

## Review Article

# Polymer Processing under Microwaves

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Over the last decades, microwave heating has experienced a great development and reached various domains of application, especially in material processing. In the field of polymers, this unusual source of energy showed important advantages arising from the direct microwave/matter interaction. Indeed, microwave heating allows regio-, chemio-, and stereo-selectivity, faster chemical reactions, and higher yields even in solvent-free processes. Thus, this heating mode provides a good alternative to the conventional heating by reducing time and energy consumption, hence reducing the costs and ecological impact of polymer chemistry and processing. This review states some achievements in the use of microwaves as energy source during the synthesis and transformation of polymers. Both in-solution and free-solvent processes are described at different scales, with comparison between microwave and conventional heating.

## 1. Introduction

Three main challenges arise from polymer science. (i) The first one consists of improving the properties of the material: According to the use the polymer is designed to, it must present adequate properties from different points of view (such as mechanical, thermal, rheological, optical, and chemical properties). (ii) The second one is the optimization of the processes involved in polymer chemistry or transformation: In order to achieve gains in time and cost, the processing parameters have to be tailored, depending on the polymer properties, to meet the goals of the process in terms of quality, productivity, and economy. (iii) The third one is compliance with the ecological requirements: Since the environmental issues are major scientific and societal challenges, both the polymer material and the process should allow a limitation of nonenvironmentally friendly substances emitted and reduce the energy consumption during the polymer synthesis or transformation.

Heating is a key parameter in both polymer chemistry and processing; the heating method can play an essential role. In that purpose, microwave (MW) heating seems to be a promis-

ing solution to fulfill the three points mentioned above, as it presents a particular heating with special features.

MW heating consists of exposing a material to electromagnetic radiation. The MW frequencies are between 300 MHz and 300 GHz, corresponding to wavelengths between 1 m and 1 mm. The use of these waves for industrial, medical, and scientific applications is regulated to avoid interferences with radars and radio communication; the 2.45 GHz frequency is the most commonly used. Like other electromagnetic fields, microwaves can interact with matter. According to their dielectric or magnetic properties, some materials are able to interact with microwaves and consequently rise in temperature.

Indeed, it is well-established that MW heating comes from the motion of charges (dipoles/ions) in the material; it is called volumetric microwave heating [1]. This mode of heating was studied by polymer scientists and has proven its efficiency. In many cases, the particularities of microwave heating offer many advantages: time and energy savings during polymer processing; fast heating rates leading to faster chemical reactions with higher yields; and chemical selectivity and easy achievement of free-solvent reactions. However,

there are some constraining aspects of MW heating, such as thermal runaway, heterogeneous heating, and difficulties in temperature measurements.

Many reviews have been published during about the use of MW heating in the field of polymers during the last decade; dealing with polymer synthesis [2], modification [3], degradation [4], and curing [5], the current review deals with the use of MWs during polymer processing. The theoretical and practical characteristics of MW heating in the field of polymers are first discussed, with a comparison between the conventional and MW heating based on sample reactions. Some applications at the industrial scale are highlighted.

## 2. Microwave-Matter Interaction

**2.1. Fundamental Aspects.** Electromagnetic waves are characterized by the free (or guided) propagation of electric  $\vec{E}$  and magnetic induction  $\vec{H}$  fields. These two components oscillate, according to the radiation frequency, and define a plane perpendicular to the wave vector  $\vec{k}$  whose intensity is inversely related to the wavelength  $\lambda$  and can be expressed by

$$k = \frac{2\pi}{\lambda}. \quad (1)$$

Based on Maxwell equations, the response of a material, submitted to an electric field  $\vec{E}$ , may be represented by the electric displacement field or electric induction  $\vec{D}$ . This vector field accounts for the effects of both free and bonded charges (dipole moment, ions and electrons) within the material. In the absence of electromagnetic field, the dipoles are randomly oriented (Figure 1(a)). If a continuous electric field comes through the material, the dipoles will be oriented in the direction of the field (Figure 1(b)). However, in the presence of an alternative electromagnetic field, the orientation of each dipole tends to follow the changes in the field direction (Figure 1(c)), leading to the oscillation of the dipole. The relative motion of dipoles is considered in the Maxwell equations by the introduction of  $\epsilon^*$ , known as the permittivity or the dielectric constant of the material. This dielectric constant links the previous field vectors according to the following equation:

$$\vec{D} = \epsilon^* \vec{E}. \quad (2)$$

As the frequency increases, the bonded charges cannot follow the oscillations, resulting in a shift between the oscillation of the dipoles and the frequency of the electromagnetic field. The permittivity can be expressed as a combination of real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts:

$$\epsilon^* = \epsilon' - j\epsilon''. \quad (3)$$

$\epsilon'$  reflects the ability of the dipoles to be polarized under the electromagnetic field and corresponds to the stored energy within the material. The dielectric loss factor  $\epsilon''$  is the dissipative

component of the dielectric constant and represents the ability of a material to dissipate the absorbed energy. The phase shift between the oscillation of the dipoles at the frequency of the electromagnetic field is represented by a shift angle  $\delta$ , called the loss angle. To describe the capability of a material to convert electromagnetic energy into heat, it is customary to express the loss factor  $\tan \delta$ , also called dissipation factor, as in the following equation [6]:

$$\tan \delta = \frac{\epsilon''}{\epsilon'}. \quad (4)$$

In the event that a material owns a nonnegligible electric conductivity ( $\sigma > 10^{-12} \text{ S}\cdot\text{m}^{-1}$ ), the free charges within the material are also impacted by the electromagnetic field. Thus, in addition of the dielectric loss, the absorbed power ( $P_{\text{abs}}$ ) can be dissipated by Joule effect and can be expressed as

$$P_{\text{abs}} = (2\pi f \epsilon^* \tan(\delta) + \sigma) |E|^2. \quad (5)$$

Despite polymer materials are, most of the time, only subjected to electric field, the use of magnetic fillers for particular applications can make the polymers sensitive to the magnetic field [7, 8]. An analogy can be made to describe the contribution of the magnetic induction  $\vec{H}$  field. In that case, thermal heating comes from the polarization of magnetic moments and the establishment of Foucault's currents. Consequently, the energy absorbed by a material under magnetic induction field may be deducted from Equation (5) by replacing  $E$  by  $H$  and the relative permittivity  $\epsilon^*$  by the relative magnetic permeability  $\mu^*$ . Therefore, the absorbed energy under magnetic field can be expressed by

$$P_{\text{abs}} = (2\pi f \mu^* \tan(\delta) + \sigma) |H|^2. \quad (6)$$

These parameters differ for each material and are highly dependent on the temperature and the frequency of the microwave field [9, 10]. In the case of polymeric materials, the dielectric constants are also dependent on the molecular weight and the molecular structure of the polymer [11, 12]. Thus, the behavior of each material is different under microwave radiation, and the knowledge of these constants and their variations is paramount when performing microwave-assisted polymerization, chemical modification of polymers, and during polymer processing under microwaves.

**2.2. Penetration Depth and Material Behavior.** It is interesting to mention that another key parameter has to be considered: the microwave penetration depth ( $D_p$ ). When the electromagnetic field passes through a material (solid or melted polymer and solvent), its intensity decreases exponentially from the free surface of the material until the transmitted power becomes too weak to cause heating (Figure 2). The absorbed power by the lossy material can be expressed as

$$P_{\text{abs}}(x) = P_{\text{in}} e^{-2(x/D_p)}, \quad (7)$$

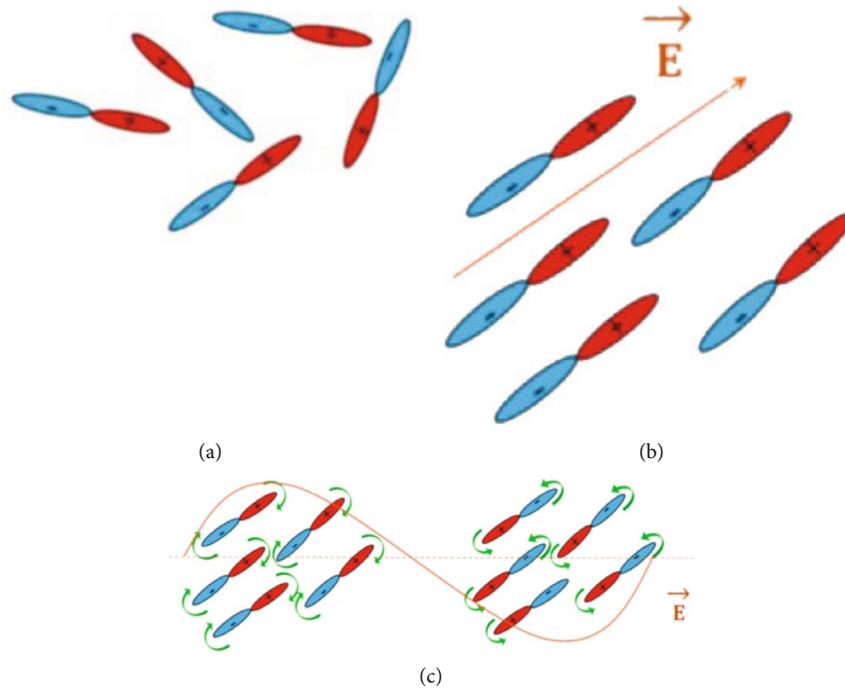


FIGURE 1: Orientation of dipoles (polar chemical moieties): (a) at rest; (b) in the presence of constant electric field; and (c) in the presence of an alternative electric field.

