

CHAPTER V

THERMAL ANALYSIS OF HYDROGENATED RUBBER PRODUCT

5.1 Introduction

The field of thermal analysis (TA) of polymers has expanded greatly since the introduction of simple, inexpensive instruments for several types of thermal measurements during the past 20 years. The term thermal analysis is frequently used to describe analytical experimental techniques, which investigate the behaviour of a sample as a function of temperature. Thermal analysis refers to conventional thermal analysis techniques such as differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetry (TG), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA) [56].

The advantages of thermal analysis over other analytical methods can be summarized as follows: (i) the sample can be studied over a wide temperature range using various temperature programs; (ii) almost any physical form of sample (solid, liquid, or gel) can be accommodated using a variety of sample vessels or attachments; (iii) a small amount of sample (0.1 μg - 10 mg) is required; (iv) the atmosphere in the vicinity of the sample can be standardized; (v) the time required to complete an experiment ranges from several minutes to several hours; and (vi) thermal analysis instruments are reasonably priced. In polymer science, preliminary investigation of the sample transition temperatures and decomposition characteristics is routinely performed using thermal analysis. Many investigators have used thermal analysis for rubber research and development in many aspects. However, research work on thermal properties of hydrogenated rubber are limited. Y. Doi et al. [35] studied the thermal properties of hydrogenated polybutadienes using $\text{RhCl}(\text{PPh}_3)_3$ by differential scanning calorimetry. Singha et al. [7] reported that the degradation temperature of hydrogenated natural rubber using $\text{RhCl}(\text{PPh}_3)_3$ increases with the degree of hydrogenation.

This Chapter focuses on a study of thermal properties of hydrogenated cis-1,4-poly (isoprene) products by thermal analysis. The thermal degradation of hydrogenated cis-1,4-

poly(isoprene) products compared with ethylene-propylene copolymers (EPDM) were investigated using thermogravimetric analysis (TGA). The differential scanning calorimeter (DSC) was used to determine the glass-transition temperature (T_g) of hydrogenated cis-1,4-poly(isoprene) products.

5.2 Experimental

5.2.1 Materials

The high molecular weight cis-1,4-poly(isoprene) with 97% *cis*-isomer was provided by Bayer Inc. The natural rubber grade TSR 5L was provided by the Rubber Research Institute of Thailand. The EPDM rubber compound was obtained from Bayer Inc. The hydrogenated cis-1,4-poly(isoprene) samples using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ (HPIOs) were prepared at the central condition as follows: $[\text{Os}] = 70 \mu\text{M}$; $P_{\text{H}_2} = 20.7 \text{ bar}$; $[\text{C}=\text{C}] = 260 \text{ mM}$; $T = 130^\circ\text{C}$. The hydrogenated cis-1,4-poly(isoprene) using $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ (HPIIr) were also prepared at the base condition as follows: $[\text{Ir}] = 90 \mu\text{M}$; $P_{\text{H}_2} = 27.6 \text{ bar}$; $[\text{C}=\text{C}] = 246 \text{ mM}$; $T = 130^\circ\text{C}$. The hydrogenated natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ (HNR) were obtained from the condition as follows: $[\text{Os}] = 80 \mu\text{M}$; [3-chloropropionic acid] = 0.06%w/v; $[\text{C}=\text{C}] = 260 \text{ mM}$; $P_{\text{H}_2} = 41.4 \text{ bar}$; $T = 140^\circ\text{C}$.

5.2.2 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis of the samples was carried out in NETZSCH STA 409C. The rubber sample (12 mg) was placed in the aluminium crucible. The temperature was raised under nitrogen atmosphere from room temperature to 800°C at constant heating rate of $10^\circ\text{C}/\text{min}$. The nitrogen gas flow rate was 50 mL/min. The onset of degradation, the weight loss due to degradation and the residue remaining at 800°C were measured. The initial decomposition temperature (T_{id}) and the temperature, at which the rate of mass loss (T_{max}) is at a maximum, were evaluated.

5.2.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was conducted using NETZSCH DSC 200. For the heat flux DSC, the instrument signal is derived from the temperature difference between the sample and the reference. The equipment was calibrated using indium. Approximately, 15-18 mg of rubber samples prepared in a crimped aluminium pan was cooled in the cell to -100°C with liquid nitrogen and then heated at a constant rate of $10^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere to 150°C . The midpoint of the base-line shift was taken as the glass-transition temperature.

