DEGRADATION OF REINFORCED AND UNREINFORCED WASTE POLYAMIDES DURING MECHANICAL RECYCLING

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The paper discusses the degradation of waste polyamides during mechanical recycling from the automotive sector. Two different polyamides were investigated: glass fibre reinforced and unreinforced. Raw materials were reprocessed twenty times and the changes in their properties were investigated as a function of reprocessing number. Considerable differences were found in relation to the specimen properties between reinforced and unreinforced waste materials. For example, the tensile strengths of reinforced and unreinforced polyamide 6.6 wastes were 84.2 and 165.2 MPa, respectively, which dropped to 38.0 and 97.0 MPa after the twentieth reprocessing cycle. Specimens from the reprocessing procedure have been investigated by Fourier transformed infrared spectroscopy in the spectral range of 400–4000 cm^{-1}. Due to mechanical stress between the rotating screw and plasticising cylinder, the reinforcements broke. The average length of the glass fibre was decreased as a function of the reusing cycle number from 1890 to 580 μm.

Keywords: polyamide, mechanical recycling, degradation, FTIR

Introduction

As a result of the continuously increasing trend in the demand for polymer worldwide, ever increasing amounts of waste polymers are generated. Polyamides (PA) are expensive engineering plastics, especially if they are reinforced. In particular, glass fibre composites are widespread among fibre-reinforced materials, as a results of their favourable mechanical and economical properties. The application of glass fibre results in improved tensile and flexural properties. Thermoplastic polyamides contain typically 10-30% glass fibres as reinforcements and are applied in many industries such as the automotive sector, civil engineering, packaging, and biomedical applications [1-9,11,16].

A grand challenge is the utilisation of plastic wastes. Polymer materials have a high resistance to different environmental and mechanical effects, which yields their favourable characteristics. Such advantageous properties can easily become disadvantage owing to waste polymers inability to decompose within a reasonable time frame. Unfortunately, a vast amount of polymer waste ends up to landfills, where non-degradable plastics together with other materials accumulate and pollute the environment [10,12-15]. The most studied recycling technologies are mechanical or chemical. Chemical recycling is a thermal process for cracking the long carbon chains of polymers into gases and liquid hydrocarbons in the absence of oxygen within in temperature range of 400-1000 °C. The other technology is mechanical recycling, when waste polymers are mixed with original granulates and newly shaped by injection moulding or extrusion. Mechanical recycling is a good option for reusing waste plastic, only when selectively collected polymers of high purity are available. Similarly to the chemical process, the polymer chains can degrade due to mechanical and thermal stresses during the pre-treating and shaping steps. Therefore, it is important to know the behaviour of polymer chains when exposed to thermal and mechanical stresses [9,11-16].

The goal of our work was to investigate the mechanical recycling of reinforced and unreinforced waste polyamides. Waste polymers have been reprocessed twenty times and the changes of mechanical amongst other properties were investigated. The effects of reinforcements on the loss of properties during the reshaping procedures were followed.

Experimental

Plastics

Glass fibre reinforced and unreinforced waste polyamides were used as raw materials. The main properties of the raw materials are shown in *Table 1*.

Table 1: The main properties of raw materials

	Reinforced	Unreinforced
MFI,* g $(10\ min)^{-1}$	15.1	11.8
Ash content, %	30.6	0.03
Tensile strength, MPa	165.2	84.2
Charpy strength, kJ m^{-2}	13.4	12.1

