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Understanding microwave interactions with polymers to enable advanced plastic chemical recycling

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ABSTRACT

The widespread adoption of plastics has led to substantial production and waste generation, raising environmental concerns. Chemical recycling offers a promising solution to enhance recycling rates, with microwave heating emerging as an attractive technology for polymer breakdown. This paper investigates the dielectric properties of various polymers and their temperature dependencies, providing insight into the effectiveness of microwave heating. Results indicate that while polymers may show low dielectric loss at room temperature, those with polar segments exhibit increasing loss at high temperatures, indicating that additional susceptors may not always necessary for effective microwave heating. Three key transitions are identified with respect to their significant impact on the dielectric properties of polymers at elevated temperatures: the glass transition temperature, the decomposition temperature, and the point where the dispersion/displacement peak exceeds the measurement frequency. Additionally, this paper introduces a new approach for utilising microwave heating for the selective, multistage recycling of mixed plastics.

1. Introduction

Plastics have become an essential part of modern life, permeating nearly every aspect of society. They are lightweight, durable, and versatile materials, making them ideal for use in a broad range of applications, from food packaging and electronics to automotive and construction. However, their success has led to the scale of plastic production and waste generation reaching unprecedented levels, with over 460 million tonnes of plastics produced worldwide in 2019, from which 353 million tonnes of waste were generated, with only 9 % of plastic waste recycled. Meanwhile, 19 % was incinerated, nearly 50 % sent to sanitary landfills, and the remaining 22 % was disposed of in uncontrolled dumpsites, burned in open pits, or leaked into the environment [1]. Thus, it is widely accepted that the current plastic production and waste management trends are not sustainable, and the development of advanced recycling strategies is urgently needed.

Mechanical recycling, currently the most dominant recycling method, transforms plastic waste into new products through a series of mechanical processes such as grinding, washing, and re-granulating [2]. However, this approach has its limitations. The heat and pressure cycles involved in mechanical recycling typically degrade the polymer's[1] quality, which limits the number of reprocessing cycles that a given polymer can undergo [3]. Additionally, ineffective sorting and washing processes as well as the presence of additives can further compromise the quality of the recycled polymer. All these factors restrict the use of mechanically recycled polymers to low-value applications, excluding them from use in areas like food-grade products [4]. Moreover, certain plastics, particularly those based on thermosetting polymers, are considered unsuitable for mechanical recycling because of their cross-linked structure which does not allow them to be re-melted and re-formed [5]. This type of processing has also been recently linked with the generation of microplastics which is an area of growing concern for the biosphere at large [6,7].

In contrast, chemical recycling has emerged as a promising

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[1] Whilst they may occasionally be used interchangeably, the term 'plastics' typically refers to materials that comprise 'synthetic polymers' as their primary ingredient, alongside optional additives. Polymers can be either synthetic or naturally occurring. Throughout this paper, the term "polymer" will refer to synthetic polymers.

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alternative to mechanical processing, with the potential to significantly enhance recycling rates. It involves breaking down the polymer into its oligomers, monomers, and/or other basic chemicals. Depolymerisation, pyrolysis and gasification are the three major chemical recycling processes [8]. Depolymerisation involves breaking down the polymer into its constituent monomers and/or oligomers, which can then be used, either on their own or blended into fresh virgin monomer, in polymerisation processes to re-form high performance plastic. Pyrolysis and gasification break down the polymer into a mixture of low-molecular-weight compounds that could be utilised to produce monomers. Pyrolysis is performed in an inert atmosphere with the aim of producing a naphtha-like product. Whereas gasification involves partial oxidation to generate a syngas that is rich in hydrogen and carbon monoxide [8]. Controlled carbonisation, which involves converting plastic waste into high-value carbon materials, is also considered one of the promising chemical recycling routes [9,10]. Chemical recycling methods can, therefore, complement mechanical recycling by targeting plastic waste streams that pose technical challenges or are economically unviable for mechanical recycling. They also provide a means to extract value from polymers that have reached their reprocessing cycle limit under mechanical recycling. All the aforementioned chemical recycling processes necessitate heating the polymeric material to induce the breakdown of the polymeric chains.

Microwave heating has attracted great interest as a promising technique for facilitating the breakdown of the polymeric chains to achieve chemical recycling [11]. Heating with microwave energy is achieved instantaneously through the interaction of the electromagnetic field with the material at molecular and/or sub-molecular (i.e., mobile electrons) levels. As a result, the material can be heated rapidly throughout its entire bulk, delivering potential advantages in energy efficiency, processing time and product quality. Consequently, a large number of studies have reported on employing microwave heating in plastic chemical recycling. In particular, pyrolysis has received a significant number of comprehensive reviews covering recent developments [12–15].

However, the lack of understanding of the dielectric properties of plastics has been identified as a major factor hindering progress towards scaling up microwave-based chemical recycling [11,16]. Dielectric properties define the interaction of a material with an applied electromagnetic field, thereby determining its heating efficiency. The dielectric constant (ε') is a measure of the material's ability to store electrical energy. It determines the material's tendency to compress the electric field and so has a significant influence over the electromagnetic field configuration within the materials and the heating cavity. Meanwhile, the loss factor (ε'') indicates how well a material converts electromagnetic energy into heat and is directly proportional to the power dissipation density [17]. Both, the dielectric constant and loss factor are influenced by many factors including temperature, frequency, and density [17,18]. Thus, knowledge of how the dielectric properties vary across the full range of process conditions adopted is an essential component required for both mechanistic understanding and the successful design/operation of microwave heating systems. This knowledge enables the optimisation of cavity design to achieve efficient and uniform heating across the material, while also avoiding the formation of hotspots and uneven heating, which can negatively impact the processes and product quality.

