Pyrolysis of WEEE using Microwave Technology: Behaviour of dielectric properties during thermal processing

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Abstract

The recycling of valuable metal-containing waste is playing an increasingly important role in the context of the circular economy and the attempts to become independent from primary raw materials. The emergence of WEEE is expected to reach up to 15 million tons per year. Printed circuit boards (PCB) count for the bigger part of WEEE's value and get in focus of new recycling technologies. Containing a high amount of organic material as well as numerous toxic components, thermal preconditioning of PCBs has proven to be a successful method of removing the organic matter and dissociating the sturdy compound of metal and ceramics. The presented study focuses on the novel application of microwave technology to generate the heat required for the pyrolysis process. This method is characterized by its special efficiency through selective heating and high energy efficiency. The present paper deals with the preliminary work for treatment by microwaves, such as the general energy input by quantifying the dielectric loss factor of the input material. During microwave treatment heating rates of up to 2,2 °C/s have been observed using active carbon as a microwave absorber. The potential of pyrolyzed PCBs acting as an absorber for continuing feeds has been evaluated. Recirculated material can be used as an effective microwave absorber, achieving heating rates of 1,67 °C/s using 25 % already pyrolyzed material in the mixture. Finally, based on experimental investigations of the thermal pre-treatment, a process model of PCB's decomposition while exposed to a microwave field has been proposed.

Introduction

Electrical and electronic devices are becoming an increasingly important part of our everyday lives. Their complexity and sheer mass are constantly increasing with the growing demand for high-tech applications in digitalization and global information technology. The pressure on the development of sustainable recycling processes is also increasing. After the devices have completed their life cycle, they are faced with a complex recycling process that aims to recover as many base, technology, and valuable metals as possible.

The amount of electronic waste has increased by about 41 % in the last decade – in 2020, about 15 million tonnes of electronic waste are now expected in Europe alone [1, 2]. Many of the elements contained in electronic scrap are lost in direct metallurgical recycling. As part of a more advanced recycling route, thermal pre-treatment processes have the potential to open up new side-streams of valuable materials [3].

Microwave pyrolysis has already been studied by many researchers. This mainly includes the treatment of biomass, such as palm kernel shells, wood chips, sago wastes, etc. [4], household plastics [5], or coffee hulls [6]. The application of microwave technology generally led to shorter treatment times and the production of high-quality pyrolysis products [7, 8]. Pyrolysis of printed circuit boards using microwaves was also carried out successfully and resulted in more efficient decomposition of the organics and a correspondingly higher metal content in the pyrolysis coke [9] and a promoted hydrometallurgical recovery of valuable metals [10].

Printed circuit boards are a complex composite of metal, glass fiber and organic materials [11]. The heterogeneous composition of the PCBs makes it difficult to predict how they interact with the microwave field. The glass fiber component, which gives the PCB its mechanical stability, is transparent to microwave radiation. The organic components such as epoxy, polyethylene or polypropylene have low loss factors and can be classified as low-loss materials [12]. The metal substrate of the PCB or metallic structures generally have a reflective effect on the electromagnetic radiation, but can reach very high temperatures locally due to gas discharges and plasma generation [13]. Furthermore, the composition of the printed circuit boards changes during pyrolysis due to thermal decomposition. The effects of this change on microwave-material-interaction have not yet been investigated.

The reviewed literature expresses concerns about commercialization, thorough economic consideration and, above all, a careful understanding of the mechanisms at work during microwave treatment of printed circuit boards. In order to set up an industrial implementation of the process of microwave pre-treatment, it is necessary to investigate the near-reality behaviour of aforementioned scrap [5, 14, 15]. The aim of this work is to carry out thorough investigations of the dielectric properties and to show process engineering possibilities to design the process of microwave pyrolysis of printed circuit boards according to the inherent characteristics of real scrap samples as they can be found after collection and comminution.