* 275 ºC, 5 kg

Figure 1: The main experimental steps

Figure 2: Tensile properties of reinforced and unreinforced polyamide 6.6 wastes: A) tensile strength, B) elongation and C) tensile modulus
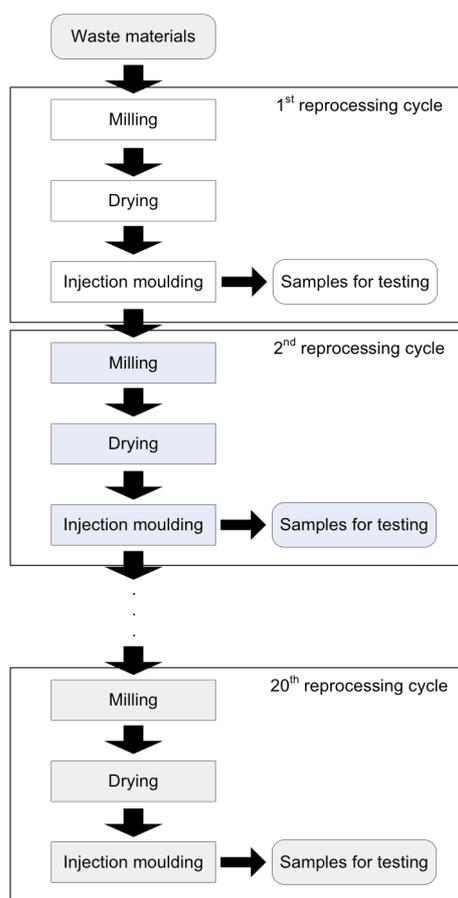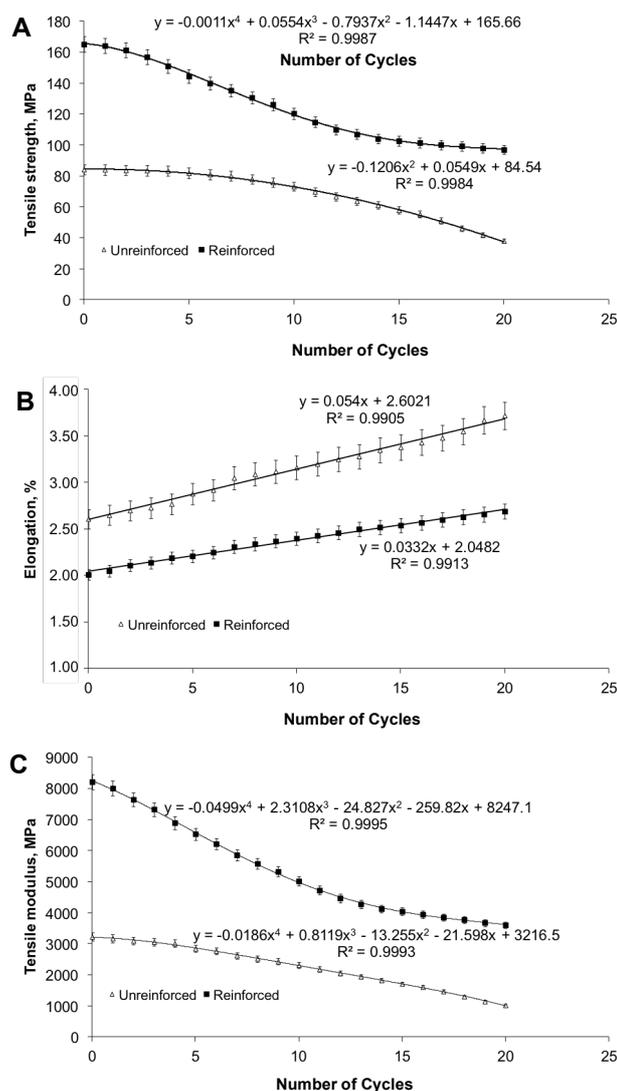
Sample Preparation

Due to PA samples being sensitive to humidity, raw materials before processing and samples before testing were dried. Drying was carried out in an air circulated drying box at 90 ºC for 2 h. The injection moulding of the specimens was carried out by a microprocessor-controlled injection moulding machine. The dimensions of dog-boned injection moulded specimens were 3 mm × 10 mm in cross-section and 50 mm in length. *Fig.1* illustrates the main experimental steps.

Methods

The tensile and three point flexural properties (mainly stress and extension) (MSZ EN ISO 527-1-4:1999, MSZ EN ISO 14125:1999) were determined using an INSTRON 3345 universal tensile testing machine. The temperature and relative humidity in the laboratory were 23 ºC and 60% respectively, during the mechanical tests. Tensile tests were carried out at a crosshead speed of 80 mm min^{-1}. During the investigation of flexural properties, the crosshead testing speed was 20 mm min^{-1}. Samples were also investigated by infrared spectroscopy with a TENSOR 27 type FTIR spectrometer (resolution: 3 cm^{-1}, illumination: SiC Globar light, detector: RT-DLaTGS type) within the 400-4000 cm^{-1} wave number range. A CEAST Resil

Impactor was applied to measure the Charpy impact strength of the produced samples according to the MSZ EN ISO 179-2:2000 standard.