The most common heating mechanisms at microwave frequencies are dipolar loss and conductive (or ionic) loss. In the case of dipolar loss, which is found in materials with permanent or induced dipoles, heat is dissipated due to molecular friction caused by the dipoles rotating to align themselves with the oscillating electric field. Conductive (ionic) loss is found in materials with free charged particles (ions and electrons) which also move to match the phase of the alternating energy.

In general, polymers are considered to be poor microwave absorbers at room temperature [12], due to their extended and complex covalently bonded molecular structure, which restricts molecular rotation in response to the electromagnetic field, and the lack of mobile electrons. However, it is believed that polymers containing polar segments may have an enhanced microwave susceptibility, particularly at higher temperatures [19]. Bur (1985) has classified the types of heating (loss) mechanisms found in polymers within the microwave region into: (a) dipolar dispersion, which is associated with the motion of polar segments of the polymeric chain, (b) dipolar loss due to polar impurities or additives, and (c) ionic loss, which is found in conducting polymers such as polyacetylene and conducting impurities or additives [19]. The difference between the dipolar dispersion, which we will refer to as dipolar 'displacement',[2] and the traditional dipolar loss is that the former occurs as a result of the local movement of the polar segments within the polymer chains instead of rotation of the whole molecule. At room temperature, the peak dielectric loss for polymers with polar segments, known as the "displacement* peak", occurs at a low frequency, with its tail extending into the microwave region [19]. The displacement peak is analogous to the relaxation peak in polar liquids [20]. While there are several other published studies on the dielectric properties of polymers [21–25], most are limited to room temperature measurements and/or to frequencies different from the industrial microwave heating frequencies.

This study reports an investigation into the temperature dependencies of the dielectric properties of a range of polymers, particularly polymers with polar segments, to provide insights into the effectiveness of microwave heating across the temperature range required for chemical recycling for plastic chemical recycling. This is important because polymers undergo substantial physical and chemical transformations during heating, which can significantly impact their interactions with the electromagnetic field. Thus, the robust design of microwave heating systems for chemical recycling necessitates an in-depth understanding of the dielectric properties of the materials involved across the range of process conditions.

2. Materials and methods

2.1. Materials

A variety of commercially available polymers were provided by Mitsubishi Chemical UK Ltd for the purpose of this study. Table 1 lists the polymers involved, along with the typical chemical structure of their repeating units.

2.2. Characterisation

Differential scanning calorimetry (DSC): DSC was utilised to gain an understanding of the structural and thermal characteristics of the investigated polymers. The analysis was carried out using a Discovery DSC 2500 system manufactured by TA Instruments. The measurements were conducted within the range of 40 °C–280 °C at a heating rate of 20 °C/min.

Dielectric Property Analysis (DEA): The dielectric properties of the polymers were measured using the cavity perturbation technique. A schematic of the measurement setup is depicted in Fig. 1. The system consists of a TM_{0n0} cylindrical cavity, vector network analyser (Agilent E5062A), tube furnace, 4 mm quartz tube, tube holder connected to a step-motor, and a computer control and data-logging system. Further details on the measurement system can be found in prior publications [26,27].

Typically, 100 mg of the sample (2 mm–4 mm particles) was loaded into the quartz test tube for measurement. The DEA was conducted at temperatures ranging from 20 °C to 400 °C and six different frequencies in the range of 400 MHz to 3 GHz. However, only the results at the industrial microwave heating frequencies (912 MHz and 2.45 GHz) are

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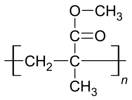
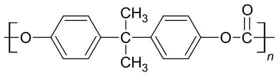
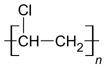
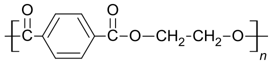
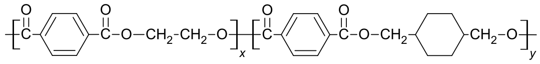
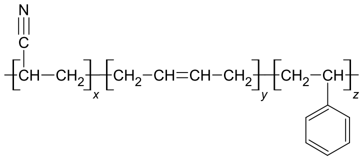
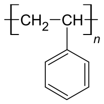
[2] The term "displacement" is used instead of "dispersion" to distinguish it from dispersion polymerisation, a common term in polymer chemistry.

Table 1
Typical chemical structure of the polymers involved in this paper.

Polymer	Acronym	Structure
Polymethyl methacrylate	PMMA	
Polycarbonate	PC	
Polyvinyl chloride	PVC	
Polyethylene terephthalate	PET	
Polyethylene terephthalate glycol	PETG	
Acrylonitrile butadiene styrene	ABS	
Polystyrene	PS	

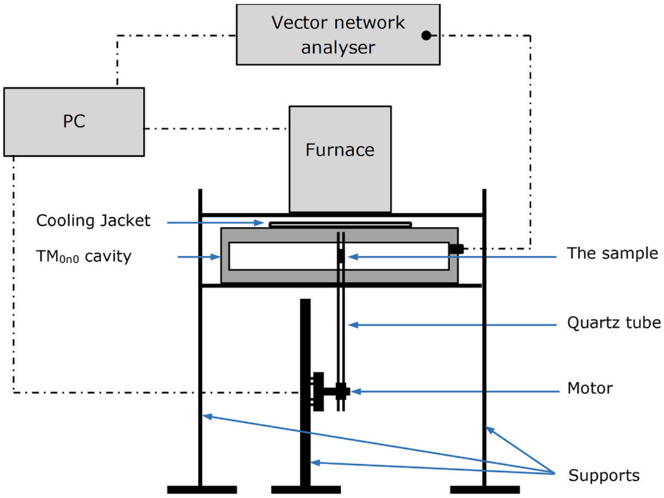


Fig. 1. Schematic of the cavity perturbation dielectric measurement system. Reprinted with permission from Ref. [26]. Copyright 2018 American Chemical Society.

presented here. The remaining results can be found in Appendix A of the Supplementary Material Document. A heat-hold-measure procedure was employed for the high-temperature measurements, where the sample was heated in the furnace to the target temperature, held for 300 s at the target temperature, then introduced into the cavity for measurement, and then moved back to the furnace for the next temperature step. The typical residence time in the cavity was less than 20 s which did not allow time for the sample temperature to significantly change during the timescale of the measurement.

