phases (crystalline and amorphous). However, it also contents soluble salts (such as NaCl and KCl): the salts presence in stabilized material requires an additional step in filler preparation, before its use in cement and concrete. Indeed, a washing process is mandatory to remove soluble salts, which are deleterious for building construction. This implies the increase in the cost and the reduction in the sustainability of the stabilization technology, in terms of both EE and CF. For this reason the use of the new filler was addressed to the plastic composites, with the aim to substitute natural fillers, such as calcium carbonate and talc; in this case, indeed, the washing process, to eliminate chloride, was avoided. A plastic composite is generally realized with the reinforcement (powders and fibers) embedded in a polymer matrix. The matrix holds the reinforcement while the filler material improves the overall mechanical properties of the composite. In accord with data about plastics demand in EU (discussed in Sect. 2.2 and shown in Fig. 2.7), polypropylene (PP) was chosen as the matrix material, for the first tests, about COSMOS reuse as a filler.

PP is a thermoplastic polymer; it can be obtained by polymerizing propylene molecules. PP possesses several useful properties like high heat distortion temperature, transparency, flame resistance, dimensional stability (Shubhra et al. 2011). The main fillers employed to realize PP composites are calcium carbonate and talc.

Talc, used for plastic composites, has generally two different sizes distributions. The first, that is due to the coarse products, is comparable to those found for the

new stabilized material (see Fig. 2.9), with a maximum size of about 75 microns. Moreover, also fine talc exists, with particles size as low as 1 micron. Generally, in application where talc is used as a filler, particles size varies in the range 0.2–6 microns (Xanthos 2010). Concerning calcium carbonate, grades of different particle sizes are used depending on the polymer, the required mechanical properties, the final application, and the fabrication method. Fine grades are generally between 3 and 7 microns (Xanthos 2010).

Polypropylene composites containing different amounts of stabilized COSMOS material were synthesized and their mechanical properties were evaluated. The experiments were made considering different typologies of stabilized materials, i.e. based on use of colloidal silica, RHA, and silica fume (Besco et al. 2013, 2014). To realize different tests, also the MSWI fly ash origin was geographically different. However the mechanical performances of the obtained composites were always comparable, suggesting that a slight variation on the COSMOS inert composition don't affect the composite mechanical characteristics.

The results about mechanical properties of the obtained PP composites are shown in Fig. 2.10 (Bontempi 2017). In particular, this figure allows comparing the results obtained in terms of mechanical characteristics, with literature data concerning PP and PP composites, also considering different fillers typologies [literature data were obtained from CES Selector (GRANTA)]. The attention was mainly devoted to calcite (calcium carbonate) and talc, as they are the main fillers already employed for PP composites. As a matrix, PP homopolymer and PP copolymer are reported in Fig. 2.10. In the first case the material is obtained by polymerization of propylene monomers. In the second case, comonomers are also added in the copolymerization of PP. This allows to decrease the EE and CF of the obtained matrix.

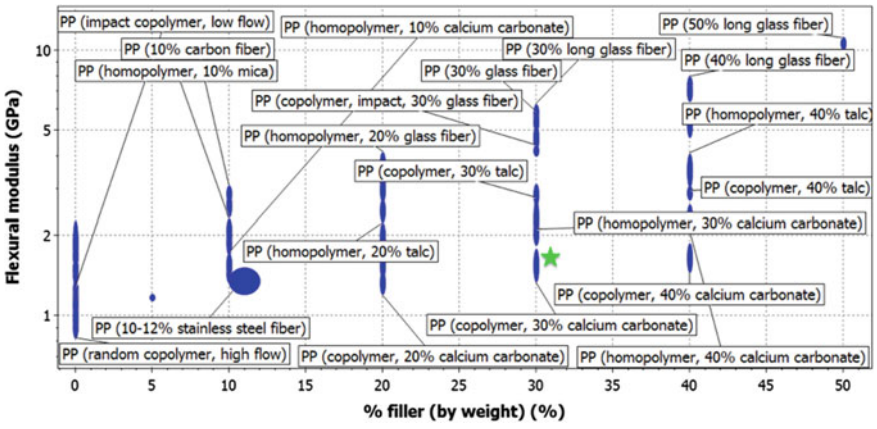


Fig. 2.10 Mechanical properties of PP and PP composites, considering different filler typologies. Data evaluated for PP-COSMOS composites are also reported as green stars (experimental data are reported only for PP composites containing 30% of COSMOS inert) (Besco et al. 2013, 2014; Bontempi 2017). Literature data were obtained from CES Selector (GRANTA)

Data reported in Fig. 2.10 highlight that the addition of a filler in the PP matrix improves mechanical resistance of the final composite. Data also show that the elastic modulus of a composites result always higher than corresponding value of the polymer matrix. The increased composite rigidity, in respect to the original polymer, can be an advantage in some applications, but it can also be undesirable for other utilizations. Data reported in Fig. 2.10 show that some fillers seem to be more effective in the improving the mechanical resistance of the final composite. For example talc seems to be more efficient in respect to calcium carbonate. This can be also attributed to the low dimensions of particles size of talc (which are generally in the order of 0.2–6 microns). The available data also consider the addition of glass fibers in the composites. Fibers allow to obtain the higher mechanical performances of PP composites, in terms of elastic modulus and mechanical strength. Considering the same filler typology (as for example talc or calcium carbonate), Fig. 2.10 also highlights that the increase in the mechanical performance (mainly in the flexural and Young moduli) of the obtained composites is dependent on the quantity of considered added filler. Results obtained for composites containing lower COSMOS amount (5, 10, and 20%), but not shown in Fig. 2.10, are generally in accord with the expected trend in mechanical performances of PP composites, which are dependent on the added filler amount. Analyzing mechanical performances of PP-COSMOS composites (represented with a green star in Fig. 2.10) it can be concluded that they are comparable to corresponding composites, obtained by using calcium carbonate as a filler. This result is extremely important, because it highlights that a possible reuse for the new proposed filler is now evident: plastic composites appears to be a very promising application field for COSMOS reuse.