Results and Analysis

Tensile Properties

The tensile properties of reshaped specimens are summarised in *Figs.2A-2C*. The tensile strength of reinforced and unreinforced polyamide 6.6 wastes were 84.2 MPa and 165.2 MPa, respectively, which were reduced to 38.0 MPa and 97.0 MPa after the twentieth reprocessing cycle (*Fig.2A*). It is important to note that the decreasing trends were considerably different in the two cases: a fourth order trend line in the case of reinforced samples and a second order one in the case of unreinforced samples were found as shown in *Fig.2A*. A short section with a barely decreasing slope can be found both at the beginning (before the third cycle) and at the end (after the fifteenth cycle) of the trend line for
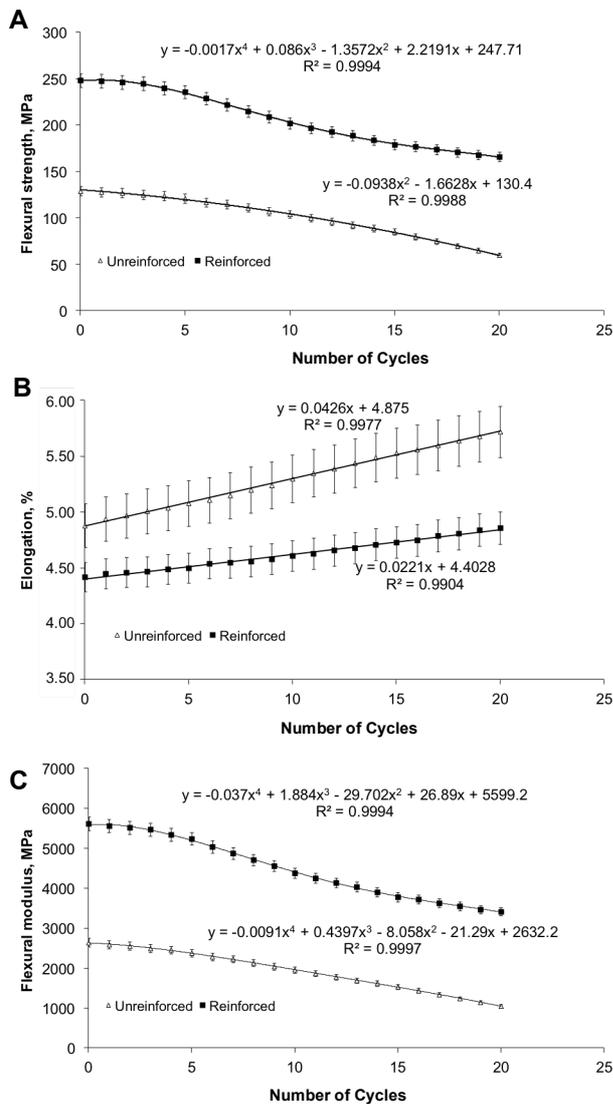
A

$$y = -0.0017x^4 + 0.086x^3 - 1.3572x^2 + 2.2191x + 247.71$$
$$R^2 = 0.9994$$

$$y = -0.0938x^2 - 1.6628x + 130.4$$
$$R^2 = 0.9988$$

△ Unreinforced ■ Reinforced

B

$$y = 0.0426x + 4.875$$
$$R^2 = 0.9977$$

$$y = 0.0221x + 4.4028$$
$$R^2 = 0.9904$$

△ Unreinforced ■ Reinforced

C

$$y = -0.037x^4 + 1.884x^3 - 29.702x^2 + 26.89x + 5599.2$$
$$R^2 = 0.9994$$

$$y = -0.0091x^4 + 0.4397x^3 - 8.058x^2 - 21.29x + 2632.2$$
$$R^2 = 0.9997$$

△ Unreinforced ■ Reinforced

Figure 3: Flexural properties of reprocessed reinforced and unreinforced polyamide 6.6 wastes A) flexural strength, B) elongation and C) flexural modulus

the reinforced specimens. In the case of unreinforced specimens a similar phenomenon was found only up to the ninth cycle.