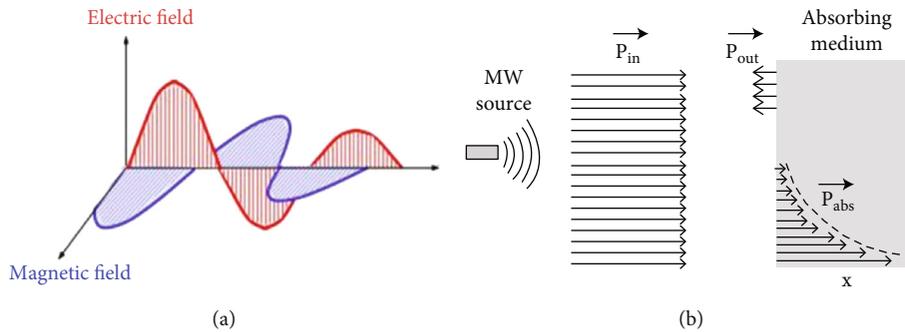


FIGURE 2: (a) Representation of the extenuation of a microwave propagating in absorbing medium. (b) Distribution of the power absorbed by a lossy material ( $P_{in}$  is the microwave incident power,  $P_{out}$  is the power reflected by the material, and  $P_{abs}$  is the power absorbed by the material).

where  $P_{in}$  represents the incoming power of the electromagnetic field transmitted at the interface of the material. Usually, the penetration depth is defined as the depth at which the intensity of the microwave field is decreased by a factor of  $1/e \approx 36.79\%$  of its surface value [9].

With the consideration of a material preferentially subjected to the electrical field  $\vec{E}$ , the estimation of the penetration depth through a given material is provided by equation 7: [13–15]

$$D_p = \frac{\lambda}{\pi\sqrt{2\epsilon'}} \left( \frac{1}{\sqrt{1 + (\epsilon''/\epsilon') - 1}} \right)^{1/2} \quad (8)$$

In the case of very low dielectric losses in comparison with the conduction loss ( $\epsilon'' \ll \sigma/\omega$ ), the penetration depth through the material can be estimated by

$$D_p \cong \frac{2}{\sigma} \sqrt{\frac{\epsilon'}{\mu'}} \quad (9)$$

In addition to the dielectric (or magnetic) properties, this concept of penetration depth allows to better understand the behavior of each material under microwave radiation. Table 1 presents the penetration depth for different kind of materials at room temperature. According to Equation 8, good electrical conductors (like metallic materials) present a small penetration depth. As a result, almost all the microwaves are reflected, leading to a very difficult heating and a

TABLE 1: Order of magnitude of the penetration depth for different materials at room temperature [15–17].

| Material           | Penetration depth     |
|--------------------|-----------------------|
| Metal              | $\leq 10 \mu\text{m}$ |
| Water              | 1.68 cm               |
| Porcelain          | $\approx 50$ cm       |
| Rubber and polymer | 5 to 350 cm           |
| Teflon             | 9200 cm               |
| Quartz             | 16000 cm              |

so called “opaque” behavior. On the contrary, water and almost all polar solvents, as well as some polymers and ceramics, are characterized by a penetration depth of a few centimeters. The penetration depth highly increases for insulating materials such as Teflon or quartz, leading to a transparent behavior.

The three possible macroscopic behaviors of a material under microwave radiation are represented on Figure 3. It is worth mentioning that the dielectric properties of materials are highly dependent on their temperature and the frequency of the microwave field. As a result, the penetration depth of the microwaves through the material may differ during microwave heating as well as the behavior of the material. Absorbing material can become transparent and vice-versa. Besides, thermal gradients within the sample may occur. For example, the  $D_p$  of 2.45 GHz frequency microwave field in water is 1.68 cm at 20°C [15] and 5.4 cm at 90°C [18]. If we consider water in a 10-cm diameter container, microwaves will reach the center of the sample at 90°C but not at 25°C. Thus, thermal gradients may occur due to the penetration depth. This is even more important in the case of solid samples since no stirring is possible. Thereby, for an efficient microwave heating, the size of the sample has to be set according to the penetration depth [19].

**2.3. The Peculiarities of Microwave Heating.** The basic knowledge having been underlined, it is now worthy to mention the peculiarities of microwave heating, especially in the case of polymers. The most commonly used heating method is the conventional conductive one. Thermal energy is transferred from a source (resistance) to the surface of a heated sample, which diffuses it from the surface to the core. This diffusion is highly dependent on the thermal conductivity of materials and remains slow in the case of polymers due to their low thermal conductivity. As microwave heating occurs through the motion of molecules, this heating process leads to specific properties [20].

**2.3.1. Microwave Heating Is a Direct Volumetric Heating.** If the polymer (or the reactant for solvent processes) is able to interact with microwaves, i.e., having dipolar moment, it will therefore heat directly. According to the penetration depth of microwaves within the material, one consequence is the obtention of an inverse temperature profile of the heated system, as represented in Figure 4. Indeed, microwave heating is known to increase the temperature in the core of the sample, and the heat diffuses to the surface,

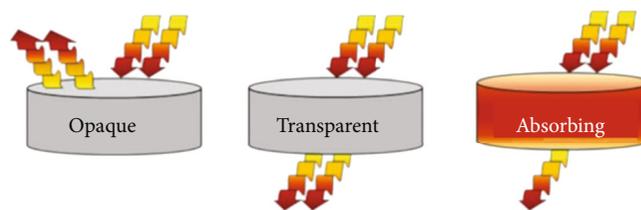


FIGURE 3: Macroscopic aspect of the microwave/matter interactions.

unlike the conventional heating in which the surface is heated first. For transparent or opaque materials, especially nonpolar polymers, the use of susceptors (graphite or SiC) as fillers or around the sample may be required. Susceptors interact preferentially with microwaves, rise in temperature, and then transfer thermal energy by radiation. If the material heats only because of the presence of the susceptors, it leads to indirect microwave heating. In the case of a material that interacts with microwaves in addition to radiative heating from the susceptors, this leads to hybrid microwave heating and limits the thermal gradient that may occur during the process.

**2.3.2. Microwave Heating Leads to Fast Heating.** The orientation of the dipoles takes place in a very short amount of time, resulting in a rapid conversion of microwave energy into heat. Thus, it allows very high heating kinetics, up to hundreds  $^{\circ}\text{C}\cdot\text{min}^{-1}$ , opening the way to new chemical reactions compared to conventional methods. In addition, microwaves can be switched off instantaneously, allowing to stop immediately the chemical reactions.

**2.3.3. Microwave Heating Is Also a Selective Heating.** In the field of polymers or material chemistry, some chemical moieties are more sensitive to the microwave field than others. It is therefore possible to heat preferentially some regions or some reactants within the sample, while other regions present lower temperatures. This property can be usefully operated in the case of some reactional systems, fostering regio-, chemio-, and stereo-selectivity [21–23] or during the heating of composites [5].

The peculiarities of microwave heating allow, in most cases, time and energy savings during polymer processing, fast heating rates leading to faster chemical reactions with higher yields, chemical selectivity, and easy achievement of free-solvent reactions, as it will be presented in the following section.

Nonetheless, microwave heating may present some constraining aspects such as heterogeneous heating and difficulties in temperature measurements. Indeed, the electromagnetic field distribution in a cavity can be highly modified by the dielectric properties of the overall mounting (sample/thermal insulator/susceptors/catalyst/medium). The antinodes of the electromagnetic field may be off-center from the sample, resulting in nonhomogeneous temperature profiles within the material. Regarding temperature measurement during microwave heating, the classical thermocouples can hardly be used because they play the role of antenna, leading most

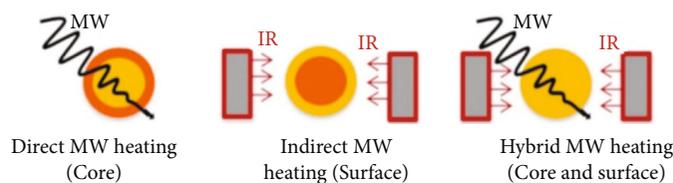


FIGURE 4: One energy, three ways of heating. Representation, at the macroscopic scale, of thermal gradients for direct, indirect, and hybrid microwave heating.

of the time to the formation of sparks inside the microwave cavity. Also, the use of optical fiber thermometers is limited to approximately 250°C, limiting its applications in the case of materials requiring high temperatures such as glass or ceramics. Thus, infrared thermometers are commonly used. The temperature at the sample surface is then obtained from the emitting radiation  $E_0$ , according to Stefan-Boltzmann law

$$E_0 = \epsilon\sigma T^4, \quad (10)$$

where  $E_0$  is the emitting radiation ( $\text{W}\cdot\text{m}^{-2}$ ),  $\epsilon$  is the emissivity of the material,  $\sigma$  is the Stefan-Boltzmann constant ( $5.6696 \cdot 10^{-8} \text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-4}$ ), and  $T$  is the temperature (K). The principle difficulty here is to determine exactly the emissivity of the heated sample along the overall thermal process. Physical characterizations and modeling may be required to address these issues, especially in the conception of models considering the temperature dependence of the properties for each system used in the cavity.

**2.4. Benefits of Microwave Heating Compared to Conventional One.** Thanks to the features listed above, microwave heating presents many advantages compared to the conventional heating in the fields of polymer processing and chemistry; several authors highlighted these benefits in their recent reviews, such as Schubert [3], Kappe [24], and Bogdal and Prociak [25].

Among these advantages, shortening drastically the times of heating is an important gain in polymer processing at industrial scale. For example, solvent-free synthesis of poly(lactic acid), by polymerization of lactic acid, in the presence of tin octoate and isoamyl alcohol, is carried out in 16 hours when conventional heating is used, against only 10 minutes under microwave heating [26] (reaction time is about hundred times shorter). Giguere et al. [27] published a comparison of reaction times between the two modes for many reactions such as Diels-Alder and ene reactions, and they noticed very important decreases when microwaves were used from a few hours to a few minutes. Calvo et al. [28] demonstrated the achievement of the synthesis of tailored mesoporous carbon xerogels in less than 5 hours under microwaves, while the same result is obtained after 24 hours when using conventional heating. In solvent-free processing, the bulk copolymerization of methyl methacrylate and hexaethyl methacrylate was studied [29]; it was found that the microwave-assisted copolymerization finished in 40 minutes against 125 minutes when the bulk was conventionally heated. Yusoff et al. [30] studied the curing time of polymeric composites made of epoxy resins and carbon fibers;

they found that the curing time is reduced from 180 to 40 minutes. Curing tung oil is a solvent-free process leading to bio-based resins, and Smith et al. [31] found that the curing time of this bio-based oil is reduced from 3 hours and 50 minutes when conventional heating was used to only 20 minutes when the oil was cured under microwaves.