To evaluate the sustainability of the PP composites shown in Fig. 2.10, their EE and CF are evaluated and reported in Fig. 2.11 [data were obtained from CES Selector (GRANTA)]. Data for unfilled polymers are also reported. It is very interesting to notice that sustainability indicators have a behaviour that is opposite if compared to mechanical performances. Indeed, both EE and CF generally decrease considering a PP composite in respect to the raw polypropylene. In addition, the increase of the filler content corresponds to a linear decrease of EE and CF of the composites. This is due to the fact that PP is a petroleum-derived product, then the increased addition of a low EE natural resource, as for example calcium carbonate, enhances the sustainability of the final obtained composite. PP composites realized with calcium carbonate appear to be the most sustainable (less EE and CF) among the reported literature data. Indeed, as already seen in Fig. 2.8, this filler has very low values of EE and CF (respectively in the range of 0.5–0.6 MJ/Kg and 0.015–0.017 kg/Kg), resulting lower more than 2 order of magnitude in respect to corresponding values of raw PP.

As expected the production of some filler materials in the synthesis of plastic composites results less sustainable than the realization of corresponding composites made with calcium carbonate (see for example talc and glass fibers PP composites shown in Fig. 2.11). The higher EE and CF of PP composites made with other fillers are in accord with data reported in Fig. 2.8, reporting EE and CF of all fillers

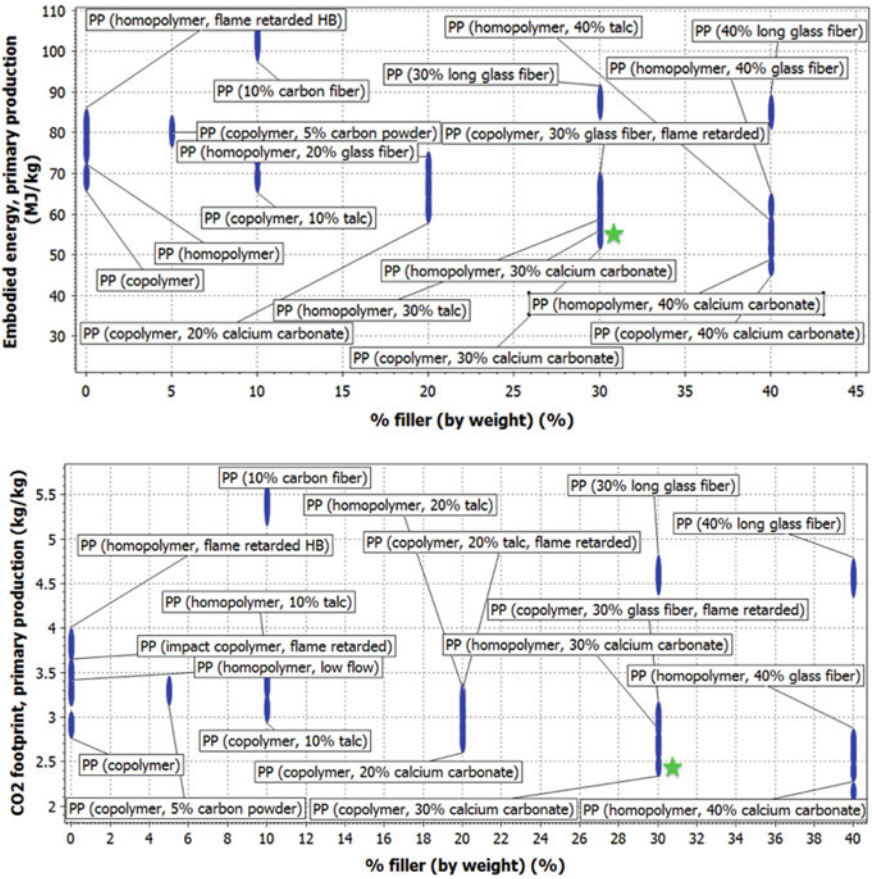


Fig. 2.11 Embodied energy and carbon footprint of PP composites. Data evaluated for PP-COSMOS composites are also reported as green stars. Literature data were obtained from CES Selector (GRANTA)

considered in this chapter. In particular, glass fibers are less sustainable than the COSMOS filler, with an EE and a CF mean value of 51.8 MJ/Kg and 2.99 kg/Kg respectively. This represents a difference of about two orders of magnitude in respect to the new proposed filler. Obviously glass fibers can be necessary to obtain PP composites with high mechanical performances, indeed fibers can guarantee improved characteristics, but with lower sustainability of final composites.

In literature other examples can be found in the use of materials obtained from waste as filler for plastic composites. However, at the best of author knowledge, no other recovered material results so convenient in term of energies and emissions involved in its production, as COSMOS.

For example pineapple leaf waste was proposed (Kengkhetkit and Amornsakchai 2014) to be added to polypropylene. However, despite that some mechanical performances of the obtained composites are similar to those obtained by using the new proposed inert, the EE for the production of the fillers from leaf waste is higher than that of COSMOS materials.

One of the most useful visualization method for materials comparison and screening is Ashby's chart (1992). Ashby usually compares the relative mechanical performance of a variety of materials for a specific constructive function. He has also introduced the use of performance indices as design criteria. Materials comparison, to screen the most suitable material for a specific application, is achieved by plotting the investigated materials characteristics and the performance indices that are typically a mathematical combination of some material properties (generally mechanical performances). For this aim Weaver (Weaver et al. 1996) introduced a performance index M, that is generally a function of two parameters. For example, the necessity to optimize flexural strength (FS), taking into account EE, can be obtained by plotting

$$M = FS/EE^{(n)}$$

The default axes of the charts that show and correlate materials properties are generally logarithmic, because material characteristics often cover large ranges of values and it is essential to show all available materials for suitable comparison.

As a consequence the previous equation can be re-written as:

$$\log FS = n \log EE + \log M$$

A line of slope n on the *log-log* plot describes the index.

To properly take into account also the environmental properties of a material (a composite in this case), during the design steps of a specific object, the mass (or volume), the cost, or life must be considered, but also environmental parameters, such as embodied energy and/or CO_2 footprint.

