
Symbiosis Users Network – SUN
Proceedings of the fourth SUN Conference

**Il ruolo della simbiosi industriale
per la prevenzione della produzione di rifiuti:
a che punto siamo?**

**The role of industrial symbiosis
for waste prevention: where are we at?**

November 4th 2020

Edited by Tiziana Beltrani and Marco La Monica



ENEA

Italian National Agency for New Technologies,
Energy and Sustainable Economic Development



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2021 ENEA

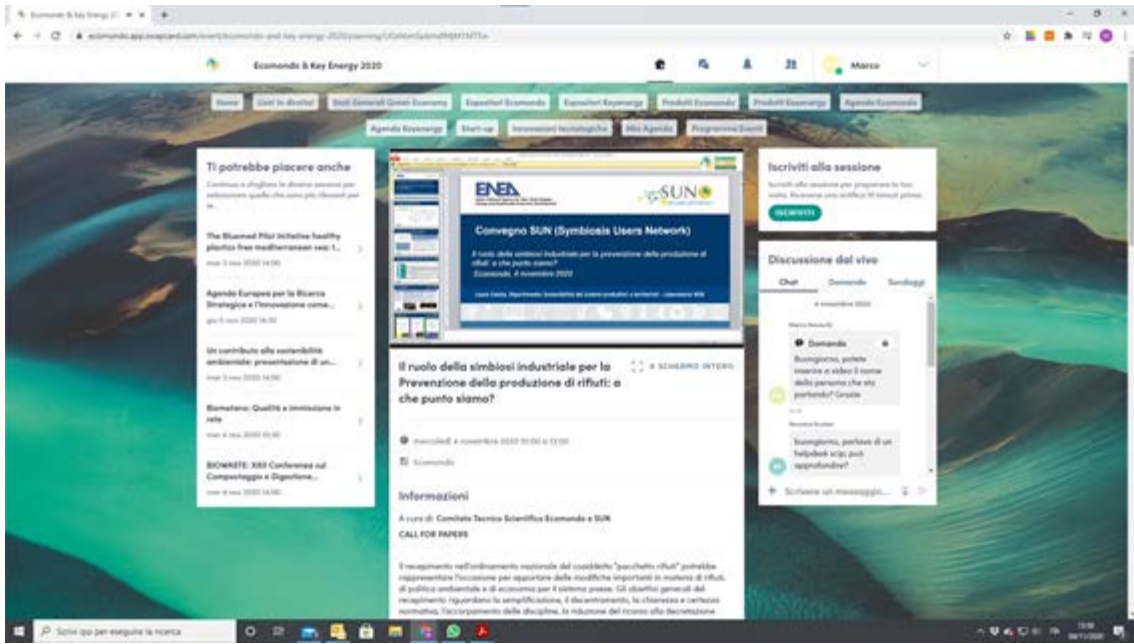
National Agency for New Technologies, Energy and
Sustainable Economic Development

ISBN: 978-88-8286-408-8

Editorial review: Giuliano Ghisu

Cover design: Cristina Lanari

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EAF SLAG AS FILLER IN VULCANIZED RUBBER

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ABSTRACT

Italy with an annual production of 20 million tons is the leading producer of electric arc furnace (EAF) steel in Europe. The geographical distribution of EAF steel producers is concentrated in Lombardy, therefore the macro sector of metallurgical industry is related to that of vulcanized rubber as it is located in the same geographical area. The aim of this work is to assess the influence of EAF slag as filler for nitrile butadiene rubber (NBR) in order to promote an alternative use of EAF slag by preventing its disposal. The processability characteristics of filled NBR are determined by the rheometric curves; the first results show that the presence of slag in NBR accelerates the crosslinking kinetics. The mechanical characterization, consisting of hardness and compression test and compression set, shows a stiffening of the material that could affect positively the gasket behavior in sealing system assembled both in load or in displacement control.