3. Results and discussion

3.1. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to gain insights into the thermal traits of the examined polymers, and so indicate the structural characteristics of the polymers such as their glass transition temperatures (T_g) [28,29] which in turn may explain certain dielectric behaviour. The T_g is the lowest or onset temperature indicating that the polymer has begun to transition from a brittle glassy state to an elastic rubbery state. The specific volume of the polymer increases significantly above its T_g and the gap between the molecular chain expands [30]. This change allows the polymeric chains some freedom of movement relative to one another. Table 2 displays the range of T_g values for the analysed polymers at temperatures from 40 °C to 280 °C. The DSC profiles from which these values were obtained can be found in Appendix B of the Supplementary Material Document.

All polymers manifested a T_g in the range between 64 °C and 150 °C, except PVC which contained a plasticiser, thus its T_g fell below the

Table 2
The T_g values for the polymers included in this study. The DSC profiles from which these values were obtained can be found in Appendix B of the Supplementary Material Document.

Polymer	T_g (°C)		
	Onset	Midpoint	End
PMMA	102	108	114
PC	149	151	154
PVC	NA	NA	NA
PET	64	73	79
PETG	70	73	75
ABS	105	108	111
PS	102	105	108

temperature range adopted in this study. Furthermore, the level of change in heat flow during the glass transition of PET at around 64 °C was relatively small indicating that the polymer has a high crystallinity. This is also evidenced by the large melting peak at ~250 °C.

3.2. The temperature dependency of dielectric properties

To explain the dielectric behaviour of the studied polymers, the polar segments within their repeating units were first identified. These segments act as the primary contributors to molecular movement under the microwave field, resulting in dielectric loss. Subsequently, the temperature-dependent changes in dielectric properties were linked to the physical and chemical transformations occurring within the polymer during heating, incorporating some findings from the DSC analysis.

Poly(methyl methacrylate) (PMMA): PMMA contains two asymmetric side groups: a methyl ($-CH_3$) group and a larger polar ester ($-COOCH_3$) group [31] (see Table 1). It was proposed that the polar ester side group served as the key segment capable of interacting with the alternating microwave field. Fig. 2 shows the dielectric constant (a) and loss factor (b) of the PMMA polymer as functions of temperature up to 400 °C.

The PMMA was observed to maintain a low dielectric loss (<0.01) from room temperature up to 100 °C after which it gradually increased and reached a peak at around 280 °C. The 240 °C–280 °C region was also the temperature at which the highest dielectric constant value was recorded. The loss factor, as well as the dielectric constant, then dropped gradually with increasing temperature. The increase in the loss factor with temperature above 100 °C was attributed to the polymer approaching its T_g (i.e., 102 °C for this PMMA grade – See Table 2). Thus, beyond this temperature range, the polymeric chains acquire an increasing degree of mobility, giving the polar segments additional freedom to interact with the electromagnetic field. The apparent reduction in both the dielectric constant and loss factor at temperatures above the 240 °C–280 °C region was attributed to the polymer's decomposition and the subsequent evaporation of the products from the test tube. The primary decomposition step for PMMA polymers starts at around 250 °C–350 °C and can continue up to 450 °C [32,33].

As indicated in Section 1, polymers with polar segments are expected to exhibit a dielectric loss-temperature behaviour similar to that of polar liquids due to some similarities in their dielectric-frequency profiles. The displacement peak for polymers, which at room temperature typically falls at low frequencies, begins to shift towards higher frequencies as the temperature is increased, as illustrated by Fig. 3.

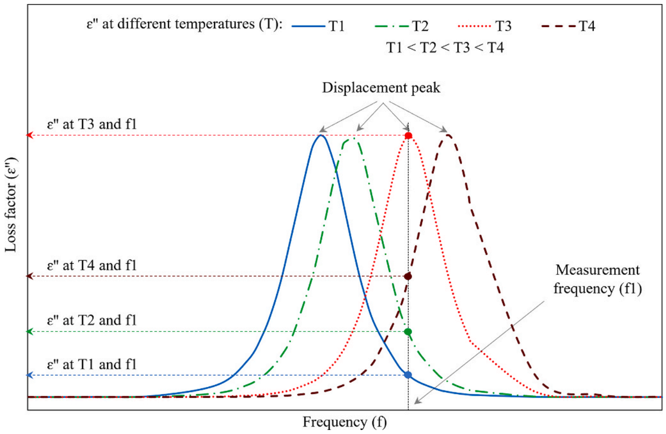


Fig. 3. Effect of temperature on the displacement peak position for polymers with polar segments. The diagram illustrates the increase in the loss factor with temperature, up to the point where the displacement peak aligns with the applied frequency (T3). A reduction in the loss factor is observed when the displacement peak surpasses the applied frequency.

This shift in the displacement peak causes a gradual increase in the loss factor when measured at microwave frequencies (f1 in Fig. 3). This gradual increase in the loss factor reflects the greater freedom offered to the polymeric chain to move, resulting in increased movement friction. The loss factor continues to rise with temperature until the displacement peak aligns with the measurement frequency (at T3 in Fig. 3). Further increases in temperature beyond this point result in a reduction in the loss factor (see values at T4 compared to T3 in Fig. 3). Mechanistically, this reduction in loss reflects the polymer's transition to a phase where the applied field is too slow to generate the optimal amount of frictional loss, given the polymer's increased specific volume and enhanced mobility of its chains. When measuring dielectric properties at two different frequencies (912 MHz and 2.45 GHz in this case), the temperature-dependent reduction in the loss factor associated with the transition in the displacement peak will be initially observed at the lower frequency (912 MHz).

