Chapter 5
Results and discussion
Determining the Söderberg electrode baking isotherm temperature

5.1 Determination of the TMA behaviour of pitch thermally pre-treated at 450 °C

Söderberg electrodes utilised in submerged arc furnaces are characterised by a critical temperature isotherm known as the baking isotherm temperature. According to literature, the baking isotherm temperature of Söderberg electrodes lies between 400 and 500 °C [Innvaer and Olsen, 1980; Walker, 1986; Fitt and Aitchison, 1993; Asphaung and Innvaer, 1997]. The baking isotherm gives the temperature at which the electrode can support itself [Beukes et al., 2013]. In order to investigate the baking isotherm temperature, the CTP samples were thermally pre-treated (as described in section 3.5.1.1) at 450, 475 and 500 °C. The measured dimensional changes of these thermally pre-treated CTP pellets indicated that pellets prepared from all the CTP samples softened during the TMA analysis, if the thermal pre-treatment temperature was ≤ 450 °C. This softening of the pellets was indicated by a sudden change in the dimensional behaviour of the thermally pre-treated pelletised CTP samples during TMA analysis as the temperature increased. Typical examples (CTP 1 to 4) of this softening behaviour observed during the TMA are indicated in Figure. 5.1.

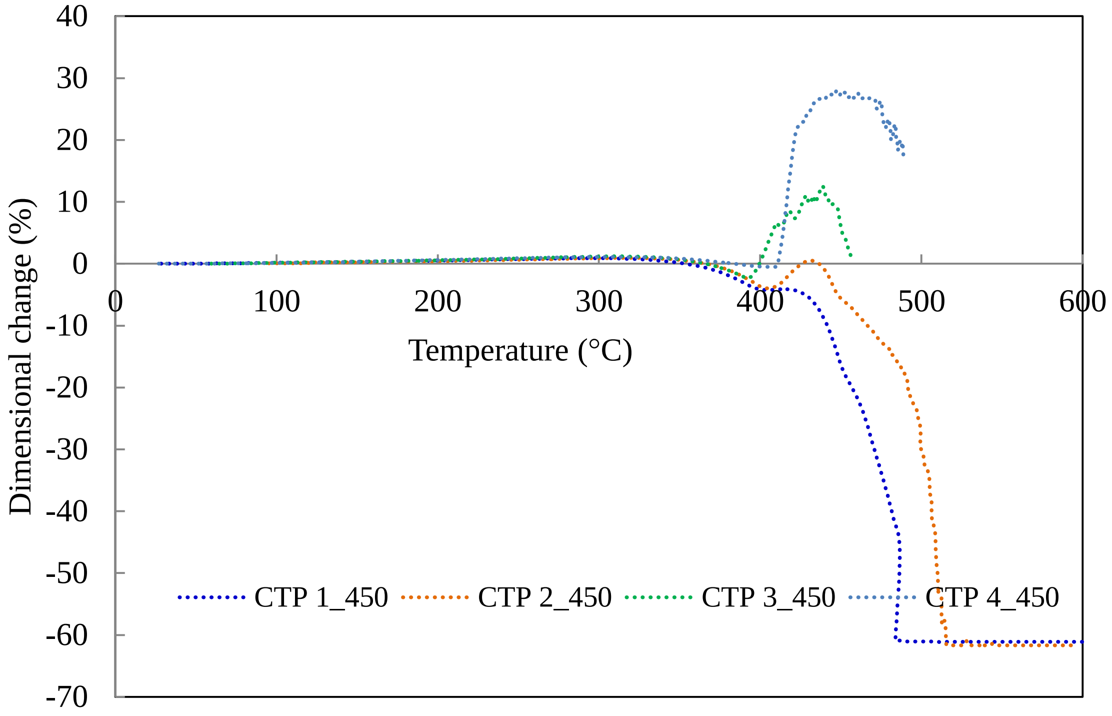

Figure 5.1 Dimensional change patterns of CTP samples pre-treated at 450 °C

As can be seen from the data presented in Figure 5.1, sample softening was indicated by a sudden decrease in dimension for some samples. However, other samples expanded due to softening. This was due to the core of the pellet melting and running out the bottom of the pellet, thereby causing the TMA instrument to measure an increase in size. All of these softening behaviours were, however, characterised by a very sudden change in pellet dimension. CTP samples 5 to 12 reacted similarly, but are not shown in Figure 5.1 to prevent the figure from becoming too crowded. As soon as pellet softening behaviour was observed, the TMA measurement was stopped in order to avoid damage to the TMA probe. Figure 5.2 shows a pellet that melted in the instrument during high temperature thermal treatment in the TMA.