Keywords: *EAF slag, filled rubber, Industrial Symbiosis, Metal industry, Rubber industry*

Introduction

In a world where demand and competition for finite and sometimes scarce resources will continue to increase, and pressure on resources is causing greater environmental degradation and fragility, Europe can benefit economically and environmentally from making better use of those resources. Moving towards a more circular economy is essential to deliver the resource efficiency agenda established under *The European Green Deal* [1]. Nevertheless, even in a highly circular economy there will remain some element of linearity as virgin resources are required and residual waste is disposed of. Industry already recognizes the strong business case for improving resource productivity. It is estimated that resource efficiency improvements all along the value chains could reduce material inputs needs by 17%-24% by 2030 [2] and a better use of resources could represent an overall savings potential of €630 billion per year for European industry [3]. Turning waste into a resource is part of 'closing the loop' in circular economy systems. The European Union has set out its political commitment to reduce waste generation, to recycle waste into a major, reliable source of raw materials

for the Union, to recover energy only from non-recyclable materials and to virtually eliminate landfilling. In this context of circular economy, the Industrial Symbiosis [4–6] is the process by which wastes, or by-products of an industry or industrial process become the raw materials for another. Application of this concept allows materials to be used in a more sustainable way and contributes to the creation of a circular economy. Through a territorial approach, industrial symbiosis involves traditionally separate industries in a business interaction process aimed at obtaining competitive advantages deriving from the transfer of resources (by-products or production waste) between two or more dissimilar industries, in which the resources being traded are not only material ones, but also energy and water [7]. In this context, the European metallurgical industry annually produces about 70 million tons of electric arc furnace (EAF) steel, where Italy is the leading European producer with an annual production of about 20 million tons. [8]. The main steel industry waste by-product is the metallurgical slag, whose production is functional to that of steel itself, and is estimated to be around 15%wt of the produced steel. The use of slag as raw material would allow an economic advantage for companies and the environment, reducing the problem of disposal and promoting the saving of natural resources. For a safe reuse of the slag it is necessary to guarantee its chemical inertia [9]. A problem is the possible release of heavy metals (i.e. Cr, V, Mo) into the environment. Due to its composition similar to that of volcanic rock, the slag is mainly used as a substitute for natural aggregates in civil engineering [10] specially in road surfaces [11–13], but unfortunately today a large amount is not reused. As highlighted in Figure 1, the geographical distribution of EAF steel plants are concentrated in Lombardy, therefore as the industrial symbiosis is implemented in limited geographical areas to avoid excessive transport costs. In addition, the macro sector of metallurgical industry is related to that of vulcanized rubber, located in the same geographical area as Sebino district that is the largest European manufacturer and supplier of gaskets. The aim of this work is to assess an innovative application of EAF slag as reinforcing filler for vulcanized rubber NBR, in order to prevent decreasing natural resource and increasing environmental degradation according to circular economy [8].