Figure 2.12 presents an Ashby plot, where flexural strength as a function of EE for PP and PP composites is shown. The selected performance index M, with $n = 1$, is also reported as resulting line, that indicates constant material performance. This line was settled to intercept PP-stabilized material containing 30% of COSMOS. As a consequence, the materials that lie on a contour have the same overall performance index (e.g. flexural strength-embodied energy) as the chosen reference material. It can be a guideline for material selection. All materials that lie above the line have a higher FS-EE and are a better choice, if flexural strength must be increased. On the contrary, materials that lie below are worse.

Ashby plot, reported in Fig. 2.12, is very useful for the following reasons (Ashby 2007): (i) it allows easily visualize some functional (generally mechanical, but in this case also EE) properties of selected materials, (ii) it concedes simplified

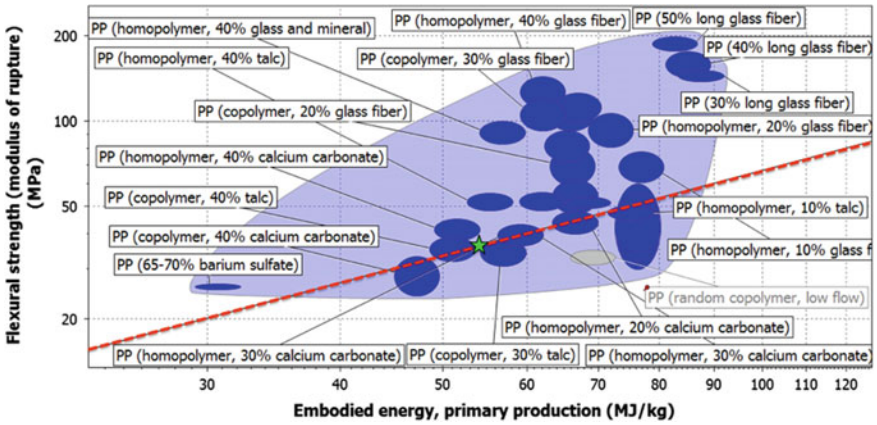


Fig. 2.12 Ashby plot of flexural strength as a function of EE for PP and PP composites. The selected performance index M, with $n = 1$, is also reported as resulting line, that indicates constant material performance. This line was settled to intercept PP-stabilized material containing 30% of COSMOS

comparison of different materials, on the basis of selected characteristics, (iii) it promotes the most efficient choice of the materials/manufacturing processes during the product design stage, and (iv) it allows to investigate possible substitution of materials that are unsustainable or very expensive, exploring the potential of one material to replace another. The last possibility is the most interesting for the aim to propose suitable substitute to some raw materials.

Ashby plot in Fig. 2.12 highlights that all PP composites, realized with the addition of calcium carbonate or talc, have comparable mechanical performances, if corresponding EE is considered. This means that generally the PP composites made with calcium carbonate, talc, and the new stabilized filler are equivalent in terms the investigated mechanical property with respect to their EE. This also means that, the increased EE of PP-talc composites, in respect for example to PP-calcium carbonate composites (see Fig. 2.12), can be justified in view of the increased mechanical performances of the final materials.

Figure 2.12 shows that the increased EE of the PP-glass fibers composites can be also justified by the high flexural strength that can be obtained for these materials, that can be necessary for some (eventually limited) applications. Similar analysis can be made in view of the performance index that must be optimized. This is an example of material selection design, that accounts also for sustainability.

The potentiality of this method lies to the fact that alternative materials for design can be compared in view of optimized performance indices, that account also for sustainability. The method also has the great advantage of being able to examine several raw materials and support on the selection of the most suitable one for each application, representing a great support to sustainable design.

2.4 A Substitute of Antimony, a Critical Raw Material

The European policy aims to reduce its economic dependency on imported raw materials, because some of these are considered critical for Europe's industries. Several activities have been encouraged to guarantee the access to raw materials within the EU and external sources, to promote resource efficiency, including recycling, to push the research to find advancing alternatives to these materials through substitution. According to an EU study (EC 2011) 14 materials are considered as critical within the EU. The definition is the following: "a raw material is labeled 'critical' when the risks of supply shortage and their impacts on the economy are higher compared with most of the other raw materials". On this basis antimony is classified as a critical raw material.

Figure 2.13 reports the annual world production of elements (with antimony that is highlighted in the figure), plotted in respect to environmental country risk Herfindahl-Hirschman Index (Rhoades 1993) evaluated in the CES Selector database (GRANTA) and calculated as:

$$\mathrm{HHI} = \sum_{c} (\mathrm{S_{ic}})^2 (10 - \mathrm{EPI_c}/10)$$

where:

$\mathrm{EPI_c}$ the value of the Environmental Performance Index (calculated by Yale University, based on the data of 2010) for the producing country *c*.

$\mathrm{S_{ic}}$ the % of worldwide production of the raw material *i* within country *c*.

This indicator represents the risk that worldwide supply of an element may be restricted in future as a result of environmental protection measures taken by any of its producing countries. Risk values are expressed qualitatively on a five-point scale: Very high (>4), High (3–4), Medium (2–3), Low (1–2), Very low (<1).

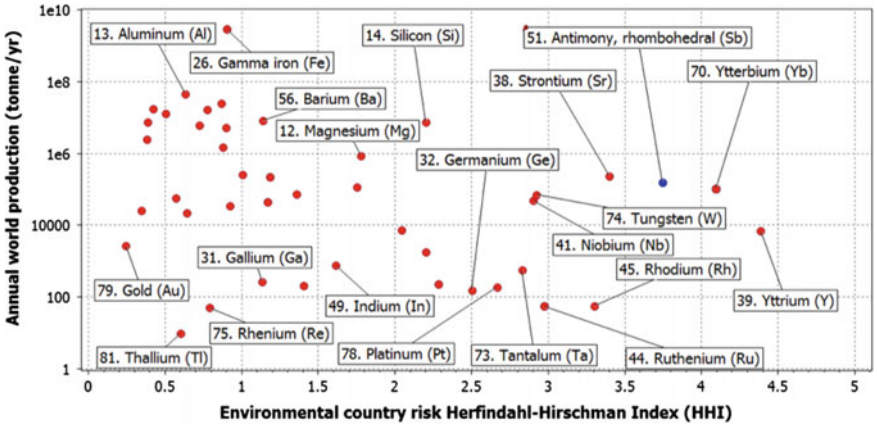


Fig. 2.13 Annual world production elements plotted in respect to environmental country risk Herfindahl-Hirschman Index (Rhoades 1993). Sb is highlighted in the figure

Figure 2.13 reports some other elements such as some rare earths (Y, Yb), W, Nb, Mg, Ge, Pt, Ga, and Si. Au is also reported as a reference. On the basis of the defined criteria, an HHI value larger than 3 represents a high environmental country risk. Sb, Y, and Yb show an HHI index higher than 3,5. However, despite that Y and Yb have a higher HHI index, in comparison to Sb, Sb is one of the most requested elements, among the critical ones (its annual world production is the higher among the most critical raw materials). Then a particular attention must be devoted to find appropriate ways for its recycle and/or substitution.

