Thermal decomposition of waste polymers

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ABSTRACT

In this work the thermal decomposition of elastomeric polymers was studied. The pyrolysis of
scrap rubber samples was carried out under nitrogen atmosphere over a temperature range of
20-800 $^{\circ}$C using a heating rate of 5 $^{\circ}$C/min. Thermogravimetric (TG) and Differential
Scanning Calorimetric (DSC) curves of rubber samples are discussed. The DTG curves show
two different peaks corresponding with the decomposition of different components presented
in the rubber blends. Using thermogravimetric data the kinetic parameters of thermal
decomposition were estimated.

Key words
Thermal decomposition, pyrolysis, kinetic of pyrolysis, scrap tyre, waste rubber

1. INTRODUCTION

The excellent properties of polymeric materials let them penetrate in all spheres of human
life; now they are completely irreplaceable and absolutely necessary for people. However,
these excellent properties represent at the same time a disadvantage of these materials: they
are not quickly decomposed under the influence of the environment aggressive factors as
light, heat, atmosphere gases, microorganisms and continue to exist in the form of a long-
living waste, inflicting an irreparable damage to the nature.
As though namely people manufacture polymeric materials to satisfy their needs, they also
have to protect the nature from a negative influence of synthetic materials. Therefore, to
continue using of polymeric material growing volumes, mankind have urgently develop
effective methods of polymeric materials utilization and disposal.
In EU the optimum waste management strategies are now becoming key political targets,
reflected by the high level of investment in both demonstrating and integrating existing
technologies, and the development of fundamental research into new ideas. European
legislation and public pressure are furthermore adding weight to the need for a sustainable
solution in the very near future.
Thermoplastic such as polyethylene (PE), polypropylene (PP), Polyethylene terephthalate
(PET), polyvinyl chloride (PVC), polystyrene etc.) are not croslinked and usually we can they
remould by simple thermal treatment. PET bottles, PE and PP coats and bags, PVC carpets,
Polystyrene foams and many others are the examples of wastes made from thermoplastics.
Wide application of polymers for polyvinylchloride window block construction have set a
new target - utilization of these window blocks after 20 years of their operation.
The three main methods of plastic recycling are:
-   Mechanical Recycling, the re-processing of the plastic materials into new products.
-   Feedstock Recycling, the processing of plastics into basic chemicals.

- Energy Recovery, the recovery of valuable energy from waste plastic through incineration.

Pyrolysis offers an alternative way of polymer recycling and a solution for recycling thermoplastics, for that other recycling methods are not effective. Recycling of polymers by pyrolysis could be an environmentally and economic attractive method. Pyrolysis belongs into feedstock recycling methods. Feedstock recycling is defined as a change in the chemical structure of the material, where the resulting chemicals are used for another purpose than producing the original material.

Used tyres and other elastomer wastes create a considerable part of croslinked thermoset polymeric wastes. Thermoset polymers cannot be simply recycled by heating and remoulding, however, a number of methods for their recycling are known [1]. Generally tyre recycling methods can be divided by the same scheme as plastic recycling:

Due to crosslinked structure of rubber vulcanizates, pyrolysis seems to be the most effective way for tyre recycling. In a pyrolysis reactor the shredded tyres are decomposed into pyrolysis products received in all three phases: solid char (30-40 wt%), liquid residue (50-60 wt%), and gases (3-20 wt%) [1].

Studying thermal decomposition of polymers in laboratory scale apparatuses let us more understand the mechanism of the pyrolysis process leading to the process optimisation.

In this work thermal decomposition of elastomeric polymers is studied. The TG (Thermogravimetric) and DSC (Differential Scanning Calorimetric) curves of different rubber samples are analyzed.