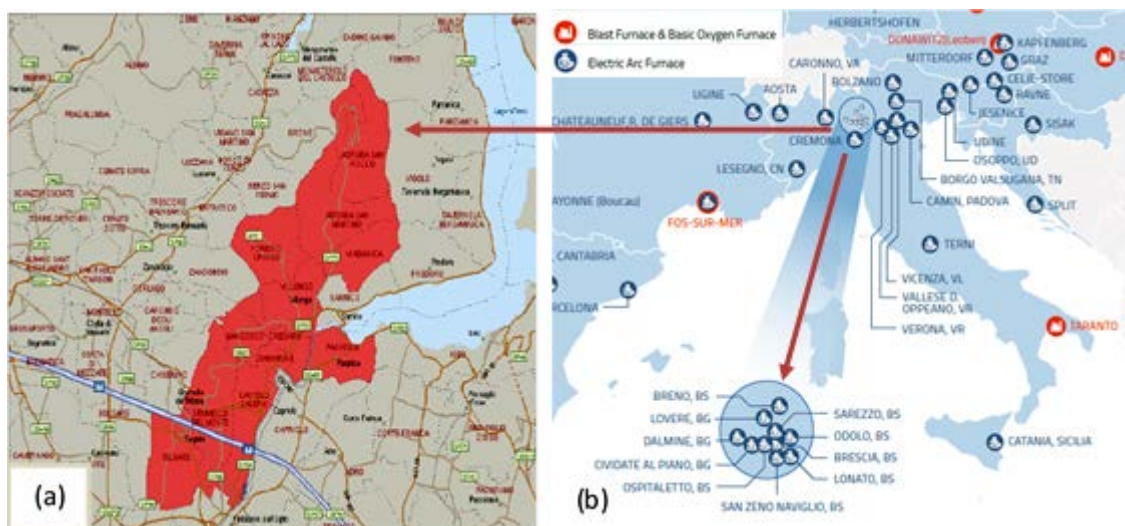


Figure 1. (a) Geographical distribution of rubber seal production sites; (b) Map of steel production in Italy

Methods

EAF slag production and characterization. The slag was supplied by the ASO Siderurgica srl (Ospitaletto BS, Italy) steelmaking plant, which produces special-grade steels. The slag employed in this research has been produced by a specific system named Slag-Rec [5,6] for dry granulating EAF molten slag. EAF slag chemical composition is determined by X-ray fluorescence spectroscopy carried out by the Thermo Scientific™ ARL™ PERFORM'X provided by Thermo Fisher Scientific. EAF slag leaching rate is determined by the leaching test according to the standard UNI EN 12457-2[9].

Compound EAF slag/NBR production and characterization: The influence of 30%V/V EAF slag as reinforcing filler for NBR has been assessed on a standard NBR (carbon black 40 phr, vulcanized with Sulfur). The compounding process has been performed to disperse the filler particles (previously grinded in a size less than 106 μm) in the standard NBR matrix. The calendaring process consists in forcing rubber and slag between two rotating cylinders (diameter of 150mm) 1mm apart at room temperature. The compound is then vulcanized by compression molding process for 15minutes at 180 °C.

The obtained compound has been mechanically characterized and its results have been compared to that of standard NBR. Moreover, the processability characteristics have been evaluated by the rheometric curve. The rheometric curve is determined by a moving die rheometer, provided by Gibitre Instruments, RHEO CHECK PROFILE for a test time of 3 minutes at 177 °C with an oscillating amplitude of 0.5 deg. Hardness is determined in Shore A scale according to the standard ISO 7619-1.

The compression set is determined by imposing a compression deformation of 25% on cylindrical samples (diameter 12mm, high 6mm) for 24h at 100 °C.

Compression tests were performed by an Instron dynamometer (mod. 3366) at room temperature and at a cross-head rate of 100 mm/min on cylindrical test samples of nominal diameter 12mm and high 6mm.

Results

EAF slag chemical composition determined by the X-Ray Fluorescence Spectroscopy consists principally of 40% iron oxides (haematite), 30% calcium oxide, 10% silicon dioxide and other minor oxides in smaller quantities. The leaching rate of heavy metals such as Mo, Cr, and V is regulated by ministerial decrees. Ministerial Decree 5/2/98 imposes the release limit of V at 0.25mg/l and Cr at 0.50mg / l for slag reuse, while Ministerial Decree 3/8/05 imposes the release limit of Cr and Mo at 0.05mg/l for landfill disposal. The rheometric curve shows the trend of the torque required to maintain the 0.5 deg. oscillation while the sample cures and provides indications regarding the processability characteristics of the tested materials. The Figure 2 shows the influence of EAF slag as filler in standard NBR. The presence of slag in reduces the time necessary for the vulcanization to be 90% complete (time 90%). This means the presence of slag as filler accelerates the crosslinking kinetics. The torque needed to maintain the imposed oscillation at complete vulcanization (maximum torque) is higher for NBR filled EAF slag, this means the filler makes the compound stiffer. The compound hardening is clearly appreciable by compressive Young modulus (E_c) determined as slope of the linear section at very low strain that increases of about 90%. The compressive test results show that filled NBR offers greater resistance to deformation compared to standard NBR, and this is noticeable in the value of stress at 50% of compressive strain ($\sigma(\epsilon 50\%)$). Similarly, hardness value of filled NBR is higher than that of standard NBR of about 10 Shore A points. The compression set results show that the presence of filler reduces the material's ability to recover an imposed deformation. The compression set of standard NBR is about 12%, while that of NBR filled EAF slag is about 18%. This is a good result due to an acceptable compression set is considered to be about 20%.

