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Physical Chemistry Supports Circular Economy: Toward a Viable Use of Products from the Pyrolysis of a Refuse-Derived Fuel and Granulated Scrap Tire Rubber as Bitumen Additives

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Abstract

The production and maintenance of road pavements consume resources and produce wastes that are disposed of in landfills. To make more sustainable this activity, we have envisioned a method based on a circular use of residues (oil and char) from municipal solid waste pyrolysis as useful additives for producing improved asphalts and for recycling old asphalts to generate new ones, reducing at the same time the consumption of resources for the production of new road pavements and the disposal of wastes to landfills. This work aims to show the feasibility of the integration of two processes (thermal treatment of municipal solid waste on one side, and that of road pavement production on the other side) where the products deriving from waste pyrolysis become added-value materials to improve the quality of road pavements. In this contribution, we presented the effect of pyrolysis product addition on asphalt binder (bitumen) preparation and aging. Solid and liquid products, deriving from the pyrolysis of two kinds of wastes (refused derived fuel (RDF) and granulated rubber tyre waste), have been used for the preparation of asphalt binder samples. Rheological tests have been performed to determine the mechanical properties of neat asphalt binder (bitumen) and those enriched with pyrolysis derived products. Measurements to evaluate possible anti-aging effects have been also performed. The collected results indicate that char addition strengthens the overall bitumen intermolecular structure while bio-oil addition exerts a rejuvenating activity.

1. Introduction

Recent legislation proposals in terms of environmental protection addressed the reduction of greenhouse gases [1] and a transition to a regenerative circular economy [2]. This implies the shift to closed cycles of materials/processes minimizing input of resources and output of wastes, refuses and emissions [3]. At present in many countries, urban wastes (household, school, industrial, hospital waste etc. [4]) are still treated by processes lacking in material re-utilization and recycling phases [5, 6]. In Italy in 2020, for example, an unacceptable amount (about 20-25%) of municipal solid wastes (MSWs) was disposed into landfills while in Germany only 1%

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[7]. This practice corresponds to pavement maintenance and transport costs (landfills are often located in remote areas), impacts human health due to the proliferation of bacteria and insects and causes pollution of soil, groundwater (due to percolation phenomena), and atmosphere (greenhouse gases (GHGs) emissions) [8-11].

Currently, the thermal treatment of wastes may therefore be seen as a valid option to the environmental threats posed by poorly managed or unmanaged waste streams. The primary target of thermal treatments is to provide for an overall reduction in the environmental impact that might otherwise arise from improper waste management. Pyrolysis has been introduced as an alternative thermoconversion technology to conventional incineration since it attempts to recover added-value materials (char, oil, syngas) from waste transformation by controlling process temperatures and pressures in specially designed reactors [12, 13]. Pyrolysis is a thermochemical conversion process performed at an average temperature between 450-600 °C that, in the complete absence of oxygen, converts the organic fraction of the feedstocks (i.e. urban wastes, tires, sludge, biomasses, plastics [14-20]) into a combustible gas mixture [21], a mixture of liquids rich in hydrocarbons and oxygenated species (here in the following oil) [22] and a carbon rich solid residue with a high calorific value (char) [23]. Anyway, although there are undisputed advantages in the use of this process [24] and no significant increase in terms of CO_2 emissions, it is not yet clear, beyond the mere exploitation for energy purposes (i.e. by combustion even if further CO_2 emissions are generated), how to achieve an economic return from the condensable fractions (oil) and solid products (char) because they are complex and heterogeneous materials difficult to exploit.

In several countries the asphalt cycle is still quite open: looking at Italy, only about 20-30% of the old asphalts are reused for new paving processes because aged asphalts are hard and brittle and no longer suitable for road paving unless expensive chemical treatments are resorted to for their regeneration. Therefore, 70-80% of old asphalts go to landfill with the aforementioned problems [25, 26].

