

Study of Aramid Fiber/Polychloroprene Recycling Process by Thermal Degradation

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ABSTRACT: Aramid fiber is an important polymer applied as reinforcement in high-performance composites, which, due its exceptional properties, becomes an excellent impact absorption material. It has been broadly utilized in aeronautic industry and ballistic protection. In aircrafts, it is mainly used in secondary structures, such as fairings, floor panels, and bullet proof structures in helicopters, whereas, in ballistic protection industry, it is applied in automotive armor and bullet proof vest. Under environmental perspective, it is worrying the development and application of composites, which generate proportional discards of these materials, whether originated from manufacturing process, spare parts or end of life cycle. High-performance composite materials like those using aramid fiber are generally difficult to recycle due to their properties and the difficulty for the separation of the components, making their recycling economically unviable. From the characteristics of composite materials and environmental viewpoint, this paper presents a new aramid fiber recycling process. The main objective of this research was to study different recycling methods in aramid fibers/Neoprene® composites. To promote the Neoprene® degradation, it was used a pyrolysis oven with controlled atmosphere and CO₂ injection. For the degraded separation, it was designed a mechanical washing machine in which the most degraded separation occurred. To complete the materials separation, it was employed a manual cleaning process, and, at least to prove the efficacy of the process, it was applied a tensile test in the yarns.

KEYWORDS: Recycling, Aramid fiber, Composite, Polychloroprene, Pyrolysis.

INTRODUCTION

The usage of composite materials is increasing with the development of new technologies due to the necessity of materials that match the needs for strength and lightness (Chawla 2012). Among the composites, the polymeric ones are advanced engineering materials composed by reinforcement fibers like aramid, glass or carbon, combined with a matrix, generally made of thermo-rigid or thermo-plastic polymeric material (Cândido *et al.* 2006).

The aramid fiber is widely applied in functions that demand a high-performance material, in different sectors, like aeronautic and automotive sectors (Boukouvalas and Wiebeck 2007).

In the aeronautic sector, this is an important material present in components that require high strength-to-weight ratio, high strain-to-failure and high temperature resistance, being commonly utilized in fairings, engine containing rings, skins, floor panels, landing gear doors, radomes, and others that need structural efficiency and suitable dielectric properties (Baker *et al.* 2004).

Structures for ballistic protection have been developed over the years, and the materials and design of these structures have evolved enough. Aramid composites have been used worldwide in production of ballistic protection due to their high capacity to absorb energy mainly on armor components in aeronautic and automotive industries (Lopes *et al.* 2007). One of those composite armors is a combination of aramid fiber (Kevlar®) with a polychloroprene resin (Neoprene®). The aramid is responsible for the mechanical and thermal endurance, and the polychloroprene provides elasticity modulus, keeping the materials united, acting as a connection element

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and protecting them against acids, ozone and other aggressive agents (Bittencourt 2011).

At the end of the life cycle, these components will be replaced by new ones, then the discarded part will be sent to disposal sites. This method of treating composites residues is becoming more expensive, and the pressure from society and environmental agencies is growing, being necessary a reassessment of the allocation of these materials (Naglis and D'Almeida 1998).

According to the Boeing Company (2007), it is expected that up to 7,200 commercial aircrafts will be retired from active service in the next 20 years and all should be available for recycling. However, in general, composites require complex recycling methods, often being sent to landfills (Cunliffe *et al.* 2003). On the other hand, aramid is a fiber with excellent mechanical properties that can be recycled and applied in another product, preserving natural resources and allowing economical gain.

The recycling of these materials is in constant development, and, nowadays, the more developed techniques are mechanical, chemical and thermal processes (Pickering 2006).

Pyrolysis is a thermal recycling process widely studied in fiber recovery. In this process, the thermal degradation of one or more constituent materials occurs, recovering the desired material for a new manufacture (Pickering 2006).

This research had the objective of showing that it is possible to carry out the separation of the components from a composite material made from aramid fiber and polychloroprene polymer without solvents usage, recycling in an ecologic way. Therefore, it was projected a washing machine capable of performing the separation of the polychloroprene degraded from the aramid fibers only with the help of simple cleaning materials.

MATERIALS AND METHODS

MATERIALS

The samples utilized in this research are strips from a composite applied in vehicle armor; the reinforcement fibers (Kevlar®) form bidirectional orientation cables, threaded in a perpendicular way one to another, arranged in 7 layers, and, between them, there are layers of the polymeric matrix (Neoprene®). Figure 1 shows, in a simplified form, the composition of the material with the respective layers. The samples were cut into strips with dimensions of 5.0×20.0 cm, weight of 2.8 kg, and then were taken to the oven where the pyrolysis process was performed.

