



Understanding and optimizing delamination/recycling of printed circuit boards using a supercritical carbon dioxide process

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ABSTRACT

A printed circuit board (PCB) is an integral component of any electronic product and is among the most challenging components to recycle. While PCB manufacturing processes undergo generations of innovation and advancement with 21st century technologies, the recycling of PCBs primarily employs 1920's shredding and separation technologies. There is a critical need for alternative PCB recycling routes to satisfy the increasing environmental demands. Previous work has developed an environmentally benign supercritical fluid process that successfully delaminated the PCB substrates and separated the PCB layers. While this work was successful in delamination of the PCB substrates, further understanding is needed to maximize the interactions between the supercritical fluid and PCB for an optimal processing scenario. As such, this research presents an exploratory study to further investigate the supercritical fluid PCB recycling process by using supercritical carbon dioxide and an additional amount of water to delaminate PCB substrates. The focus of this study is to test delamination success at low temperature and pressure supercritical conditions in comparison to the previous studies. Furthermore, material characterization methods, such as differential scanning calorimetry, dynamic mechanical analysis, and Fourier transform infrared spectroscopy, are included to study the delaminating mechanisms. Results from the recycling process testing showed that the PCB substrates delaminated easily and could be further separated into copper foils, glass fibers and polymers. Surprisingly, the material characterization suggested that there were no significant changes in glass transition temperature, crosslink density, and FTIR spectra of the PCBs before and after the supercritical fluid process.

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1. Introduction

Widespread use of electronic equipment and shortening of product life cycles have created the challenging task of dealing with the ever-increasing quantity of obsolete electronic equipments. The huge amount of electronic wastes (E-wastes) generated each year and the lack of established methodologies capable of handling the increasing volumes of the E-wastes pose a severe environmental threat. Among the challenges to successful electronic equipment recycling, printed circuit board (PCB) recycling is recognized as one of the most difficult tasks because of their complex construction and complicated material composition (Pitts and Mizuki, 1996). PCB scraps are generated from almost all kinds of end-of-life (EOL)

electrical and electronic products. It is reported that about 50,000 tons of PCB scraps are produced each year in the United Kingdom and only 15% of those are currently subjected to any form of recycling, while the remaining 85% is consigned to landfill (Goosey and Kellner, 2003).

This paper presents an exploratory investigation of an environmentally benign process for PCB recycling by using supercritical carbon dioxide (CO₂). As part of this research, a background in current PCB recycling processes will be discussed along with past work for an environmentally benign means for PCB recycling. Particularly, this research looks to expound the work of Zhang et al. (2006) by processing PCBs at lower supercritical conditions (i.e. temperature and pressure) and by further investigating the supercritical CO₂ process with detailed material characterization methods, such as differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and Fourier transform infrared spectroscopy (FTIR). Such tests are anticipated to provide a better understanding of the interactions between the PCB substrates and supercritical CO₂.

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2. Background

PCBs contain three basic components regardless of their construction: 1) a non-conducting substrate or laminate, 2) conductive circuits printed on or inside the substrate and, 3) mounted components. The most widely used substrate is (flame retardant) FR4, which is made up of glass fiber reinforced epoxy resin with a brominated flame retardant in the epoxy matrix. FR2 is another type of commonly seen substrate which is made up of paper reinforced phenolic resin with added flame retardants. It is worthwhile to note that PCBs contain not only a significant amount of precious metals (gold, silver, palladium, etc.) and base metals (copper, iron, aluminum, tin, etc.) but also hazardous elements such as lead, mercury, antimony, cadmium, chromium, and beryllium (Jianzhi et al., 2004). Improper recycling processes for PCB disposal containing these toxic elements could lead to serious environmental contamination.

Interestingly, while PCB manufacturing processes undergo generations of innovation and advancement with 21st century technologies, the recycling of PCBs still primarily employs 1920's shredding, smelting, and separation technologies (Yu and Zhang, 1998). The traditional PCB recycling technology focuses more on roughly separating objective metals and fiber glasses but pays less attention to efficiency and economic returns and more importantly, poorly satisfies environmental demands. For instance, most recycling processes can only recover 28 wt% metals from PCBs, resulting in more than 70% of PCB scraps not being efficiently recycled and ending up in landfill (Jianzhi et al., 2004). A traditional PCB recycling process usually includes three steps: pretreatment, shredding/separation, and mechanical/chemical refining (Jianzhi et al., 2004). The pretreatment stage includes a composition analysis and disassembly of the reusable and hazardous components. Since the main objective of the recycling is to minimize the damage to the environment and maximize material recovery, a composition analysis is necessary not only to obtain the detailed material information of PCBs, but also to give an estimation of the cost incurred and profit realized from the PCB recycling. The purpose of disassembly is to remove reusable and hazardous components in order to isolate them from subsequent treatments. Shredding/separation is the next alternative step after disassembly. The PCB substrates are treated with shredding machines to be fragmented into small particles typically between 100 and 300 μm (Jianzhi et al., 2004). These particles can be further separated by