5.3 Results and Discussion

5.3.1 Thermogravimetric Analysis

Thermogravimetric analysis of cis-1,4-poly(isoprene), hydrogenated cis-1,4-poly(isoprene) using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ and $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ (HPIOs and HPIIr), hydrogenated natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$, and EPDM rubber compound were conducted under nitrogen atmosphere. The TG curve of rubber samples is shown in Figure 5.1 and 5.2. The TG curve of all rubber samples is one-step and provides a smooth weight loss curve. This indicates that the degradation could be an overall one-step reaction. Under nitrogen, there is no weight loss up to 400°C , indicating the stability of hydrogenated cis-1,4-poly(isoprene) and hydrogenated natural rubber in this temperature range. An initial weight loss occurs between $420\text{-}450^{\circ}\text{C}$ due to the degradation. A 100% weight loss occurred at 500°C , where at this stage all the hydrocarbon elements of rubber change to carbon and gases indicating total degradation.

The initial decomposition temperature (T_{id}) was determined from the intersection of two tangents at the onset of the decomposition temperature. The maximum decomposition temperature (T_{max}) was evaluated from the peak maxima of the derivative of the TG curve. Table 5.1 summarizes the T_{id} and T_{max} of all rubber samples. The degradation temperature (T_{id} and T_{max}) of hydrogenated cis-1,4-poly(isoprene) using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ and $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ and hydrogenated natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ are higher than that of cis-1,4-poly(isoprene) and natural rubber. The results suggest that the

degradation temperature increased with increasing the reduction of carbon-carbon double bond in the cis-1,4-poly(isoprene) and natural rubber. It can be explained that the C=C bond in cis-1,4-poly(isoprene) and natural rubber consist of strong σ bond and a weak π bond and that the hydrogenation reaction involves the break of a weak π bond by the hydrogen molecule to a strong C-H σ bond, which demonstrates its higher thermal stability.

The ^{13}C -NMR characterization of hydrogenated cis-1,4-poly(isoprene) in section 2.3.1 shows that the quantitative hydrogenation of cis-1,4-poly(isoprene) leads to an alternating ethylene-propylene copolymers. Comparing with the standard EPDM rubber compound, the degradation temperature of hydrogenated cis-1,4-poly(isoprene) using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ and $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ and hydrogenated natural rubber become very close to an EPDM rubber compound. It can be concluded that the quantitative hydrogenation of cis-1,4-poly(isoprene) and natural rubber provides a facile entry to alternating ethylene-propylene copolymers. The thermogravimetric analysis of hydrogenated cis-1,4-poly(isoprene) and hydrogenated natural rubber agrees very well with the results of Singha et al. [7] that the degradation temperature of hydrogenated natural rubber using $\text{RhCl}(\text{PPh}_3)_3$ increased with increasing degree of hydrogenation.

Table 5.1 The Degradation Temperature of Rubber Samples.

Rubber sample	T_{id} ($^{\circ}\text{C}$)	T_{max} ($^{\circ}\text{C}$)
Cis-1,4-poly(isoprene)	346.2	367.0
Natural rubber	360.8	385.6
HPIOs	427.1	448.0
HPIIr	420.0	440.0
HNR	426.6	458.3
EPDM	447.4	455.0

