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ARAMID FIBER RECOVERY FROM WASTE COMPOSITE BY PYROLYSIS

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Abstract

Due to their outstanding mechanical properties and temperature resistance, aromatic polyamides are widely used for reinforcement in composite materials. The high consumption leads to an increasing waste generation. The recycling of composites requires a complex process, therefore the investigation of aramid fiber recovery is still in the middle of attention. In this study, the pyrolytic behavior of a waste aramid composite was investigated. Then laboratory-scale pyrolysis experiments were performed in a tubular reactor at 400 °C.

Keywords: *aramid, composite, pyrolysis*

1. Introduction

There is a great demand for composites with outstanding physical and chemical properties. The aromatic polyamides or so-called aramids are widely used as reinforcement during composite production. In *Figure* **1** the most common types of aramids can be seen, namely poly(p-phenylene terephthalamide) (PPTA), poly(m-phenylene isophthalamide) (MPIA), and copoly(p-phenylene/3,4'-diphenylether terephthalamide) (ODA/PPTA) [1], [2].

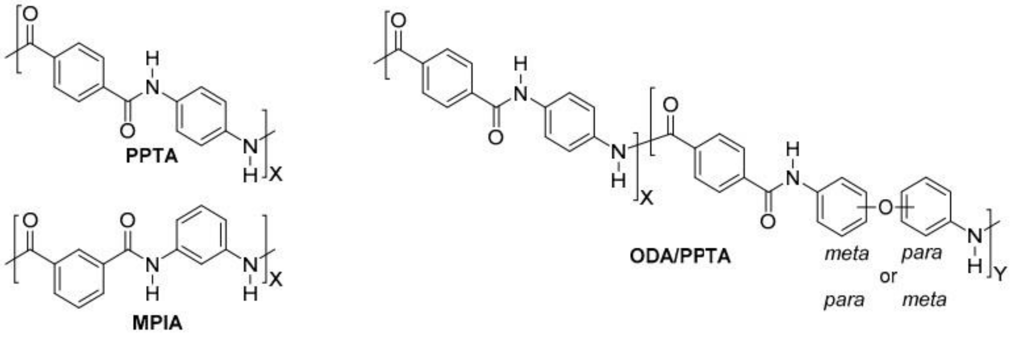

Figure 1. *Structure of the most common aramid types* [1]

The main advantages of aramids that they are cost-effective and keep their excellent physical and chemical properties even at high temperatures [3], [4]. Aramid fibers are sensitive to ultraviolet light, therefore ultraviolet absorbers or light screeners are often added to the fibers during manufacture [5]. The DuPont company developed the first commercial aramid, a meta-aramid in the 1960s and named Nomex. A decade later the same company produced a para-aramid with higher tenacity. This was introduced to the market under the name Kevlar [6]. Due to their high strength-to-weight ratio and temperature resistance, aramids are important materials in the military, aerospace and automotive industries [7], [8]. On an equal weight basis aramids have better mechanical properties, compared to steel and glass fibers [9].

According to the market research report [10] of the Research and Markets company in the next years further increase is expected in the demand for aramid fibers due to the advancements in the automotive and defense industries. Although, the rising production leads to higher waste generation, and composites require complex recycling processes. Depending on the composition of the composite, pyrolysis can be a possible way of aramid fiber recovery. In the recovery process, the matrix resin decomposes, while the reinforcement is left behind.

The pyrolysis process is conducted in the absence of oxygen to prevent the oxidation of the material. During the thermal degradation of the non-desirable components of the composite waste, oil, and gases are produced. According to the literature, after pyrolysis of fiber-reinforced polymers, the remaining fibers are contaminated and need a post-treatment in a furnace to burn the char particles [11].

Dabkiewicz et al. [7] studied a recycling method in aramid fibers/Neoprene composites *(Figure 2)*. They aimed to remove the Neoprene layer by pyrolysis. This step was followed by a washing process to remove the degraded Neoprene from the fibers. The thermal degradation was performed in 2 stages. In the first stage, the oven was heated up to 300 °C and remained at this temperature for 15 hours. Before the second stage, the 7 layers of the material were separated to create a larger contact area. Then, the furnace was heated up to 300 °C with a 5 °C/min heating rate. Then, the heating rate was decreased to 3.33 °C/min until the temperature reached 350 °C. The furnace was kept at this temperature for 5 hours. Although the separation was successful, a deterioration of the mechanical properties of the fibers was observed.

