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Review

Microwave heating processes involving carbon materials

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ABSTRACT

Carbon materials are, in general, very good absorbents of microwaves, i.e., they are easily heated by microwave radiation. This characteristic allows them to be transformed by microwave heating, giving rise to new carbons with tailored properties, to be used as microwave receptors, in order to heat other materials indirectly, or to act as a catalyst and microwave receptor in different heterogeneous reactions. In recent years, the number of processes that combine the use of carbons and microwave heating instead of other methods based on conventional heating has increased. In this paper some of the microwave-assisted processes in which carbon materials are produced, transformed or used in thermal treatments (generally, as microwave absorbers and catalysts) are reviewed and the main achievements of this technique are compared with those obtained by means of conventional (non microwave-assisted) methods in similar conditions.

Contents

1. Introduction to the microwave heating of carbons

Microwaves lie between infrared radiation and radiowaves in the region of the electromagnetic spectrum. More specifically, they are defined as those waves with wavelengths between 0.001 and 1 m, which correspond to frequencies between 300 and 0.3 GHz. The microwave band is widely used in telecommunications. In order to avoid interference with these uses, the wavelengths of industrial, research, medical and domestic equipment are regulated both at national and international levels. Thus, the main operating frequency in the majority of countries is 2.450 (+/−0.050) GHz [1,2].

Dielectric heating refers to heating by high-frequency electromagnetic radiation, i.e., radio and microwave frequency waves. The interaction of charged particles in some materials with the electric field component of electromagnetic radiation causes these materials to heat up. The heat resulting from this interaction is mainly due to two different effects. In the case of polar molecules, the electric field component of the microwaves causes both permanent and induced dipoles to rotate as they try to align themselves with the alternating field (2450 million times per second). This molecular movement generates friction among the rotating molecules and, subsequently, the energy is dissipated as heat (Dipolar Polarization). This is the case of water and other polar fluids. In the case of dielectric solid materials with charged particles which are free to move in a delimited region of the material, such as π-electrons in carbon materials, a current traveling in phase with the electromagnetic field is induced. As the electrons cannot couple to the changes of phase of the electric field, energy is dissipated in the form of heat due to the so-called Maxwell–Wagner effect (Interfacial or Maxwell-Wagner Polarization) [1,2].

The materials which interact with microwaves to produce heat are called microwave absorbers. The ability of a material to be heated in the presence of a microwave field is defined by its dielectric loss

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tangent: $\tan\delta = \varepsilon''/\varepsilon'$. The dielectric loss tangent is composed of two parameters, the dielectric constant (or real permittivity), ε', and the dielectric loss factor (or imaginary permittivity), ε''; i.e., $\varepsilon = \varepsilon' - i\varepsilon''$, where ε is the complex permittivity. The dielectric constant (ε') determines how much of the incident energy is reflected and how much is absorbed, while the dielectric loss factor (ε'') measures the dissipation of electric energy in form of heat within the material [1,2]. For optimum microwave energy coupling, a moderate value of ε' should be combined with high values of ε'' (and so high values of $\tan\delta$), to convert microwave energy into thermal energy. Thus, while some materials do not possess a sufficiently high loss factor to allow dielectric heating (transparent to microwaves), other materials, e.g. some inorganic oxides and most carbon materials, are excellent microwave absorbers. On the other hand, electrical conductor materials reflect microwaves. For example, graphite and highly graphitized carbons may reflect a considerable fraction of microwave radiation. In the case of carbons, where delocalized π-electrons are free to move in relatively broad regions, an additional and very interesting phenomenon may take place. The kinetic energy of some electrons may increase enabling them to jump out of the material, resulting in the ionization of the surrounding atmosphere. At a macroscopic level, this phenomenon is perceived as sparks or electric arcs formation. But, at a microscopic level, these hot spots are actually plasmas. Most of the time these plasmas can be regarded as microplasmas both from the point of view of space and time, since they are confined to a tiny region of the space and last for just a fraction of a second. An intensive generation of such microplasmas may have important implications for the processes involved.