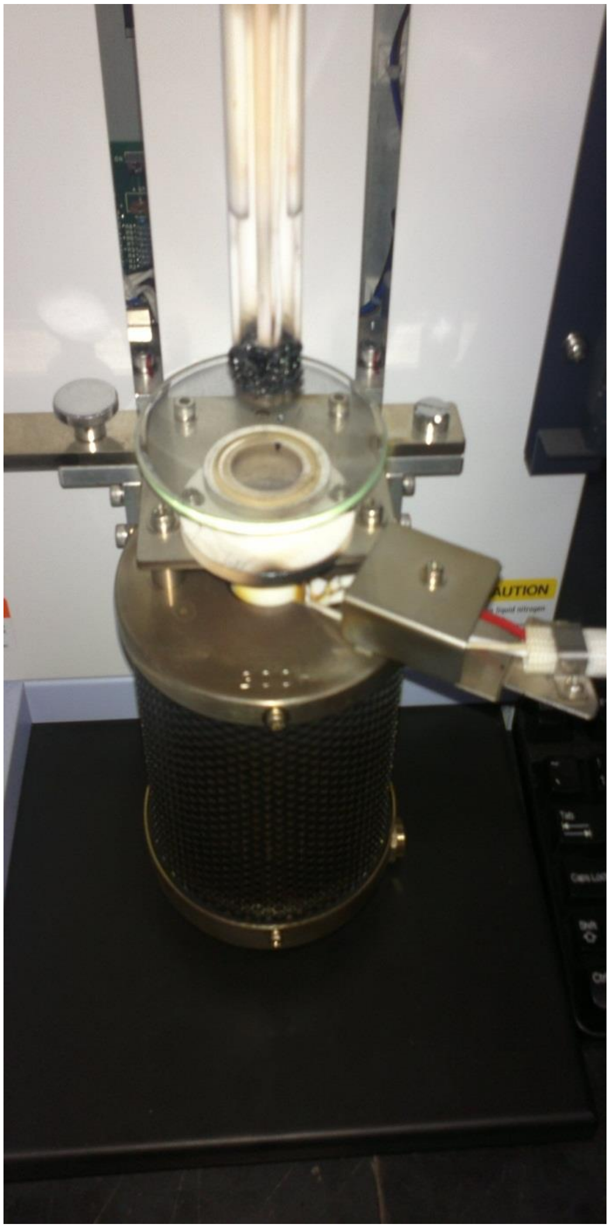

Figure 5.2 An example of a CTP pellet that had melted in the TMA

5. 2 Determination of the TMA behaviour of pitch thermally pre-treated at 475 and 500 °C

In contrast to the above-mentioned results (Section 5.1), none of the pelletised thermally pre-treated CTP samples indicated any softening behaviour during TMA analysis, when the pre-treatment temperature was ≥ 475 °C. An example of such a TMA thermally-treated CTP pellet that did not soften is shown in Figure 5.3.