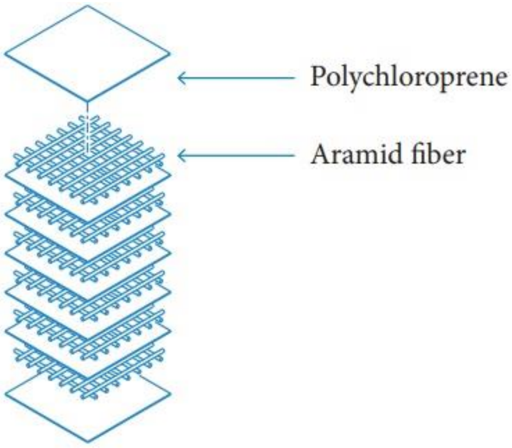

Figure 2. *Structure of the aramid/polychloroprene composite*

According to Blazsó et al. [12] the decomposition of aramids occurs at temperatures above 500 °C. However, the decomposition temperature range depends on the type of aramid. Zhang et al. [13] published their comparative analysis of the thermal degradation of Kevlar- and Nomex-type aramid fibers. The results showed that there is a difference in the thermal degradation process and temperatures of the two materials. Compared to Nomex, Kevlar showed a higher degradation temperature.

Villar-Rodil et al. [14] also studied the pyrolysis behavior of Nomex fibers. They observed a slight weight loss (~1%) starting at around 270 °C and probably related to water release from the rupture of hydrogen bonds. At higher temperatures, two slightly overlapping peaks were observed. The second decomposition stage started at 420 °C and the third stage ended at approximately 607 °C.

Wang et al. [15] investigated the thermal degradation behavior of meta- and para-aramid fibers using TGA-DTA/MS technique. They found that the degradation of meta-aramid occurred in 3 stages both in air and argon. Compared to meta-aramid, the mass loss of para-aramid was greater when the temperature reached 1,000 °C.

2. Materials and methods

In this study, the thermal behavior of the aramid-based composite sample was examined using a MOM Derivatograph-C type device with a heating rate of 10 °C/min in a nitrogen (8 L/h) atmosphere. The TG and DTG curves are shown in *Figure 3*. The TG curve illustrates the mass loss of the sample with increasing temperature. While the DTG curve – as the derivative of TG – shows the rate of sample mass loss.

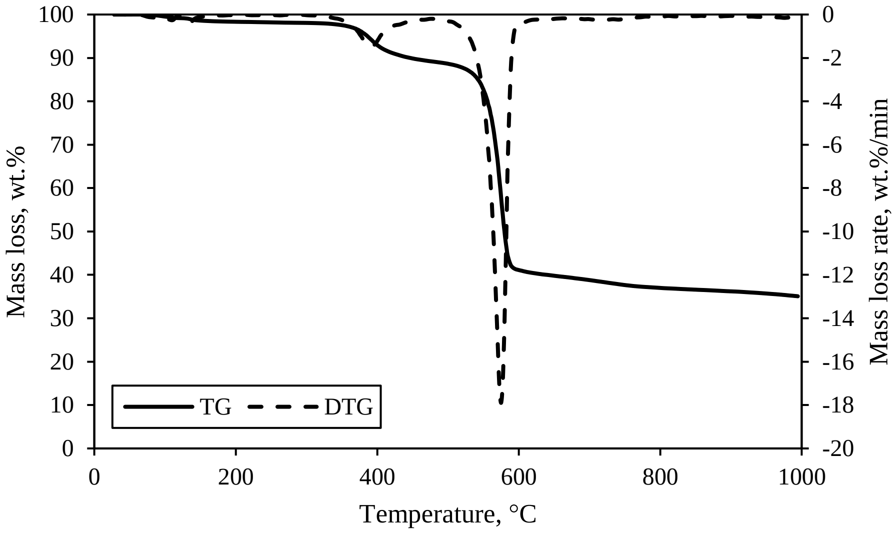

Figure 3. *TG and DTG curves of aramid composite waste*

The first weight loss belongs to the release of moisture. The pyrolysis of the aramid composite occurred in two temperature stages according to the two distinct peaks observed on the DTG curve. The first peak was located between ~350 °C and ~480 °C with a maximum mass loss rate of 1.5 wt.%/min at ~392 °C. While the second peak centered at ~575 °C had an onset temperature of ~490 °C and ended at ~615 °C.