Fig. 2 showed that even after its apparent drop at high temperatures (above 280 °C), the loss factor of PMMA at 912 MHz remains higher than at 2.45 GHz, indicating that the displacement peak remained below 2.45 GHz throughout the studied temperature range. This suggested that, if there were no reduction in the amount of sample within the test tube, the loss factor would be expected to steadily increase with temperature up to 400 °C.

Polycarbonate (PC): Polycarbonates are a group of thermoplastic polyesters containing polar carbonate linkages due to the presence of the carbonyl functional group. A common commercial PC was used in this study, which was determined to have a T_g of 149 °C (see Table 2). This explained the rapid increase in its loss factor above this temperature, as displayed in Fig. 4. Decomposition of PC begins at temperatures above 400 °C [34], hence, its loss factor at 2.45 GHz and the dielectric constant at both frequencies continued to increase with temperature up to 400 °C, as shown in Fig. 4.

The differential in loss factor behaviour above 300 °C, i.e., decrease at 912 MHz compared to a continued increase at 2.45 GHz, indicated that the displacement peak over this temperature range lies between these two frequencies as explained by Fig. 3. Therefore, unlike PMMA, the drop in the loss factor at 912 MHz could indicate a potential slowdown in the heating rate above 300 °C during microwave heating.

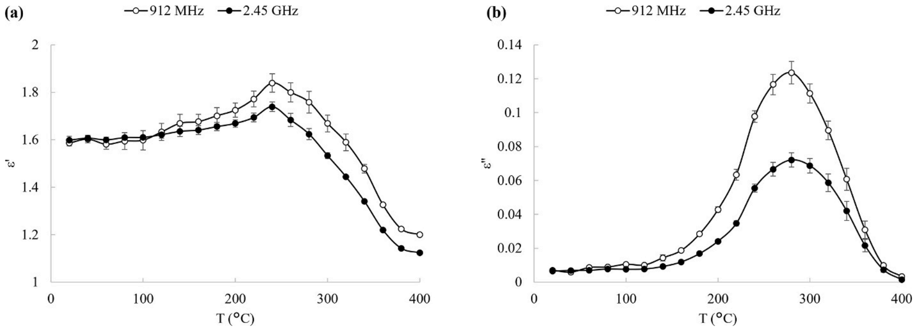


Fig. 2. Dielectric constant (ε′) and loss factor (ε″) of clear cast PMMA as a function of temperature, measured at 912 MHz and 2.45 GHz.

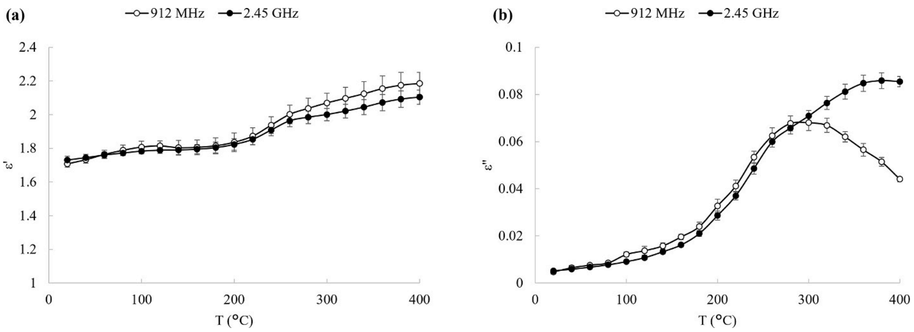


Fig. 4. Dielectric constant and loss factor of PC as a function of temperature, measured at 912 MHz and 2.45 GHz.

Poly(ethylene terephthalate) (PET): PET is one of the most common polyesters and the grade used in this study had a high degree of crystallinity as discussed earlier in Section 3.1. The molecular structure of PET contains polar ester groups (–COO–) that are polar as they contain a carbonyl (C═O) functional group. Additionally, there will be either/both polar carboxylic acid (-COOH) and hydroxyl (-OH) end-groups that may be retained in the final structure that are also polar and may have additional influence on the dielectric properties of lower molecular weights materials.

The study of this PET material determined that the dielectric constant and loss factor increased gradually with temperature, as shown in Fig. 5. This increase became more rapid, particularly for the loss factor, above the glass transition range (>80 °C). A further, limited acceleration in the rate of increase for both properties was observed from 240 °C to 280 °C, which covers the melting range of this PET polymer. Despite the high degree of crystallinity of the polymer suggested by its DSC profile, the increase in the loss factor up to the melting point was apparently larger than the increase observed over the melting range itself. This highlights the significant influence of the amorphous regions of this semi-crystalline polymer in the dielectric response at high temperatures.

The loss factor at 2.45 GHz surpassed the corresponding 912 MHz value at 220 °C and continued to increase up to 280 °C before it started to decrease (Fig. 5). This indicated that the displacement peak in the temperature range of 220 °C–280 °C lay between 912 MHz and 2.45 GHz. Therefore, the reduction in the loss factor above 280 °C was attributed to the displacement peak becoming greater than 2.45 GHz. Furthermore, as PET starts to decompose at a temperature exceeding 350 °C [35], the decrease in the dielectric constant and a portion of the reduction in the loss factor above 360 °C would also be associated with the diminishing sample size due to decomposition.