2. EXPERIMENTAL

Materials and samples

Rubber samples prepared from two parts (side wall and tread) of a used MATADOR passenger car tyre for TG and DSC analysis.
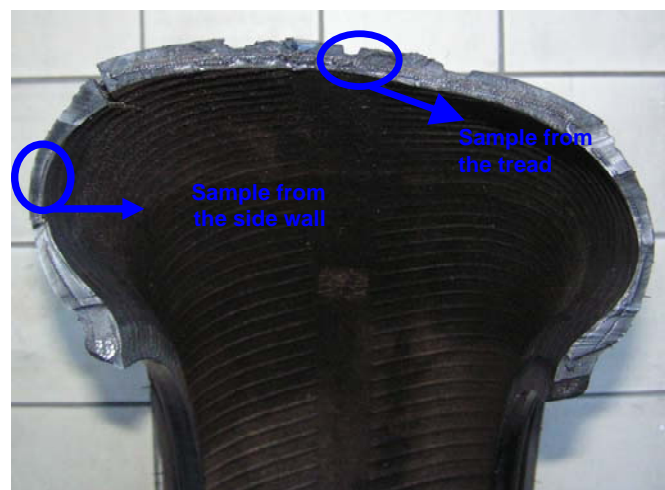

Figure 1: Degradation temperature region during rubber pyrolysis

Experimental method

The simultaneous TG/DSC analyser NETZSCH STA 409PC, was used for both thermogravimetric and differential scanning calorimetric analyses performed simultaneously. The weight of the sample war around 50 mg. As inert atmosphere for thermal decomposition

0.99999 nitrogen with a total flow rate 40 ml/min was used. The behaviour of the thermal decomposition was studied in a temperature range from 20 to 800°C using a heating rate of 5 K/min.
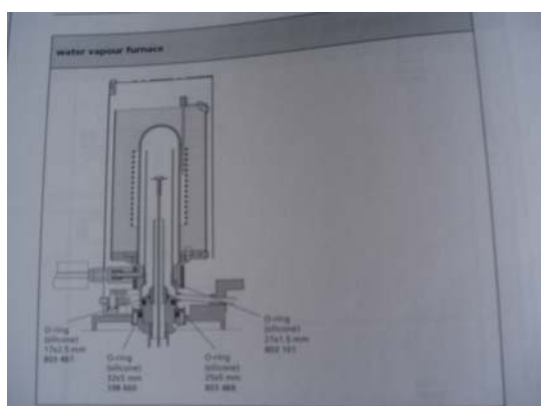

Figure 2: simultaneous TG/DSC analyser

3. RESULTS AND DISCUSSION

The behaviour of the thermal decomposition of rubber is generally studied by thermogravimetric analysis. From the thermogravimetric analysis provided by various authors [2][3] [4] results that more than one degradation temperature region during rubber pyrolysis is recorded. As it is shown in Figure 5, our measurements sustain this fact.

The behavior of the TG and DSC curves of two different scrap tyre samples measured simultaneously is shown in Figures 3 and 4. The TG curve of sidewall sample indicates that its thermal decomposition begins at a temperature of 210°C and practically finishes at 510°C. In the temperature range from 210 to 315°C volatile additives are released. From 315°C probably also decomposition of NR starts, this suggest the derivative thermogravimetric (DTG) curve of this sample (Figure 5). The DTG curve of the sidewall sample shows two peaks one with an extreme at 370°C and one with an extreme at 445°C. By comparing these values with the results of thermal degradation of individual types of rubbers in the literature [5] (for NR 375°C, for SBR 445°C, and for BR 465°C), we see that the first peak corresponds with the decomposition of NR and the second peak with the decomposition of SBR. However, Seidelt et al. [5] reported, that SBR is decomposed in two steps. The first step starts at 360°C and represents the release of styrene, and the second step represents the release of the main butadiene decomposition product, 4-vinylcyclohexane,which starts at 420°C. For this reason the first peak in DTG curve of the tyre sidewall can be caused also by a release of styrene from SBR.

The DTG curve of the sample from the tyre tread (Figure 6) does not show clearly two peaks. This curve, however, reveal the release of volatiles in the temperature range (200-330°C). The only dominant peak with a maximum at 440 ^{o}C represents a release of SBR, which is in tyre tread the main type of polymer.