Although above 615 °C no more peaks were observed, the weight of the sample further decreased from 40.6 wt.% to 35.1 wt.%.

Considering the mass losses and decomposition temperatures, the first peak belongs to polymer resin, while the latter peak shows the pyrolysis of the aramid fibers. The distinct peaks suggest that the removal of the resin should be viable without the decomposition of the fibers. Based on the maximum peak temperature in the first decomposition stage the final temperature of our experiments was determined at 400 °C and held for 1 hour.

The laboratory-scale pyrolysis system shown in *Figure 4* consisted of a stainless-steel tube with approximately 20-30 g capacity and two tube furnaces with a maximum temperature of 900 °C. The role of the second furnace was to increase the heated length, therefore ensuring a longer residence time for the volatiles to break down and maximize the gas production. The waste composite samples were placed into the heated section of the tubular reactor. Outside the furnaces, the reactor was insulated by Insulfrax ceramic blanket. K-type thermocouples were used to measure the surface temperature of the stainless-steel tube and the data was recorded using a four-channel data logger. Before each experiment, the system was flushed with nitrogen to provide an inert atmosphere for pyrolysis. After flushing was completed, the furnaces were heated up to 400 °C.

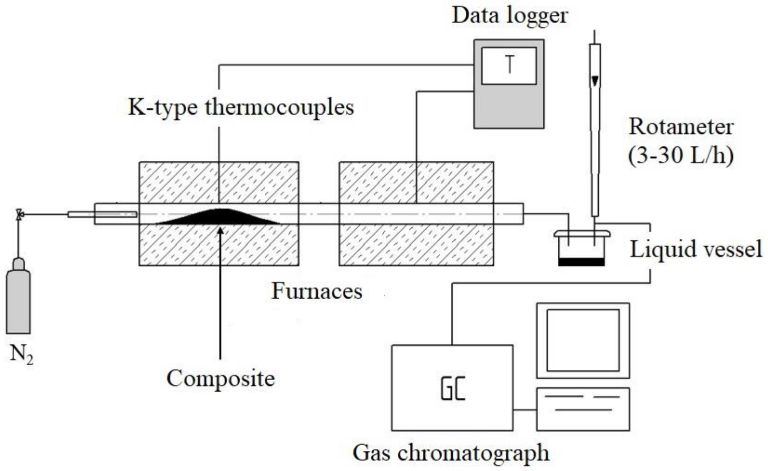

Figure 4. *Laboratory-scale pyrolysis apparatus*

The released volatiles left the heated zone and entered a water-cooled vessel, where the liquid product condensed. The volume flow of the produced gas was measured using a rotameter with a measurement range of 3-30 L/h. The composition of the pyrolysis gas was determined by an Agilent 490 Micro GC gas chromatograph equipped with thermal conductivity (TCD) detector and 2 columns (PoraPLOT U, CP-CO_x). The composition analysis of the solid samples was performed using a Carlo Elba EA1108 elemental analyzer.

3. Results and discussion

In *Figure 5* the composite samples are shown before (a) and after (b) pyrolysis. The difference between the two materials is not well defined at first sight. Following pyrolysis, no significant contamination was observed on the surface, and no signs of damage were visible. The fibers became more separated than before the treatment. By the end of the thermal treatment, 88.2 wt.% of the composite remained as a solid residue.