Polyethylene terephthalate glycol (PETG): PETG is an amorphous copolymer, similar in structure to PET, that contains an additional glycol group along the backbone, introduced via the poly (1,4-cyclohexylenedimethylene terephthalate) (PCT) reagent [36]. Both reagents that copolymerise to form PETG (i.e., PET and PCT) contain polar carbonyl (C═O) functional groups. In comparison to PET, PETG is highly amorphous, as evidenced by its distinct T_g at around 70 °C (see Table 2 and Appendix B of the Supplementary Material Document). This relatively low T_g facilitated the rapid increase in the loss factor with temperature below 100 °C, as displayed in Fig. 6. PETG decomposition is initiated at approximately 400 °C [37], which accounts for the reduction in the dielectric constant observed at 400 °C in Fig. 6. The drop in the loss factor at lower temperatures was attributed to the displacement peak surpassing the measurement frequency as explained by Fig. 3. This occurs at 220 °C and 280 °C for the 912 MHz and 2.45 GHz frequencies, respectively. This indicates that during the microwave heating of this polymer, the heating rate would potentially begin to slow down before decomposition starts.

Polystyrene (PS): PS lacks strong polar segments within its polymeric chain, hence, previous studies pointed out that it does not exhibit a low-frequency displacement peak [19]. Fig. 7 shows that PS maintained a very low dielectric loss up to 200 °C, with only a limited increase observed above this point. Notably, both the dielectric constant and loss factor showed a sharp decline above 360 °C, a trend that is consistent with the thermal decomposition of PS, which typically occurs between 300 °C and 500 °C [38].

Acrylonitrile butadiene styrene (ABS): ABS is a terpolymer composed of three monomers: acrylonitrile, butadiene, and styrene. The acrylonitrile monomer contains a polar cyano group (-CN), which renders this segment of ABS polar [19]. Neither the butadiene nor the styrene segments contain polar groups. The data in Fig. 8 demonstrates that both the dielectric constant and loss factor begin to increase progressively with temperature above 120 °C. This rise is defined as being when the test temperature went beyond the materials T_g (~105 °C, see Table 2).

The decrease in dielectric constant above 360 °C was linked to polymer decomposition, which commences within this temperature range for ABS [39]. Meanwhile, the reduction in loss factor at lower temperatures (starting just above 320 °C at 912 MHz) was again attributed to the displacement peak surpassing the measurement frequency.

Poly(vinyl chloride) (PVC): The repeating unit in PVC features a polar chloride group (-Cl) capable of interacting with the alternating microwave field. Fig. 9 illustrates that PVC exhibits a relatively high loss factor at room temperature compared to the other polymers studied in this

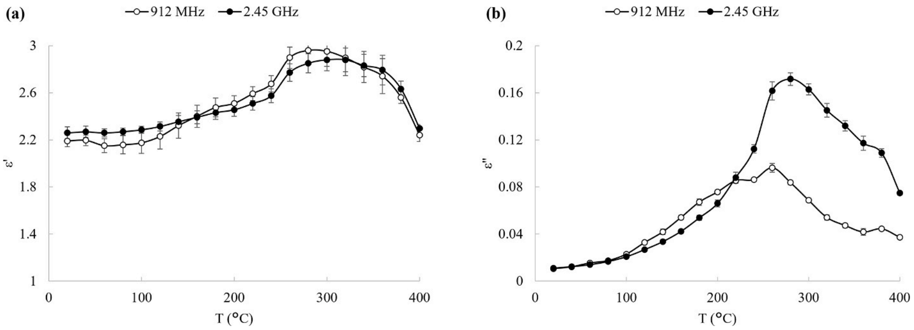


Fig. 5. Dielectric constant and loss factor of PET as a function of temperature, measured at 912 MHz and 2.45 GHz.

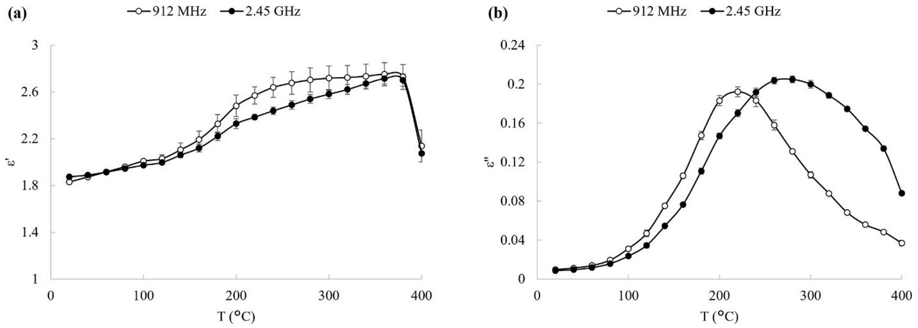


Fig. 6. Dielectric constant and loss factor of PETG as a function of temperature, measured at 912 MHz and 2.45 GHz.

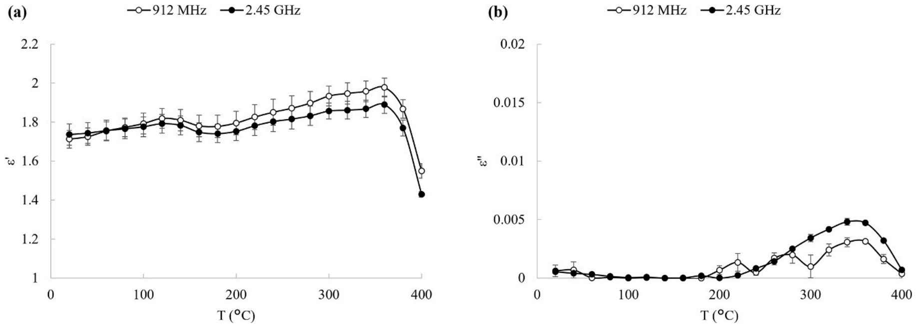


Fig. 7. Dielectric constant and loss factor of PS as a function of temperature, measured at 912 MHz and 2.45 GHz.