Thermal Conditioning: Pyrolysis

Pyrolysis is a promising option for pre-treatment of printed circuit boards. It is defined as the chemical decomposition of organic material under the external application of heat. The process must take place in the absence of oxygen to prevent burning and oxidizing of the feed [16]. The main products of pyrolytic decomposition are a carbon-rich solid residue (pyrolysis coke), a non-condensable gas and condensable components called pyrolysis oil. The general conversion of organic material can be described by the following formula [17].

$$C_nH_mO_p + Heat \rightarrow \sum_{liquid} C_aH_bO_c + \sum_{gas} C_xH_yO_z \sum_{solid} C$$

Pyrolysis takes place at temperatures above 300 °C. Here, the structure of the polymers begins to break down and form smaller intermediates. This decomposition of the long-chain molecules is called cracking. If enough energy is added to the process, the cracking eventually leads to the formation of elemental carbon, which is called pyrolysis coke [18]. Important parameters influencing thermal decomposition are primarily temperature, heating rate and reaction time. They dictate the composition and distribution of the end products [19].

Microwave Technology

Various aggregates are available for the implementation of the pyrolysis process. Ovens based on microwave technology have attracted more and more attention in recent years. In contrast to conventional heating, microwave units offer the possibility of faster and more efficient material conversion [20].

Microwaves are electromagnetic waves in the frequency range from 300 MHz to 300 GHz. The corresponding wavelengths range from 1 m to 1 mm. Two frequencies have become established in industrial heating processes: 2.45 GHz and 915 MHz. The generated field corresponds to the frequency. Materials interact with the microwave field depending on their dielectric characteristics [20].

In this work, printed circuit boards are exposed to the microwave field in order to perform the thermal decomposition described above. Therefore, an understanding of the mechanisms that lead to heat generation is of great importance. In principle, all materials can be classified into four categories based on their interactions with the microwave field.: (I) reflective materials, such as metals, which reflect the microwaves with low loss and react weakly with them, (II) transparent materials, such as glass, certain ceramics or air, which are permeable to electromagnetic radiation, (III) absorbent or “lossy” materials that interact strongly with the microwave field and convert the electromagnetic energy into heat, and (IV) magnetic materials that interact with the magnetic component of the microwave field. Effective heat conversion in lossy materials occurs through frequency-dependent polarization mechanisms. The dominant polarizations in the range of microwave radiation are orientation and dipole polarizations. Here, molecules that have a constant di-pole moment are excited and aligned by the microwave field. The molecules follow the fluctuating wave, but due to their inertia they generate a frictional resistance that macroscopically leads to a heating of the material [12, 20].

A measure of the ability of a material to be polarized by electromagnetic waves and to convert the supplied energy into heat is the dielectric loss factor $\tan\delta$. If this dimensionless value of a substance is above 0.05, it is generally said to be well suited to be heated by microwaves. The loss factor is made up of two measurable quantities, which together give the complex relationship of permittivity: the dielectric constant ε' and the dielectric loss ε'' [12, 21].

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

One way of heating materials with a low dielectric loss factor in the microwave field is to use absorbers. Here, lossy components are added to the feed, whose dielectric properties allow the electromagnetic radiation to be absorbed, converted into heat and indirectly transferred to the surrounding material. These absorbers generally allow a significant time gain, which in most cases is followed by lower energy consumption. As a result, the process becomes more efficient and economically competitive. Of great importance for this work are carbon-rich absorbers, such as graphite, carbon black or activated carbon, whose dielectric loss factors range from 0.02 to 1.00. Therefore, these materials are suitable as microwave absorbers [22].

Materials and Methods

The feedstocks treated in this work are class 2 printed circuit boards. The material was provided by a local recycler. As can be seen in Figure 1 on the left, the samples consist of fractions of different sizes. The largest parts are pieces of circuit board, 1 to 6 cm wide, consisting of epoxy resin, glass fiber and metal contacts, as well as plastic plugs a few centimeters in size. Smaller parts up to 1 cm are metal connectors, crushed components of microchips and plastic. Some copper wires from transformers and cables with plastic coating can also be found in the samples. Figure 1 on the right shows pieces of printed circuit boards. Their basic substance, consisting of epoxy resin (green) and glass fibers, can be seen. Metal contacts and solder joints are exposed.