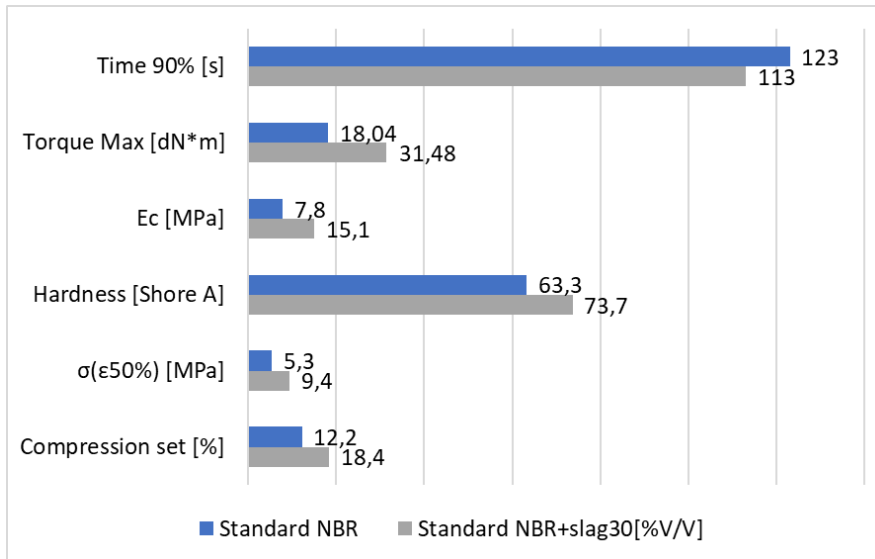


Figure 2. Standard NBR and compound NBR+30%slag V/V comparison

Discussion and Conclusion

The aim of this work is to characterize an innovative compound in vulcanized rubber NBR filled EAF slag in order to pave the way to a new EAF slag application economically and environmentally convenient. The results of this preliminary characterization are encouraging both from the point of view of compound production process and from the point of view of mechanical properties.

The marketing of a new compound with EAF slag as a filler for vulcanized rubber would allow the implementation of the industrial symbiosis model: slag as the major waste (output) of metallurgical industries becomes raw material (input) for rubber sector (Figure 3).

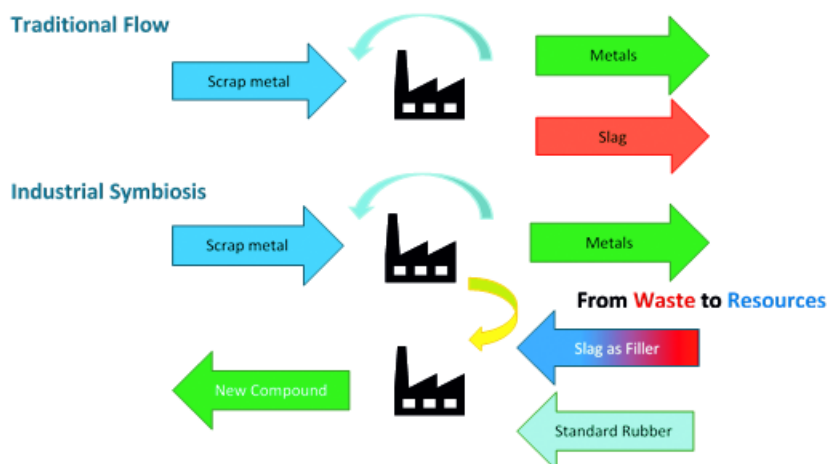


Figure 3. Model of Industrial Symbiosis between metal sector and rubber sector in Lombardy

Acknowledgements

The authors thank ASONEXT SpA and Novotema SpA for their collaboration in carrying out the experiments.

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