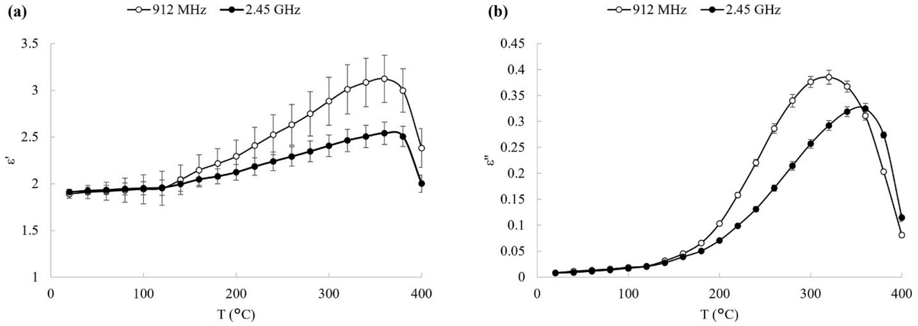


Fig. 8. Dielectric constant and loss factor of ABS as a function of temperature, measured at 912 MHz and 2.45 GHz.

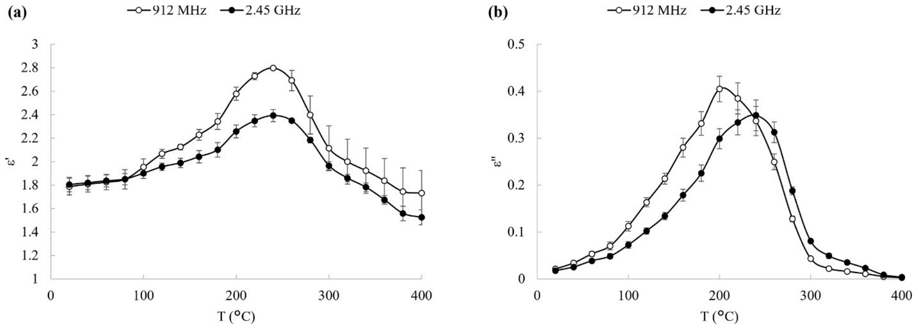


Fig. 9. Dielectric constant and loss factor of plasticised PVC as a function of temperature, measured at 912 MHz and 2.45 GHz.

paper. This observation was attributed not directly to the T_g of the base polymer, but due to the presence of plasticisers in the polymer matrix.

Plasticisers are low-molecular-wight compounds that are incorporated into the polymer matrix to make them more flexible and less brittle which typically involves lowering the apparent T_g [40,41]. They act as “molecular ball bearings”, i.e., they introduce more free volume between the chains, both reducing interchain interaction and so allowing a greater level of interchain movement. Thus, the polymer chains can have a greater ability to interact with the electromagnetic field, thereby increasing the dielectric loss. Furthermore, many plasticisers may also interact with the microwave energy themselves, i.e., acting as susceptors. Such behaviour has already been reported by the authors to result in the microwave-induced annealing of polymer matrices [42].

Both the dielectric constant and loss factor increased with temperature, reaching a peak at around 240 °C. The earlier drop in the loss factor at 912 MHz indicated that the displacement peak aligns with the measurement frequency at 200 °C. The reduction in both the dielectric constant and loss factor above 240 °C was attributed to decomposition. It is well-documented in the literature [43–46] that the decomposition of PVC occurs in two stages. The first stage involves the dehydrochlorination of the polymers, which removes most of the chloride present in the polymer as hydrogen chloride. The second stage involves the degradation of the remaining dechlorinated polymer. The dehydrochlorination stage occurs in the temperature range between 250 °C and 350 °C, while the decomposition of the remaining polymers continues up to 525 °C [46]. Given that the chloride group constitutes the polar element responsible for the dielectric loss within the polymer, the dehydrochlorination stage resulted in a sharp decrease in the loss factor of the polymer, as shown in Fig. 9 (b). Stripping out the chloride group from the polymer leaves it nearly lossless.

Comparative dielectric response of various polymers: The loss tangent (tan δ) is defined as the ratio of the loss factor and the dielectric constant and is commonly used to compare the efficiency of energy conversion among different materials. Fig. 10 compares the loss tangent at 2.45 GHz as a function of temperature for all the polymers involved in this study, which highlights some commonalities of behaviour and some clear differences.

One of the observed similarities was that, with the exception of PVC due to the presence of plasticisers, all polymers start with a low dielectric loss at room temperature. All the polymers containing polar segments (PS not included) showed a significant increase in the dielectric loss with temperature, particularly above their T_g.

The temperature at which the polymer reaches its tan δ peak (i.e., the onset of its decline) is determined by two factors. Firstly, thermal decomposition and the subsequent loss of material from the test sample. Secondly, a transition in the displacement peak at which it overtakes the measurement frequency (as illustrated by Fig. 3). The behaviour exhibited by the polymer tested was concluded to fall into one of three types. In the case of the grade of PMMA studied, the tan δ peak is at 300 °C. This position was largely attributed to polymer decomposition at temperatures of about 300 °C. Meanwhile, for the PC sample, the tan δ peak is only reached at 400 °C (observed as a plateau at the highest temperature measurement). This was concluded to be caused by the transition in the displacement peak to be higher than the measurement frequency because the main decomposition stage for polycarbonate occurs above 400 °C [34]. For the remaining polymers, this position of the peak (i.e., the onset of the reduction in tan δ values) is caused by a combination of both these two factors. It is worth noting that the reduction in the loss caused by decomposition does not necessarily lead to a reduction in heating rate during microwave processing under continuous operation mode. The continuously fed fresh polymer compensates for the amount that has decomposed and left the microwave cavity which is the primary cause for the reduction is the dielectric loss in this case. By comparison, the reduction caused by the transition in the dispersion peak will likely result in a reduction in heating rate.