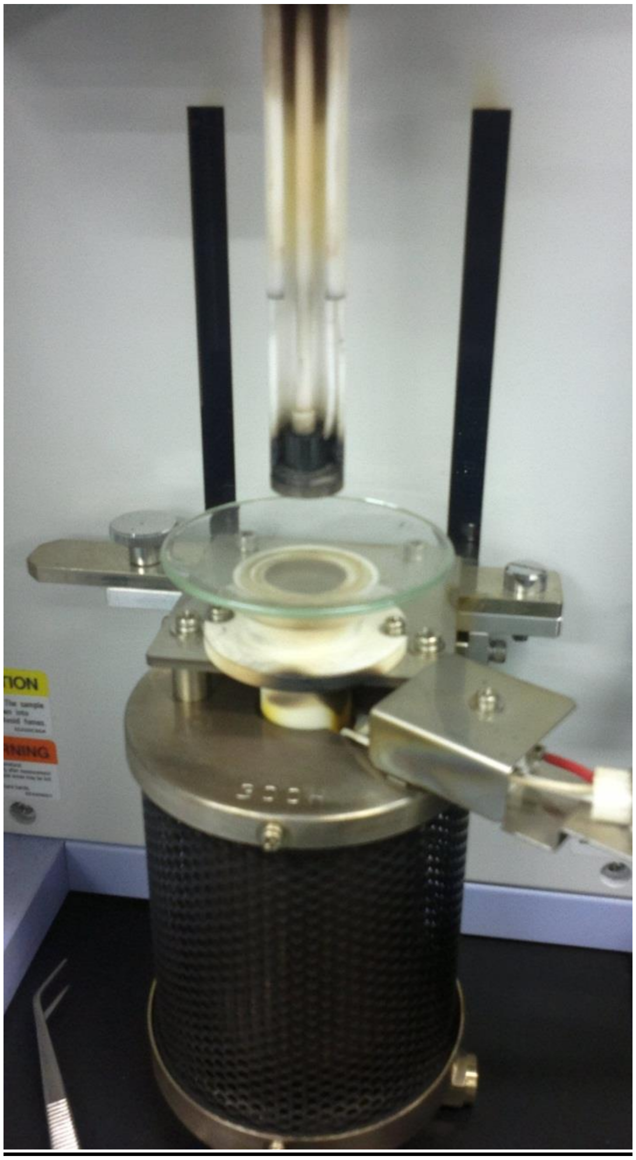

Figure 5.3 An example of a pellet prepared for CTP pre-treated at 475 °C that did not indicate softening during TMA analysis

Typical TMA curves of samples thermally pre-treated at 475 and 500 °C are indicated in Figures 5.4 and 5.5, respectively. Again, four samples (CTP 2, 4, 5 and 6) pre-treated at 475 °C and two samples (CTP 1 and 2) pre-treated at 500 °C were selected for illustration purposes, since the other samples reacted similarly. In contrast to the pre-treated samples that indicated softening behaviours (Section 5.1), which were characterised by sudden dimensional changes, these samples exhibited gradual dimensional changes.