Another advantage related to the volumetric characteristic is that in the conventional heating method, the external surface of the heated polymer rises in temperature faster than the core, and the difference in temperature lasts long; thus, thermal degradation often occurs at the surface of the material on one hand. On the other hand, many properties become different between the surface and the core, such as chemical reactions yield and mechanical properties. These drawbacks are avoided by using microwave heating; the same feature is revealed in the case of chemical reactions in solution, where the reactional medium is more efficiently heated thanks to microwaves and the reaction proceeds uniformly throughout the heated system, reaching completion simultaneously in the whole reactional volume [32]. In addition, microwave-assisted polymer synthesis, and overall reactions in organic chemistry, provides products with higher purities and reduces side reactions, both in solution and bulk [33–36].

Regarding the properties of the obtained products, Sierra et al. [37] studied the emulsion polymerization of methyl methacrylate. The authors found that the average molecular weights of the obtained polymers are higher in the case of microwave-assisted reactions than with conventional heating. They also noticed that the polydispersity indexes values were clearly lower when microwaves were used. Several works show that microwave heating leads to polymers with better mechanical properties. Smith et al. [31] prepared tung oil-based/carbon nanotube composite samples and studied them by dynamic mechanical analysis at 25°C, and they found that the storage modulus of the microwave-cured composite was definitely higher than the one of the analog sample cured in convection oven. Tanrattanakul and Jaroendee [38] performed a comparison between microwave and thermal curing of glass fiber-epoxy composites; they measured Young's modulus, tensile strength, flexural modulus, and flexural strength of their samples and found that all these parameters are of higher values in the case of microwave curing.

Energy saving is a major issue in polymer synthesis and processing. It results in savings on production costs on one hand, and on the other hand, it is an ecological approach meeting environmental requirements. Replacing conventional heating methods in polymer preparation or

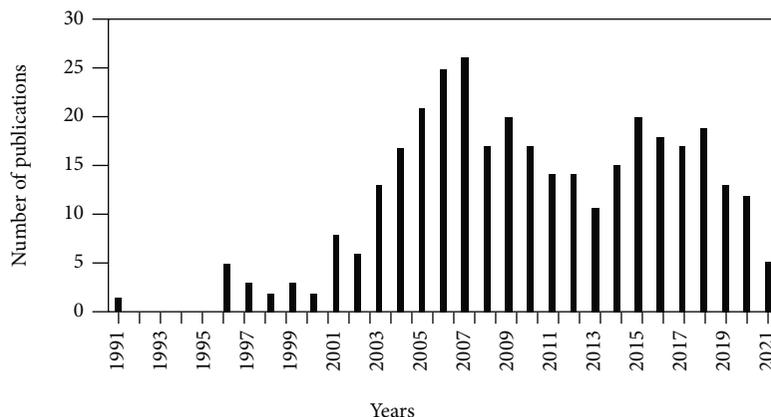


FIGURE 5: Evolution of the number of published research articles and reviews containing “microwave” and “polymerization” in their title (from Web of Science).

transformation by microwave heating showed a decrease in energy consumption; Moseley et al. [39] measured the energy consumption of four reactions: alkylation, Diels-Alder, nucleophilic aromatic substitution, and Heck reaction in conventional heating reactor then in microwave reactor. When the power of the microwave reactor was set to 1600 W, the authors noticed a drastic decrease in energy consumption compared to the conventional reactor; for example, the energy efficiency of the Heck reaction was  $0.56 \text{ mol}\cdot\text{kW}^{-1}$  in the conventional reactor against  $1.24 \text{ mol}\cdot\text{kW}^{-1}$  in 1600 W microwave reactor (increased by a factor of 2.2). In solvent-free processing, the curing of glass fiber-reinforced polymer matrix was studied by Rao [40], and the author found that the total curing of this material requires 8 kWh in conventionally heated continuous reactor; however, the achievement of the same process with the same rate requires only 2.8 kWh when the curing is carried out under microwaves.

Another interesting advantage of microwave heating is the selectivity. Characteristically, polar substances are quickly heated, while nonpolar moieties are not sensitive to this field. Thus, this technique provides chemo-, regio-, and stereo-selectivity [41], allowing a wide range of possibilities in organic chemistry and polymer processing even in solution or in bulk.

At the end, microwave systems and reactors are compact and require a small equipment footprint, which is easy to maintain; they can be turned on or off instantly avoiding warm-up or cool-down phenomena and act without contact with the heated materials. These striking advantages make microwave heating technology a promising technique in the fields of polymer chemistry and processing and allow an interesting application of the interaction between matter and electromagnetic waves.

### 3. Microwaves in Polymer Chemistry

*3.1. Polymerization under Microwaves.* Microwave-assisted polymerization has gained a large interest and has become a mature and useful technique. Figure 5 shows the increase in the number of research articles and reviews, during the

last four decades, containing “microwave” and “polymerization” in their title; this result was obtained by using the keywords “microwave” and “polymerization” in Web of Science.

In the last ten years, many reviews were published dealing with polymerization under MWs; including free radical polymerization [42], RAFT polymerization [43], step-growth polymerization [44], and ring-opening polymerization [45].

The growing interest in the use of MWs as energy source during polymerization is due to their main advantage: the great increase in reaction speed compared to conventional heating. As consequences of this advantage, higher polymerization yields, better selectivity, and fewer by-products are obtained. Many studies were carried out to compare the MW-assisted polymerization kinetics to the conventional method.

Schubert and co-workers [46] highlighted the usefulness and the potential of MWs during different polymerizations: reversible addition-fragmentation chain-transfer polymerization (RAFT), atom transfer radical polymerization (ATRP), free radical polymerization, ring-opening polymerization (ROP), and step growth polymerization. All these reactions can benefit from the peculiarities of the MW heating with respect to the polarities and dielectric properties of both monomers, catalysts, initiators, and solvent.

In a comparative study, Chia et al. [47] achieved the bulk polymerization of methyl methacrylate monomer by using MWs and by conventional heating; they followed the evolution of the monomer conversion and the temperature in the bulk (Figure 6). The polymerization was carried out in the presence of AIBN as initiator; the temperature was set at  $69^\circ\text{C}$  in a thermal oven at the beginning of the conventionally heated reaction. In the MW-heated system, the power was set to 500 W with 2.45 GHz frequency. Being exothermic, an elevation of temperature was observed after about 40-minute reaction in the thermally heated system; this elevation is also involved in the MW-irradiated system and contributed to heat the reaction mixture. By comparing the two graphs, a remarkable difference in the percentage conversion can be noticed: after 20 minutes, it reaches only 10% in the conventionally heated system versus about 80%

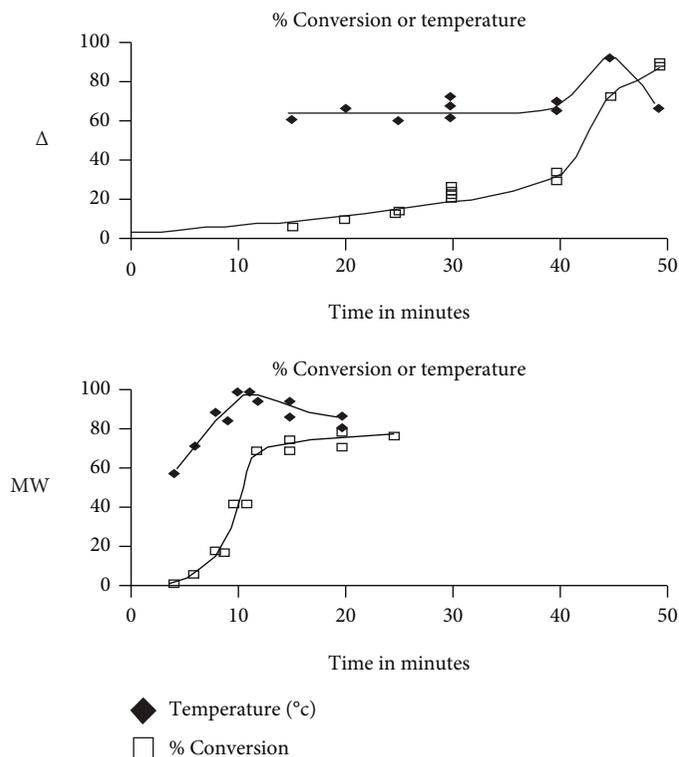


FIGURE 6: Conversion of methyl methacrylate and evolution of the temperature in the reaction mixture;  $\Delta$ : by conventional heating; MW: microwave-assisted (reprinted from Chia et al. [47] with permission. Copyright ©1995, Elsevier B.V.)

in the case of MW heating. According to the authors, the increase in the reaction rate under MWs is not purely related to the temperature rise in the sample. NMR analyses of the activities of the obtained polymers were carried out and led to similar results, suggesting that the polymerization mechanism is the same in the two cases and that only the reaction kinetic changes.

In another paper [48], the same authors realized a comparative study of the polymerization of styrene under MWs and in conventional thermal oven. The temperatures at the beginning of the reactions were set to about 80°C in the two cases for the comparison. Figure 7 shows the results of monitoring the monomer conversion and the temperature. Based on similarity in the reaction conditions, the authors noted that the reaction rate enhancement (the ratio of conventional reaction time by microwave reaction time) was of 190% when a 500 W MW field was applied (Figure 7). They also conclude that this enhancement is dependent on the power of the MW field; they obtained 120% when 300 W power was used.

Another comparative kinetic study was achieved by Velmathi et al. [49]; they investigated the polymerization of succinic acid with butane-1,4-diol, under nitrogen atmosphere, without solvent, in the presence of a catalyst, both by conventional heating (oil bath) and under MWs (with regulation of temperature). To make a comparison, in the two cases, the temperature was set to 200°C, and all the reaction conditions were the same. The authors follow the increase in the molecular weight of the synthesized poly(butylene succinate) by size exclusion chromatography and obtain the results as shown

in Figure 8. A ten-fold increase in the rate of the polymerization was observed. The authors suggested that the polymerization mechanism was the same under MWs as well as by conventional heating since no ionization or electronic excitation was possible by MW energy. They attributed the drastic increase in the rate of the polymerization to the effective interaction between MWs and the water eliminated during the polymerization reaction (Figure 9): MW energy results in the removal of water molecules; thus, the reaction equilibrium is driven in the polymerization direction.