The main diffused Sb ore is stibnite (Sb_2S_3), with valentinite (Sb_2O_3) phase, that is a product of the stibnite oxidation, also quite extensively distributed in soils (Filella et al. 2002). Antimony is generally employed as oxide. In particular, antimony trioxide (Sb_2O_3) is primarily used as a fire retardant in plastic as well as electronic devices and household appliances. The use as flame-retardant in plastics accounts for about 72% of Sb employ (see Fig. 2.14). It can also be used as a filling agent for various rubber, ceramic and fiber products, as a pigment in oil paints, and as a catalytic agent in organic synthesis. According to the U.S. Geological Survey, China is the largest producer of Antimony metal, with 86% of antimony being mined in China; followed by 3% in Tajikistan and Bolivia; 2% in Russia and South Africa and 1% in Australia and Turkey. It is evident that, depending on the changing on the government policies, China can affect the market of Sb, by changing its price. In Fig. 2.14, the fluctuation of the last years price of Sb is reported (USAC). This is due to the Chinese policy about the antimony export. It is evident that this fluctuation could seriously affect the EU economy based on this metal. Several other countries have restrictions concerning trade with antimony. The world natural resources of this metal are expected to be exhausted in the several 8 years, then Sb is the first critical raw material with the higher urgency of substitution (EC 2011). As a consequence also British geological survey has listed Sb on the top of three critically high-risk elements.

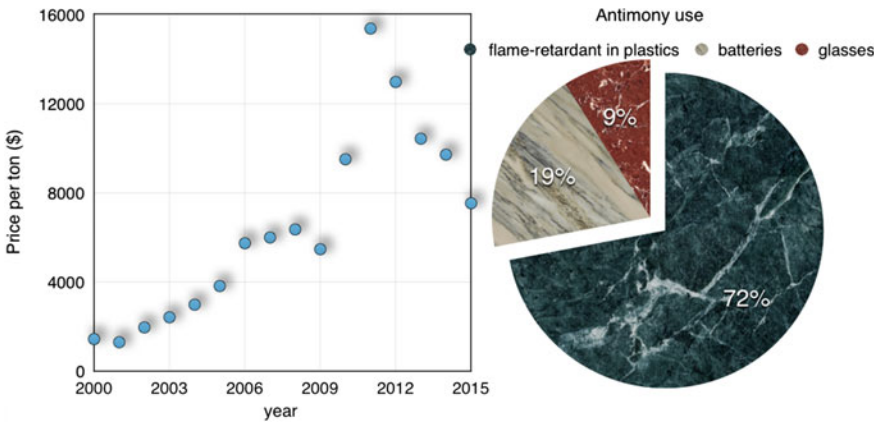


Fig. 2.14 Antimony price per tons in the last 15 years. Sb main uses are also reported (in percent)

As already reported, antimony is mainly used in flame retardants. Indeed, most of the polymers used in our society are petroleum-based and hence are flammable. Therefore, EU regulatory framework has developed some restriction about flame behaviour of all objects made on plastics. Flame-retardants are materials added or applied to reduce flammability, and to delay ignition of the obtained final products. They are necessary to meet the legal requirement concerning safety conditions. The main fire-retardants commercially available are based on halogens, then they are diffusely employed. Brominated flame retardants (BFRs), for example, have been widely used in electronic and electric equipment, furniture, construction materials, and other commercial products (Brits et al. 2016). Antimony is mainly employed in the form of antimony trioxide, as a catalyst, with halogen fire-retardants, to speed the release of bromine or chlorine radicals. As a consequence, it is used as synergists with other materials. It also reacts with the halogen radicals, forming antimony halogens that help remove the high-energy H and OH radicals, thus helping suppress the fire (BuildingGreen). Antimony is used also in power transmission equipment, batteries, and alloys.

With the increasing use of polymeric materials in construction, electronic and computer equipment, global market demand for the flame-retardants has increased substantially in the last years. As an example, the global market demand for BFRs in 1990 was 145,000 tonnes (Pettigrew 2000). It grew to over 310,000 tonnes in 2000 (BSEF) which represents an increase of over 100% in one decade.

From an environmental point of view, Sb is a toxic metal. Antimony is a carcinogen and is comparable to arsenic for its chemical properties and its toxicity (Westerhoff et al. 2008).

Due to adverse health effects, produced by antimony and its compounds, Sb was listed as priority pollutants by the US Environmental Protection Agency (USEPA) and the European Union (EU) (Wu et al. 2012).

Since 1997, the number of papers reporting the distribution, accumulation and toxicity of brominated flame retardants and Sb has grown exponentially.

Research papers have demonstrated that also brominated flame retardants are persistent and bioaccumulative. They have been found in different environmental media and in biota (Besis and Samara 2012). The world diffused distribution of some flame-retardants, including their revelation in remote areas such as deep oceans and the Arctic catches now the attention not only of the scientific community, but also of the public and politicians (de Boer et al. 1998). Several studies in the indoor environment have focused on BFRs presence in dust (Wilford et al. 2004). Moreover, the humans are exposed to these pollutants also by diet (Domingo 2004). It was already shown that some plastics bottles containing drinking-water can produce co-leaching of brominated compounds and antimony (Andra et al. 2012).

The concerns about these substances are very high due to their toxicity. Moreover also the environmental cost, due to their disposal is very onerous. For example, in construction and demolition waste management, most construction materials are inert, and can be considered as nonhazardous waste. On the contrary, other building materials contain hazardous substances, as for example flame

retardants in wires and cables. As a consequence, this limit the recycling and recovery possibilities of all waste building, increasing the cost for their management. There are also several risks that these contaminants will be released into various environmental media (e.g. water, sediment, and soil) when hazardous construction and demolition wastes are landfilled.