Recently, the physico-chemical bases [27, 28] of:

1. the improving effects of char addition on the mechanical characteristics of asphalt [29, 30];

2. the char antioxidant and anti-aging properties on asphalts [31-33];

3. the regenerative properties of pyrolysis oil against aged asphalts [34];

have been identified and more details on each aspect are reported in the following.

Asphalt concretes are biphasic systems, with the predominant phase (c.a. 93–96% w/w) made by macro-meter sized inorganic aggregates (size from microns to millimeters) held together by small amounts (c.a. 5% w/w) of binding bitumen which constitutes the second phase.

The addition of small particles (high surface-to-volume ratio, tuneable chemical constitution, etc.) can exert significant effects on the rheological properties of asphalt components [35-37]. In particular, it has been demonstrated that the addition of nanoparticles can increase the load capacity of the pavement and decrease the formation of cracks due to fatigue during the pavement operation life. Carbonaceous particles are expected to give better results thanks to their chemical compatibility with the asphalt binder chemical nature (they both are carbon-based materials). Since char is characterized by a porous and fibrous structure [38] it is expected to give rise to a strong interaction with the binder [27, 28] and to reinforce the bitumen structure.

The strict interactions between char and asphalt binder components can exert also an anti-aging effect. Indeed, the presence of char can slow-down the aging processes hindering their dynamics. In particular, the interaction of apolar char nanoparticles with the maltenic phase of bitumen will drug the latter to more restricted dynamics typical of the stiffened asphaltene-dominated structure. Here, it is important to stress the role of those amphiphilic molecules (resins) present in the bitumen [39, 40]. Thanks to the simultaneous presence, within amphiphilic molecular architecture, of both polar and apolar moieties, amphiphilic species can bind on one side the polar phase (asphaltenes and their clusters), and on the other side, the apolar one. The overall result of these simultaneous interactions proved to be effective in the stabilization of clusters of polar molecules [41, 42], of inorganic ionic species [43], even of metal [44] or of composites of different natures [45] dispersed in apolar solvents, thus being expected to reduce the aging processes. It must be noted that, due to the confinement effect, even the state of the polar species stabilized by amphiphiles/resins can change according to the size of their assemblies [46] which, in turn, reflects the overall stability.

Under aging, cracking or fracture can take place [47] in asphalts, since binder chemical components become less and less mobile to flow under the applied stress. After aging, the bitumen original physical properties can be somehow restored by the simple addition of softening (usually called fluxing) agents like flux oil, soy oil, slurry oil, lube stock, etc. [48, 49] which restore the original ductility/viscosity. Anyway, more sophisticated methods try to restore the original chemistry of the neat asphalt binder and its original inter-molecular structure [50] (rejuvenation) by pushing back the oxidations, agglomerations and self-assembly processes that occurred during the whole aging.

Pyrolysis oil has all the characteristics to effectively act as a fluxing agent [51]. Indeed, the amphiphilic molecules present in pyrolysis oil can interact with those already present in the asphalt binder. The interaction between different types of amphiphiles can vary, due to the complex nature of such molecules, and with marked effects especially if acidic and basic molecules come into contact within the system, due to a favourable energetic push towards strong H-bond formation or, even, a definite proton transfer with the formation of charged species [52]. The interesting interplay among all these interactions can trigger peculiar, and usually unexpected, self-assembly with consequent changes in the mechanical properties [53].

The use of both oil and char from pyrolysis processes can reasonably help in producing better and longer-lasting asphalts, as well as regenerate them on site once exhausted without additional burden on CO_2 emissions. The environmental impact is attributable to the production of paving grade bitumen is well known [54]. Crude oil production is the main contributor to the potential impacts of total climate change (149.6 kg CO_2 eq.), energy demand (45,015 MJ), ozone depletion associated with the trichlorofluoromethane (CFC-11) emission (1,07E-05 kg CFC-11 eq.), acidification (1.75 mol H^+ eq.) and photochemical ozone formation associated to non-methane volatile organic compounds (NMVOC) emission (1.32 kg NMVOC eq.). It is also known that the use of recycled waste in the production of asphalt pavements or in the rejuvenation of bitumen significantly mitigates negative environmental impacts and leads to economic and resource savings [55, 56].