Emulsion polymerization of methyl methacrylate was also investigated for the purpose of comparing the polymerization kinetics under MWs to its conventional analog; the study was conducted by Sierra et al. [37]. The reaction was carried out in the presence of potassium persulfate as initiator. The temperature was set to 50°C both in the MW oven for MW-assisted polymerization and in the water bath for the conventionally heated mixture. Figure 10 shows the results from following the conversion of the monomer during the polymerization, and the reaction rate is clearly much faster when using MWs than with conventional conductive heating; a total conversion (100%) of methyl methacrylate was obtained after a 12-minute MW-assisted reaction, while only 74% limiting conversion was observed when conventional conductive heating was used and for seven times longer delay (90 minutes). According to the authors, this difference is due to the fact that in the emulsion, MWs heat selectively the molecules of water and the monomers, because of their polarity and high dielectric constants. Since water is the major component of this emulsion, MW heating

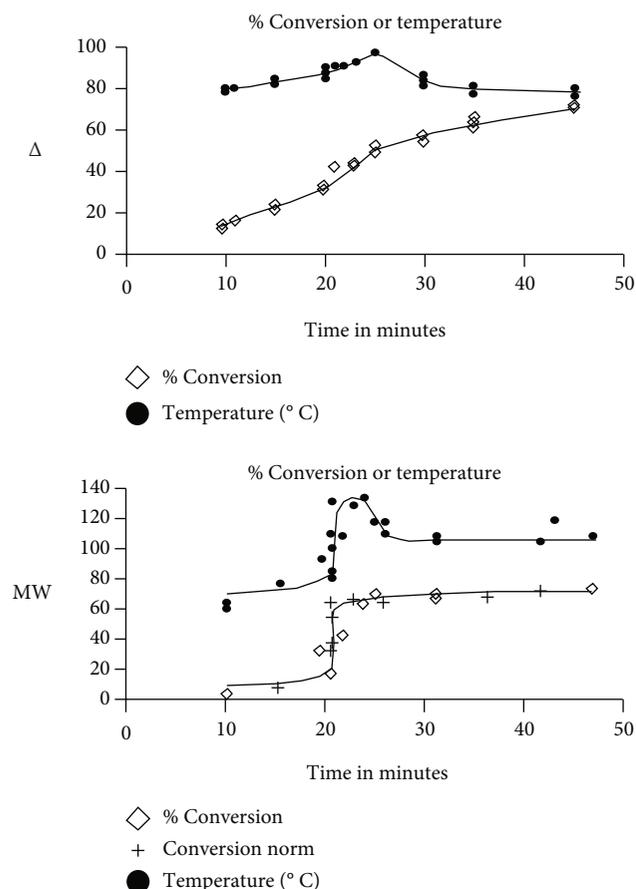


FIGURE 7: Conversion of methyl methacrylate and evolution of the temperature in the reaction mixture;  $\Delta$ : by conventional heating; MW: microwave-assisted (reprinted from Chia et al. [48] with permission. Copyright © 1996 John Wiley & Sons, Inc.).

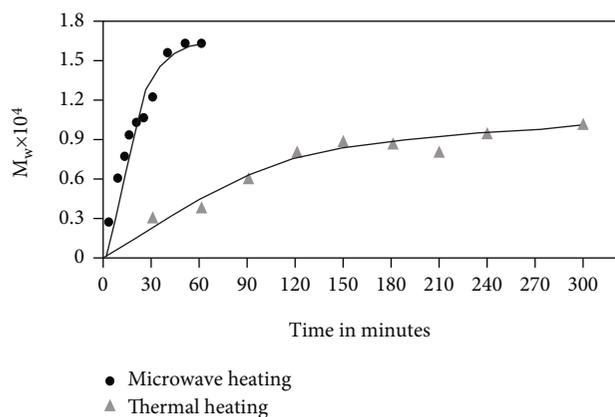


FIGURE 8: Poly(butylene succinate) molecular weight evolution during its synthesis (reprinted from Velmathi et al. [49] with permission. Copyright © 2005, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

produces a local increase in temperature and consequently reduces the local viscosity of the aqueous continuous media. The decrease in the viscosity allows the diffusion of radicals (produced from the monomers and the initiator) inward the

micelles that represent the reaction sites. Once arrived inside the micelles, the radicals are consumed very quickly during the monomer propagation.

Microwave-assisted inverse emulsion polymerization was studied by Xing and co-workers [50]. The authors prepared a Cd(II)-containing aqueous mixture of  $\beta$ -cyclodextrin and acrylamide as monomers. They added an emulsifier to form inverse emulsion. After adding a crosslinking agent and initiator, the reaction mixture was placed under MWs to obtain Cd(II) ion imprinted polymers. The obtained material showed the ability to adsorb Cd(II) from water with adsorption capacity reaching more than 100 mg/g depending on pH and temperature. The authors reported a good adsorptive selectivity for this polymers when tests were made in the presence of mixtures of Cd(II)/Pb(II) and Cd(II)/Zn(II). In a more recent work [51], Xing et al. achieved a MW-assisted inverse emulsion polymerization of methacrylic acid and salicylaldehyde Schiff base as monomers in the presence of crosslinking agent and magnetic Pb(II) ions, and the authors obtained a Pb(II)-imprinted-poly(Schiff base-co-MMA) which showed a high efficiency for absorption of Pb(II) from water (more than 100 mg/g) with high selectivity.

The MW-assisted free radical polymerization of styrene was investigated by Schubert and co-workers [52] in the context of developing eco-friendly syntheses of polystyrene. Styrene is a monomer which can be autopolymerized; two monomers can undergo Diels-Alder reaction and generate radicals without needing initiator. This self-initiation requires high temperatures ( $>100^{\circ}\text{C}$ ). The authors succeeded to initiate this polymerization by using MW as heating source, without initiator, and obtained polystyrenes with controlled molecular weights and polydispersities ranging from 1.4 to 2. These results demonstrate the possibility of a fast and environmentally friendly method to synthesize polystyrene.

In a more recent study, Tomovska and coworkers [53] experienced the free radical polymerization of methyl methacrylate (MMA), butyl acrylate (BA), styrene (St), and vinyl ferrocene (Vf) which is an organometallic monomer. Reactional mixtures were made of different monomer couples: MMA/BA, MMA/St, and MMA/Vf. Each couple was subjected to two copolymerization methods (MW-assisted copolymerization and conventional one), and a sophisticated device was used to keep equal temperature profiles and reaction conditions between the two methods. The authors found that there is no difference neither in the reaction kinetics nor in the reached molecular weight between the two methods for the MMA/BA and MMA/St couples. But the MMA/Vf couple showed higher reaction rates and reached higher molecular weights when its copolymerization is MW-assisted. Furthermore, it is noted that this enhancement depends also on the solvent in which the reaction occurs. The authors explained these results by the difference in the dielectric properties of the monomers; contrary to MMA and St, Vf is an organometallic monomer with higher polarity; thus, it is able to absorb more MW energy and convert it to heat more quickly. Based on that result, the authors conclude on the existence of MW-specific effects in free radical polymerization.

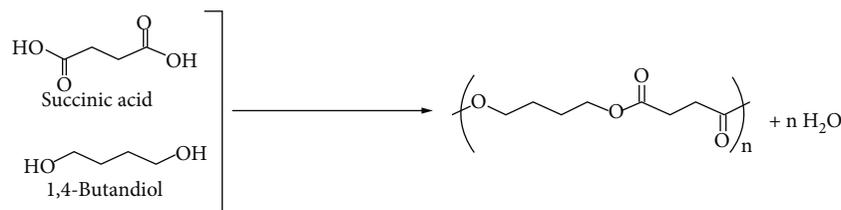


FIGURE 9: Poly(butylene succinate) synthesis reaction.

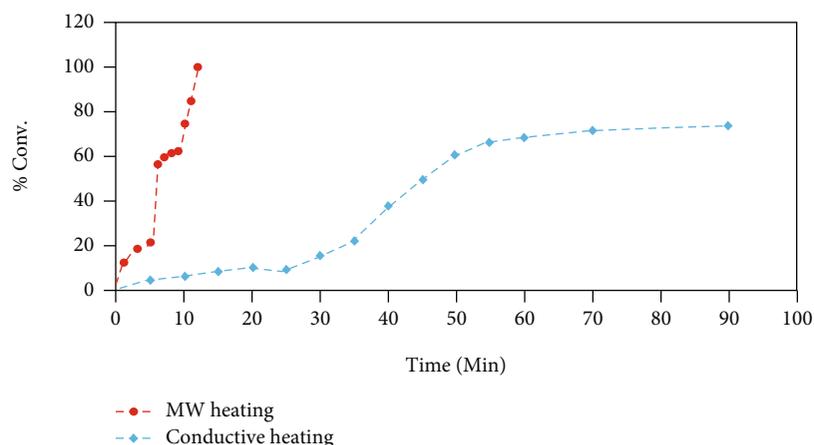


FIGURE 10: Methyl methacrylate conversion monitoring, reproduced from the results given as table by Sierra et al. [37] with permission (copyright © 2006, Taylor &amp; Francis Group, LLC).

Polycaprolactone (PCL) is a biodegradable polymer known for their good mechanical, rheological, thermal, and good processing properties; it is used in numerous applications from medical to packaging. It is synthesized from the monomer of caprolactone. The caprolactone monomer contains a carbonyl group which is polar and thus able to convert microwave energy to heat; this is the main reason why polymerization of caprolactone (Figure 11) is accelerated by microwaves. This reaction has long been studied at small scale until Xu et al. [54] achieved it at large scale. The authors carried out the ring-opening polymerization of  $\epsilon$ -caprolactone in bulk under microwaves; the reactors were batch with an amount of 2.45 kg of the monomer each time. They found that the thermal behavior of the reaction mixture was similar to that observed at small scale; they also noticed that the temperature and the time of the reaction can be controlled by adjusting the microwave power. The reaction yield was over 93%, and the average molecular weight of the obtained PCL was controllable by adjusting the reactant ratios, proving the possibility of industrialization of this process.