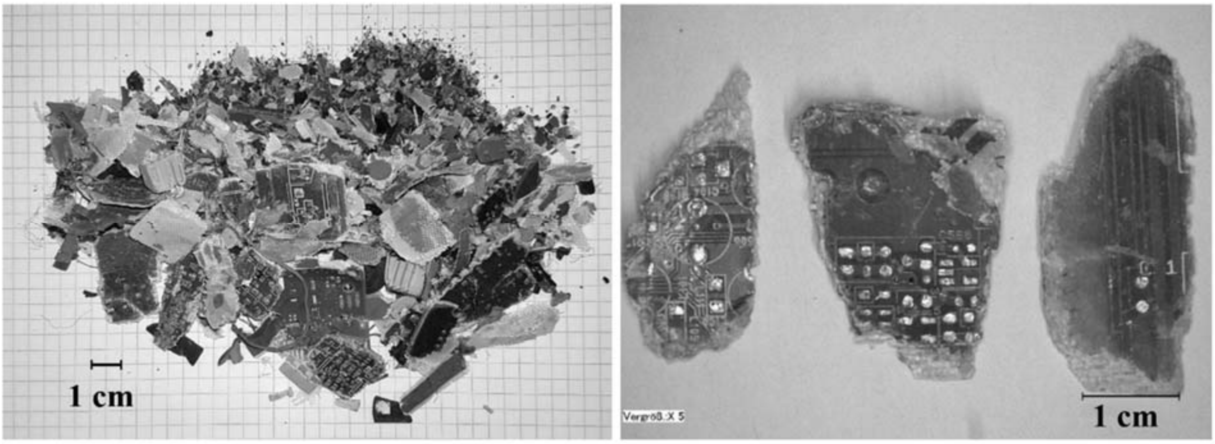

Figure 1: PCBs used in the experiments

Furthermore, the use of a microwave susceptor was tested. For this purpose, activated carbon in the form of pellets was used, which was mixed with the PCB material (Figure 2). The pellets were 0.5 – 2 cm long with a diameter of about 0.35 cm.