The ultimate goal of the proposed approach is the integration of the urban waste and asphalt cycles by optimizing processes of use of pyrolysis by-products, as shown in Fig. 1.

According to the proposed strategy, the waste currently produced by urban activities is processed to obtain raw materials suitable for reuse in the asphalt cycle. In particular, wastes undergo the pyrolysis process to produce gas, oil and char. The gaseous mixture can be transformed into electricity and heat to meet the energy consumption of the entire asphalt production cycle. Pyrolytic oil and char are introduced into the cycle of production, improvement and rejuvenation of asphalts. The possible benefits endowed by the proposed approach are many and varied. Environmental benefits: the mitigation of environmental impacts derives both from avoiding the production of virgin asphalts, and from the reuse of wastes otherwise destined for landfills. On-site rejuvenation of exhausted asphalts prevents the production of new virgin asphalt, thus reducing the energy process consumption, avoiding

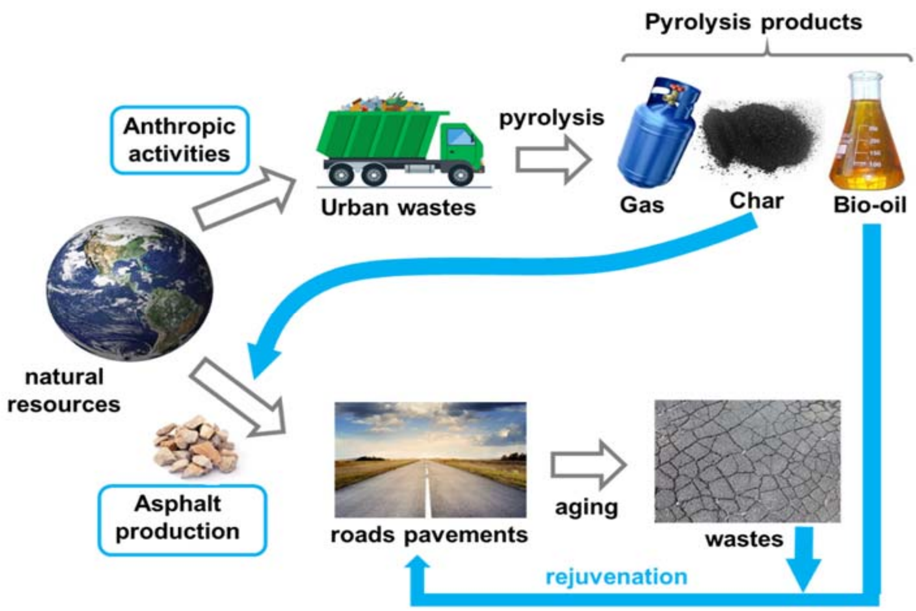

Fig. 1. Scheme showing the integration of pyrolysis and roads pavement production processes.

the extraction of virgin oil and natural resources and improving environmental indicators, such as CO_2 emission, due to the disposal of old asphalts and MSWs in landfills.

Economic benefits: the cost reduction of virgin material and production processes are the main items of economic savings. The overall cost savings over the entire life cycle of the asphalt pavement are attributable to the lower energy consumption in the material and construction phases, to the minor production cost due to the replacement of natural resources with recycled waste, and to the reduction of the costs of transporting materials following on-site processing of rejuvenation of exhausted asphalts. Further economic benefits are also due to the savings in the disposal costs of old asphalts, and MSWs, including transport costs to landfills.

Technical benefits: the use of rejuvenating agents derived from waste rather than from non-renewable virgin resources improves the performance of the asphalts. In fact, adding waste pyrolysis derived char to the bitumen improves the mechanical, chemical and rheological properties and the longevity of asphalts. As a consequence, it is possible to produce asphalt that is more resistant to atmospheric conditions during its use, such as oxidation, high or low temperatures and ultraviolet (UV) rays.