The derivative differential scanning calorimetric (DDSC) curves of both samples (Figure 7) show an endothermic character in general with one main endothermic peak, and also one exothermic peak located before the main endothermic peak. This endothermic character of the thermal decomposition was expected. The exothermic peak can be caused by oxidation of released volatiles by oxygen liberated during the thermal decomposition or by some residual oxygen in the apparatus due to its insufficient remove from the device. The heats of thermal

decomposition calculated for the tyre sidewall and the tyre tread sample are 291 J/g and 324J/g, respectively.
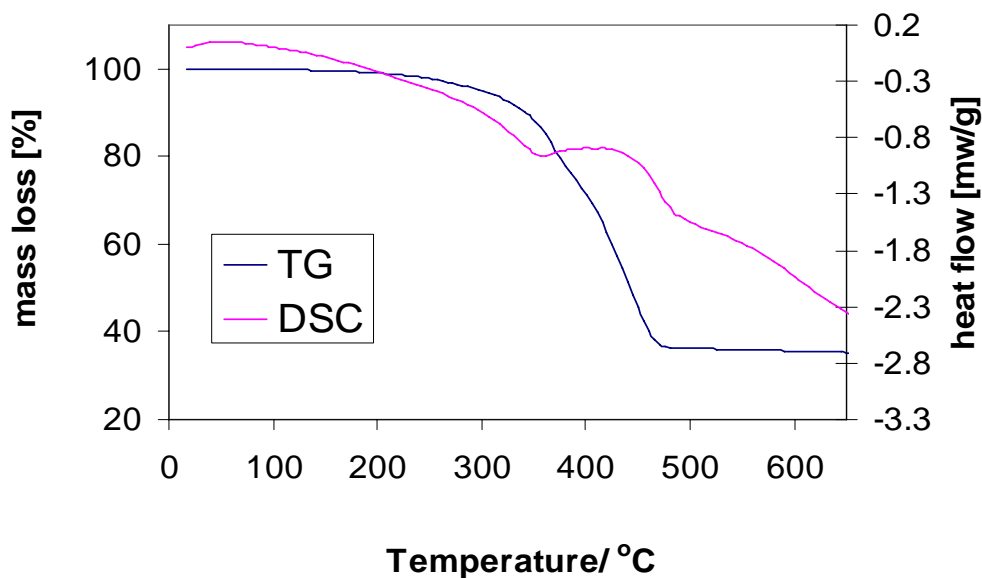

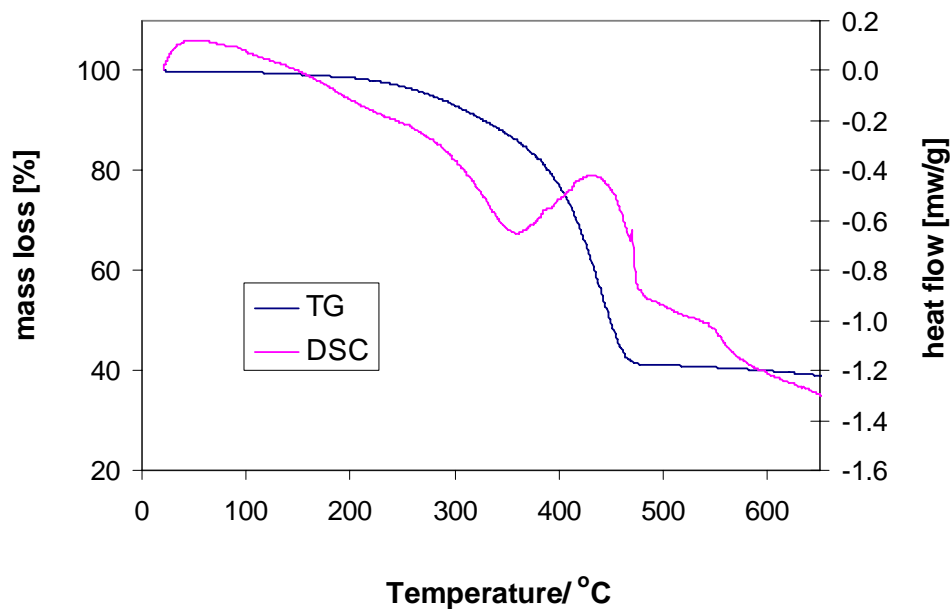Figure 3: TG and DSC curves of tyre sidewall sample