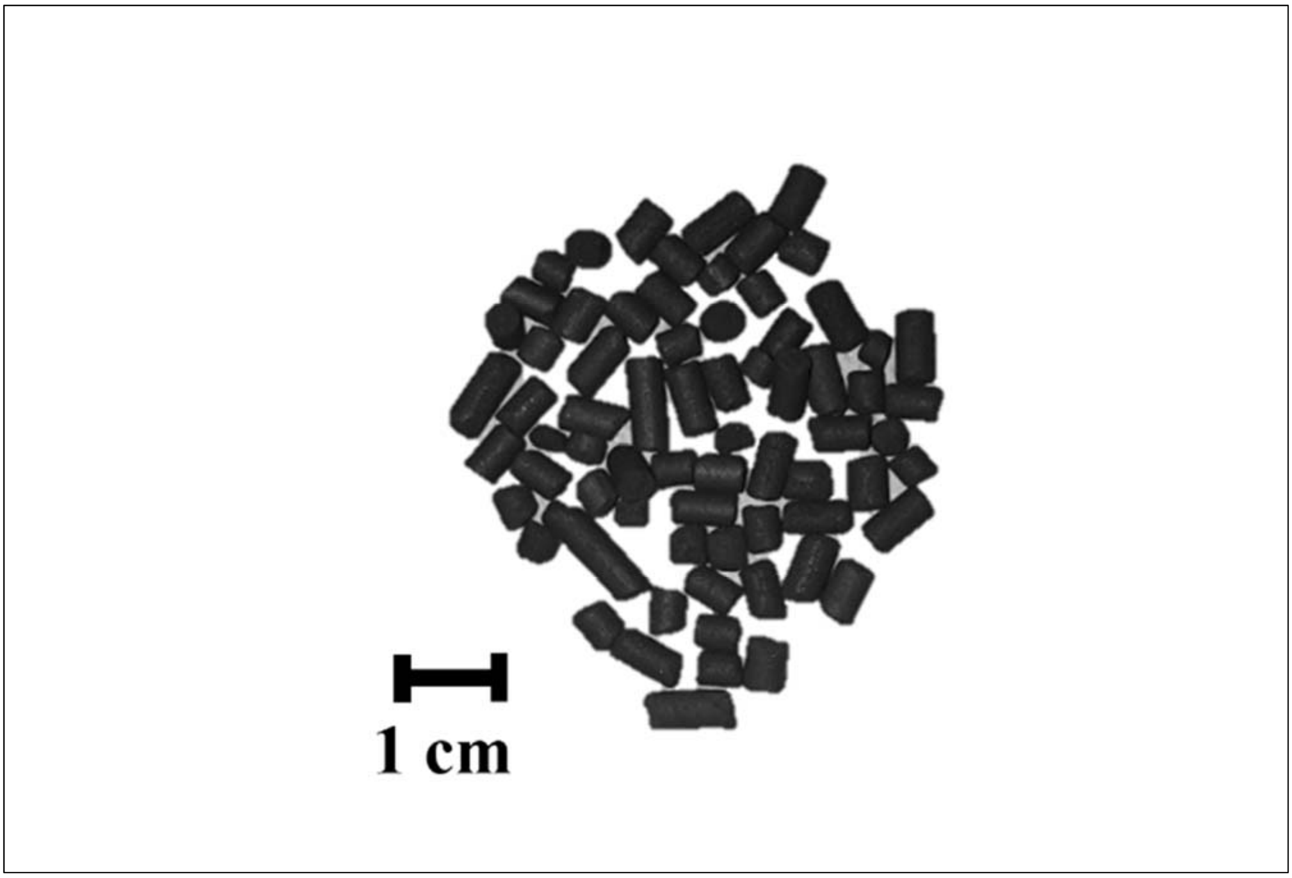

Figure 2: Active carbon used as a microwave absorber for indirect heating

Experimental Setup

Conventional Pyrolysis and Measurement of Dielectric Properties

In order to understand the behavior of a material in the microwave field, an evaluation of the dielectric properties becomes very important. First, the PCB scrap was cryogenically ground to < 4 mm to homogenize the samples and enable charging. 30 grams of the samples were pyrolyzed at 300 – 800 °C each in 100 °C steps in a gas-tight, resistance-heated oven. A constant inert gas flow of argon was used to displace oxygen and to remove pyrolysis gases (6 l/min). The holding time was 30 minutes.

Figure 3: Cryogenically crushed PCBs for conventional pyrolysis prior to the measurement of dielectric characteristics

The investigation of the dielectric properties was carried out using the “Open-Ended Coaxial Probe” (Reflection Method). In this method, a coaxial probe is brought into contact with the material to be analyzed. A broadband EM field is induced in the material via the probe. Network analyzers measure the reflected signal and translate it into a value for the relative permittivity of the sample. An impedance meter calculates the real and imaginary parts of the permittivity and finally the dielectric loss factor. The investigated frequency was chosen according to the common microwave frequencies 2.45 GHz and 915 MHz.

Microwave Pyrolysis

The microwave pyrolysis was carried out in a gas-tight microwave furnace at the IME Institute. Microwave energy is supplied by eight magnetrons with a maximum power of 6 kW each. For the experimental procedure, a beaker made of DURAN glass was used, which keeps the effective gas space for the resulting pyrolysis gas low while being transparent to the applied microwave field. The feed to be pyrolyzed is placed in a thermal shock resistant crucible made of Al_2O_3 and SiO_2. At the beginning of the experiment, the microwave chamber was flooded with argon to displace the atmospheric oxygen. Afterwards, a constant flow rate of 6 l/min Ar was set to remove the emerging pyrolysis gases. The furnace and a schematic of the experimental set-up are shown in Figure 4.

Samples of 150 grams each have been treated in the microwave field. A treatment of printed circuit boards without susceptor served as a reference experiment and for generating a sample of pyrolyzed material. Batches of 25 % activated carbon and 25 % of the previously pyrolyzed material were used to investigate the influence of microwave absorbers. Furthermore, tests were carried out in which the

PCBs were heated up for a few seconds using microwaves to observe the heat development at the beginning of the treatment.