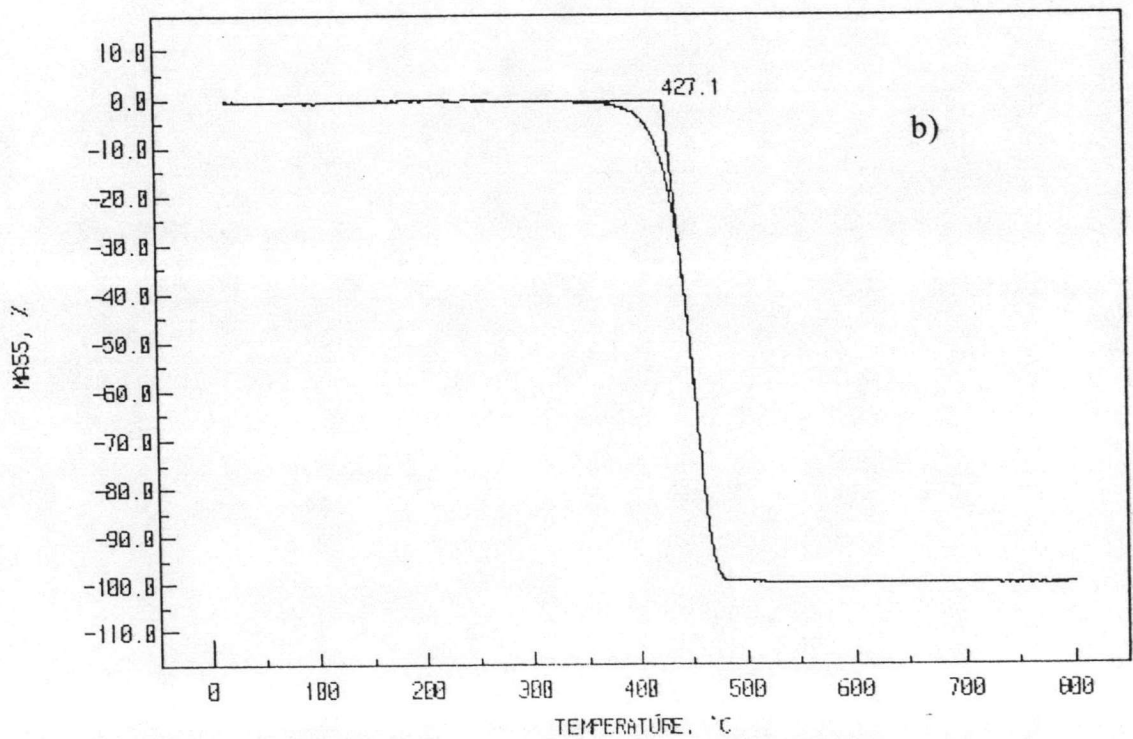
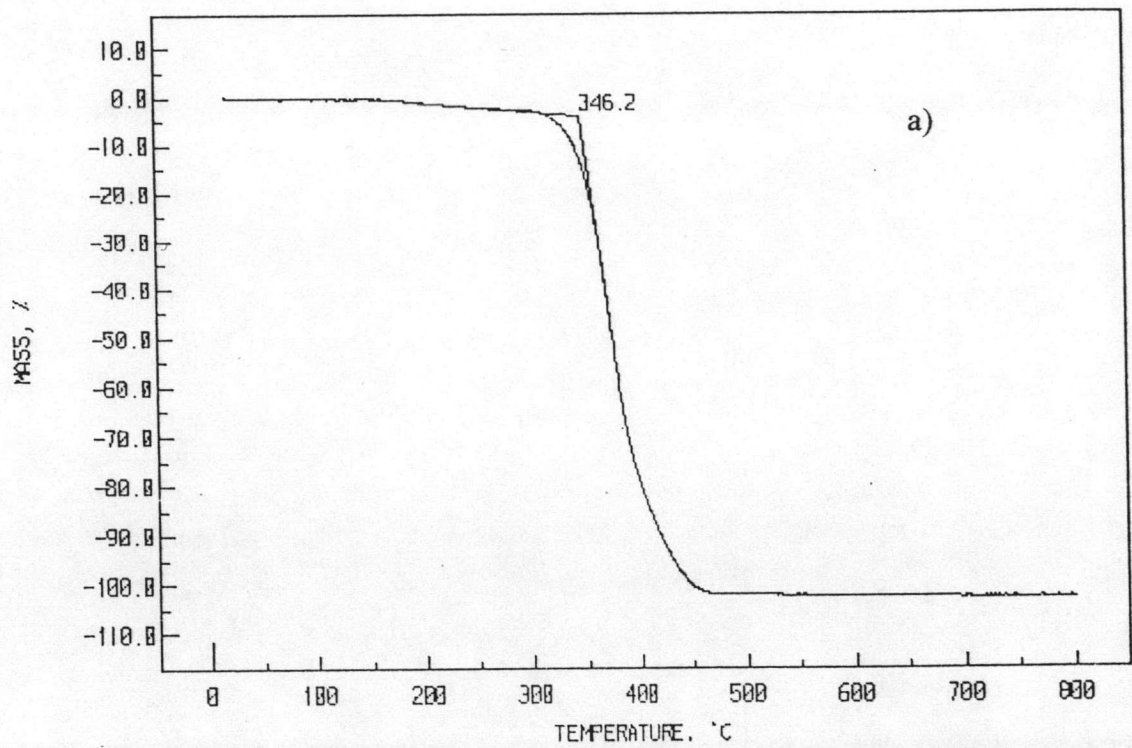


Figure 5.1 The thermogravimetric curve of rubber samples. a) cis-1,4-poly(isoprene) b) HPIOs c) HPIIr and d) EPDM.