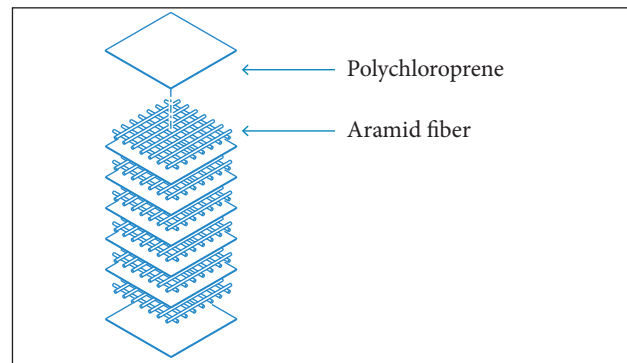


Figure 1. Material composition.

PYROLYSIS PROCESS

The pyrolysis was performed in 2 stages, in a controlled temperature oven, with injection of CO_2 in a volume of $300 \text{ mL}\cdot\text{L}^{-1}$. In the first stage, the oven was programmed to a heating ramp of 300°C , reaching this temperature and remaining at this value for 15 h (Fig. 2). At the end of this stage, the material was again weighed and analyzed.

In the second pyrolysis stage, the 7 layers of the material were separated as illustrated in Fig. 1, resulting in a larger contact surface. Then, the oven was heated at 300°C for 1 h. After that, the temperature was increased at 350°C for 15 min, remaining 5 h at this value (Fig. 3).

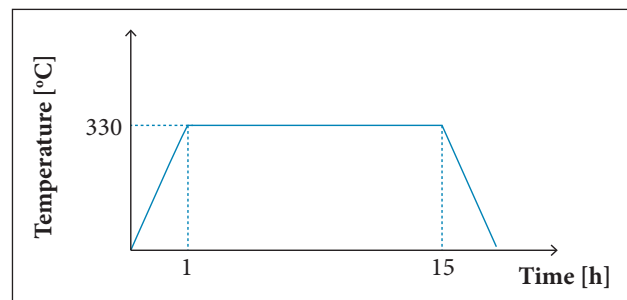


Figure 2. First pyrolysis stages.

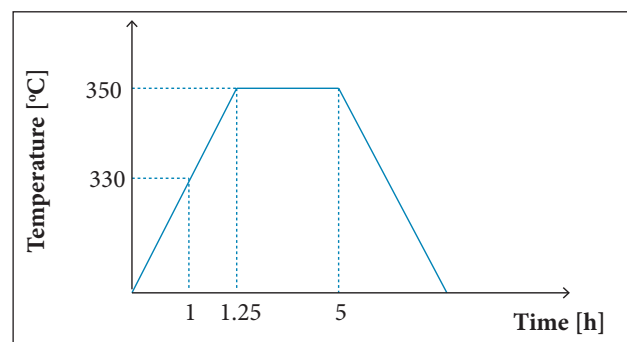


Figure 3. Second pyrolysis stage.

SAMPLES WASHING

After the pyrolysis process, the samples were subjected to the mechanical washing process for the degraded Neoprene® separation from the Kevlar®. In this process, 2 different techniques were employed: the mechanical washing and then the manual washing.

Mechanical Washing

This washing method was employed with the objective of performing the separation of degraded products from the pyrolysis. Then, for this purpose, it was built a mechanical action washer where metal spheres and rollers promote the required friction for the material separation. In this washing step, soap powder and water were utilized together with the spheres and rollers. In order to avoid water saturation, after 3 h of washing, the water and the soap were replaced, and the washing was performed for a further 3-h period.

Manual Washing

After the mechanical washing, the samples were rubbed with a sponge to remove possible traces of the degraded polychloroprene.

MECHANICAL TENSILE TEST

The mechanical tensile test was employed to determine the integrity of Kevlar® during each step of the recycling process; therefore, samples were collected from the starting material after pyrolysis, after the mechanical washing and after the manual washing.

The following aramid reference values were utilized: linear mass density of 1.27 cN/dtex, density of 1.44 g·cm⁻³, and diameter of 12.0 µm. These values are comparable to the results obtained in the test (DuPont® 2011). The linear mass density of 1.27 cN/dtex was applied to determine the pre-tension, which set a pre-tensioning claw of 50.0 mg used in the Textechno Vibromat equipment in order to obtain the filament linear mass density.

Thus, with the linear mass density determined, the tensile test was performed using the Textechno Fafergrhaf equipment. For

this test, ten samples of each step of the recycling process were collected: ten from the original material (before any recycling process), ten after pyrolysis and ten after washing.

The equipment was set to perform tests in filaments of 20 mm, with a speed of 50.0 m·min⁻¹, 10.0% of minimum and 30.0% of maximum elongation compared to the initial length of the filament and maximum strength of 45.0 cN.