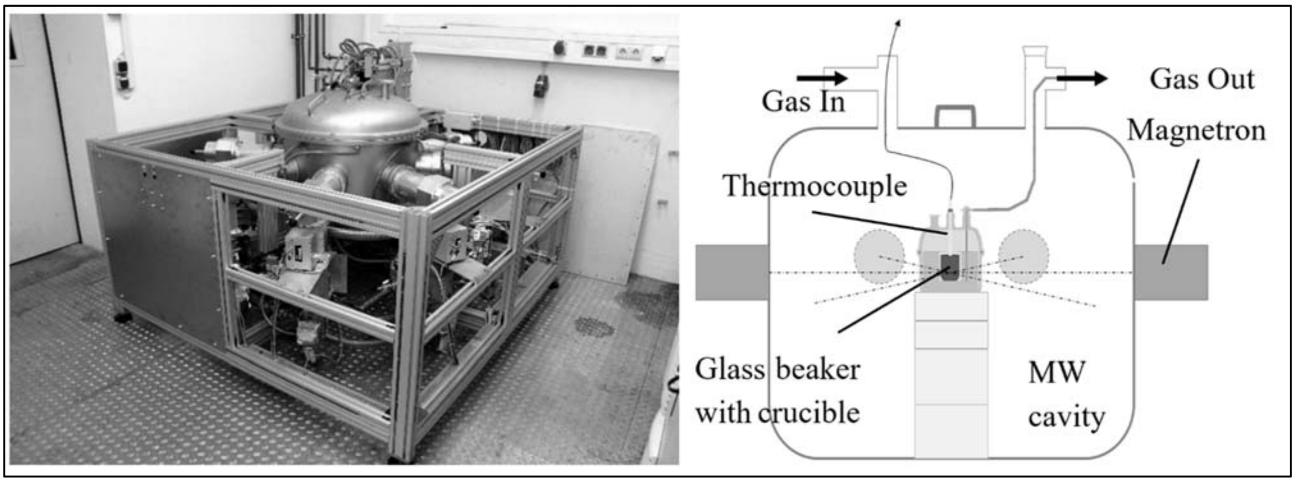

Figure 4: Microwave furnace at the IME Institute (left), experimental setup for MW-pyrolysis (right)

Measuring temperature in the microwave field is challenging due to interference and volumetric heating. In this work, the temperature of the feedstock was measured using a shielded type K thermocouple. A 1 cm copper cylinder shields the measuring tip of the thermocouple. Additionally, the metallic wire of the thermocouple was embedded in a protective Al_2O_3tube filled with granulated ZrO. This prevents interference with the microwave field but contributes to the inertia of the thermocouple. The thermocouple was suspended centrally in the bulk of the circuit boards.

Results and Discussion

Figure 5 shows the results of the measurement of the dielectric properties of pyrolyzed lead plates as a function of the pyrolysis temperature. A steady increase of the dielectric properties with increasing pyrolysis temperature can be seen. The measurements of the sample pyrolyzed at 700 °C are an exception. Here the dielectric properties decrease compared to the next colder temperature (600 °C). However, the increasing trend continues at higher temperatures (800 °C). All values of the loss factor for a working frequency of 2.45 GHz are above 0.05. The measurements at 915 MHz exceed this value. The measurements at 915 MHz only exceed this value from 500 °C. The maximum values for the dielectric loss factor are reached at 800 °C at 0.2 (2.45 GHz) and 0.16 (915 MHz). At all times, the values for 915 MHz are below those for 2.45 GHz.

The basis for the evaluation of the measurement results is the assumption that the degree of pyrolysis of the PCB increases with increasing temperature. Due to the decomposition processes, which are favored by a higher energy supply, a more intensive cracking of the organic components takes place. This is directly related to an increased proportion of elemental carbon in the pyrolysis coke. This is consistent with the observations of other researchers [23]. The generated pyrolysis coke converts the microwave radiation into heat more efficiently due to higher dielectric losses than the incompletely decomposed organic material at lower pyrolysis temperatures.

The measurements show that the operating frequency of 2.45 GHz is more suitable than 915 MHz for the effective heating of printed circuit boards. The increasing degree of pyrolysis and the resulting increased carbon concentration in the samples leads to a significant increase in the dielectric losses of the sample.