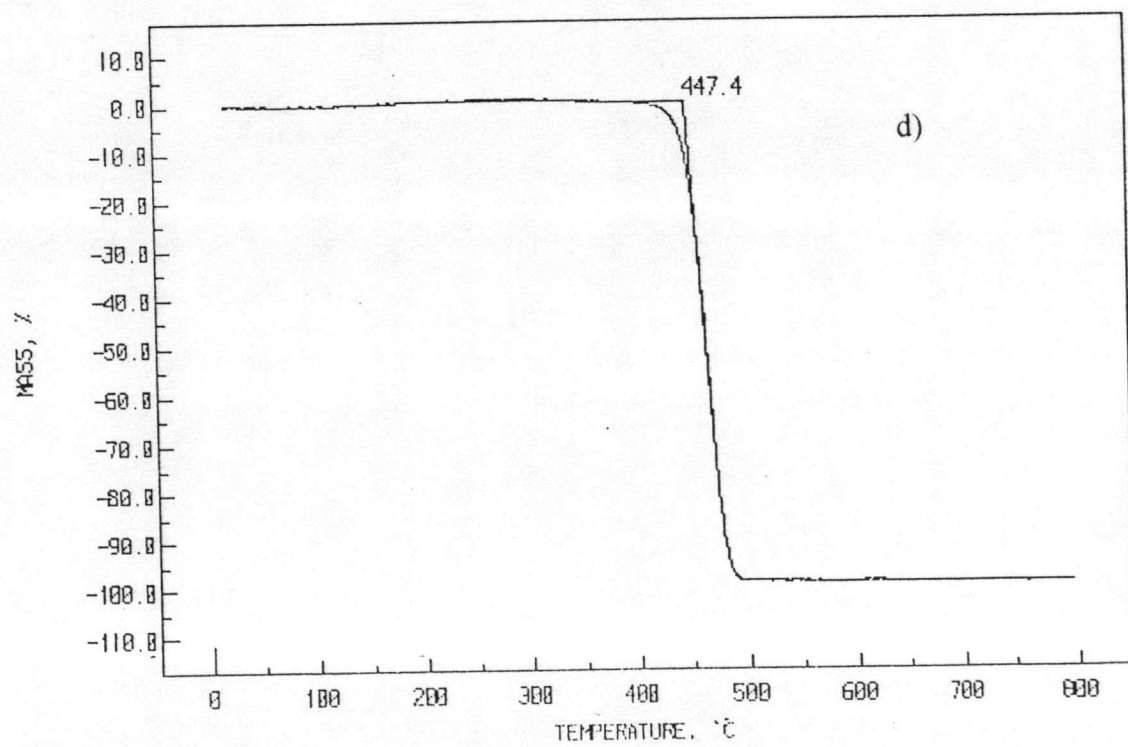
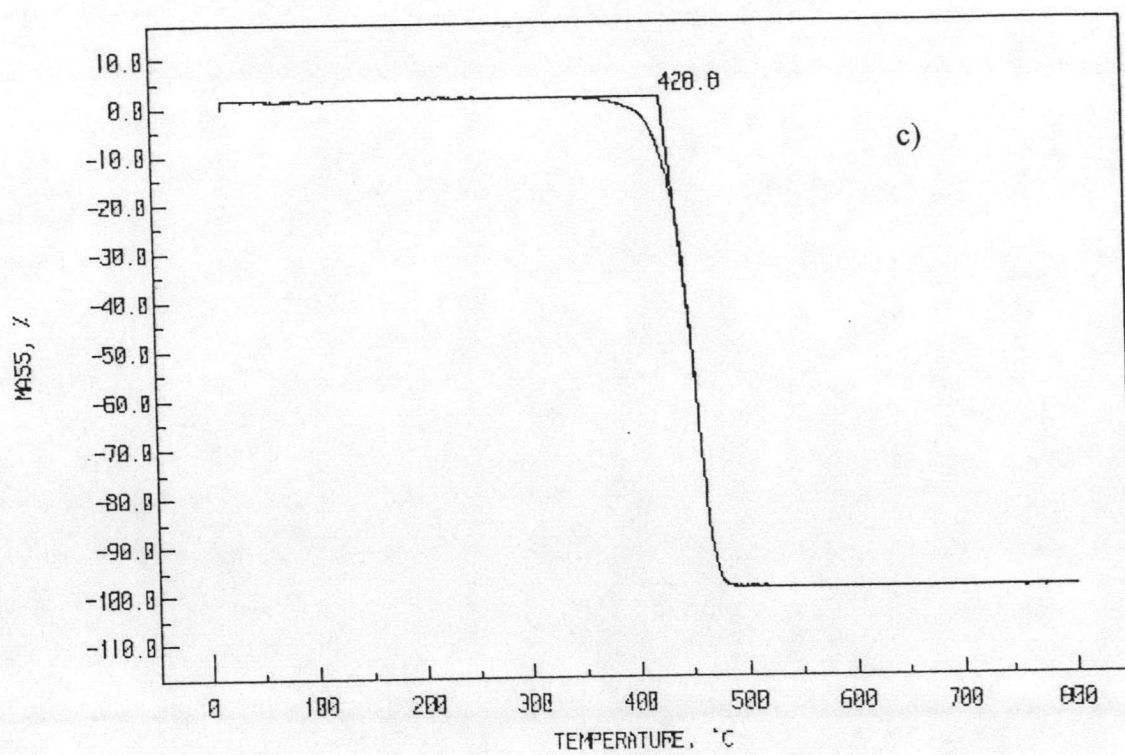