The microwave heating of a dielectric material, which occurs through the conversion of electromagnetic energy into heat within the irradiated material, offers a number of advantages over conventional heating such as: (i) non-contact heating; (ii) energy transfer instead of heat transfer; (iii) rapid heating; (iv) selective material heating; (v) volumetric heating; (vi) quick start-up and stopping; (vii) heating from the interior of the material body; and, (viii) higher level of safety and automation [3]. Due to these advantages, microwaves are used in various technological and scientific fields in order to heat different kinds of materials [2–4]. Most of the industrial applications of microwave heating are based on heating substances that contain polar molecules, for example: food processing, sterilization and pasteurization, different drying processes, rubber vulcanization, polymerization or curing of resins and polymers by elimination of polar solvents, etc. In addition, solid materials with a high dielectric loss factor, i.e., microwave absorbers, can be subjected to different processes based on microwave heating. Among these materials, carbons are, in general, very good microwave absorbers, so they can be easily produced or transformed by microwave heating. Moreover, carbon materials can be used as microwave receptors to indirectly heat materials which are transparent to microwaves. Thus, carbon materials have been used as microwave receptors in soil remediation processes, the pyrolysis of biomass and organic wastes, catalytic heterogeneous reactions, etc. The high capacity of carbon materials to absorb microwave energy and convert it into heat is illustrated in Table 1, where the dielectric loss tangents of different carbons are listed. As can be seen, the loss tangents of most of the carbons, except for coal, are higher than the loss tangent of distilled water ($\tan\delta$ of distilled water = 0.118 at 2.45 GHz and 298 K). The search and compilation of these data is not a straightforward matter. Although this parameter is helpful for the study of microwave heating, few research groups have determined the dielectric loss tangents of carbons and the data that can be found are scattered throughout bibliography.

The first commercial microwave oven was developed in 1952, although it was during 1970s and 1980s when the widespread domestic use of microwave ovens occurred, as a result of Japanese technology transfer and global marketing [18]. Curiously, the industrial applications of microwaves were initiated by the domestic ovens. However, in recent years, the number of processes that combine the use of carbons and microwave heating to obtain benefits with respect to other traditional methods based on conventional heating has increased enormously. Thus, as can be seen from Fig. 1, the number of scientific publications related to these topics was very low until the late 1990s, but interest has risen drastically in the last decade and especially so in the last five years.

Table 1
Dielectric loss tangents for different carbon materials at a frequency of 2.45 GHz and room temperature, ca., 298 K.

Carbon material	$\tan\delta = \varepsilon''/\varepsilon'$	Reference
Coal	0.02–0.08	[5,6]
Carbon foam	0.05–0.20	[7]
Charcoal	0.11–0.29	[8,9]
Carbon black	0.35–0.83	[10,11]
Activated carbon	0.57–0.80	[9,12,13]
Activated carbon[a]	0.22–2.95	[14]
Carbon nanotube	0.25–1.14	[15,16]
CSi nanofibres	0.58–1.00	[17]

[a] Activated carbon at a mean temperature of 398 K.

The aim of this work is to review examples of different microwave-assisted processes involving carbon materials. In these processes, microwave heating is used either to produce or modify different carbon materials or is employed in combination with carbons acting as microwave absorbers to enhance different processes in technological applications. The amount of published work is relatively large, so an effort has been made to be representative rather than comprehensive. Thus, the synthesis of a wide range of carbon materials by microwave techniques is reviewed in Section 2. Due to the widespread use of activated carbons, their production, modification and regeneration is treated in a separate section (Section 3). The use of microwave heating in various metallurgical and mineral processes is presented in Section 4. Moreover, microwaves can be used not only to treat and modify solid carbons but also for purposes of revaluation, to obtain other products of high added value, such as gases. This is the case of thermal valorisation of biomass and biosolids, which is dealt with in Section 5. Finally, the use of microwaves to enhance the reactions catalyzed by carbons is growing in importance and is discussed in Section 6.

2. Synthesis of carbon materials

Microwave plasma-enhanced chemical vapor deposition (CVD) has been widely used for growing carbon nanotubes [19,20] or diamond deposition [21]. Although very few works have been

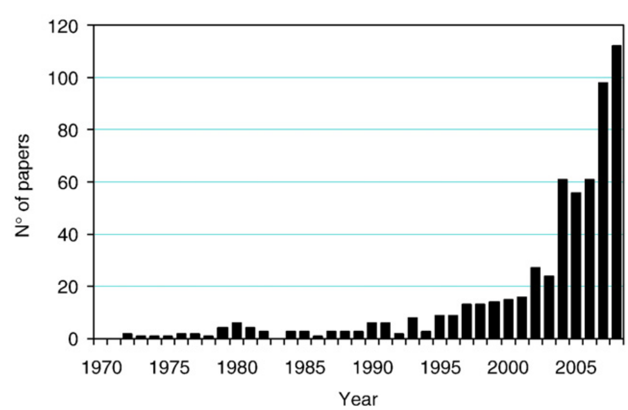

Fig. 1. Evolution of the number of research papers published on microwave-assisted processes involving carbon materials.
(Source: Scopus®).