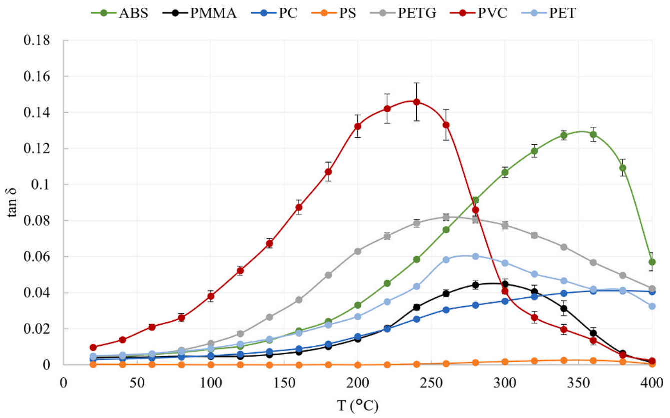


Fig. 10. Loss tangent of a range of polymers as a function of temperature, measured at 2.45 GHz.

3.3. Effect of particle size and heating rate

The influence of particle size and heating rate on the dielectric properties was further investigated. Fig. 11 compares the tan δ values for PMMA granules (2 mm–4 mm) with that of a powdered sample (0.5 mm–1 mm).

It is evident from the data that the granules exhibit notably higher loss than the powder, particularly above 200 °C. The increased tan δ of the larger particles was attributed to mass transfer factors, where lower molecular weight decomposition products that exhibit higher dielectric properties due to their increased molecular freedom, primarily methyl methacrylate (MMA), diffuse out of the particles and leave the measurement apparatus at a slower pace. Thus, the retained MMA contributes to an overall increase in the sample's dielectric loss due to its greater loss compared to the polymer. The shift of the dielectric loss peak towards higher temperatures in the larger particles was attributed to heat transfer limitations arising from their smaller specific surface area. This results in a slower rate of heat transfer and a larger surface-to-centre temperature gradient. Consequently, the larger particles decompose at a slower rate, resulting in a later decline in the dielectric loss.

To further explore the analysis of these heat and mass transfer factors, the dielectric properties of clear cast PMMA were examined at various heating rates. This was achieved by adjusting the holding time in the experiments. The default holding time employed in all previously presented results has been 300 s, whilst Fig. 12 shows the tan δ value change as a function of temperature for PMMA powder (0.5 mm–1.0 mm) at three distinct holding times (60, 150 and 300 s).

The data demonstrates that reducing the holding time led to a considerable increase in tan δ, particularly beyond 260 °C, and caused a shift in the loss peak towards higher temperatures. Notably, decreasing the holding time appears to yield similar effects on the dielectric-temperature behaviours as those observed when increasing the particle size. A longer holding time typically suggests that the particles get closer to the target temperature throughout the entire volume of the particle. These factors also facilitate the diffusion of more decomposition products out of both the particles and the test apparatus.

It is important to emphasise that the high-temperature dielectric measurements were conducted using a conventional electric oven. Microwave heating can offer significantly accelerated heating rates compared to traditional heating methods. What may take hours in an

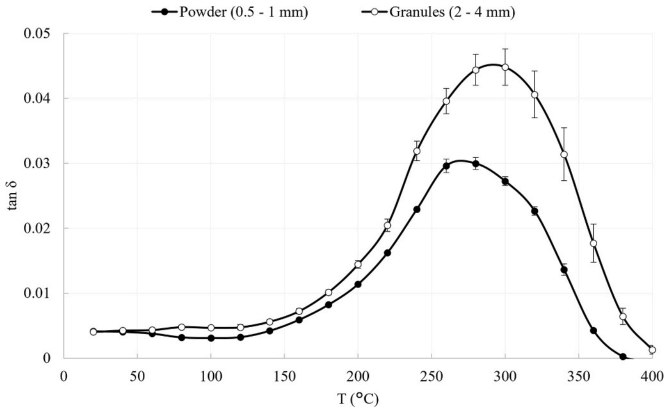


Fig. 11. Effect of particle size on the loss tangent of clear cast PMMA at 2.45 GHz.

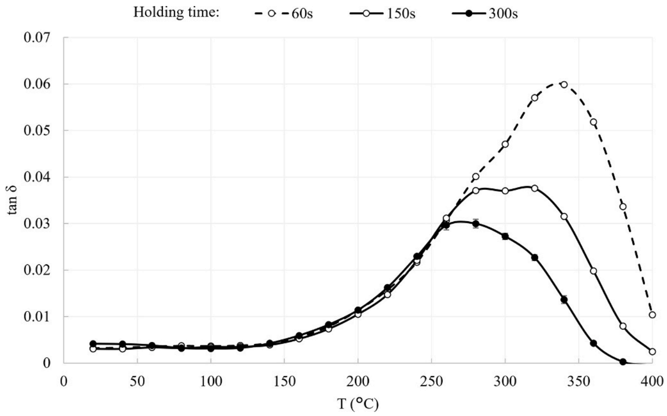


Fig. 12. Loss tangent of clear cast powder (<1 mm) as a function of temperature at 2.45 GHz and different holding times.

electric oven can be achieved within minutes using microwave heating. The implication of this is that the actual dielectric loss during microwave heating could surpass the values obtained from measurements in a conventional electric furnace. Robinson and co-workers [47] have recently highlighted the impact of variations in heating rate between microwave and conventional heating techniques on the mass transport of the decomposition products during the pyrolysis of woody biomass. They observed significant differences in the dielectric properties measured under the two heating techniques.