An interesting characteristic of the new filler (COSMOS) is related to its capability to improve the polypropylene thermal stability.

To test the polypropylene composite fire-resistance property, UL 94 Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances was applied. This test is widely used both in industry and academic research centers. It is released by Underwriters Laboratories of the United States. It covers tests for flammability of polymeric materials used for parts in devices and appliances and it is used to group materials into categories based on their flammability. This standard can be used as a preliminary indication of a material acceptability with respect to flammability for a particular application (UL94). In addition it is a very useful test, because it is quite simple to be realized, don't requiring specific apparatus. The test is used to verify the flammability of the composites in vertical position, in accord to the schema reported in Fig. 2.15. At least 10 different specimens for each test are generally used for statistics. Their dimensions are: length 125 ± 0.5 mm, width 13 ± 0.5 mm, and thickness 1.6 mm. They are fixed in vertical position at a distance of 10 mm from the bunsen, with the test flame impinging on the bottom of the sample. After the flame ignition, the bunsen is removed. The time required for flame extinction can be evaluated and the eventual sample drip is collected on cotton. To achieve a V rating (e.g. V-0, V-1, or V-2) the samples must extinguish within specified times, not burning to the top clamp or dripping molten material which ignites a cotton indicator. Composites prepared with MSWI fly ash and with stabilized MSWI fly ash were tested. All samples were synthesized by using 25% of the filler in a polypropylene matrix. Results, made on at least 10 specimens for each test, showed that composites containing the new filler can be classified as V-2. On the contrary, composited containing raw MSWI fly ash were not classified (N.C.).

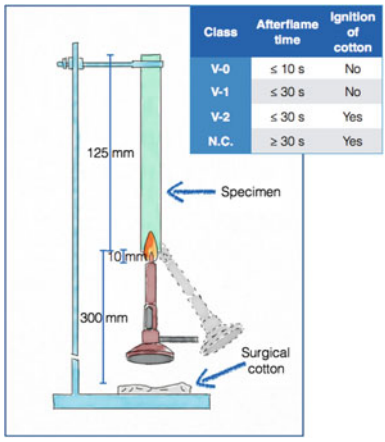


Fig. 2.15 Schema of the apparatus used for UL 94 Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances. Classifications of tests results are also reported

These preliminary results are very promising, suggesting that this filler has great potentialities to be used to increase the thermal stability of polymer composites. Because COSMOS is generally employed as a filler, then in higher quantities in respect to the commercial flame-retardants and Sb, it would be very interesting, in the near future, to investigate the synergic effect of using COSMOS with sustainable flame retardants, other that BFRs and antimony oxide.

Additionally the inorganic nature of the new filler makes it more suitable for combustion, in respect to organic compounds. Indeed, during the process of interference with flame, BFRs can reach high temperature, with consequent decomposition. Decompositions of BFRs have produced some concerns, with regard to the release of toxicants compounds, as for example brominated dibenzodioxins and furans (Thoma et al. 1986).

Thermogravimetry analysis (TGA), that measures the amount of weight change of a material, as a function of increasing temperature, showed that degradation of the BFRs starts with the formation of Br-radicals and the abstraction of hydrogen by radical transfer reactions, with HBr being the main product of the fire retardant degradation. The elimination of HBr was generally reached at about 500 °C. Brominated aromatic compounds, that are harmful, are generally formed between 270 and 400 °C (Grause et al. 2008).

TGA and corresponding derivative thermogravimetric analysis (DTG) diagrams obtained from stabilized sample (COSMOS inert) are shown in Fig. 2.16. The 1st derivative of the TGA curve, DTG, gives the decomposition rate and is useful to precisely highlight the mass loss steps. From TGA curve it is evident that a weight

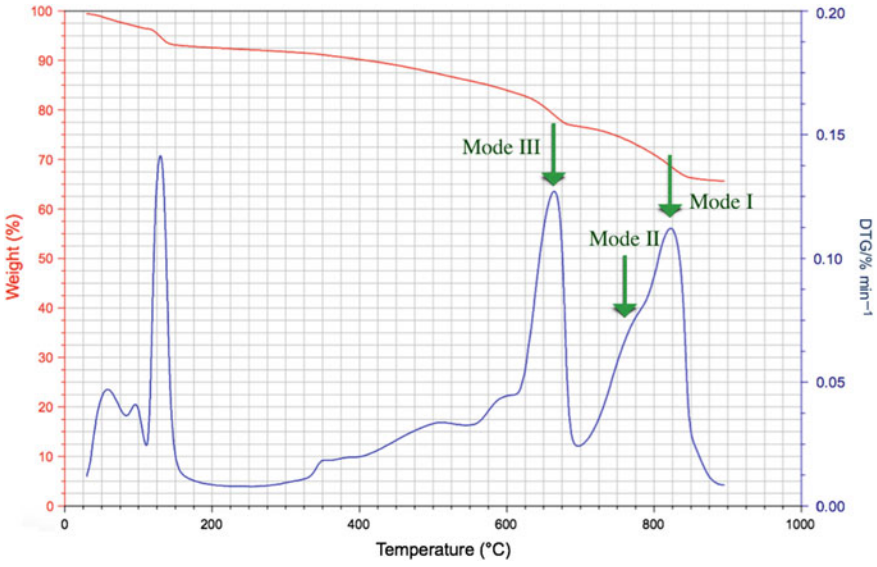


Fig. 2.16 Thermogravimetry analysis (TGA) and corresponding derivative thermogravimetric analysis (DTG) diagrams obtained from stabilized sample (COSMOS inert)

loss of the sample gradually occurs, when the temperature increases. Some peaks are present in the DTG diagram. The first peaks appears at temperature lower than 200 °C. Other peaks can be found in the range of about 600–700 and 700–900 °C. Some bumps in the region of 350–600 °C are also visible. These curves (TGA and DTG) are very similar to those already found for samples, that were stabilized by using the same technology, but some different raw materials (Benassi et al. 2017). Indeed, as already discussed, the proposed stabilization technology, that was optimized by using several by-products, can be realized by using different raw materials, on the basis on the local materials availability.