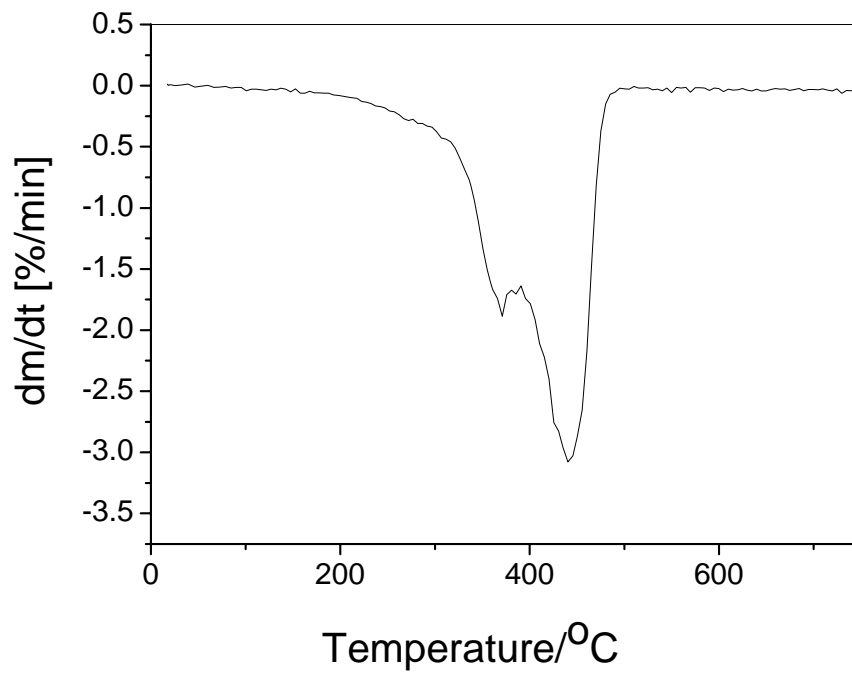Figure 4: TG and DSC curves of tyre tread sample
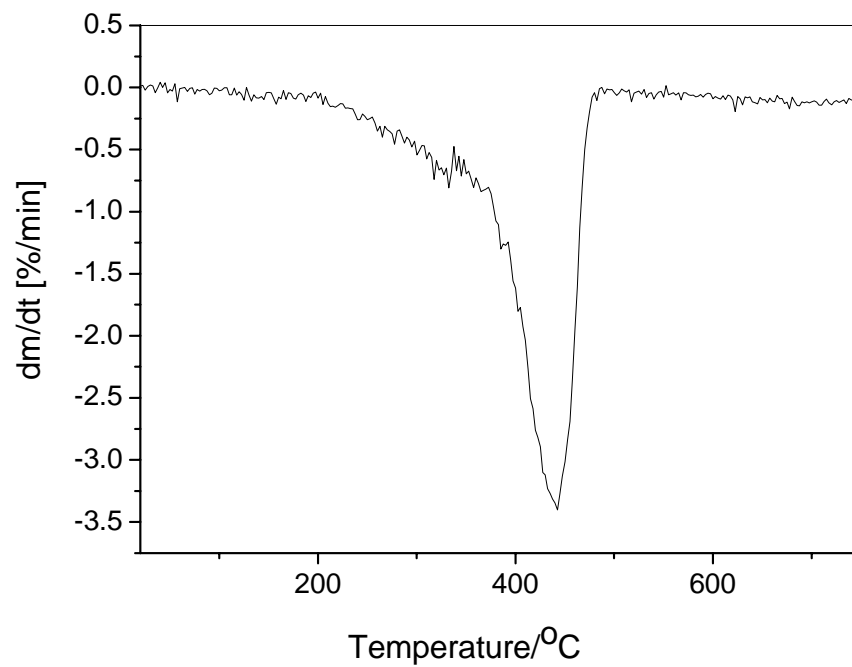
Figure 5: DTG curve of tyre sidewall sample