The elongations of specimens are shown in *Fig.2B*. Owing to the rigid property of polyamides the relative elongations are rather small (below 3.8%). As results demonstrate the change in elongations was rather linear, but the gradient was different when the reinforced (tan $\alpha =$ 0.033) and unreinforced (tan $\alpha = $ 0.054) raw materials were investigated; because a slower ratio in change was found in the presence of glass fibres in polyamide wastes.

As demonstrated by the tensile strength, tensile moduli show a decreasing trend as well. Furthermore, the trend line is highly similar to the measured data for tensile strength. The E-modulus of reinforced and unreinforced wastes was 8219 MPa and 3226 MPa, respectively. Those were decreased to 3606 MPa and 1022 MPa according to the mathematical equations in *Fig.2C*.
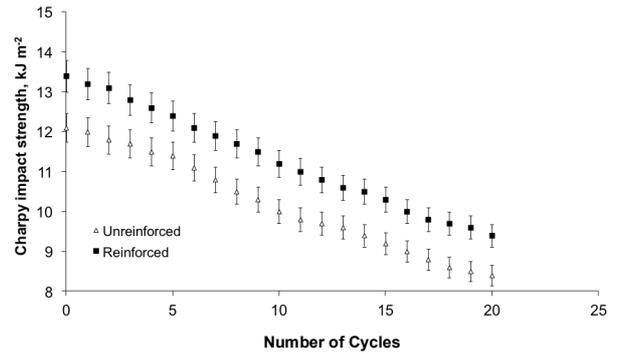

△ Unreinforced
■ Reinforced

Figure 4: Charpy impact strength of reprocessed reinforced and unreinforced polyamide 6.6 wastes

Flexural Properties

The flexural properties of reshaped specimens are summarised in *Figs.3A-3C*. The change in both flexural strength and E-modulus followed a decreasing trend, while the trend in terms of elongation was rather increasing. The results were similar to the tensile properties discussed above. It is important to note that the shapes of trend lines were also similar to results demonstrated before. When reinforced polyamide 6.6 waste material was reprocessed the flexural strength, elongation and E-modulus changed from 248.5 MPa, 4.42% and 5622 MPa to 166.0 MPa, 4.86% and 3416 MPa, respectively. By taking into consideration the results of both tensile and flexural tests it can be concluded that the glass fibre reinforcement helps to keep the high values of strengths and E-moduli in the case of reinforced polymers at the start of property curves as a function of processing cycle number. Approximately after the third-to-fifth reprocessing cycles, the dropping ratio was increased step by step. Presumably this was the consequence of the glass fibres degrading into pieces. On the contrarily, a relatively constant dropping ratio was found in the unreinforced case.

Charpy Impact Strength

The Charpy impact strength test is one of the most widely specified mechanical tests of polymeric materials to provide information about impact properties. Results of Charpy tests were summarised in *Fig.4*. The change in Charpy impact strength followed a decreasing trend in both cases. Moreover, a similar trend in the changes could be found, because the gradients were 13.38 and 12.18 for reinforced samples and unreinforced specimens, respectively. The Charpy impact strengths were 12.1 kJ m^{-2} and 13.4 kJ m^{-2} without any reprocessing, and decreased to 8.4 kJ m^{-2} and 9.4 kJ m^{-2} respectively by the end of the procedure. Naturally the reinforced samples gave higher values of impact strength.