techniques based on component differences in size, density, magnetic, electrostatic, eddy current and gravitational properties (Goosey and Kellner, 2003). Finally, thermal, mechanical or chemical (or combined) processing will be employed to collect the final recycled products. It is worthwhile to note that the shredding process is neither efficient in energy consumption nor optimized for environmental demands. It requires a large amount of energy but only separates about 75–80% of the precious metals from the shredded mixtures; it also results in significant dust and noise pollution (Yuan, 2004). The dust pollution can cause significant lung damage to animals and human beings. In addition, the glass fiber particles can cause skin irritation is heavy metal dusts may initiate various occupational diseases (Tomasko et al., 2003).

While current PCB recycling methods provide these overwhelming challenges concerning human health and the environment, there has been work that provides an environmentally benign solution for PCB delamination and recovery. One such method has been with the use of supercritical fluids (SCFs). A SCF is defined as a substance above its critical temperature (T_c) and critical pressure (P_c), where it remains as a single phase, having gas-like diffusion rate, viscosity, and liquid-like densities. The gas-like and liquid-like properties combined together can give the SCF appropriate thermodynamic properties that make it highly useful as an environmentally benign solvent for various applications. For example, it has been found that near-critical and supercritical water oxidation techniques can partially or completely break down rubber waste materials (Park et al., 1999). Furthermore, electronic wastes can be disassembled with zero emission using supercritical water oxidation. Up to 50% reduction in weight can be achieved and organic epoxy resin material can be converted into carbon dioxide, water, nitrogen and bromide (Eyerer and Elsner, 1998). In the same effort, work performed by Zhang et al. (2006) presents a supercritical fluid (SCF) carbon dioxide (CO_2) based process to delaminate the PCBs at high temperatures and pressures such that the metals and glass fibers retain their original form and can be recovered.

3. Experiment

As per the work performed in Zhang et al. (2006) a supercritical CO_2 process was used to delaminate/recycle PCBs. Fig. 1 is a schematic diagram of the supercritical CO_2 process. The main components in the process include a HiP (High Pressure Equipment

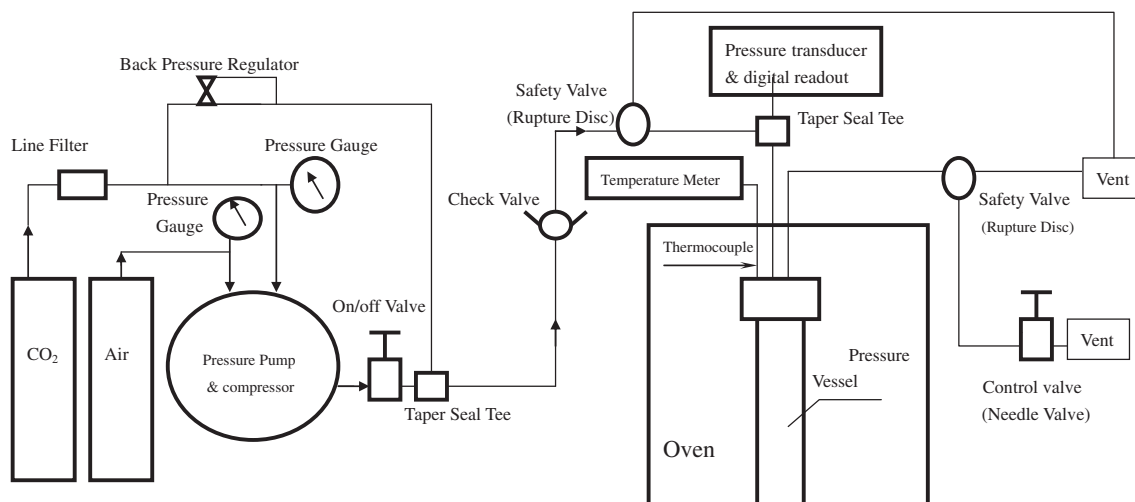


Fig. 1. A schematic diagram of the supercritical CO_2 process for delaminating/recycling PCBs.