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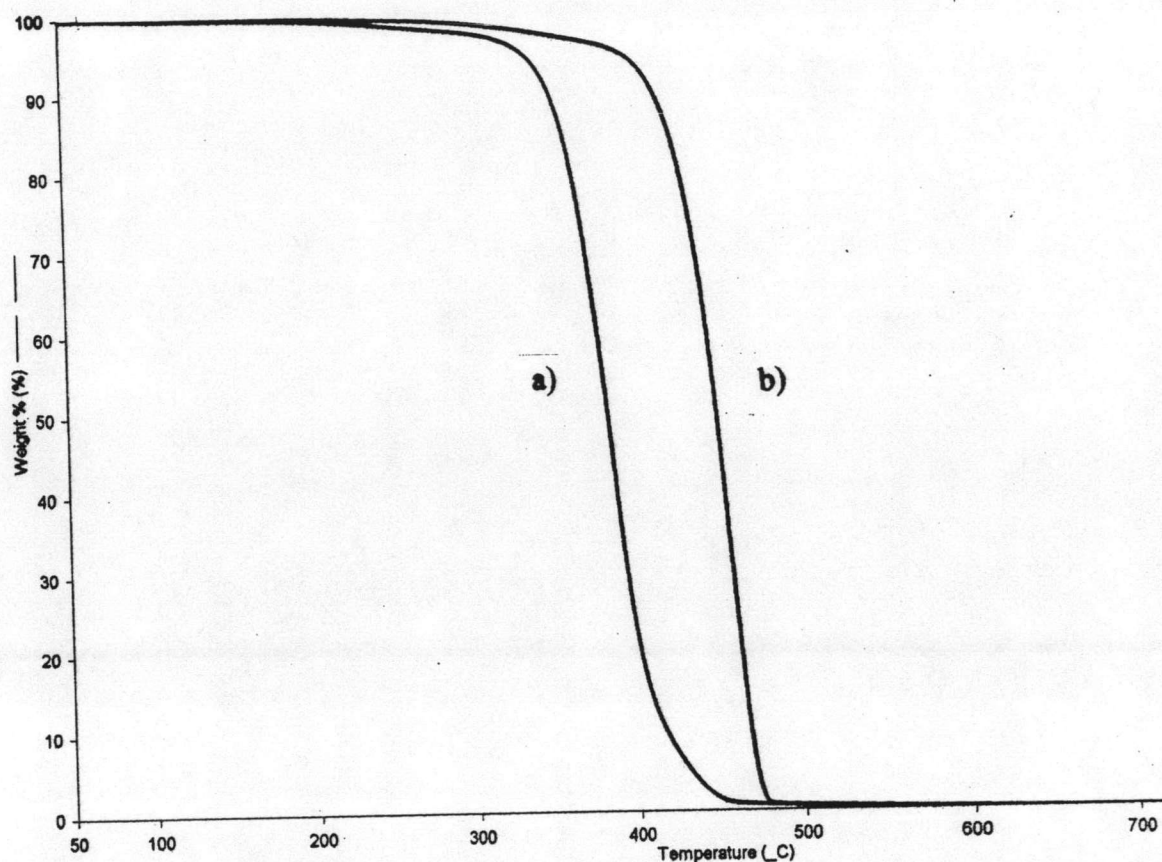


Figure 5.2 The thermogravimetric curve of rubber samples. a) natural rubber and b) hydrogenated natural rubber.