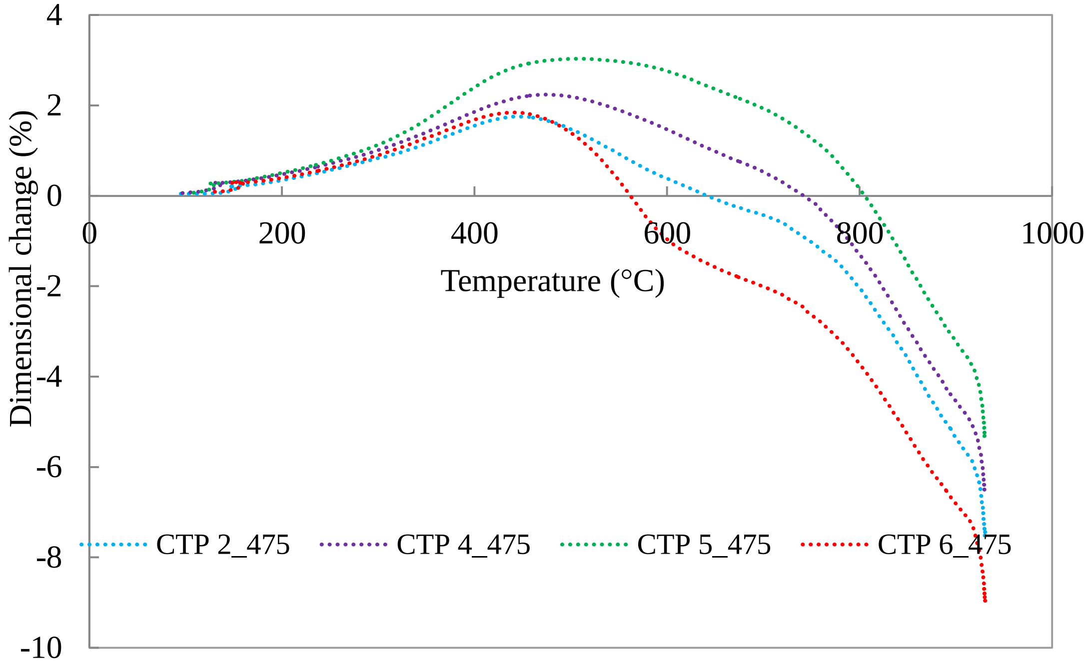

Figure 5.4 Dimensional changes for CTP samples thermally treated at 475 °C

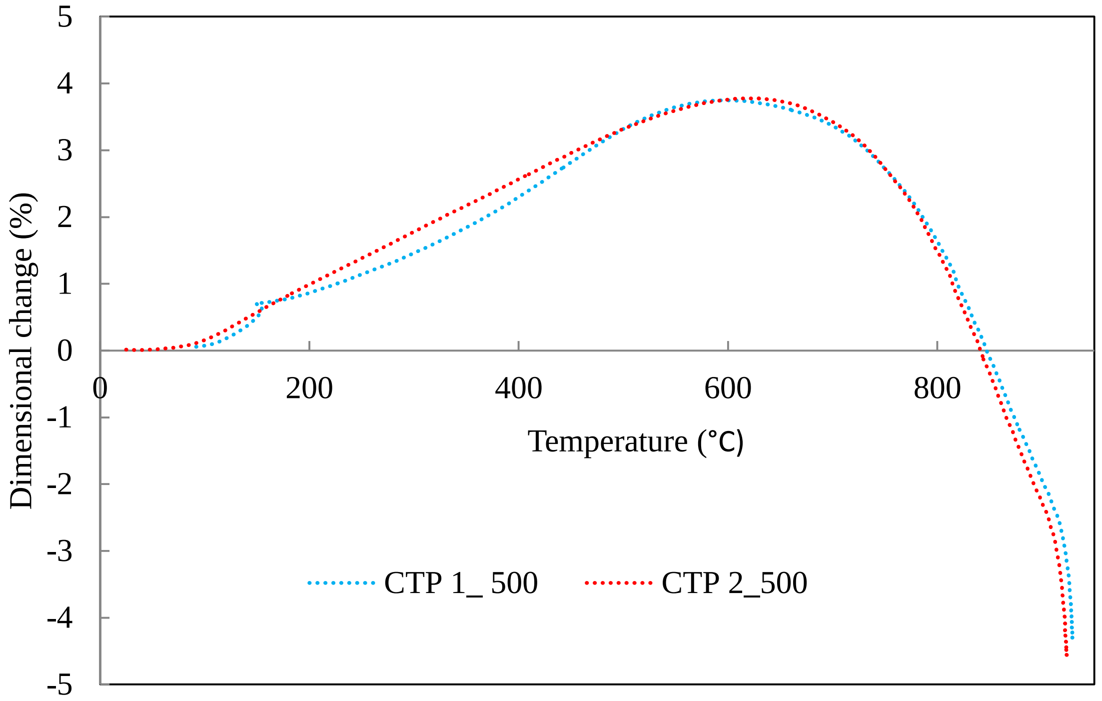

Figure 5.5 Dimensional change of CTP samples thermally pre-treated at 500 °C

The fact that none of the pelletised pre-treated CTP samples softened when the thermal pre-treatment temperature was 475 °C indicates that solid carbonaceous material is formed between 450 and 475 °C. By comparing the TMA thermal behaviour of the pellets prepared from thermally pre-treated CTP at maximum temperatures in the range of 400 to 450 °C and those that were pre-treated at a maximum temperature of 475 °C, it can be deduced that the baking isotherm temperature of CTP used as a binder in Söderberg electrodes lies between 450 and 475 °C. It is acknowledged that the thermal behaviour of the mixture of filler (e.g. calcined anthracite or coke) and binder (CTP) in Söderberg electrode paste might differ from the characteristics of the CTP, but the softening behaviour of the paste is likely to be linked to the CTP rather than the filler. Beukes et al. [2013], who developed the TMA method employed in this study, also reported the baking isotherm temperature of two CTP samples to be between 450 and 475 °C.