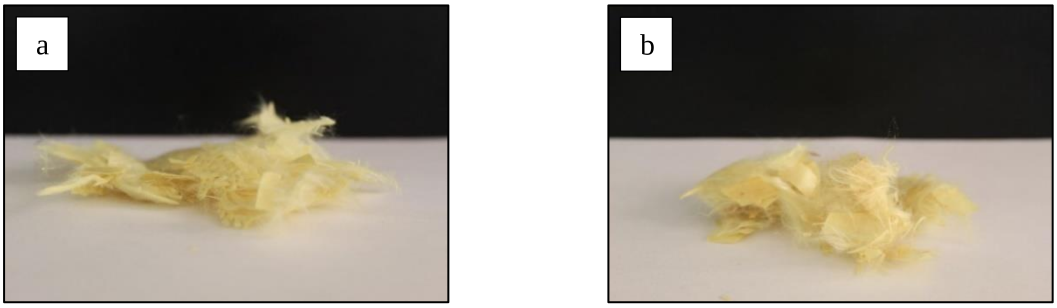

Figure 5. *Aramid composite samples before (a) and after (b) pyrolysis*

In *Figure 6*, the elemental composition analysis of the solid samples is presented. Initially, the sample consisted of 66.3 ±0.3 wt.% carbon, 5.8 ±0.1 wt.% hydrogen, 9.1 ±0.1 wt.% nitrogen, and 0.2 ±0.0 wt.% sulfur. Due to the pyrolysis, 6.9 wt.% of the initial carbon was converted into a gas and liquid product. The conversion of hydrogen was even more intense, although it includes the hydrogen content of the moisture of the analyzed sample. The nitrogen content did not change significantly. Approximately 56.6 wt.% of sulfur remained in the solid phase.

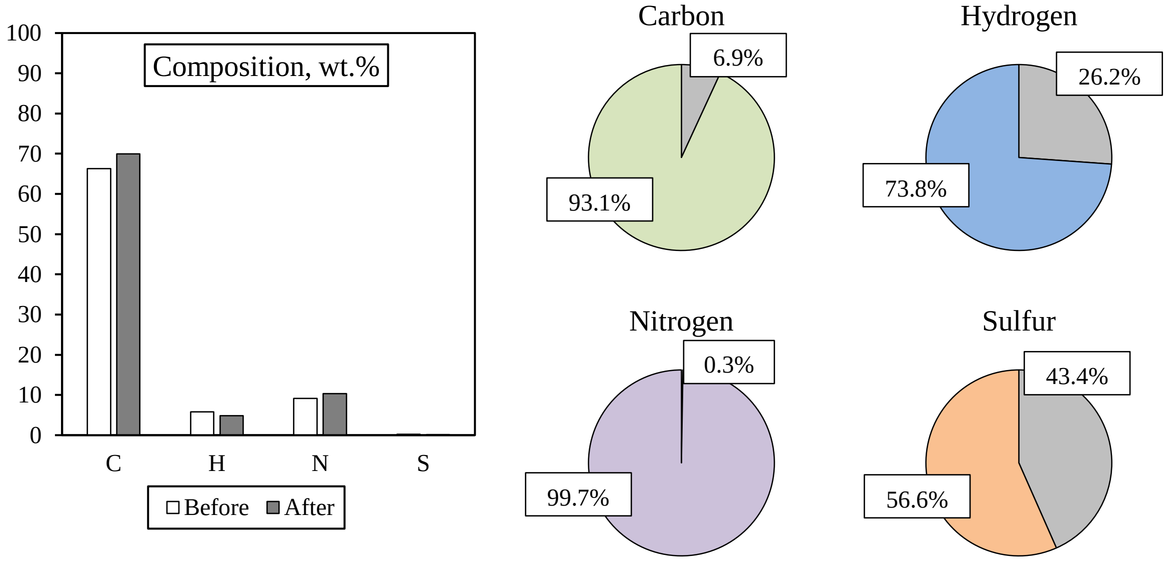

Figure 6. *CHNS composition of the solid samples before and after pyrolysis and the conversion of the elements*

Figure 7 shows the microstructure of the treated composite. The polymer resin was removed partly from the fibers, although the degradation was not completed in every part of the sample, as can be seen in the left figure.