RESULTS AND DISCUSSION

PYROLYSIS

After the first stage of pyrolysis, it was observed that the weight of the samples decreased 21.0% compared to the original material; in the second stage, after the delamination, the samples were weighed, and it was observed that they lost 0.20 kg, weighing at last 1.60 kg. At this point, it was observed that the polychloroprene degradation occurred more significantly, with a weight loss of 14.0% compared to the resulting material from the first stage (Table 1).

SAMPLE WASHING

In the mechanical washing process, tests were carried out with different washing times and different cleaning products to set the most efficient method. Thus, it was observed that the most efficient washing process refers to that in which the samples were treated during a total of 6 h. Thus, to avoid the water saturation, at the end of 3 h, the water and the soap were changed, and the washing was carried out for more 3 h. To execute the washing process, it was used public distribution water and Omo Multiaction® washing powder, which is a commercial cleaning product that reduces the surface tension of the water, allowing its deeper penetration into the material. At the same time, this washing powder is able to attract debris through its polarity, increasing the washing efficacy (Souza *et al.* 2010).

It was observed that the mechanical washing removed the most part of the degraded Neoprene® from the fibers (Fig. 4); however, it was necessary the use of manual washing for the complete removal of the degraded remains.

Table 1. Pyrolysis stages.

Pyrolysis	Mass loss (g)	Time (h)	Temperature (°C)	Flow rate of CO ₂ (mL·L ⁻¹)	Results
Stage 1	680	16	330	300	The material became malleable
Stage 2	0.050	6	350	300	The polymeric matrix degraded and obtained a shattered appearance

After performing tests to determine the best manual washing method, the sponge was the one which presented the best efficiency, with which the fibers showed coloration near to their natural yellow (Fig. 5).



Figure 4. Material after mechanical washing.

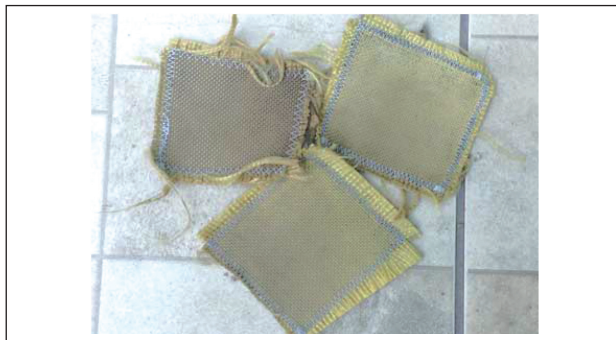


Figure 5. Material after manual washing.

TENSILE TEST

Through the analysis of the tensile tests results, it was observed that the pyrolysis process employed in recycling degraded the fibers. The fiber became fragile, and values of tenacity and tensile strength became very close. The samples lost some of their properties, occurring a decrease of 64.0% in tensile strength, 64.0% in tenacity, 84.0% in elongation and 87.0% in the time required for rupture (Table 2).

It was observed that all plastic and almost the entire elastic region from the material were lost after pyrolysis, making the

fiber a fragile material. One explanation for this degradation is the conditions and parameters adopted for the pyrolysis of the material and the properties of the fiber.

The aramid fiber begins to decompose at 427 °C, losing only humidity. In quick exposures, it would bear the maximum temperature employed in the process (350 °C); however, when the temperature exposure occurs over a long period, the aramid begins to decompose in a range between 147 and 177 °C (Cunliffe *et al.* 2003).

It can be observed that the exposure to elevated temperatures leads to the loss of the fibers' properties, making 22 h of exposure in the oven sufficient for their degradation.

CONCLUSIONS

The proposed material separation for this study was successfully done; however, the fibers suffered significant loss of mechanical properties, especially in their main features.

Regarding the toughness, a critical feature of the fiber for impact absorption, a decrease of 80.13% has occurred. The tensile strength decreased by 79.80%, also limiting the fiber application in structural efforts. The pyrolysis degraded the polychloroprene impregnated into the fibers satisfactorily, allowing the subsequent complete removal by the washing process; however, the aramid fibers were also partially degraded during the pyrolysis process, resulting in decreased mechanical strength.

The mechanical action washer did not completely removed the degraded polychloroprene as expected, requiring a subsequent removal from it with a manual method.

These conclusions allow making some considerations about this research. The loss of aramid fiber mechanical strength properties during the pyrolysis process has been caused by exposure to high temperatures for a long period. The mechanical washing proposed in this study is not able to perform the complete separation of the materials, being necessary to improve the washing method.

Table 2. Tensile test results.

Sample	Rupture time (s)	Linear mass density (dtex)	Tensile strength (cN)	Angular coefficient (°)	Tenacity (cN/dtex)	Stretching (%)
Starting material 1	4.59	1.00	21.49	10	21.49	8.52
Pyrolysed 1	0.58	1.00	7.73	10	7.73	1.48
Washed 1	0.63	1.00	12.35	10	12.35	1.73

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