No data are available in literature to compare the results about thermal analysis of stabilized MSWI fly ash samples. However, a comparison can be made with thermal investigations directly made on MSWI fly ash. An interesting difference between TGA curves of stabilized fly ash and the corresponding raw fly ash material can be attributed to the absence of a fast reduction of mass between 531 and 660 °C, for stabilized sample, that can be attributed to the decomposition of calcium hydroxide. Indeed, in the stabilized samples, this phase is transformed into calcium carbonate, by carbon dioxide sequestration, to due carbonation process involved in the stabilization reactions. For MSWI fly ash, a mass loss between about 950 and 1240 °C, is caused by decomposition and/or volatilization of chlorides (mainly NaCl and KCl), that are present in large amount in this ash typology. This temperature range was not investigated for the present sample.

For samples stabilized with COSMOS technology, a mass spectrometer was also employed to evaluate which gases are emitted during the heating process at the same time of sample volatilization. Then, TGA analysis was coupled with a mass analyzer, in order to detect and analyze these gases over a temperature range. The results obtained are discussed in a very recent work (Benassi et al. 2017), and they are very similar to those reported in Fig. 2.16.

It was shown that, in the investigated range of analysis, the main detected gases are H_2O, CO_2 and SO_2. In particular, the analysis reveals that the mass decrease till to about 200 °C is attributed to water evaporation. Then the first peaks till about 200 °C are due to the removal of physical adsorbed water. In TGA curves made on raw MSWI fly ash, some peaks are found in the range of 350–550 °C and they are attributed to the removal of hydration and institutional water as well as burning of organic substance (Haiying et al. 2010). In the present case only some bumps in the region of 350–600 °C are visible. Other peaks can be associated to CO_2 evaporation, then to calcium carbonate decomposition. Indeed, according to literature results, three modes of calcium carbonate decomposition can occur (Thiery et al. 2007). They can be separated when the level of sample carbonation increases: mode I (780 °C < T < 990 °C), mode II (680 °C < T < 780 °C), and finally, mode III (550 °C < T < 680 °C). Mode I is attributed to the decomposition of calcite, the highly crystalline $CaCO_3$ phase. Mode II is associated to the decomposition of a calcium carbonate phase with lower crystallinity, as for example vaterite (Šauman 1971), in respect to $CaCO_3$. Finally, mode III decomposition is referred to the presence of amorphous calcium carbonate (Thiery et al. 2007). These three decomposition modes can be found in the DTG curve shown in Fig. 2.16. These

three modes can be clearly distinguished also in the DTG diagrams of all stabilized samples (Benassi et al. 2017), made by using wood pellet ash. In addition, mass spectroscopy referring to CO_2 evaporation showed a behaviour that is consistent with the DTG trend from about 500 °C to about 900 °C. This result is very important, because it is shown that stabilized samples contain large amount (also higher than 40%) of calcium carbonate (Benassi et al. 2017), which is obtained by carbon dioxide sequestration of the realized mixture during the stabilization process. In addition, mass analysis shows that the main detected gases are H_2O, CO_2 and SO_2, with the last gas produced at high temperatures (in the range of 780–990 °C) and attributed to the decomposition of sulphate phases. As a consequence the eventual new filler decomposition don't produce environmental concerns, if the COSMOS filler will be used as commercial flame-retardants composites.

It is clear that, in view of these results about the high amount of calcium carbonate phases present in COSMOS samples, the carbon footprint (CF) of the material obtained by the proposed stabilization technology should be revised. In particular, due to the carbonation relations that allow sequestering carbon dioxide in the stabilized material, a lower CF should be attributed to the obtained new filler.

Figure 2.11 shows some interesting results about the use of flame-retardants in plastic composites, that weren't discussed before. These compounds have high embodied energy (EE) and carbon footprint. This can be clearly appreciated considering PP, with no filler addition. It results that also for nearly pure PP (with the addition of only flame-retardants) these compounds contribute to increase CF and EE of the matrix.

As a consequence, all the composites containing conventional flame-retardant additives are placed in the higher regions of Fig. 2.11. In conclusion, the substitution of commercial flame-retardants, made on Sb and BFRs, will permit not only to preserve natural resources, but also to increase the sustainability of the final obtained composites.

References

Andra SS, Makris KC, Shine JP, Lu C (2012) Co-leaching of brominated compounds and antimony from bottled water. Environ Int 38:45–53. doi:10.1016/j.envint.2011.08.007

Ashby MF (1992) Materials selection in mechanical design. Pergamon Press, Oxford, UK

Ashby MF (2007) The CES EduPack Database of Natural and Man-Made Materials. http://www.grantadesign.com/download/pdf/biomaterials.pdf

Belevi H, Stampfli D, Baccini P (1992) Chemical behaviour of municipal solid waste incinerator bottom ash in monofills. Waste Manag Res 10:153–167. doi:10.1016/0734-242X(92)90069-W

Benassi L, Franchi F, Catina D, Cioffi F, Rodella N, Borgese L, Pasquali M, Depero L, Bontempi E (2015) Rice husk ash to stabilize heavy metals contained in municipal solid waste incineration fly ash: first results by applying new pre-treatment technology. Materials (Basel) 8:6868–6879. doi:10.3390/ma8105346

Benassi L, Dalipi R, Consigli V, Pasquali M, Borgese L, Depero LE, Clegg F, Bingham PA, Bontempi E (2017) Integrated management of ash from industrial and domestic combustion: a new sustainable approach for reducing greenhouse gas emissions from energy conversion. Environ Sci Pollut Res. doi:10.1007/s11356-017-9037-y

Bergna HE (1994) Colloid chemistry of silica: an overview. In: Advances in Chemistry. Wilmington, pp 1–47

Besco S, Brisotto M, Gianoncelli A, Depero LE, Bontempi E, Lorenzetti A, Modesti M (2013) Processing and properties of polypropylene-based composites containing inertized fly ash from municipal solid waste incineration. J Appl Polym Sci 130:n/a-n/a. doi:10.1002/app.39692