Company) GC-21 high pressure vessel and a high temperature laboratory oven. For processing, the PCBs, supplied from the S1 Technology Inc., along with water acting as a co-solvent, were placed in the high pressure vessel and brought to supercritical CO₂ conditions (starting at 31 °C and pressure of 73.8 bars (Rothman et al., 2002)) for a defined processing time. As a point of contrast from the work seen in Zhang et al. (2006), which used predominantly high pressures and temperatures (i.e. 225–250 °C and 414–552 bar), it was decided that lower processing temperatures and pressures should be investigated. For this research, testing was thus performed at processing temperature, pressure, and time variation from 100 to 260 °C, 100–379 bar, and 3–6 h, respectively, with water co-solvent additions.

A number of material characterization methods were incorporated to analyze the supercritical CO₂ PCB recycling process including:

- DSC was used to quantify the glass transition temperatures. The measurements were performed in a nitrogen atmosphere using TA Instruments SDT Q600. Temperature and heat flow calibrations were performed following standard procedures. After a heating and cooling cycle up to 240 °C at 10 °C/min to eliminate the thermal history, the glass transition temperature was analyzed from the data of the second heating scan from 25 to 240 °C at 10 °C/min, with the TA Universal Analysis software.
- DMA was used to determine the glass transition temperature and crosslink density of the PCBs before and after supercritical CO₂ processing. Experiments were performed in a tension mode using a TA Instruments Q800. Thin films of delaminated PCB samples were mounted onto the tension clamp and the temperature was ramped from 25 to 250 °C at a rate of 3 °C/min.
- With the addition of water as a co-solvent, FTIR was used to determine water absorption by the PCB during supercritical CO₂ processing. Processed PCBs were disassembled, the polymeric parts were scraped off, grinded and pressed with Potassium bromide (KBr) to form pellets. FTIR spectra were

scanned over the range of 400–4000 cm⁻¹ with these pellets loaded into a Bruker IFS 66V/S FTIR spectrometer.

4. Results and discussion

A combination of low/medium processing temperature, pressure, and time proved to be sufficient to delaminate the PCBs. Typically, a combination of temperature as low as 180 °C and pressure as low as 138 bar could successfully delaminate PCBs and enabled subsequent recycling. This provides a contribution to the continuing efforts for supercritical CO₂ PCB recycling as previous work has only relied on higher temperature and pressure studies. In addition, a small amount (7 vol. %) of water as co-solvent improved the effectiveness of delaminating the bonding materials with the process temperature and pressure being below the critical temperature and pressure of water ($T_{c, \text{water}} = 374 \text{ °C}$ and $P_c = 221 \text{ bar}$ (Rothman et al., 2002)).

DSC analyses showed no significant differences in glass transition temperatures between the control (untreated) samples and processed samples (See Fig. 2). This is surprising since it is known that a SCF process can cause a subsequent chain scissoring, often referred to as degradation, which produces resin fragment with shorter chain length and lower molecular weight. For example, recycling of high value carbon fiber from polymer composites using supercritical n-propanol (Jiang et al., 2009) and near critical and supercritical water (Piñero-Hernanz et al., 2008) have been reported; both works suggest polymer degradation as the primary mechanism for fiber and resin separation. Since polymer degradation leads to significant changes in physical properties such as glass transition temperature and crosslink density, the DSC results do not support such a hypothesis when the PCB substrates undergo a supercritical CO₂ process at 172 bar, 150–200 °C and 7 vol. % water.

DMA analyses determined the storage modulus, loss modulus, and tan delta values (See Fig. 3). The peak value of the tan δ curve was used to determine the glass transition temperature. The DMA experiments also suggested that there was no significant difference in glass transition temperature when comparing the samples