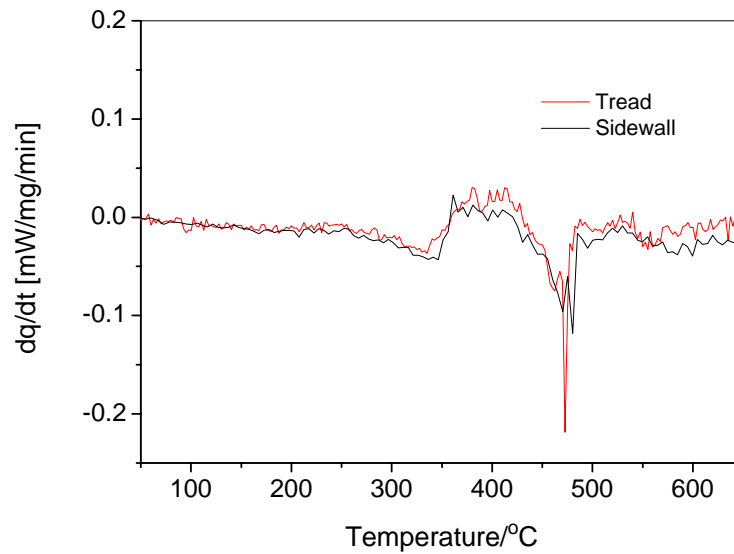

Figure 6: DTG curve of tread sample

Figure 7: DDSC curves of tyre samples

Kinetic properties of the scrape tyre thermal decomposition

Due to a very complex composition of rubber compounds used in the tyre and also due to multiple unknown chemical reactions during the tyre decomposition, usually the kinetics of this process is described by the use of experimental thermogravimetry data. The first order reaction based on the Arrhenius theory is commonly assumed by researchers in the kinetic analysis of data for tyre decomposition. The rate of decomposition may be expressed by:

$$\frac{dX}{dt} = k.\left(1-X\right)^n \tag{1}$$

The rate coefficient is calculated by the Arrhenius equation:

$$k = A.\exp^{\left(-\frac{E}{R.T}\right)} \tag{2}$$

In this equation k is the rate constant; A is the apparent pre-exponential factor, E is the apparent activation energy, n is the reaction order, R and T are the universal gas constant and absolute temperature, respectively. The reaction conversion (X) was calculated according to the following equation:

$$X = \frac{m_0 - m_i}{m_0 - m_{final}} \tag{3}$$

where m_0 is the initial sample mass, m_i is the sample mass at arbitrary time and m_{final} is the final mass of the sample.

In the case of multistep decomposition, a multistep rate equation, which is a sum of individual step's rate equations could be used (equation 4). However, estimating kinetic parameters from this equation requires separation of thermogravimetric data into intervals for individual reactions. This kind separation of thermogravimetric data is usually very difficult.

$$\frac{dX}{dt} = \sum_{i=1}^{s} \frac{dX_i}{dt} = \sum_{i=1}^{s} A_i \exp\left(-\frac{E_i}{RT}\right)(1-X_i)^n \qquad (4)$$

In equation 4 s represents the number of mass loss regions or decomposition steps.

The distance between the first and the second pyrolysis stage depends on the composition of the tyre rubber. Due to a small distance between the first and the second pyrolysis stage of our samples, we modelled the thermal decomposition as a single stage process. The parameters of equation 1 and 2 were obtained using experimental thermogravimetric data and an optimization programme developed in MATLAB.

In Table 1 are shown the estimated kinetic parameters and also for comparison kinetic parameters obtained by other authors. Compared to results of other authors our results show similar values of apparent activation energy and lower values of apparent per-exponential factor.

Table 1: Kinetic parameters of the scrap rubber decomposition

Author	Activation energy E (kJ/mol)	Pre-exponential factor, A (min-1)	Reaction order, n
This paper, sidewall	105.0	6.84×10^6	1
This paper, tread	96.0	1.52×10^6	0.8
Leung and Wang [3]	99.1-218.7	1.02×10^7-1.13×10^{17}	1
Yang et al. [4]	152 - 215	8.82×10^9-3.89×10^{16}	1-2
Kim et al. [6]	42.1 – 203.9	1.44×10^3- 2.04×10^{14}	-
Chen et al. [7]	147.6-148.1	5.02×10^{10}-$7.57*10^{10}$	1.63-1.98
Wiliams and Besler [8]	102.8-145.0	5.58×10^9-1.26×10^{10}	-

4. CONCLUSIONS

The TG, DTG, DSC and DDSC analyses of two different types of tyre rubber material were investigated. The DTG curve of the sample from the tyre sidewall can be characterized by two separate peaks with a maximum at 370 and 445°C, which correspond to a release of NR and SBR. The DTG curve of tyre tread sample shows only one dominant peak, but the release of volatiles also caused a deformation of this curve.

By analyzing DSC and DDSC curves the overall reaction heat of thermal decomposition was estimated. Values of 291J/g for sidewall rubber and 324 J/g for tread rubber was calculated. However, for both rubber materials also an exothermic peak was observed.

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