The circular economy benefits: the application of the proposed approach fully respects the fundamental principles of the circular economy model based on the “take, make, use and recycle” strategy. In particular, MSWs are subjected to a thermochemical transformation (pyrolysis) to produce an energy vector (gaseous mixture) and two pyrolytic by-products (oil and char). The energy carrier (syngas) can be used to partially meet the energy needs of the asphalt production process, avoiding the exploitation of fossil energy resources, while the pyrolysis products are used as additives to produce new and improved asphalt binders or as agents to rejuvenate old asphalts. In this way, municipal solid wastes and old asphalts are re-inserted in the production system avoiding their disposal into landfills.

Undoubtedly, the simultaneous integration of the waste and asphalt cycles not only mitigates the impact on the country’s landscape by encouraging the use of pyrolysis as waste process treatment thus reducing landfill, but also meets the needs of the circular economy, which have become more stringent in the post-COVID era.

Diverting waste from landfills through their use in asphalt pavements [57] can offer various environmental, technical and economic advantages according to the concept of circular economy [58]. In particular, several studies have been reported on the use of MSW incinerator ash [59], waste tire and plastic pyrolytic chars [60], bio-oil [61] and bio-char [62-64], the latter both generated by the pyrolysis of biomass [65], as an aggregate substitute, modifier or additive to improve some properties of asphalt binder (bitumen). To date, no studies have been carried out on the use of char obtained from the pyrolysis of a refused derived fuel (RDF) as an additive in asphalt binder preparation.

In this work, we report some insights into the feasible utilization of pyrolysis products to produce better and longer-lasting asphalts. To accomplish this goal, char and bio-oil samples deriving from the pyrolysis of a RDF and granulated waste tyre rubber (WTR) have been tested for the preparation of asphalt binder samples.

2. Materials and methods

2.1 Asphalt binder additives production and characterization

Char and bio-oil samples were produced from a refused derived fuel (RDF) derived from MSW and granulated rubber tyre waste (WTR). The RDF was supplied by Calabra Maceri e Servizi S.p.A, Rende (CS), Italy). Both feedstocks underwent a fast pyrolysis process (heating rate 30 °C/min, N_2 atmosphere) up to 530-550 °C in a lab scale reactor as detailed elsewhere [66].

Pyrolysis products were characterized by elemental and proximate analyses, thermogravimetry (both in inert and oxidative atmospheres) and gas-chromatography coupled with mass spectrometry (GC-MS) as reported elsewhere [67].

2.2 Rheological properties evaluation

Bituminous samples were prepared by adding 6% wt of char to a neat 50/70 penetration grade (according to ASTM D946) kindly supplied by Loprete Costruzioni Stradali (Terranova Sappo Minulio, Calabria, Italy). The neat bitumen was produced in Italy and the crude oil was from Saudi Arabia.

Mechanical properties of the bituminous samples were evaluated by Rheology Time Cure tests, performed in a temperature ramp at a constant heating rate of 1 °C/min, are reported. Tan δ (loss factor) = G’’/G’ [68] was measured in the regime of small amplitude oscillatory shear at a frequency of 1Hz by dynamic stress-controlled rheometer – SR5, Rheometric Scientific, Piscataway, NJ, USA – equipped with a parallel plate geometry – gap 2 mm, diameter 25 mm, temperature controlled by a Peltier element, uncertainty ±0.1 °C. Such conditions are those generally adopted for accurate studies on bitumen mechanical properties [69, 70].

The data obtained during a small amplitude oscillatory rheometry test include the complex shear modulus G*, which is a measure of the total energy required to deform the specimen and is defined as:

$$|G^*| \; G'_2 + G''_2$$

where G′ is the elastic modulus (or storage modulus), a measure of the energy stored in the material during an oscillation, and G′′ is the viscous modulus (or loss modulus), a measure of the energy dissipated as heat. The temperature dependence of the experimental G′ and G′′ measured at 1 Hz can give several information.