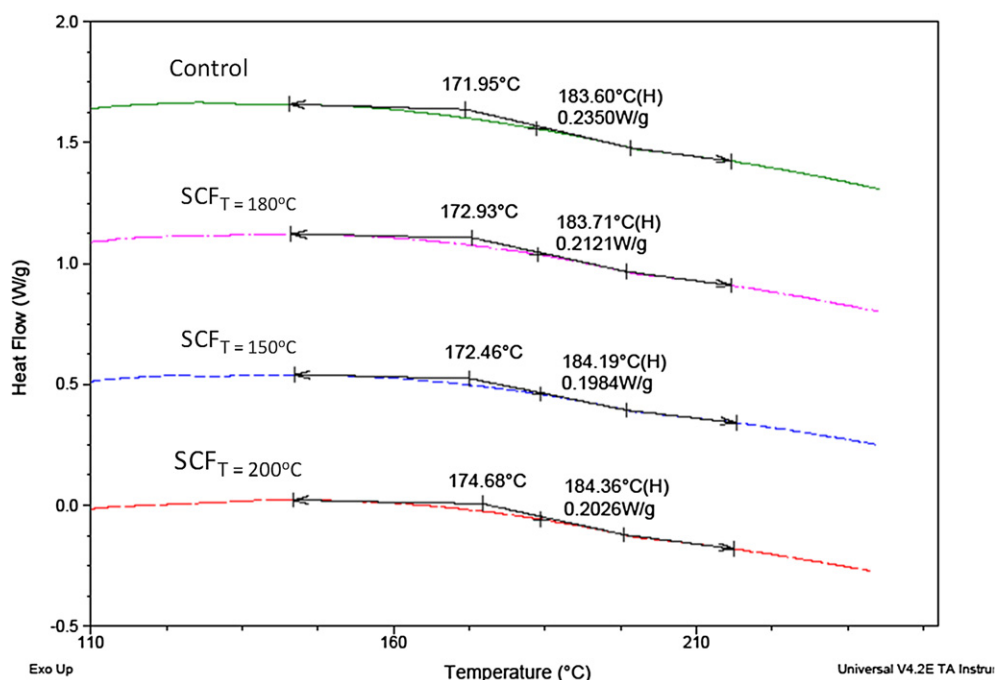


Fig. 2. Differential scanning calorimetry (DSC) overlay of the control and the PCBs going through SCF process at 172 bar, 7% water, at various temperatures.

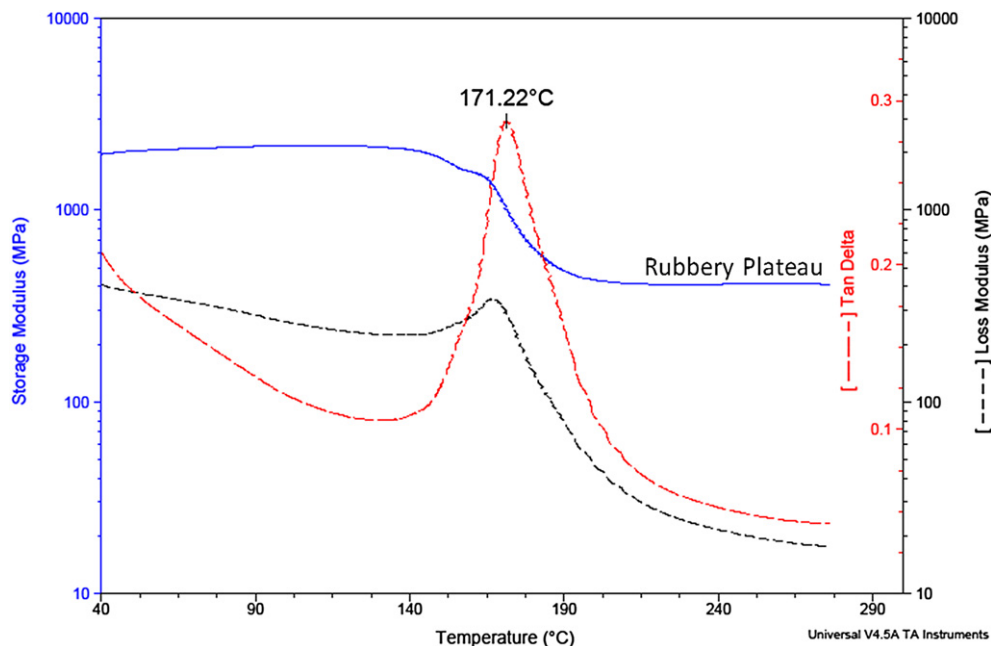


Fig. 3. A representative dynamic mechanical analyzer (DMA) run of PCB after going through a supercritical carbon dioxide process at 180 °C, 172 bar, and 7% water. The experimental frequency is 1 Hz.

before and after the supercritical process (same process conditions as those samples in the DSC experiments). It is also worthwhile to note that we characterized the crosslink density through its correlation with rubbery plateau (E'), $3\rho RT/E'$, where ρ is the density, R is the gas constant, and T is the temperature. Taking into account the standard deviation of results, the samples did not reveal meaningful difference in crosslink density, which further eliminated the hypothesis chain scissoring under such process conditions.