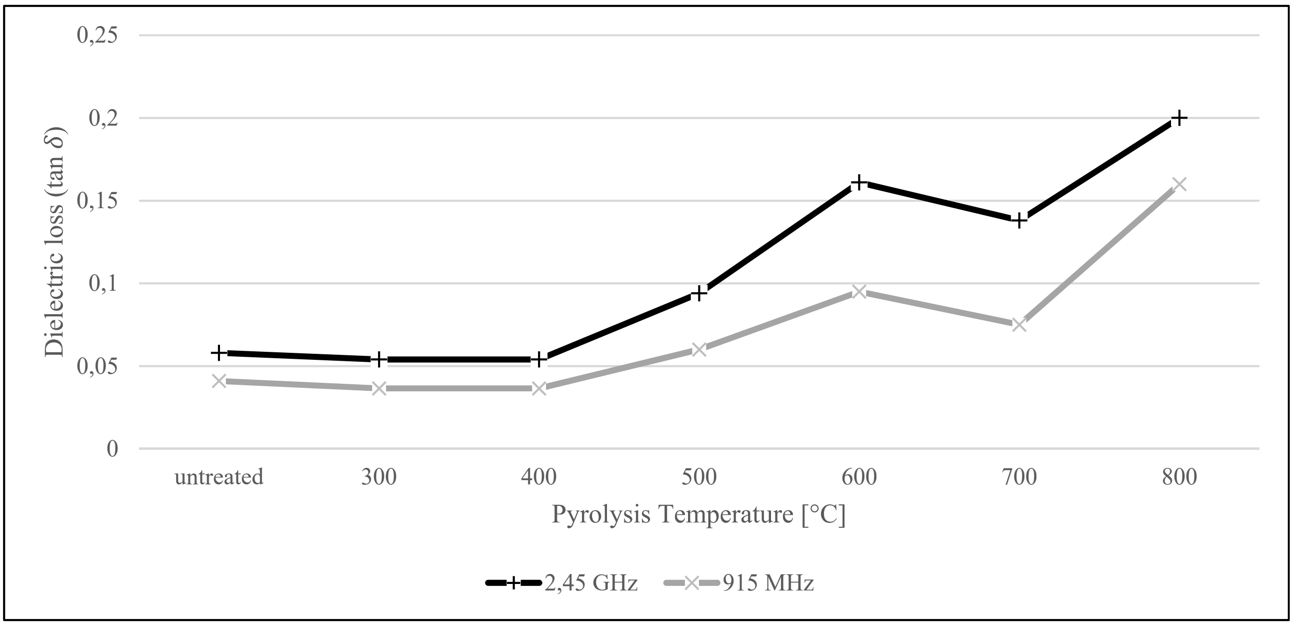

Figure 5: Results of dielectric loss measurement of pyrolyzed PCB at 2,45 GHz and 915 MHz

The influence of the use of microwave absorbers can be seen in Figure 6. The influence of the use of microwave absorbers can be seen in Figure 6. Heating rates of 1.05 °C/s without absorber, 2.20 °C/s with activated carbon and 1.67 °C/s with recirculated material were achieved. For safety reasons and to protect the glass beaker, the microwave power was switched off at 600 °C.