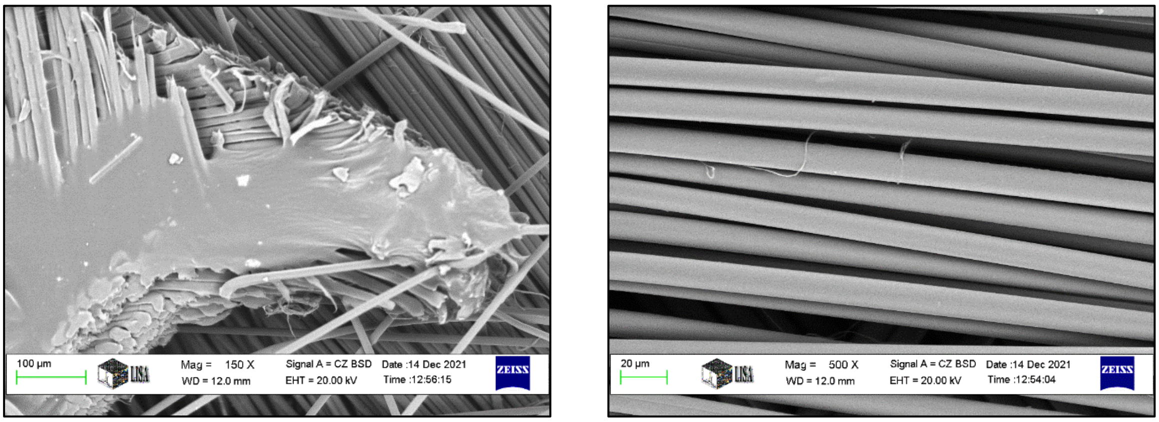

Figure 7. *SEM micrographs of the waste composite after pyrolysis*

EDS (energy dispersive X-ray spectroscopy) analysis was also conducted. Based on the EDS spectrums we identified the presence of carbon, nitrogen, oxygen, sodium, and sulfur. The detection of the latter two components suggests potential contamination on the aramid fibers. In the sample coated with resin, we only detected the presence of oxygen and calcium, in addition to 91.5 wt.% carbon.

Due to the limited sample size, gas generation remained insufficient to reach the lower detection limit of the variable-area flow meter (<3 L/h). The results of the gas chromatography analysis are shown in *Figure 8*.

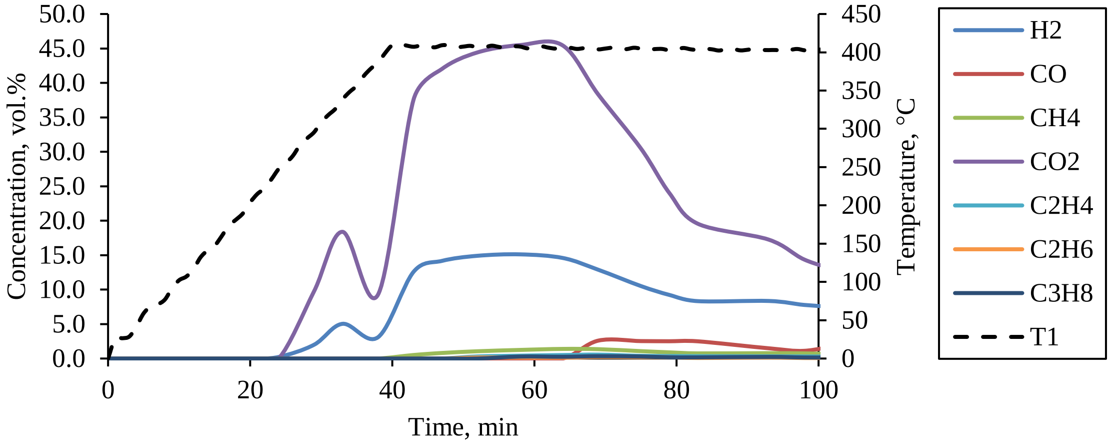

Figure 8. *Pyrolysis gas analysis*

Based on the analysis, the pyrolysis gas release started after the outer temperature of the reactor tube reached approximately 240 °C. The main component of the pyrolysis gas was CO_2, followed by H_2.

4. Conclusion

In this paper, the thermal treatment of an aramid reinforced composite was studied. The thermal treatment was performed in a laboratory-scale tubular pyrolysis reactor. We aimed to examine the recovery of the aramid fibers and at the same time analyze the properties of the pyrolysis gas originating from the thermal decomposition of the polymer resin. Before the experiments, the composite was examined using a derivatograph to determine the optimal temperature for the thermal treatment. Based on the results, the experiments were performed at 400 °C. By the end of the pyrolysis, 88.2 wt.% remained as a solid product and 6.9 wt.% of the initial carbon content was converted into a gas or liquid product. According to the SEM images, the degradation of the polymer resin was not completed, therefore for the next series of experiments, the pyrolysis temperature or the residence time needs to be raised.

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