Besco S, Bosio A, Brisotto M, Depero L, Lorenzetti A, Bontempi E, Bonora R, Modesti M (2014) Structural and mechanical characterization of sustainable composites based on recycled and stabilized fly ash. Materials (Basel) 7:5920–5933. doi:10.3390/ma7085920

Besis A, Samara C (2012) Polybrominated diphenyl ethers (PBDEs) in the indoor and outdoor environments—a review on occurrence and human exposure. Environ Pollut 169:217–229. doi:10.1016/j.envpol.2012.04.009

Bonen D, Khayat KH (1995) Characterization and pozzolanic properties of silica fume stored in an open pond. Cem Concr Res 25:395–407. doi:10.1016/0008-8846(95)00025-9

Bontempi E (2017) A new approach for evaluating the sustainability of raw materials substitution based on embodied energy and the CO_2 footprint. J Clean Prod 162:162–169. doi:10.1016/j.jclepro.2017.06.028

Bontempi E, Zacco A, Borgese L, Gianoncelli A, Ardesi R, Depero LE, Tenini S, Depero LE (2010) A new method for municipal solid waste incinerator (MSWI) fly ash inertization, based on colloidal silica. J Environ Monit 12:2093. doi:10.1039/c0em00168f

Bontempi E, Depero LE, Bosio A, Gianoncelli A, Cioffi F (2015) An inert material, a production method thereof from waste materials and industrial uses thereof. EP 2879813 A1

Bosio A, Rodella N, Gianoncelli A, Zacco A, Borgese L, Depero LE, Bingham PA, Bontempi E (2013) A new method to inertize incinerator toxic fly ash with silica from rice husk ash. Environ Chem Lett 11:329–333. doi:10.1007/s10311-013-0411-9

Bosio A, Gianoncelli A, Zacco A, Borgese L, Rodella N, Zanotti D, Depero LE, Siviero G, Cinosi A, Bingham PA, Bontempi E (2014a) A new nanotechnology of fly ash inertization based on the use of silica gel extracted from rice husk ash and microwave treatment. Proc Inst Mech Eng Part N J Nanoeng Nanosyst 228:27–32. doi:10.1177/1740349913490683

Bosio A, Zacco A, Borgese L, Rodella N, Colombi P, Benassi L, Depero LE, Bontempi E (2014b) A sustainable technology for Pb and Zn stabilization based on the use of only waste materials: a green chemistry approach to avoid chemicals and promote CO_2 sequestration. Chem Eng J 253:377–384. doi:10.1016/j.cej.2014.04.080

Brits M, de Vos J, Weiss JM, Rohwer ER, de Boer J (2016) Critical review of the analysis of brominated flame retardants and their environmental levels in Africa. Chemosphere 164:174–189. doi:10.1016/j.chemosphere.2016.08.097

Brunner PH, Rechberger H (2015) Waste to energy—key element for sustainable waste management. Waste Manag 37:3–12. doi:10.1016/j.wasman.2014.02.003

BSEF Bromine. Powering science and technologies. http://bsef.com/. Accessed 27 May 2017

BuildingGreen Flame Retardants Under Fire. https://www.buildinggreen.com/feature/flame-retardants-under-fire. Accessed 27 May 2017

Calkins M (2009) Materials for sustainable sites: a complete guide to the evaluation, selection, and use of sustainable construction materials. Wiley, New York

Carran D, Hughes J, Leslie A, Kennedy C (2012) A Short history of the use of lime as a building material beyond Europe and North America. Int J Archit Herit 6:117–146. doi:10.1080/15583058.2010.511694

Chandler AJ, Eighmy TT, Hjelmar O, Kosson DS, Sawell SE, Vehlow J, Sloot HA van der, Hartlén J (1997) Municipal solid waste incinerator residues. Elsevier

COP21 Paris France Sustainable Innovation Forum 2015 working with UNEP. http://www.cop21paris.org/. Accessed 27 May 2017

COSMOS-RICE Cosmos Rice. http://www.cosmos-rice.csmt.eu/

de Boer J, Wester PG, Klamer HJC, Lewis WE, Boon JP (1998) Do flame retardants threaten ocean life? Nature 394:28–29

Diamond S, Sahu S (2003) Densified silica fume—is it what you think it is?. In: Proceedings of the engineering foundation conference on advances in cement and concrete IX. Copper Mountain, CO

Diamond S, Sahu S, Thaulow N (2004) Reaction products of densified silica fume agglomerates in concrete. Cem Concr Res 34:1625–1632. doi:10.1016/j.cemconres.2004.01.031

Domingo JL (2004) Human exposure to polybrominated diphenyl ethers through the diet. J Chromatogr A 1054:321–326. doi:10.1016/j.chroma.2004.03.042

EC (2011) Critical raw materials—european commission. https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_it. Accessed 21 May 2017

EN (2002) 12457-2:2002 characterisation of waste—Leaching—compliance test for leaching of granular waste materials and sludges—Part 2: one stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size)

Eurostat-Your key to European statistics. http://ec.europa.eu/eurostat. Accessed 21 May 2017

Fernández Bertos M, Li X, Simons SJR, Hills CD, Carey PJ, Carey PJ (2004) Investigation of accelerated carbonation for the stabilisation of MSW incinerator ashes and the sequestration of CO_2. Green Chem 6:428–436. doi:10.1039/B401872A

Filella M, Belzile N, Chen Y-W (2002) Antimony in the environment: a review focused on natural waters: I. Occurrence. Earth Sci Rev 57:125–176. doi:10.1016/S0012-8252(01)00070-8

Funari V, Braga R, Bokhari SNH, Dinelli E, Meisel T (2015) Solid residues from Italian municipal solid waste incinerators: a source for "critical" raw materials. Waste Manag 45:206–216. doi:10.1016/j.wasman.2014.11.005

GRANTA CES Selector 2016. https://www.grantadesign.com/it/products/ces/. Accessed 21 May 2017

Grause G, Furusawa M, Okuwaki A, Yoshioka T (2008) Pyrolysis of tetrabromobisphenol-a containing paper laminated printed circuit boards. Chemosphere 71:872–878. doi:10.1016/j.chemosphere.2007.11.033