When the temperature is increased, all the materials become progressively softer with G′ decreasing more quickly than G′′ therefore causing a parallel increase of Tan δ. For temperature high enough, at a certain point G′ suddenly drops so no storage of energy can be afforded anymore by the sample. This is revealed by the steep increase in Tan δ. For higher temperatures, the binder can be considered almost as a Newtonian fluid. From the microscopic point of view, for temperatures higher than this transition temperature (T*) the molecular thermal agitation, and consequently, the molecular relaxation rate, is sufficiently high to let the system accommodate for the mechanical distortion/perturbation. This gives purely flowing behaviour and causes any elastic storage of mechanical energy to vanish.

In order to evaluate the potentialities of the bio-oil as rejuvenator, bitumen aging was performed by the Rolling Thin-Film Oven Test (RTFOT) procedure, according to ASTM D2872-04, with the aim to simulate the natural aging occurring in a period of about 10-12 years under operating conditions RFTOT was extended to 225 min [71], then modified by adding 6% wt of bio-oil to the hot aged bitumen (~ 150 °C) and mixed by mechanical stirrer (RW 20 Digital, IKA, Germany), around 600 rpm for 15 minutes.

3. Results and discussion

3.1 Asphalt binder additives characteristics

The char samples were characterized by a high carbon content (around 80 wt.% for char from granulated rubber tyre waste and around 45 wt.% for char from RDF) and a quite high temperature of burn-off (above 550 °C for char from WTR and above 400°C for char from RDF). In both char samples the ash content was not negligible [66]. In the WTR-char also a not negligible content of sulphur was detected [66]. Both char samples contained ashes:12.5 wt.% in WTR-char and 49.2 wt.% in RDF-char [66].

The bio-oil sample from RDF was rich in plastic derived species [67] and oxygenated species derived from cellulose-containing materials (paper and wood), while the one from WTR was richer in aromatic species such as stable monoterpenes like limonene [72].

3.2 Effects of char addition

Through temperature-sweep measurements, the evolution of the loss tangent (Tan δ = G′′/G′) is monitored during a temperature ramp at a constant heating rate of 1°C per minute and at a frequency of 1 Hz, in order to observe the shift in transition temperature from viscoelastic to liquid (T*). The results are reported in Fig. 2, where the bitumen blended with 6% of the char coming from the pyrolysis of RDF and WTR is compared with the neat bitumen.

As it can be seen from Fig. 2, Tan δ diverges at higher temperatures in bitumens containing the chars, demonstrating their role as bitumen modifiers. The increased temperature transition indicates a higher temperature resistance and a strengthening of the overall chemical structure of the modified bitumens.

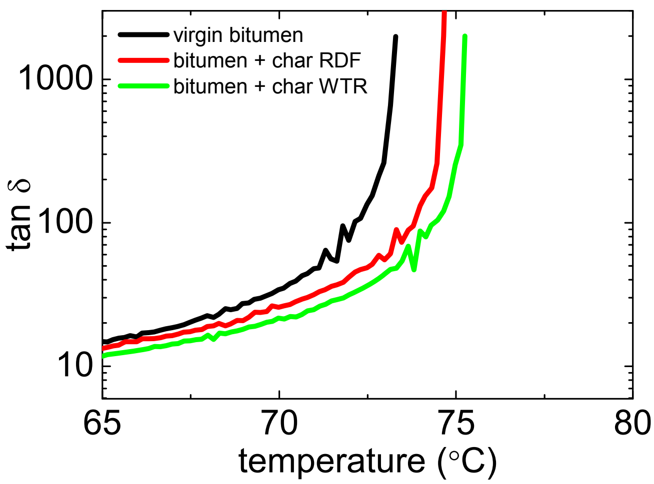

Fig. 2. Tan δ as a function of temperature for the bitumen as is (black line) and the same modified by the char coming from the pyrolysis of RDF (red line) and WTR (green line).