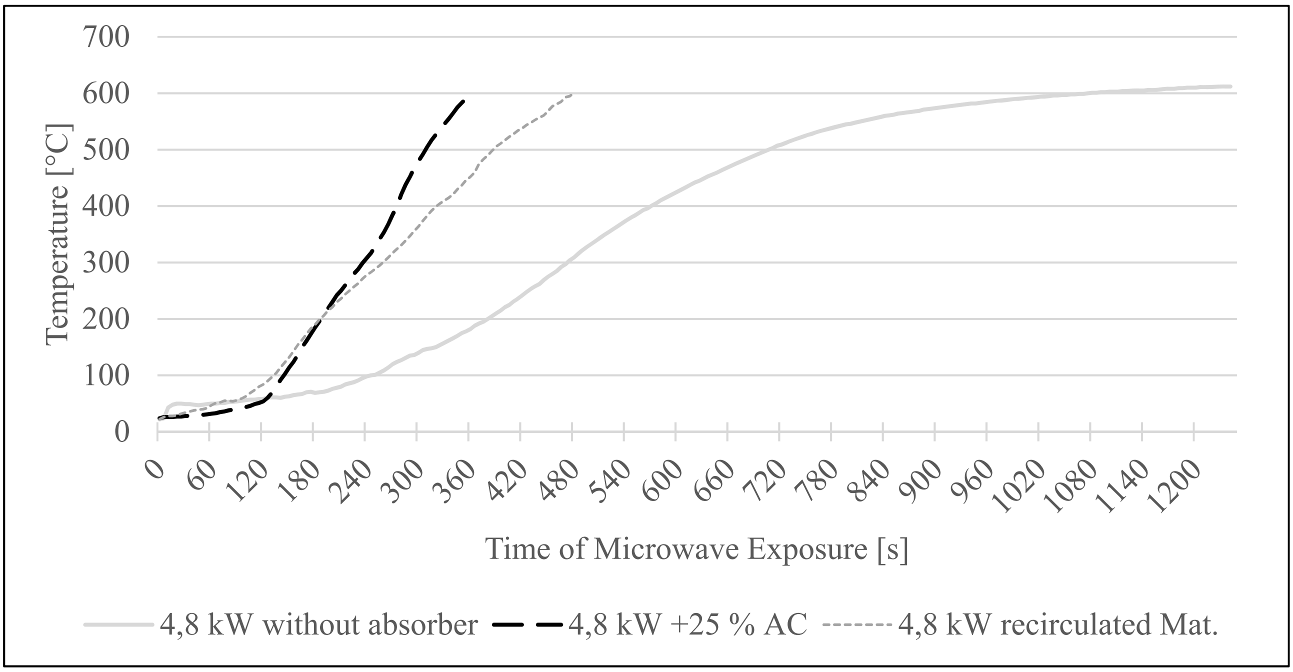

Figure 6: Temperature Measurement during pyrolysis of PCB using microwave absorbers when indicated

Without the addition of absorber, the temperature of the sample rises slowly at the beginning, but with the help of activated carbon or recycled material a rapid temperature development can be observed. This is consistent with the measurements of the dielectric properties. Initially, the PCB shows a low dielectric loss, which means that it only heats up slowly. As the degree of pyrolysis increases, decomposition of the organics occurs, and carbon-free pyrolysis coke is formed. This coke is heated more efficiently by the microwave power and dissipates the heat to the surrounding material. The more the pyrolysis process advances, the more coke is formed followed by a significant increase in the heat absorption of the material. When the PCB is completely pyrolyzed, the sample reaches a temperature maximum. By using a carbon-based absorber, the temperature development is accelerated due to the higher absorptive nature of the material in total. Apparently, in addition to activated carbon, already pyrolyzed printed circuit boards are also suitable for serving as an additive. The recycled material achieves a similar temperature increase or time gain, which makes it suitable as an absorber.

Figure 7 shows PCB pieces after a few seconds in the microwave field. The pyrolysis process can be recognized by the black pyrolysis coke that forms. Obviously, the thermal decomposition started near a solder contact and spread from there over the PCB. This may be due to local overheating caused by arcing. However, a direct visual inspection of the material was not possible due to the construction of the oven.

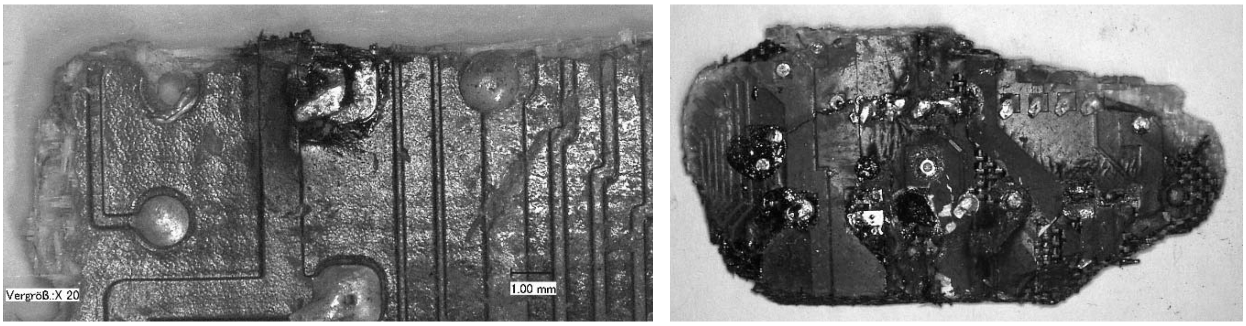

Figure 7: Partially pyrolyzed PCBs after a few seconds (left) and 2 minutes (right) exposed to the microwave field

Conclusion

As shown, the dielectric properties of PCBs were investigated at increasing pyrolysis levels. Resulting behaviors in a microwave field were verified in experiments in a microwave furnace. The following conclusions are drawn from this work:

- The elemental carbon produced during the pyrolysis of printed circuit boards improves the dielectric properties of the input material. as the degree of decomposition increases, the ability of the material to be polarized by the microwave field increases.
- During microwave pyrolysis of PCBs using high loss absorbers, the temperature increased significantly faster resulting in a faster decomposition of organics. Heating rates of up to 2.2 °C/s were achieved.
- Already pyrolyzed printed circuit boards are suitable as microwave absorbers. A heating rate of 1,67 °C/s was achieved. In industrial implementation, this has the advantage that the starting material does not have to be mixed with foreign substances prior to microwave pyrolysis to ensure efficient and rapid thermal pre-treatment.