5.3.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was used to determine the glass transition temperature (T_g) of hydrogenated rubber. The glass transition temperature is the temperature at which the amorphous domains of a polymer take on the characteristic properties of the glassy state—brittleness, stiffness, and rigidity [57]. This was determined from the midpoint of the base-line shift of the DSC thermogram. The DSC thermograms of the cis-1,4-poly(isoprene), hydrogenated cis-1,4-poly(isoprene) using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ and $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$, and EPDM rubber compound are shown in Figure 5.3. The DSC thermograms

of the natural rubber and hydrogenated natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ are presented in Figure 5.4. The DSC thermograms of all rubber samples show only one step base-line shift, which demonstrates a single glass transition temperature. A single glass transition temperature of hydrogenated rubber products suggests that possibly that no side reactions occurred during the catalytic hydrogenation process.

Table 5.2 The Glass Transition Temperature Value of Rubber Samples

Rubber sample	T_g ($^{\circ}\text{C}$)
Cis-1,4-poly(isoprene)	-55.5
Natural rubber	-57.0
HPIOs	-52.2
HPIIr	-52.6
HNR	-56.3
EPDM	-29.7

The glass transition temperature as obtained from DSC thermogram is presented in Table 5.2. The cis-1,4-poly(isoprene) and natural rubber which has a the T_g of -55.5°C and -57.0°C , respectively demonstrate the rubber properties at room temperature and the glass properties at below T_g . The standard EPDM rubber compound having the higher T_g of -29.7°C exhibits more degree of crystallization in the polymer structure than that of the cis-1,4-poly(isoprene) and natural rubber. The hydrogenated rubber samples display a slight decrease of T_g compared to the T_g of the cis-1,4-poly(isoprene) and natural rubber. It can be concluded that the hydrogenation of cis-1,4-poly(isoprene) and natural rubber do not affect the glass transition temperature. The hydrogenated rubber products still demonstrate high amorphous properties. This agrees very well with the results of natural rubber hydrogenation using $\text{RhCl}(\text{PPh}_3)_3$ where no effect on the T_g of the hydrogenated natural rubber product was observed [7].