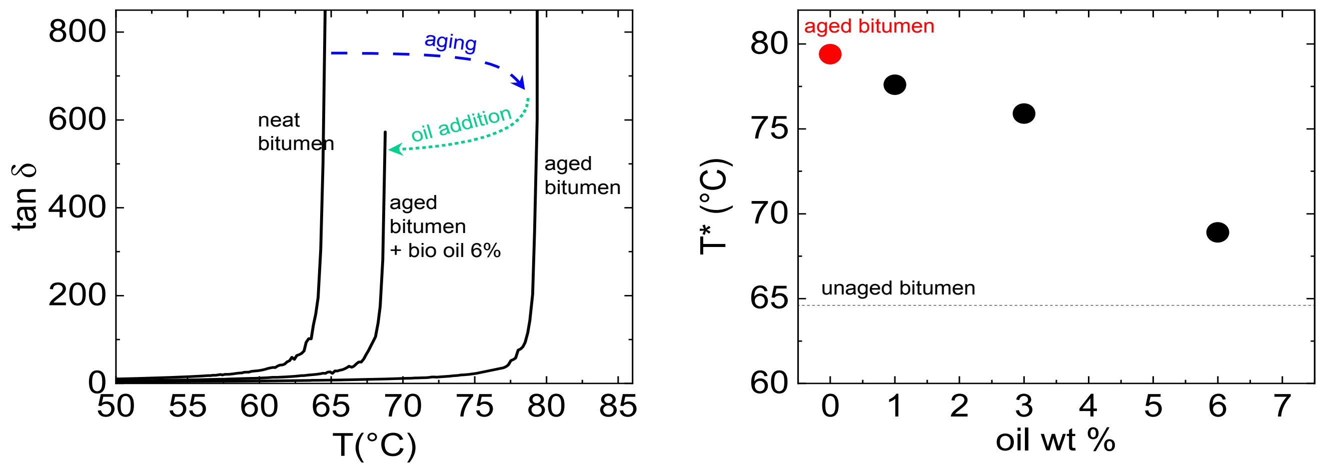

Fig. 3. Left panel: Tan δ as a function of temperature for the neat bitumen, for aged bitumen and the latter after addition of bio-oil 6% wt; right panel: transition temperature (T*) for aged bitumen before (red point) and after (black points) oil addition.

3.3 Effects of oil addition

The effect of the addition of oil to aged bitumen is shown in Fig. 3. Bitumen was subjected to artificial aging by the RTFOT procedure. In this work, the standard RTFOT procedure was extended up to 225 min (normally it is 75 min, according to ASTM D2872-04) to obtain a bitumen rigid enough to simulate a prolonged aging process of about 10-12 years, which is a period typical of recycled asphalts.

Figure 3 shows that aging implies an increase in the transition temperature (T*) because that the physico-chemical processes involved in aging cause an increase in rigidity [43].

The progressive addition of oil causes a shift of T* to lower temperatures, due to the partial restoring of initial mechanical properties. The bitumen therefore tends, after oil addition, to recover its initial viscosity and plasticity. This shows the effectiveness of the approach we are proposing, suggesting that after its life cycle, a road pavement can be restored instead of being landfilled. Further studies are advisable to clarify if the effect is a simple reduction of viscosity (fluxing effect) or, rather, a real change in the microscopic molecule-based structure is obtained, with an effect associated with a real rejuvenation of the bitumen [73].

For this, as the cited article shows, more specialized methods of investigation are needed, which probe the real physico-chemical state of the asphaltene clusters.

4. Conclusions

In accordance with the circular economy perspective, we envisioned developing a virtuous use of both solid (char) and liquid (oil) products derived from the pyrolysis of urban waste, which represents the barrier technology of the entire process, to produce bitumens and asphalts (i.e. bitumen blended with inorganic particles) more durable over time and highly performing. This would guarantee all motorists greater road safety. This activity matches the scope of the Circular Economy Package dated 4/7/2018 with the final aim of material recovery ("tertiary recovery").

The collected results show that the addition of char leads to a strengthening of the overall intermolecular structure, resulting in a higher temperature of transition to the molten state and that the bio-oil can be used as a rejuvenating agent.

This approach will foster the use of multi-functional and multi-effect additives with benefits for society, which will benefit from safer and longer-lasting roads, with reduced maintenance and production costs, and reduced waste to landfill as a result of their superior use.

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