Guarienti M, Gianoncelli A, Bontempi E, Moscoso Cardozo S, Borgese L, Zizioli D, Mitola S, Depero LE, Presta M (2014) Biosafe inertization of municipal solid waste incinerator residues by COSMOS technology. J Hazard Mater 279:311–321. doi:10.1016/j.jhazmat.2014.07.017

Guarienti M, Cardozo SM, Borgese L, Lira GR, Depero LE, Bontempi E, Presta M (2016) COSMOS-rice technology abrogates the biotoxic effects of municipal solid waste incinerator residues. Environ Pollut 214:713–721. doi:10.1016/j.envpol.2016.04.053

Haiying Z, Youcai Z, Jingyu Q (2010) Thermal characterization of fly ash from one municipal solid waste incinerator (MSWI) in Shanghai. Process Saf Environ Prot 88:269–275. doi:10.1016/j.psep.2010.03.004

Iler RK (1979) Silica gels and powders. The chemistry of silica. Wiley, New York, pp 462–729

Jancar J, Fekete E, Hornsby PR, Jancar J, Pukánszky B, Rothon RN (eds) (1999) Mineral fillers in thermoplastics I. Springer, Berlin

Kamath SR, Proctor A (1998) Silica gel from rice hull ash: preparation and characterization. Cereal Chem J 75:484–487. doi:10.1094/CCHEM.1998.75.4.484

Kengkhetkit N, Amornsakchai T (2014) A new approach to "Greening" plastic composites using pineapple leaf waste for performance and cost effectiveness. Mater Des 55:292–299. doi:10.1016/j.matdes.2013.10.005

Le Forestier L, Libourel G (1998) Characterization of flue gas residues from municipal solid waste combustors. Environ Sci Technol 32:2250–2256. doi:10.1021/ES980100T

Mitchell DRG, Hinczak I, Day RA (1998) Interaction of silica fume with calcium hydroxide solutions and hydrated cement pastes. Cem Concr Res 28:1571–1584. doi:10.1016/S0008-8846(98)00133-1

Pettigrew A (2000) Flame retardants, halogenated. In: Kirk-Othmer (ed) Encyclopedia of chemical technology. Wiley, Hoboken, NJ, USA

PlasticsEurope, Association of Plastics Manufactures. http://www.plasticseurope.org/. Accessed 27 May 2017

Rhoades SA (1993) The Herfindahl-Hirschman index. Fed Reserv Bull 188–189

Rodella N, Bosio A, Dalipi R, Zacco A, Borgese L, Depero LE, Bontempi E (2014) Waste silica sources as heavy metal stabilizers for municipal solid waste incineration fly ash. Arab J Chem. doi:10.1016/j.arabjc.2014.04.006

Rodella N, Pasquali M, Zacco A, Bilo F, Borgese L, Bontempi N, Tomasoni G, Depero LE, Bontempi E (2016) Beyond waste: new sustainable fillers from fly ashes stabilization, obtained by low cost raw materials. Heliyon. doi:10.1016/j.heliyon.2016.e00163

Šauman Z (1971) Carbonization of porous concrete and its main binding components. Cem Concr Res 1:645–662. doi:10.1016/0008-8846(71)90019-6

Shubhra QT, Alam A, Quaiyyum M (2011) Mechanical properties of polypropylene composites: A review. J Thermoplast Compos Mater 26:362–391. doi:10.1177/0892705711428659

Siddique R, Khan MI (2011) Supplementary Cementing Materials. Springer, Berlin Heidelberg

Srivastava VC, Mall ID, Mishra IM (2006) Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. J Hazard Mater 134:257–267. doi:10.1016/j.jhazmat.2005.11.052

Thiery M, Villain G, Dangla P, Platret G (2007) Investigation of the carbonation front shape on cementitious materials: Effects of the chemical kinetics. Cem Concr Res 37:1047–1058. doi:10.1016/j.cemconres.2007.04.002

Thoma H, Rist S, Hauschulz G, Hutzinger O (1986) Polybrominated dibenzodioxins and -furans from the pyrolysis of some flame retardants. Chemosphere 15:649–652. doi:10.1016/0045-6535(86)90013-5

UL94 Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances. https://standardscatalog.ul.com/standards/en/standard_94_6. Accessed 27 May 2017

USAC Antimony Prices. http://www.usantimony.com/pricing.htm. Accessed 27 May 2017

Weaver PM, Ashby MF, Burgess S, Shibaike N (1996) Selection of materials to reduce environmental impact: a case study on refrigerator insulation. Mater Des 17:11–17. doi:10.1016/0261-3069(96)00024-6

Westerhoff P, Prapaipong P, Shock E, Hillaireau A (2008) Antimony leaching from polyethylene terephthalate (PET) plastic used for bottled drinking water. Water Res 42:551–556. doi:10.1016/j.watres.2007.07.048

Wilford BH, Harner T, Zhu J, Shoeib M, Jones KC (2004) Passive Sampling Survey of Polybrominated Diphenyl Ether Flame Retardants in Indoor and Outdoor Air in Ottawa, Canada: Implications for Sources and Exposure. Environ Sci Technol 38:5312–5318. doi:10.1021/ES049260X

Wu F, Sun F, Wu S, Yan Y, Xing B (2012) Removal of antimony(III) from aqueous solution by freshwater cyanobacteria Microcystis biomass. Chem Eng J 183:172–179. doi:10.1016/j.cej.2011.12.050

Xanthos M (2010) Functional fillers for plastics, 2nd edn. Wiley-VCH

Zacco A, Gianoncelli A, Ardesi R, Sacrato S, Guerini L, Bontempi E, Tomasoni G, Alberti M, Depero LE (2012) Use of colloidal silica to obtain a new inert from municipal solid waste incinerator (MSWI) fly ash: first results about reuse. Clean Technol Environ Policy 14:291–297. doi:10.1007/s10098-011-0401-1

Zacco A, Borgese L, Gianoncelli A, Struis RPWJ, Depero LE, Bontempi E (2014) Review of fly ash inertisation treatments and recycling. Environ Chem Lett 12:153–175. doi:10.1007/s10311-014-0454-6

http://www.springer.com/978-3-319-60830-3

Raw Materials Substitution Sustainability

Bontempi, E.
2017, IX, 101 p. 43 illus., 41 illus. in color., Softcover
ISBN: 978-3-319-60830-3