Poly(lactic acid) (PLA) is a commercial, bio-based, biodegradable, biocompatible, and compostable polymer. This competitive polymer presents many other advantages such as good processability and low cost, making it a very attracting polymer for researchers [55]. The most used method to synthesize this polymer is the ring-opening polymerization of lactide using metal catalysts (based on tin, aluminum, or zinc) in a suitable solvent such as toluene. These methods led to products with traces of toxic substances and reduce

the application field of PLA [56]. Several works were carried out to find cleaner processes for the synthesis of PLA while remaining efficient, and microwaves seemed to be a good alternative for the ROP of lactide [57, 58]. Dubey et al. [59] recently (2017) published an interesting attempt to carry out this synthesis in a continuous reactive extrusion process combined to microwave energy. The microwave generator was implemented in a section of the twin-screw extruder to facilitate the ROP of lactide (Figure 12). They used  $\text{Sn}(\text{Oct})_2$  as catalyst, triphenylphosphine ( $\text{PPh}_3$ ) as co-catalyst, and dodecanol as initiator for the ROP. The temperatures were 160 and 180°C, the authors obtained a conversion of the lactide of about 15% higher than the one obtained without MW heating zone, and the produced PLA was of about 50000 g/mol average molecular weight, stating the improvements due to the addition of the microwave zone. They performed simulations of this process using Ludovic®, and the results of the simulation agreed with the experiments.

Polyoxazolines are polymers with particularly interesting properties; thanks to their structural versatility, many reviews reported the possibilities offered by these polymers when it comes to the ease of the synthesis methods [60], the control of the macromolecular architectures and design of the copolymers [61], the modulation of the hydrophilicity of the polymer chains [62], making self-assemblies and hydrogels [63, 64], and biocompatibility and applicability in the biomedical domains [65]. These polymers are now usually synthesized by cationic ring-opening polymerization of oxazolines; a polymerization reaction that has greatly

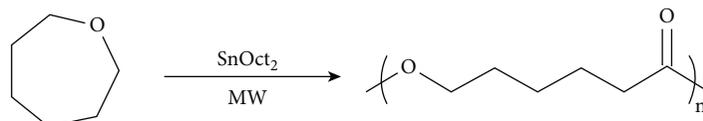


FIGURE 11: Polymerization reaction of caprolactone under microwaves.

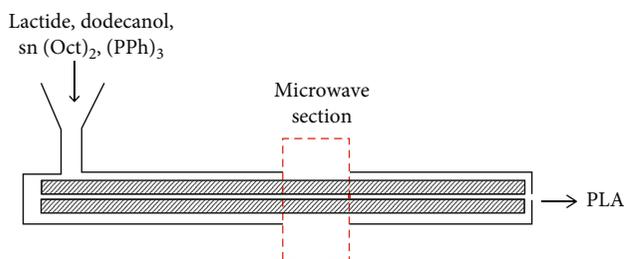


FIGURE 12: Implementation of the microwave generator in the twin-screw extruder for the ROP of lactide.

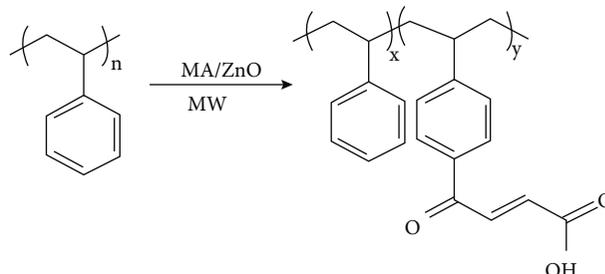


FIGURE 13: Grafting maleic anhydride on polystyrene.

benefited from the emergence of MW heating in the polymer chemistry notes that the synthesis of polyoxazolines by conventional heating suffered for a long time from low kinetics before multiplying its rate by 400 thanks to MWs. In a recent review, Wiesbrock and co-workers [66] estimate that 2-oxazolines and poly(2-oxazoline)s are, respectively, the most investigated monomers and polymers in the research works on MW-assisted polymerization. The first MW-assisted ROP of oxazoline monomer was achieved by Schubert and co-workers [67], and the authors used the 2-ethyl-2-oxazoline as monomer and methyl tosylate as initiator in acetonitrile as solvent. The authors found that the polymerization rate can be accelerated by a factor of 350 when the mixture was heated in a single mode microwave oven, with keeping the living character of the polymerization. In a recent work, Lapinte and co-workers [68] used MW-assisted ROP of oxazolines to develop interesting architectures of amphiphilic copolymers. The authors used a tosylate-functionalized coumarin as long-chain hydrophobic initiator to the ROP of 2-methyl-2-oxazoline. This reaction took 30 minutes in a microwave reactor at 140°C. The targeted molecular weight of 4000 g.mol<sup>-1</sup> was reached. After dimerization of the coumarin chain ends, the authors obtained triblock amphiphilic copolymers with two pendent hydrophobic parts and a hydrophilic one in the middle. These copolymers were subsequently used to make nanoparticles. In another work [69], the same authors used MW-assisted CROP to synthesize poly(2-methyl-2-oxazoline)s with coumarin pendent groups. The obtained amphiphilic diblocks showed a good self-assembling property, and the authors used them to make nanovectors for the UV-controlled drug delivery.

**3.2. Functionalization and Grafting.** In the field of polymer chemistry, MWs are also used to graft on or to functionalize both synthetic and natural polymers. When used for this purpose, the advantages of MWs are still the same as cited above, including improvement of reaction kinetics, yields, and heating efficiency. Polystyrene was functionalized by radical grafting of maleic anhydride (MA) on its aromatic cycle

(Figure 13), in the presence of zinc oxide (ZnO) as catalyst and MWs as energy source [70]. The authors noticed that the main advantages from this strategy are low cost, nontoxicity, time and energy savings, and also the reusability of the catalyst after simple washing. After functionalization, the obtained material (grafted polystyrene) presented improved anticorrosive properties; the authors suggested that this functionalization methodology could be achieved with all polymers containing aromatic cycles in their structure.

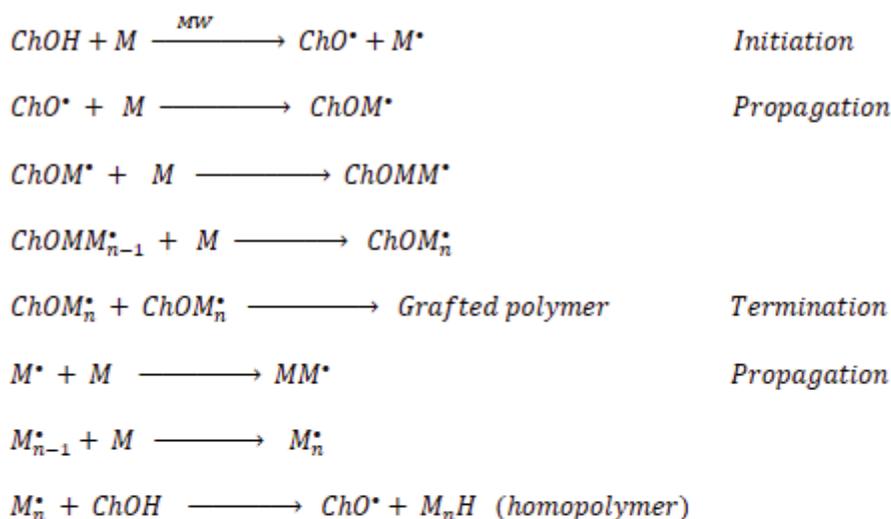
Grafting of acrylamide monomers on chitosan was carried out under MWs and under conventional conditions by Singh et al. [71]. Conventionally, this grafting reaction is carried out in the presence of a mixture of potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) and ascorbic acid as a redox initiator, Ag<sup>+</sup> ions as catalyst, and the atmospheric oxygen as co-catalyst; the reaction takes about 1 hour in these conditions; however, in this work, the grafting was successfully achieved without any initiator or catalyst thanks to MW heating, and the reaction was achieved after only 1 minute and 10 seconds. The authors compared the percentage of grafting in the two cases (conventional vs MW); the calculation was done according to

$$\% \text{Grafting} = \frac{W_1 - W_0}{W_0} \times 100 \quad (11)$$

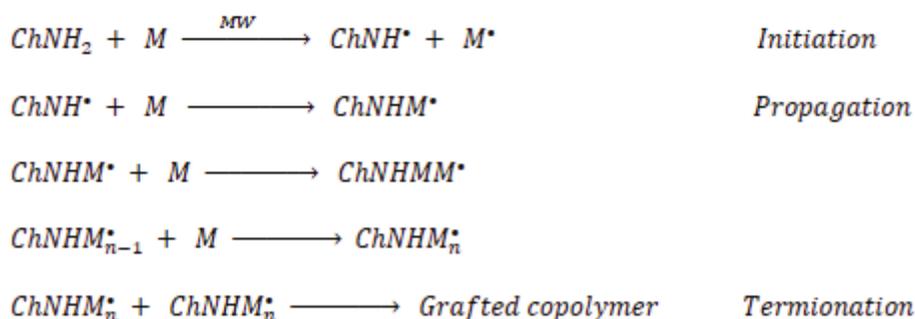
where  $W_0$  and  $W_1$  are, respectively, the weights of original and grafted chitosan.

They found a percentage of grafting of 168% when MWs were used, against only 82% in the conventional conditions. This result shows that in addition to simplifications in the grafting process (without neither initiator nor catalyst), the use of MWs led to better efficiency. To explain the yield improvement, the authors noticed that there are two MW-susceptible pendant groups in the structure of chitosan: hydroxyl (-OH) and amine (-NH<sub>2</sub>). These polar groups heat quickly, and the energy amount they absorb is sufficient to break the O-H and N-H bonds creating radical sites at, respectively, oxygen and nitrogen atoms. Once radical sites created, they undergo propagation and termination steps

-Grafting at O-H groups of chitosan:



-Grafting at NH<sub>2</sub> groups of chitosan



SCHEME 1: Mechanism of acrylamide MW grafting at hydroxyl and amine groups of chitosan (Ch stands for Chitosan, M stands for acrylamide, and MW stands for microwave irradiation).

to complete the radical mechanism (Scheme 1). In terms of the properties of the obtained product, this acrylamide-grafted chitosan is intended for application as  $\text{CA}^{2+}$  and  $\text{Zn}^{2+}$  absorber from waste and natural water; the authors found that MW grafting leads to more efficient absorption than the conventional method.