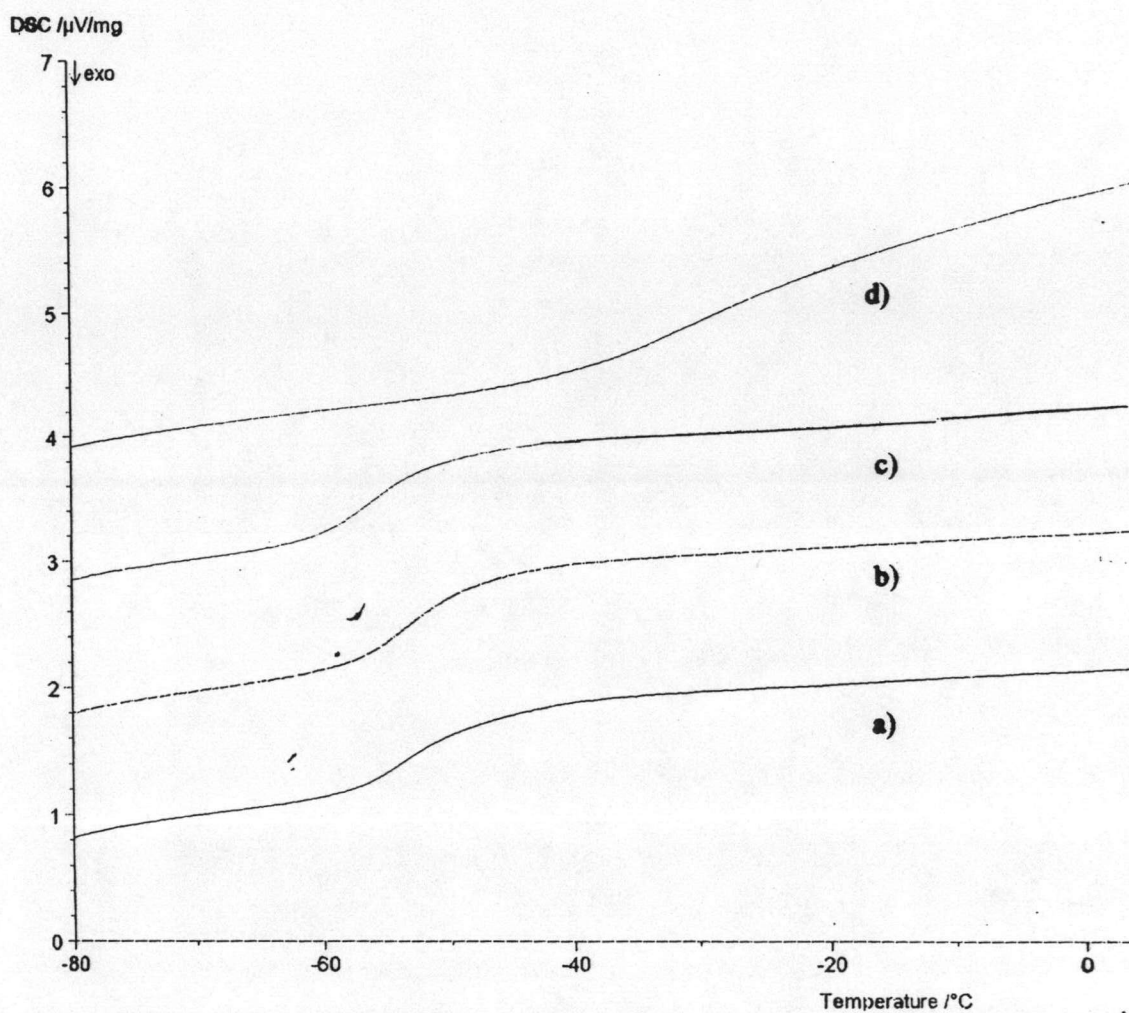


Figure 5.3 The DSC thermogram of rubber samples. a) cis-1,4-poly(isoprene) b) HPIOs. c) HPIIr and d) EPDM.