However, since these authors [Beukes et al., 2013] only considered two case study CTP samples, they could not deduce with certainty that this would be valid for other CTPs.

Considering the vast differences in fundamental properties (Table 4.1) and the chemical composition (Tables 4.2 and 4.3) of the CTP samples used in this study, it was somewhat surprising to find that the baking isotherm temperatures of all the CTP samples evaluated were between 450 and 475 °C. However, the results led the candidate to believe that although there might be differences in the chemical composition and fundamental properties of the untreated CTP samples ((Tables 4.2 and 4.3), the inert atmosphere heat treatment led to the loss of organic compounds with similar functional groups from all the CTP samples, resulting in the formation of a solid carbonaceous matrix. This implies that the temperature of the Söderberg electrode paste baking isotherm is independent of the initial chemical composition and the fundamental properties of the CTP (Table 4.1). In order to prove/disprove this hypothesis, FT-IR analyses of the as-received CTP samples (Fig 4.2), as well as the CTP samples pre-treated at 475 °C (Figure 5.6), were obtained to determine the organic functional groups present in the samples.

5.3 FT-IR analysis of CTPs thermally treated at 475 °C

The thermal treatment of carbonaceous materials results in chemical changes taking place in the material [Belekov, 2001]. The changes in the CTP structure on thermal treatment can be characterised by FT-IR analysis [Guillen et al., 1992]. All the CTP samples were investigated for changes in functional groups after the thermal pre-treatment at 475 °C, since it was proven in sections 5.1 and 5.2 that transformation to a solid carbonaceous material had then taken place. The FT-IR spectra for samples CTP 2, 5, 8 and 10 that had been thermally pre-treated at 475 °C are presented in Figure 5.6.