3.4. *Implications of the findings on microwave processing of polymers*

The findings presented in this paper suggest that (a) while polymers may exhibit a low dielectric loss at room temperature, the dielectric loss of polymers containing polar segments steadily increases with rising temperatures and (b) the peak heating rate during microwave heating of polymers with polar segments can be more than an order of magnitude greater than the heating rate at room temperature. Given that the amount of dissipated power during microwave heating is directly proportional to the loss factor [17], this jump in the loss factor at high temperatures would translate into a corresponding enhancement in the heating rate. This suggests that polymers with polar segments can be directly heated with microwave energy without a need for an additional susceptor. However, this means that the transition from ambient to a temperature at which the material is microwave-receptive needs to be considered. Preheating the polymer conventionally has been previously suggested as an approach to accelerate this transition and enhance the microwave heating efficiency of polymers [48]. In addition, additives that can improve chain mobility, such as plasticisers, are thought to enhance the microwave susceptibility of polymers at room temperature. Such influence of plasticisers was observed in the dielectric loss of the PVC sample studied in this work.

It is important to highlight that pyrolysis and gasification, two major chemical recycling technologies, typically require no or minimal additional chemicals. However, other methods, such as glycolysis, acidolysis, and hydrothermal liquefaction, involve using chemicals like liquid solvents and/or catalysts. These additives can influence how microwave heating is achieved.

For example, water and polar organic solvents, in their liquid state, are considered good microwave absorbers. When mixed with polymers, these solvents are selectively heated (i.e., heated at a much faster rate). However, it is well-established that the dielectric loss factor of low-molecular-weight polar solvents, including water, decreases with increasing temperature. This is linked to their relaxation frequency at room temperature being higher than the industrial frequencies [20,49]. As a result, at elevated temperatures, especially above the polymer's T_g, the dielectric loss of the polymer can exceed that of the solvent, leading to selective heating of the polymer itself. Indeed, recent publications have demonstrated that biomass materials can be selectively heated at high temperatures even when submerged in polar liquids, despite the solvents having a higher loss factor at room temperature [50,51].

The variations in the dielectric properties between the different polymers shown in this study, along with the differences in decomposition temperatures, offer a promising avenue for the development of selective, multistage pyrolysis processes targeting mixed plastic waste streams. To explain the concept, which is visually represented in Fig. 13, consider a simple plastic waste stream containing PET, PVC, PS, and polyolefins (polyethylene and polypropylene), which is not an uncommon mixture for mixed plastic waste and accounts for approximately 70 % of global plastic production [52].

PET and PVC are considered good microwave absorbers, particularly above their T_g. Unless they contain polar or conductive additives, PS and polyolefins are considered poor microwave absorbers, as they lack polar segments within the polymer repeating units. During microwave heating, such waste stream will first be selectively dechlorinated by removing the chloride in the PVC in the temperature range of 250 °C–350 °C. The side product from this stage will be an HCl-rich gas stream. The next stage will be the selective depolymerisation of PET, resulting in an oxygen-rich side product stream. One of the primary products from PET pyrolysis is terephthalic acid which is one of the monomers used to make PET [53]. The second pyrolysis stage leaves behind a dechlorinated and deoxygenated polymer that is a poor microwave absorber.

The third pyrolysis stage may require an additional microwave absorber to enhance the heating rate. This could be achieved by recycling the char produced from this third stage. However, the char generated in the first two stages might be enough to facilitate the heating needed to complete this pyrolysis stage. The vapour product from the third stage will likely be a mixture of aliphatic and aromatic hydrocarbons (naphtha-like product), which can be further processed to produce platform chemicals. These can subsequently be used to produce polymers and/or other chemicals.

4. Conclusions

The findings reported in the paper revealed that while polymers may initially exhibit a low dielectric loss at room temperature, those containing polar segments experience a rapid increase in dielectric loss as temperatures rise, particularly above their T_g, indicating that additional susceptors might not be essential for microwave heating of certain plastics. The reduction of the loss factor at high temperatures was believed to be due to one or a combination of two causes. The first is the thermal decomposition and the subsequent loss of material from the test tube. The second is the displacement peak surpassing the applied frequency.

Particle size and heating rate were found to have a significant influence on the dielectric properties, particularly beyond the initial decomposition temperatures, which was linked to heat and mass transfer factors.

This paper also introduced a concept for employing microwave heating technology for the selective recycling of mixed plastics, utilising the differences in dielectric properties across different plastics, paired with their distinct decomposition temperatures. Such an approach holds the promise of revolutionising plastic chemical recycling by enabling selective pyrolysis and in-situ fractionation of products from mixed plastic waste streams.

CRediT authorship contribution statement

Mohamed Adam: Writing – review & editing, Writing – original draft, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Nicklas Hjalmarsson:** Writing – review & editing, Resources, Project administration,

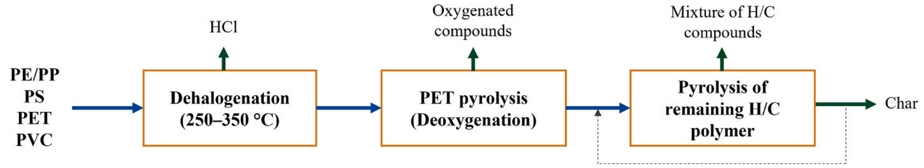


Fig. 13. A potential configuration for a process for selective, multistage pyrolysis of a mixed plastic waste stream.

Methodology, Conceptualization. **Chai Siah Lee:** Writing – review & editing, Formal analysis. **Derek J. Irvine:** Writing – review & editing, Methodology, Conceptualization. **John Robinson:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Eleanor Binner:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2024.108483.

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