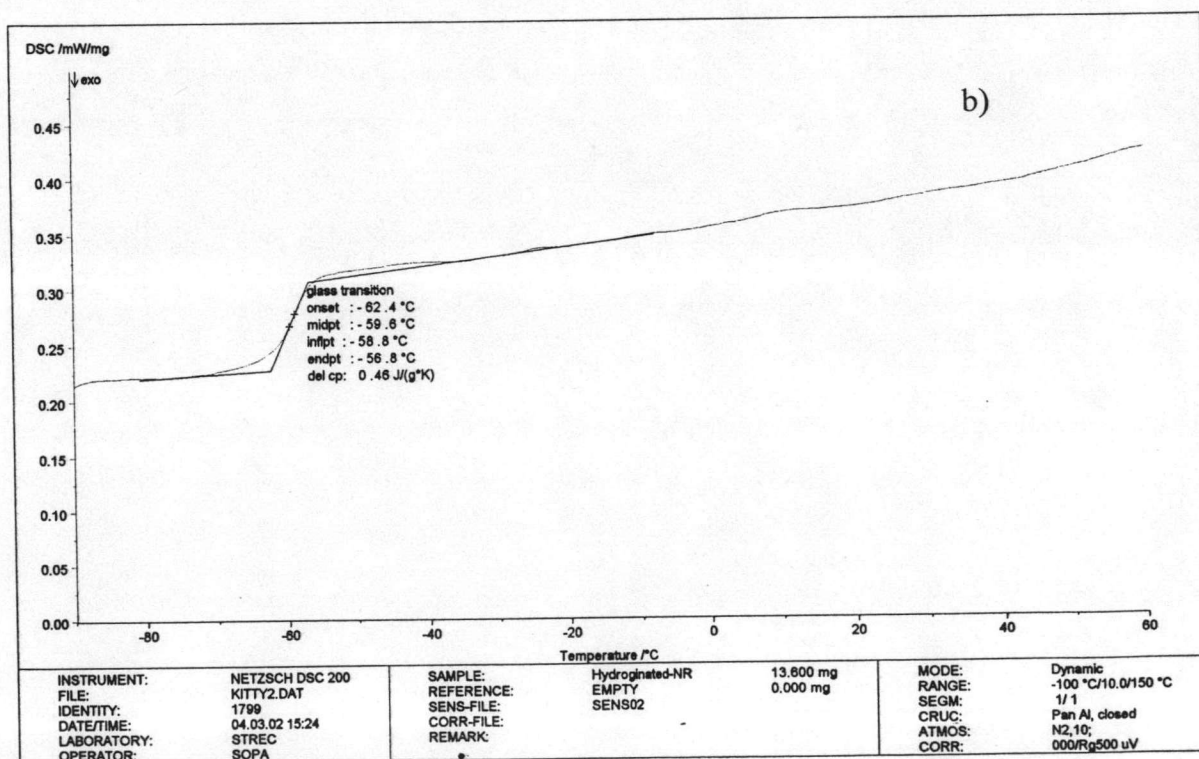
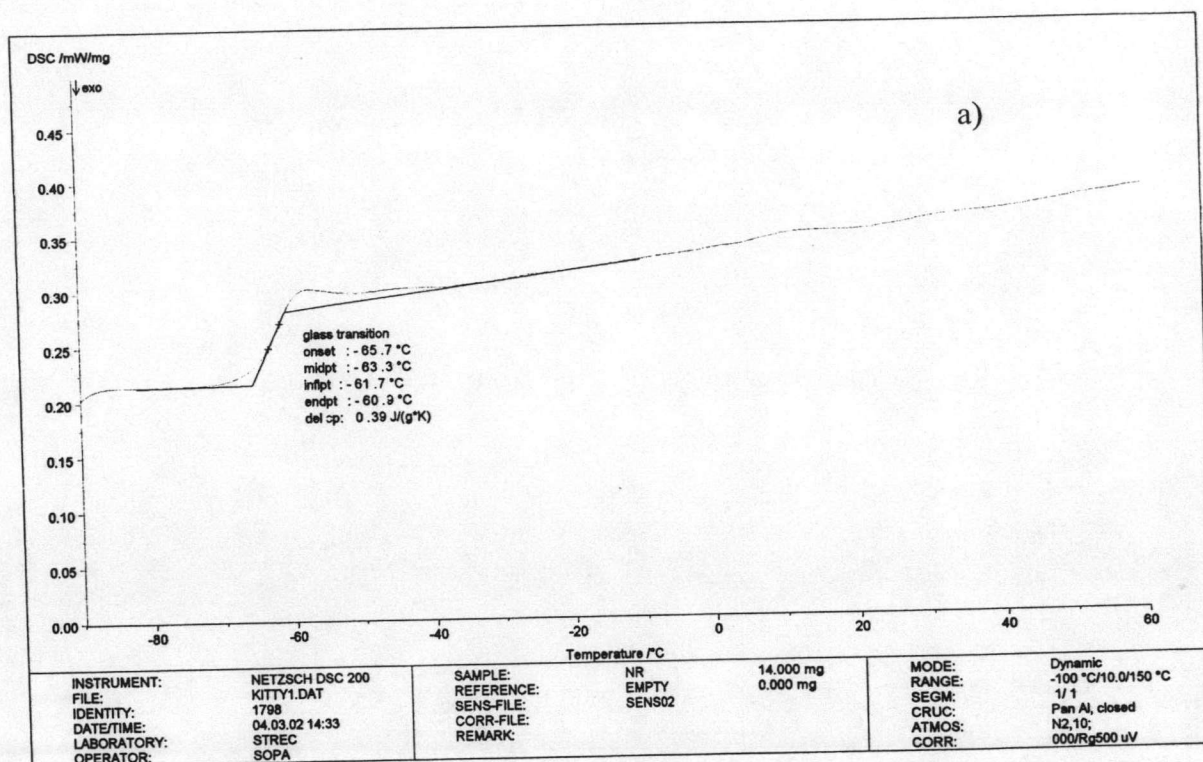


Figure 5.4 The DSC thermogram of rubber samples. a) natural rubber and b) hydrogenated natural rubber.

5.4 Conclusions

Thermogravimetric analysis and differential scanning calorimetry were used to characterize the thermal properties of hydrogenated cis-1,4-poly(isoprene) using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ and $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ and hydrogenated natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$. The increase in the degradation temperature (T_{id} and T_{max}) of hydrogenated rubber products demonstrates that hydrogenation increases the thermal stability of cis-1,4-poly(isoprene) and natural rubber. The glass transition temperature (T_g), measured from DSC, is consistent with the compositional analysis from TGA. A single T_g value of hydrogenated rubber products suggested that there was possibly no side reaction during the hydrogenation process. The hydrogenation reaction did not affect the T_g value of the hydrogenated cis-1,4-poly(isoprene) and hydrogenated natural rubber.