**3.3. Depolymerization and Polymer Degradation under Microwaves.** Depolymerization is a widely used technique to recycle both natural and synthetic polymers. This reaction may need catalysts or other reagents, and in almost all cases, it needs heating; this is why microwave-induced depolymerization is of a great interest, and many authors investigated this method. Poly(ethylene terephthalate) was subjected to many depolymerization studies under microwaves since this polymer is ubiquitous in plastic wastes, and it can be depolymerized following different reactions: hydrolysis, aminolysis, and glycolysis. The hydrolysis of soft drink bottle poly(ethylene terephthalate) under microwaves and high pressure was investigated by Ikenaga et al. [72], and the reaction was achieved in 30 minutes at a temperature of 223-232°C under a pressure of 2.3-3.0 MPa. The authors obtained better depo-

lymerization rate under MWs when compared to conventional heating; they explained this enhancement by a possible more effective diffusion of water molecules through the polymer matrix which undergoes relaxation due to MW irradiation. The same polymer, from fiber waste and soft drink bottle waste, was subjected to aminolytic depolymerization under MWs by Pingale et al. [73], and the reaction was achieved using an excess of ethanolamine with simple catalysts such as sodium acetate, sodium sulfonate, and sodium bicarbonate. The authors obtained depolymerization yields of about 90% after only 4-minutes reaction. The authors highlighted the advantages of the potential application of this technology in recycling poly(ethylene terephthalate) and production of its monomer: high yields, short reaction times, low-energy consumption, and the use of cheap catalysts rather than heavy metals. The glycolytic depolymerization of poly(ethylene terephthalate) was also successfully achieved under MWs by Achilias et al. [74] with the aim of recycling waste bottles. The reaction was carried out in the presence of diethylene glycol; the complete depolymerization was reached after 2 minutes under MW radiation against about 4 hours with conventional heating. These

experiments show real merits of MW heating in depolymerization and recycling of one of the most used polymers.

Bio-based polymers were also subjected to MW depolymerization with the aim of recovering their constituting monomers. Hirao et al. [75] achieved the depolymerization of polylactic acid following a hydrolysis reaction under MWs in the presence of water. The authors compared the effectiveness of this process to the same one with conventional heating. At the same temperature of 170°C, the lactic acid (the monomer) yield reached saturation at 45% after more than 13-hour reaction in the conventional process, whereas only 2 hours was required to reach the same yield under MW heating; the authors noticed that MW heating led also to L-lactic acid with higher optical purity. Orozco et al. [76] investigated the depolymerization of cellulose and cellulosic biowaste under MWs, and hydrolysis reactions were achieved in the presence of phosphoric acid; the authors found that the use of MWs allows faster reactions and higher yields.

At the industrial scale, an applicator of a continuous MW depolymerization of poly(ethylene terephthalate) was recently designed by Ramopoulos et al. [77] with a production rate of more than 12.5 kg/h. The applicator contains an Archimedean screw to move the materials through a 250-mm diameter cylindrical glass tube (Figure 14). The applicator works at 2.45 GHz, and the depolymerization reaction is achieved at temperatures of 150–220°C. Other prototypes are being developed for the large-scale MW-assisted depolymerization, known as Pyrowaves.

## 4. Microwaves in Polymer Processing

**4.1. Microwave Heating of Polymers.** Whether in solution or in melt phase, there are two ways to cause an increase of the temperature of the polymer chains by using microwaves. The first and most used one acts indirectly by heating the dipoles surrounding the polymer chains, such as solvent molecules in solution or polar fillers in melt phase, and then, the heat is transferred to the polymer: the indirect microwave heating. The second one acts directly on the polymer chains by increasing their motion when their polarity is sufficient: the direct microwave heating.

The effectiveness of the indirect mode depends on the dielectric properties of the media surrounding the polymer chains. In solution, this mode of heating is generally used for modification or functionalization of polymers. Different solvents could be used; Table 2 lists some of the most used ones for different polymers, their dielectric constants, and the reached temperatures by microwave heating.

In the melt phase, the indirect mode involves the use of polar fillers such as metals, metal oxides, and carbon fillers. Table 3 lists different fillers used for microwave heating of different polymers.

**4.2. Solution Processing.** This processing mode is commonly used when chemical reactions are involved, such as synthesis of polymers, polymer functionalization, and other chemical modifications. In this case, microwave energy is used to increase the temperature of the reaction medium, reactants,

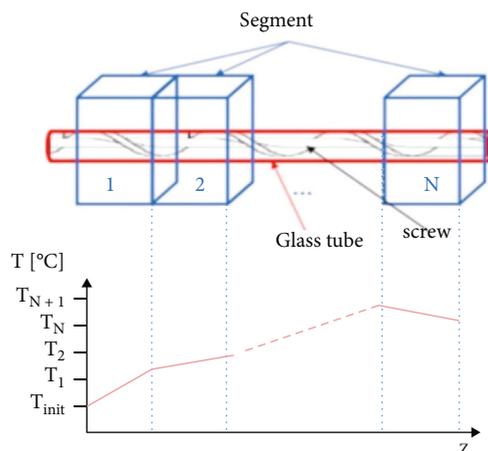


FIGURE 14: Schematic representation of the microwave applicator developed by Ramopoulos et al. [77] with the temperature profile (reprinted with permission. Copyright © Cambridge University Press and the European Microwave Association 2018).

or catalysts and consequently initiate or increase the rate of the desired chemical reactions. This type of process is generally performed in microwave ovens that act as batch reactors; there are few continuous systems for the synthesis or chemical modification at the pilot scale.

Ertec (Poland) developed a continuous process to synthesize high molecular weight epoxy resin under microwave (Figure 15). The reaction occurs between bisphenol A and low molecular weight epoxy resin in solution with the presence of a catalyst. The reactor consists of four microwave cavities crossed by a rotating quartz tube. Each cavity is equipped with a magnetron which can be switched on or off in order to ensure continuous regulation of the temperature in the reaction medium while saving energy. The quartz tube was of 2 m long with 12 cm inner diameter. The flow of the reaction mixture through this tube was 8 kg/h, but experiments showed that it can be increased without changing the properties of the obtained resin [93].

### 4.3. Solvent-Free Processing

**4.3.1. Polymer Resins Synthesis.** Recently (2019), an interesting attempt to develop a MW batch reactor for the synthesis of polymer resins, at the kilo-scale, was published by Buttress et al. [95]. The reactor was equipped with a 2.45 GHz and 2 kW MW generator (Figure 16). A fiber optic probe was placed within the reactor and connected to a control unit allowing the adjustment of the delivered MW power and the control of the temperature of the mixture during reaction. The main body of the reactor was also surrounded by an oil-heated jacket providing conventional heating. The authors obtained up to 4.1 kg of product per batch. They indicated that it was a polyester resin without information about its chemical structure or applications; they precised that this information cannot be disclosed. For comparison, the authors conducted the polymer synthesis using conventional heating mode (oil-heated jacket) and using MW radiation mode. The rate of the increase in temperature during

TABLE 2: Systems used to heat polymers in solution.

| Solvent         | The used frequency (GHz) | Dielectric constants of the solvent at the used frequency |                    | Dissolved/dispersed polymer    | Temperature reached by microwave heating (°C) |
|-----------------|--------------------------|---|--------------------|--------------------------------|---|
|                 |                          | $\epsilon'$   | $\tan \delta$      |                                |   |
| Water           | 2.45                     | 76.0 at 25°C [78]   | 0.158 at 25°C [78] | Cellulose                      | 100-260 [79]                                  |
|                 |                          |   |                    | Polyhydroxybutyrate            | 150 [80]                                      |
| Ethylene glycol | 2.45                     | 13.9 at 25°C [82]   | 1.150 at 25°C [82] | Poly(vinyl alcohol)            | 100 [81]                                      |
|                 |                          |   |                    | Poly(vinyl alcohol)            | ~197 [83]                                     |
| Ethanol         | 2.45                     | 8.91 at 30°C [84]   | 0.898 at 30°C [84] | Polyhydroxybutyrate            | 140 [85]                                      |
| Methanol        | 2.45                     | 24.02 at 30°C [84]  | 0.522 at 30°C [84] | Polyhydroxybutyrate            | 110 [85]                                      |
| Toluene         | 2.45                     | 2.4 at 25°C [86]  | 0.04 at 25°C [86]  | Poly(ethylene-co-acrylic acid) | 220 [85]                                      |

TABLE 3: Fillers used for indirect microwave heating of some polymers, with the improvements observed.

| Filler  | Polymer matrix       | Improvements observed  |
|---|----------------------|--|
| Mixture of carbon nanotube with barium titanate | Epoxy resin          | Increased permittivity, enhanced conductivity [87]   |
| Carbon black-magnetite                          | Natural rubber       | In the investigated frequency range (1-12 GHz), the addition of the filler decreases the reflection coefficient of the rubber, increases the attenuation coefficient and thus enhance the shielding effectiveness [88] |
| Carbonyl iron particles                         | Polydimethylsiloxane | The MW energy absorption was increased by increasing the particle content in the polymer matrix [89]   |
| Aluminum powder                                 | Polyester resin      | When heated by microwaves, the cured composite showed higher tensile strength compared to the product obtained by conventional heating [90]  |
| Nickel oxide                                    | Polycaprolactone     | $\epsilon'$ and $\epsilon''$ increase by increasing the nickel oxide content in the polycaprolactone matrix [91]   |
|   | Polypyrrole          | $\epsilon'$ , $\epsilon''$ and $\tan \delta$ increase by increasing the nickel oxide content in the polypyrrole matrix [92]  |



FIGURE 15: The Ertec continuous microwave reactor for the synthesis of high molecular weight epoxy resin (reprinted from Bogdal et al. [94] with permission. Copyright © 2022 American Chemical Society).

MW heating was adjusted to meet the one of conventional heating (6°C/min), and the reaction was then carried out at 230°C in the two cases. After analyzing the obtained products, the authors found that when MW heating was used, the reaction takes only 8 hours and 20 minutes, and the synthesized polymer resin was of 2100 g/mol molecular weight; however, the same amount of resin could be obtained by conventional heating during 22 hours with a molecular weight of only 1200 g/mol. This enhancement was attributed to the volumetric heating of the whole reaction volume by

microwaves, as predicted by the simulation of the power density distribution of the electromagnetic field within the reaction volume (Figure 17).