Based on the findings from the experiments conducted, a mechanism is proposed to describe the behavior of printed circuit boards in a microwave field: Figure 8. The unpyrolyzed printed circuit board has a low dielectric loss factor at the beginning. The organic part is still intact before decomposition, there is no elementary carbon. If the material is now exposed to a microwave field with sufficient power, thermal decomposition begins at metallic contacts or solder points. This local overheating leads to decomposition of the surrounding laminate. One decomposition product is elemental carbon, which can effectively convert the microwave radiation into heat due to its dielectric properties. This heat generation leads to progressive decomposition of the organic material.

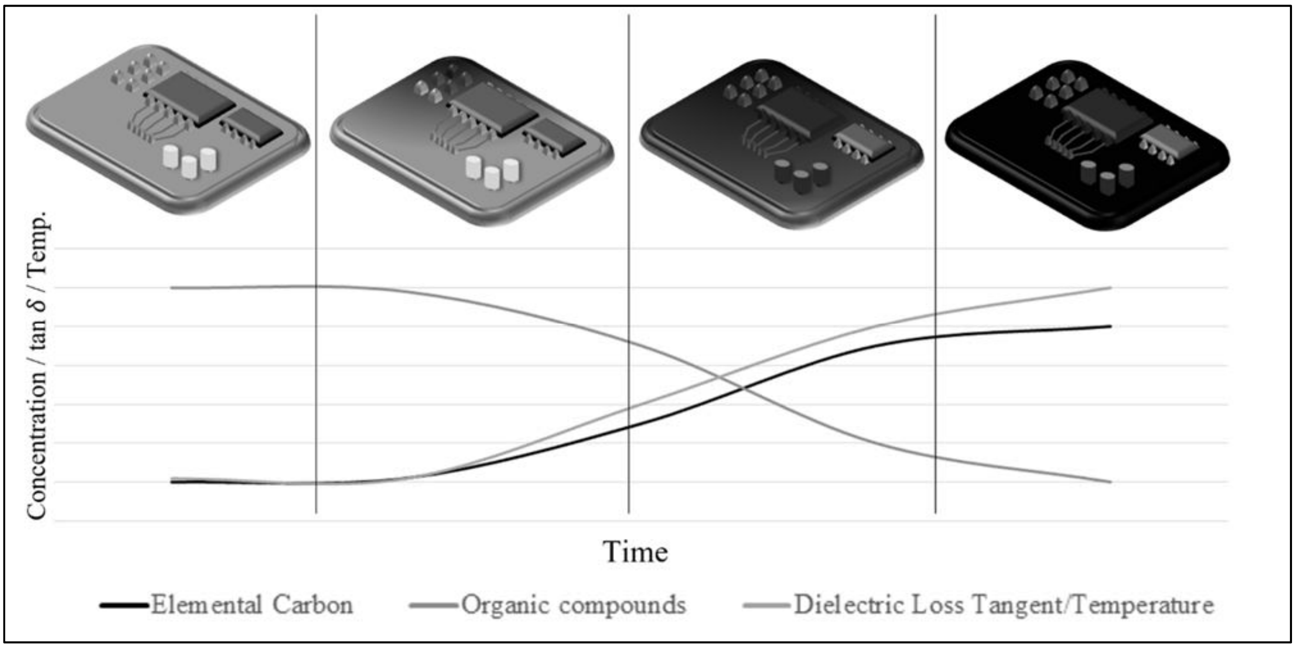

Figure 8: Suggested process of Microwave Pyrolysis of PCB resulting from observations

Finally, the thermal pre-treatment of metal-containing scrap using microwaves is still in the development phase. The mixture of carbon-containing materials as absorbers offers great potential for saving energy and time. Their use makes it possible to heat low-loss materials. Microwave processes involving carbon-rich materials also have the potential to catalyze certain reactions [22]. In the case of PCB pyrolysis, for example, this could be used for the systematic production of a high-quality pyrolysis gas or even high amounts of hydrogen.

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