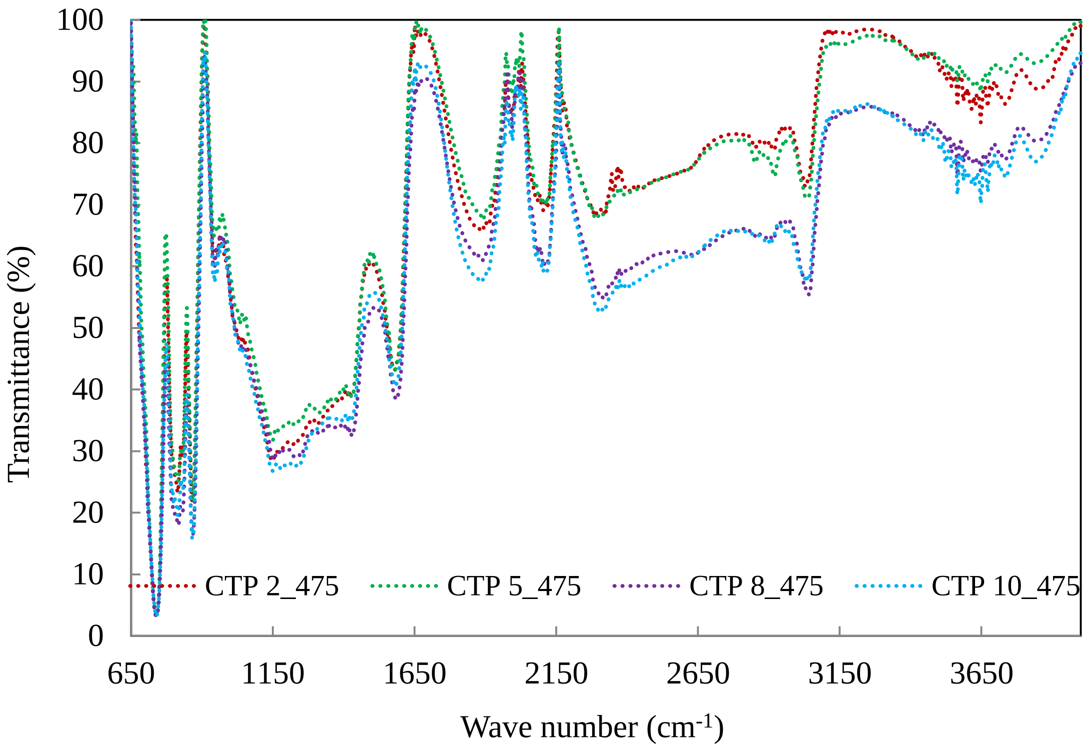

Figure 5.6 FT-IR spectra of CTP thermally pre-treated at 475 °C

From Figure 5.6, it is evident that the FT-IR spectra obtained for the various samples thermally pre-treated at 475 °C are similar. These spectra are also typical of carbonaceous materials [Guillen et al., 1995]. If the spectra of these thermally pre-treated CTP samples are compared to the FT-IR spectra of the raw CTP samples (Figure. 4.2), it is clear that a reduction in some functional groups occurred, as well as the formation of new groups characterised by peaks in the region 2400 to 1900 cm^{-1}. The compounds in this band could not be identified, as we were unable to find literature indicating the possible nature of functional groups with peaks in this region. The bands in the region of 3896 to 3442 cm^{-1} could be assigned to N-H stretching [Guillen et al., 1992, 1995]. 3050 cm^{-1} and the weak peak at 2923 cm^{-1} could be assigned to aromatic and aliphatic C-H stretching vibrations [Alcañiz-Monge et al., 2001; Strydom et al., 2011]. Bands in the region ranging from 700 to 900 cm^{-1} were assigned to out-of-plane aromatic compounds [Papole et al., 2012]. Peaks at 1436 cm^{-1} are due to CH_3 and CH_2 linkages [Guillen et al., 1992, 1995; Alcañiz-Monge et al., 2001,]. Peaks at 1597 cm^{-1} are due to carbonyl compounds, as well as aromatic C=C. The peak at 1253cm^{-1} is due to aryl ethers, aryl oxygen [Ibara et al., 1989], with bands at 1173 and 1065 cm^{-1} being assigned to clay minerals.

In order to visualise the differences between the FT-IR spectra of the raw (as-received) and CTP samples thermally pre-treated at 475 °C, the FT-IR spectra of a raw and 475 °C pre-treated CTP samples are shown in Figure 5.7. Only the relevant FT-IR spectra for CTP 2 and 3 are indicated. Similar results were obtained for all the other CTP samples. However, these specific samples (CTP 2 and 3) were chosen since the peak intensities at approximately 3000 cm^{-1} were almost the same, which helps to identify significant differences.