**4.3.2. Rubber Vulcanization.** The vulcanization of rubber was among the first industrial applications of microwaves in solvent-free polymer treatment; during this process, the polymer chains of the raw rubber are crosslinked by chemical bonds giving a three-dimensional network. The obtained product shows high thermal and chemical resistance and good mechanical properties. In the presence of a catalyst, at a temperature of 120-200°C, the bridges between raw rubber chains can be created by using peroxide which forms carbon-carbon bridges and metal oxides that form ether bonds or sulfur which is the most used one and leads to form sulfur-sulfur bridges (Figure 18); at the end, the rubber is transformed from plastic material, which undergoes permanent deformation, to elastic one which is hard and resistant to plastic flow.

Before the development of continuous microwave systems, the vulcanization of rubber was carried out by using hot air or liquids. However, rubber is a poor conductor for thermal energy, and many problems were encountered such as long times of vulcanization, thermal degradation of rubber due to nonuniform temperature distribution within it, and nonhomogeneous vulcanization yield in the whole volume of rubber. By introducing microwaves, the volumetric

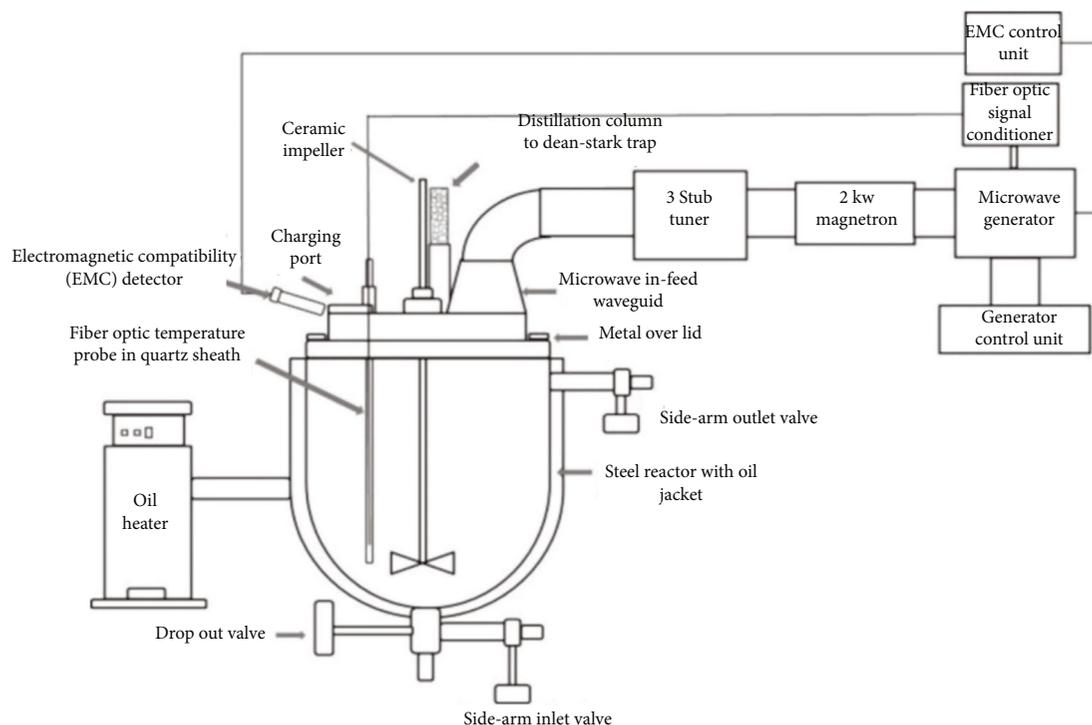


FIGURE 16: Schematic representation of the reactor with MW generator and oil-heated jacket (reprinted from Buttress et al. [95] with permission. Copyright © 2019 Elsevier Ltd.).

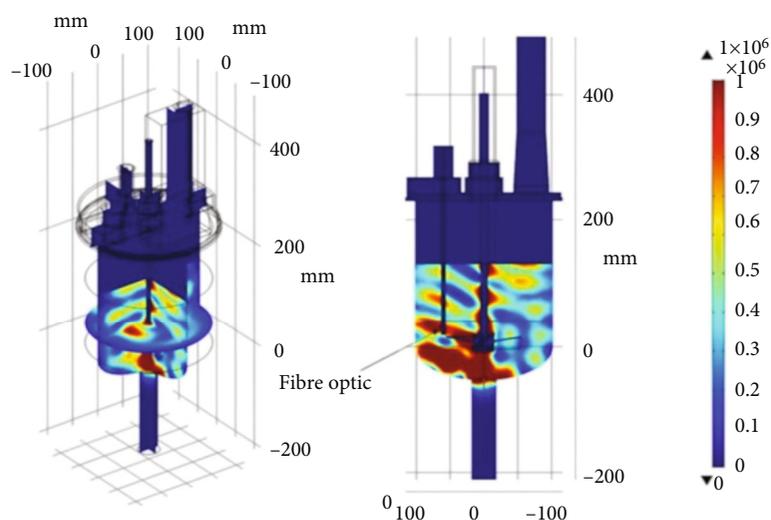


FIGURE 17: Simulation of electromagnetic field power density in the reaction volume (a) and in a section of the reaction volume (b) (reprinted from Buttress et al. [95] with permission. Copyright © 2019 Elsevier Ltd.).

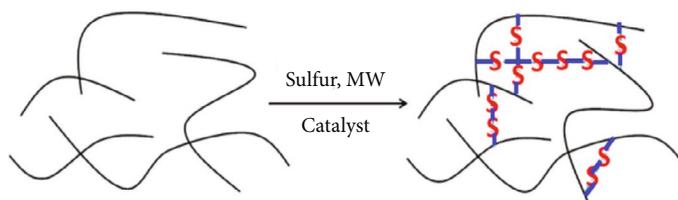


FIGURE 18: Reaction scheme of the rubber vulcanization.

heating allowed short-time heating, homogeneity of the temperature within the rubber, energy savings, and better properties of the obtained rubber. Microwave radiation is mainly used just after the extrusion of rubber profiles.

Somme rubbers are sufficiently polar and can be easily heated by microwaves due to their high loss factor; neoprene and nitrile are good examples (direct microwave heating mode). But there are many other types of rubber that are not enough polar (low loss factor) and have low microwave receptivity such as styrene-butadiene rubber. In this case (low polarity), polar fillers are added to the rubber in order to improve its microwave susceptibility (indirect microwave heating mode); the commonly used one is carbon black which is also and fortunately used in all automotive components as a filler to improve their mechanical properties.

Nowadays, rubber vulcanization by microwaves is a mature process which is used at large scale; many plants are implanted in the world.

**4.3.3. Pyrolysis.** Microwave pyrolysis of polymer materials and plastic-containing wastes is potentially a solution for their disposal; this technique leads to recover some gases, oils, and solids that can be used as products or as energy sources. Despite the numerous benefits of the microwave pyrolysis of polymers with respect to conventional one, no successful application at the industrial scale was found. This may be due to the limitations of this technique such as the nonuniform distribution of temperature caused by the hot spots, inaccuracy in the measurement of temperatures, and the difficulty to design appropriate systems. However, several studies at the laboratory scale and many attempts to scale-up this method were achieved showing its advantages.

The MW pyrolysis of PLA was studied by Undri et al. [96] in a MW oven working at 2.45 GHz, and the oven was equipped with an infrared thermometer which measures the temperature inside the oven but not within the sample. The authors used three different MW absorbers, tire, carbon, and iron, and the pyrolysis temperatures were between 365 and 535°C. As products of PLA pyrolysis, they obtained high amounts of gases and liquids with low amounts of solid when the MW absorber was carbon. Equivalent quantities of gases, liquids, and solids were obtained with iron as MW absorber; however, small amount of gases was obtained when tire was used as MW absorber. The obtained liquid was rich in lactide which can be polymerized again to obtain renewed PLA.

Al Shara'ah and Helleur [97] investigated the MW pyrolysis of cellulose at low temperature (200–280°C), first without addition of any MW absorber, and then with water or activated carbon. They obtained bio-oil, biochar, and gases as products. The bio-oil yield was about 50 wt.% of the product, and its composition was very close to conventional bio-oils derived from cellulose. MW-assisted catalytic pyrolysis of cellulose was also studied by Wang et al. [98] for the purpose of producing phenol-rich bio-oil. The role of the catalyst was to increase the rate of the pyrolysis reactions; they used silicon carbide as MW absorber. The pyrolysis was carried out at 600°C during 10 minutes under 1000 W power MW filed. The yield of bio-oil was close de 70 wt.%, containing about 21% of phenols.

High-density polyethylene was also subjected to MW-assisted pyrolysis [99], the process was achieved in a MW reactor with activated carbon particle bed, 3 kW 2.45GHz magnetron was used, and the pyrolysis temperature was between 400 and 600°C. The authors noticed that the presence of activated carbon particle bed allowed greater cracking of polyethylene chains, giving smaller carbon chains as the transport fuels petrol and diesel, representing a high potential commercial value. Activated carbon was also used as MW absorber for the pyrolysis of low-density polyethylene [100] in the presence of natural zeolite as catalyst; the samples were heated to temperatures ranging between 300 and 550°C; the pyrolysis times were variable from 45 to 90 minutes. The highest yield of the liquid products was 28.12%; this liquid fraction was found to be rich in aromatic compounds.

The production of tires reaches currently about 3 billion annuals; the concern of recycling this product imposes itself. Tire pyrolysis by conventional heating is a well-known process used at industrial scale, but it suffers from some limitations such as high-energy consumption and low quality of the pyrolysis products. Many studies were achieved on the MW pyrolysis of tires and showed major advantages with respect to the conventional method. The results from different authors are consistent, and the conclusions are that MW pyrolysis of tires is definitely cleaner than the conventional one since it limits the production of nonenvironmentally friendly substances and needs less energy to be achieved; it allows the conversion of scrap tires rubber into a useful solid, liquid, and gaseous fractions, especially as fuels to energy production [101–104].