Results for FTIR were used to understand why a small amount (7%) of water improved effectiveness of delamination of the bonding materials when the process temperature was significantly below the critical temperature and pressure of water (T_c water = 374 °C and P_c = 221 bar). The commonly used bonding material is brominated bisphenol-A epoxy based material, which includes a basic epoxy resin, crosslinking component, and brominated fire retardants.

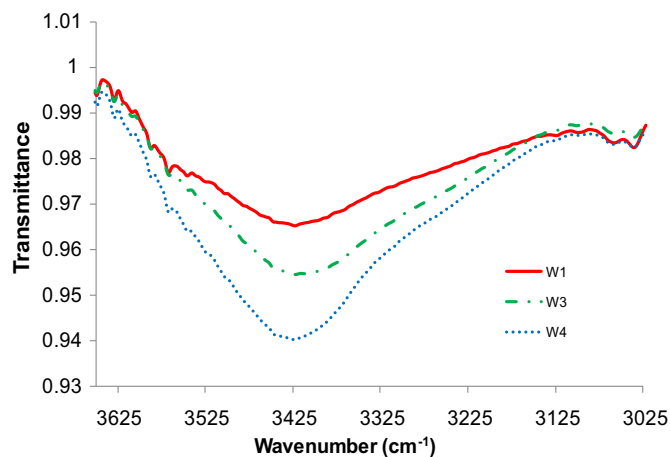


Fig. 4. Overlay of Fourier transform infrared spectrum (FTIR) of PCB boards after going through different SCF processes. $T = 180$ °C; $P = 172$ bar; water percentage: W1: 0%, W3: 20%; W4: 31%. The water percentage was increased solely for the purpose of studying mechanisms.

Water has recently been identified as a unique agent under sub- and super-critical conditions (Shibasaki et al., 2004; Thomason and Modell, 1984; Shaw, 1991; Postorino et al., 1993; Hoffmann and Conradi, 1997; Fang et al., 2000; Huisman et al., 2000; Tester et al., 1993; Goedkoop and Spiensma, 2000; Bellissent-Funel, 2001). For example, sub- and super-critical water has effectively converted an epoxy resin into carbon dioxide and water through a hydrolysis and oxidation mechanism (Fromontel et al., 2000). Recovery of waste polystyrene to styrene monomer by supercritical water partial oxidation has also been performed (Lilac and Lee, 2001). Diphenylether can be decomposed into phenol in the reaction of supercritical water with the addition of a base compound Na_2CO_3 (Shibasaki et al., 2004). Surprisingly, this work suggested that water caused neither additional chemical reaction nor additional decomposition of the epoxy resins under the tested conditions, likely due to the fact that the process was operated at a non-supercritical condition of water.

The FTIR spectrums suggested that the PCB boards, which went through a high percentage of water during the supercritical CO_2 process, contained a high tracer amount of water molecules. This was evidenced by the more prominent peaks at the wave number of 3450 cm^{-1} (where water molecule resonates), as shown in Fig. 4. However, the FTIR scans revealed signals of neither formation of any new substances nor changes of other molecular “finger prints” over the experimental wavelength range. The evidence of no formation of new substances such as hydrocarbons and noxious gases commonly found in the pyrolysis of PCBs (Chien et al., 2000), further reinforced the environmentally benign nature of the developed supercritical CO_2 process.

5. Conclusion

An environmentally benign supercritical CO_2 process has been investigated and validated for PCB recycling. Using supercritical carbon dioxide as a solvent and with an additional small amount of water, the PCB scraps delaminated easily and separated into copper foil, glass fiber and polymer which can then be further recycled. In addition, a systematic study of the effects of process conditions such as pressure, temperature, time and co-solvent on PCB

delamination/recycling has been performed. Of particular importance is the successful delamination of the PCBs at lower temperatures and pressures of supercritical CO₂ conditions (180 °C and 138 bar). This is a significant advancement beyond previous works because with lower temperatures and pressures less energy will be used correlating to a more economic and environmentally friendly process. From the experimental results of DSC, DMA and FTIR, neither chain scissoring nor additional reaction were detected during the developed supercritical CO₂ process. We thus hypothesize that the delamination is likely due to a foaming mechanism and work is in progress to test such hypothesis.

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