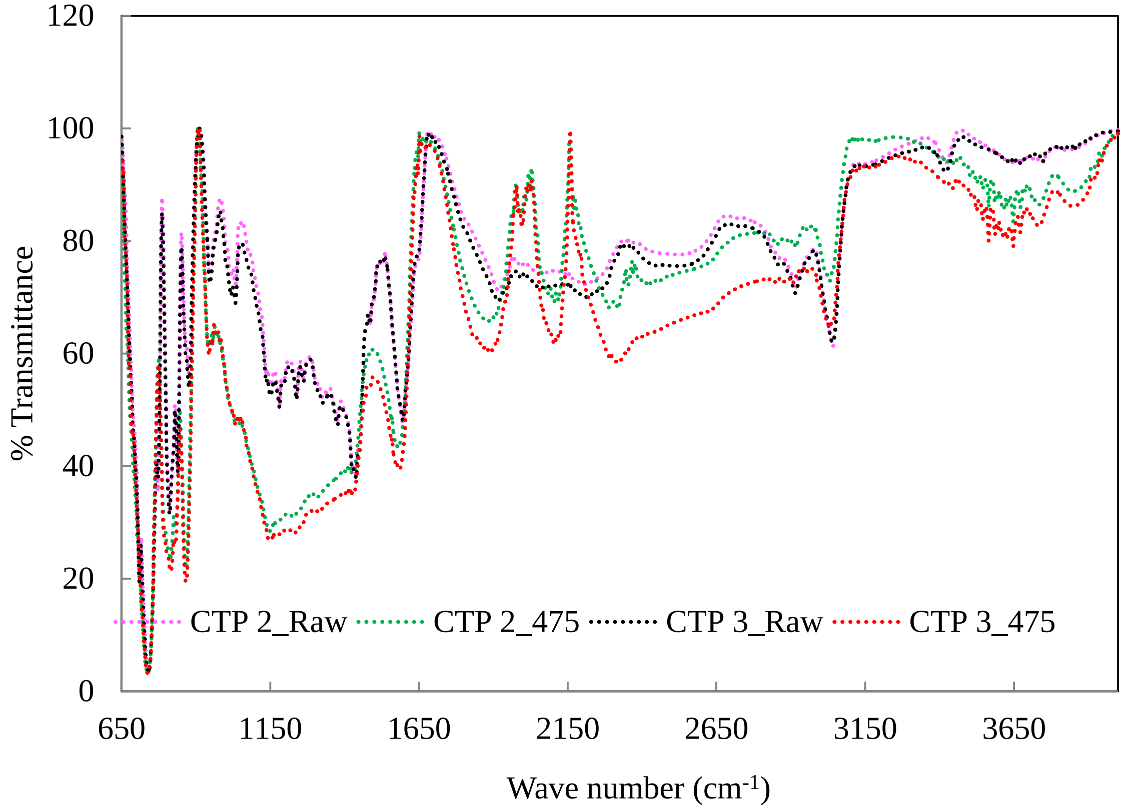

Figure 5.7 Comparison of FT-IR spectra of raw and thermally pre-treated (at 475 °C) CTP for CTP samples 2 and 3

During thermal treatment of CTP, polymerisation, poly-condensation, thermal degradation reactions, as well as fragmentation of organics occur. These reactions lead to a loss of some functional groups such as OH groups. Aromatic, aliphatic modes as well as CH_3 and CH_2 linkages are broken during thermal treatment. These are converted into volatile components, which were evolved and observed during thermal treatment [Yue and Watkinson, 1998; Alcañiz-Monge et al., 2001]; therefore, a reduction in the peak intensities of the above-mentioned functional groups in thermal treated pitch samples. The reactions that take place during thermal treatment can also lead to the formation of new compounds (see section 2.3.3 for the reaction path way during the carbonisation of CTP).

5.4 Conclusions

The results presented in this chapter confirmed that TMA is a useful tool to assess the dimensional behaviour of CTP samples. Thermal pre-treatment and subsequent TMA analysis indicated that the baking isotherm temperature of CTP used as a binder in Söderberg pastes lies between 450 and 475 °C. It was found that this temperature is independent of the initial physical and chemical composition of the CTP. As far as the candidate could assess, this is a novel finding, which will help operational personnel at smelters utilising Söderberg electrode systems to manage their electrodes better. A better defined temperature range for the baking isotherm temperature will allow more precise electrode management and therefore lead to improved operational stability and reduced safety risks. These findings also provide researchers with new questions that need to be answered to better understand these complex systems.

Although FT-IR analysis could not be used to quantify the different functional groups in the CTP samples, it indicated that the raw CTP samples were similar in composition, only differing in terms of the fractional composition of the various functional group compounds as confirmed by NMR (Figure. 4.1 and Table 4.4). The 475 °C pre-treated CTP samples also had similar FT-IR spectra (Figure.5.6), but these spectra differ from that of the raw CTP samples. This indicates that the organic functional groups (mainly in the triple bond region, i.e. 1909 -2350cm^{-1}) present in the CTP samples changed as a result of the thermal pre-treatment. This also implies that similar functional group compounds are lost (no peaks observed at 2913 cm^{-1} correlating to aliphatic and alicyclic CH_3, CH_2 and CH groups) and that new ones are formed (new peaks observed at 2691 cm^{-1} in thermally treated CTP at 475°) during the transition of a molten CTP to a solid carbonaceous material, irrespective of the initial composition of the CTP.