Microwave-assisted pyrolysis of biomass is also a mature process for production of various gases, bio-oils, biofuels, biochar, and energy from raw biomass feedstocks such as agricultural waste. This process was long carried under conventional heating before seeing the advantages of microwave pyrolysis; for example, the energy consumption during conventional pyrolysis of woody biomass is about 2.7–3.1 kJ/g, while the same degree of pyrolysis is reached in microwave-assisted process with energy consumption of about 2.2–2.5 kJ/g and can even decreased to 1.07 kJ/g by increasing the power density of the microwave field [105]. The dielectric properties of the biomass feedstocks vary drastically from one sample to another and depend on temperature; some batches absorb efficiently the microwave energy and heat quickly; however, in some cases, the value of  $\tan \delta$  is too low, and it is essential to add microwave absorbing additives (microwave absorbers) such as carbon black, activated carbon, char, metal oxides, and graphite. The Scandinavian Biofuel Company (SBC) has scaled up a MW pyrolysis process for the conversion of woody biomass into biofuel (Figure 19); in this process, the biomass is conveyed by a rotating ceramic disc through a spiral shaped tunnel in which a quick microwave treatment occurs with great power. The capacity of this process is 25000 tons per year.

**4.3.4. Foaming.** Foaming is a much-used process in polymer industry; this technology leads to materials with designed structures and properties, low weight, and low cost. The achievement of this process requires heat energy and also

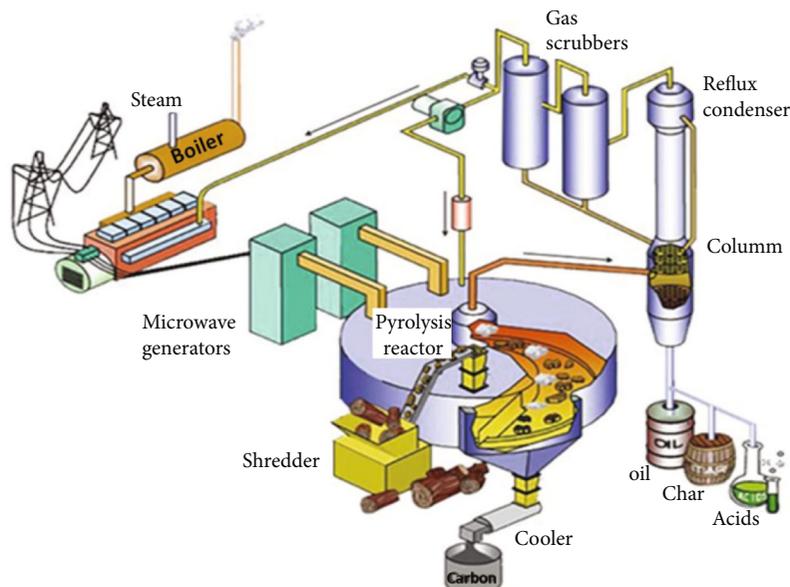


FIGURE 19: The pyrolysis process based on the rotating ceramic disc concept of SBC. With permission (copyright © 2007-2012 <http://SBioFuel.com>).

physical or chemical blowing agents. Currently the conventional heating is used at industrial scale to make polymer foams, the use of MW heating for this purpose still remains at the laboratory scale, and several studies are conducted on this emerging field [106].

The most involved polymers in the foaming processes are polyurethanes, and these polymers are generally able to absorb MW energy to a sufficient extent to be heated; however, some authors used MW absorbers as fillers to enhance the heating efficiency under MW. Prociak et al. [107] experimented the polyurethane foaming under MW heating, and they used carbon black as MW absorber to heat the polymer; the blowing agent was azodicarbonamide. The product was of good properties as well as its conventional counterpart; the authors however emphasized that above a certain limit of black carbon content the mechanical properties of the obtained foam can be altered. Polypropylene was also subjected to foaming under MW heating in a recent work [108]. Composites of polypropylene/carbon black were prepared in a first step by using a twin-screw extruder, the obtained granulated composites were then mixed with a blowing agent, and the mixture underwent a second extrusion process in a single screw extruder (Figure 20); the wire outcoming from the extruder passes through a MW cavity in which it undergoes microwave heating and foams. Besides the enhancement of polypropylene foaming due to MW heating, the authors conclude that by changing the content of the MW absorber in the composite, the final product properties change, and they also noticed the formation of hot spots within the MW-heated composite altering the temperature measurements. Yet, this process shows numerous advantages with respect to the conventional one, and the incorporation of MW heating may lead to foams with tailored properties.

On the side of bio-based polymers, starch was tested by Peng et al. [109] in a MW foaming process. Pellets of starch

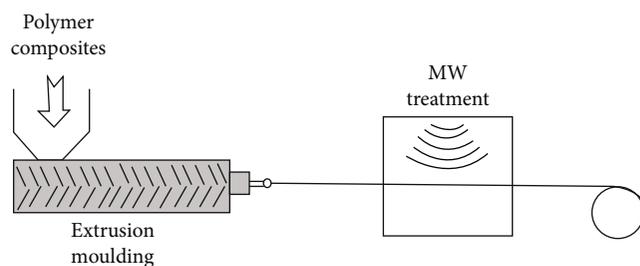


FIGURE 20: Schematic representation of the process of polypropylene foaming within a MW cavity coupled to extruder.

with additives were made after an extrusion step. The pellets were then heated in a cylindrical MW resonant cavity with frequency range between 2.3 and 2.7 GHz equipped with a fiber optic temperature sensor and a power meter. The authors achieved simultaneously the heat and the measurements of dielectric properties of the starch within the MW cavity; they noticed that  $\tan \delta$  changes drastically by increasing the temperature. In the second part of this study [110], the authors found that the presence of glycerol as additive in starch did not alter the foaming performance, while its content is lower than 10%, and that the presence of about 5% of polyvinyl alcohol in the starch pellets may improve the MW foamability, but above the limit of 10%, this additive also deteriorates the starch MW foamability. The authors explained these phenomena by the interactions that occur between starch and the used additives, and these interactions restrict the mobility of the polymer molecules and decrease the foaming performance.

**4.3.5. Polymer Drying.** Thanks to their advantages, MWs are likely to be used as energy source in drying materials, especially when a fast drying is required without impacting the properties of the material. Polymers are good candidates to

be dried under MWs for two reasons: the first one is that most polymers are not good absorbers of MW energy due to their low dielectric loss factor, and the second one is that the solvents to remove from the polymers (water in general) are polar with high dielectric loss factor, making them good absorbers of MW energy, and their temperature rises quickly under a MW field. As a consequence, when a polymeric material is subjected to MW drying, the solvent is heated much faster than the polymer itself and then removed without degrading or considerably heating the polymer; this efficient selective heating leads to well-dried polymers with minimal effects of the treatment.

Polymer drying is an important step in the majority of polymer processes since the engineered plastics are often hygroscopic; the presence of moisture (or other volatiles) can cause damages to the material as well as to the process devices. MW-assisted drying is a mature process that is now used at the industrial scale [111]; the effects of the electromagnetic MW field on the properties of polymers during the drying process are widely investigated and highlighted in recent reviews [112, 113].

To show the added value of this method, Kast et al. [114] studied the kinetics of a MW drying process for five different polymers in form of pellets: polyamide 6 (two grades), polyethylene terephthalate, polylactic acid, and polyhydroxybutyrate. The experiments were achieved in a pilot scale dryer filled with 50 kg polymer for each test. Samples were taken at different drying times to determine their moisture content, and the results were compared to those obtained by using a desiccant dryer. By using MW power ranging from 1.2 to 3 kW, the authors succeeded to dry the five polymers and remove all the moisture they contained. They also found that the drying speed depends on the temperature only below a specific threshold temperature from which the drying rate becomes temperature-independent; this effect was observed in MW drying and not in the desiccant process.

For the five polymers, and in accordance with the finding cited above, the authors found that the MW drying is more efficient than the desiccant one at low temperatures, but at higher temperatures and above a specific threshold for each polymer, this trend is inverted, and the desiccant drying becomes faster than the MW one. The authors explained this result by the fact that the desiccant dryer was a mature system; however, the MW dryer was still a prototype which suffers from many defects such as constructive inefficiencies. In order to evaluate the effects of the two drying modes on the properties of the polymers, the authors achieved mechanical and rheological analyses. They noticed a slight decrease in the Young's modulus for the two polyamides and PET with no considerable difference between the two drying modes. However, significantly smaller values of the modulus were obtained after MW drying compared to desiccant one in the cases of PHB and PLA. For the rheological properties, the zero shear viscosity was measured before and after drying the polymers; a decrease in the viscosity was observed for all the polymers due to the drying process, but the two modes lead to no significantly different values between each other. The authors attributed the decrease in the viscosity to a decrease in the molecular weights of the polymers; they

also found that the drying time affects the viscosity more than the temperature does.

## 5. Conclusion

This review put forward some theoretical and practical characteristics of microwave heating. Compared to the conventional heating, microwave heating is known to be fast, volumetric, and selective. Therefore, this technology appears to be very interesting in the fields of polymer processing and chemistry. Many attempts have been successfully adopted at lab or industrial scales. Microwave heating already proved its benefits in terms of energy and time saving, increasing the chemical reactions rate and yield, limiting side reactions, and in some cases providing products with high purities and better properties.

Microwave heating is based on the interaction between electromagnetic waves and matter, depending on the dielectric properties of the last. In the case of polar polymers, this technology allows many applications such as drying, polymerization, functionalization, or chemical modification of polymers. Even nonpolar polymers (that cannot directly interact with microwaves due to the absence of free or bonded charges) may be heated by microwaves by adding microwave absorbers [115] within the polymer in the case of solvent-free processes or by using polar solvents. They play the role of microwave susceptors and heat the polymers, indirectly, faster than in conventional heating.

Despite all its benefits in polymer processing and chemistry, one of the biggest challenges to succeed the involvement of this technology is the temperature calibration and regulation. Optical fiber and infrared thermometers are commonly used to measure temperature during microwave heating. Efforts in metrology are therefore required to calibrate and regulate temperature during the overall process. Besides, as dielectric properties of polymers are dependent on temperature, thermal gradients or overheating may occur, leading to a difficult control of the processing temperature. Modeling is therefore a powerful approach that may be developed to consider the temperature dependence of the dielectric properties of each polymer system and to better understand the behavior of polymers under microwave irradiation.

## Data Availability

No data were used to support this study.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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