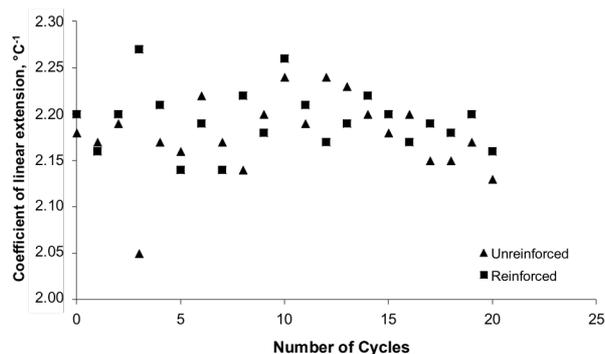*Figure 5*: Coefficient of linear heat extension of reprocessed reinforced and unreinforced polyamide 6.6 wastes
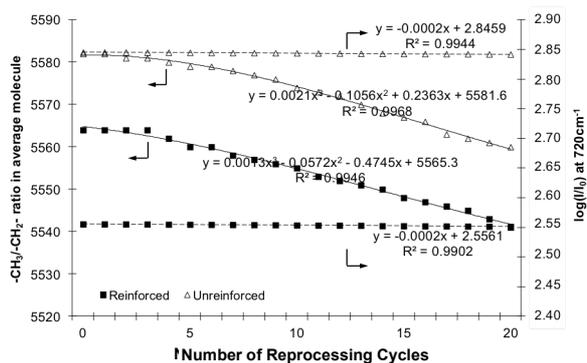

Figure 7: The change in the –CH$_3$/–CH$_2$– ratio of an average molecule and the value of log(I/I_0) from FTIR spectra at 720 cm^{-1} as a function of the reprocessing cycles in the cases of reinforced and unreinforced polyamides

Figure 6: FTIR spectra of reinforced (A), and unreinforced polyamide (B)

Linear Extension Coefficient

The coefficient of thermal expansion describes the change in dimensions of samples against changing temperature at a constant pressure. Regarding polymers the linear extension coefficient is used to classify the materials. As it is known, thermal expansion decreases with increasing bond energy and the thermal extension of the amorphous phase is higher than that of the crystalline phase, because rearrangements in the structure can be achieved at the glass transition temperature. A change in ratio of amorphous and crystalline phases occurs. The coefficients of linear extension are demonstrated in *Fig.5*. Results demonstrate well that the coefficient changes randomly in both cases between 2.05 and 2.27 with approximately the same average value of 2.18 °C^{-1} for the reinforced and unreinforced specimens within 0.01 °C^{-1}. Presumably no rearrangements in the structures of the tested materials occurred during the reprocessing and the ratio of the amorphous to crystalline phases remained similar. In other words, the specimens a have relatively permanent stability of shape.

Fourier Transformed Infrared Spectroscopy

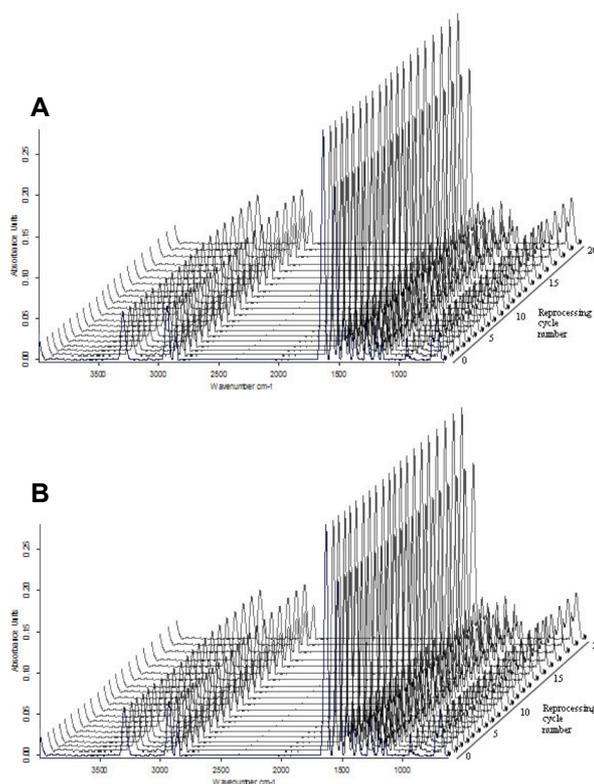Samples from the reprocessing procedure were also investigated by Fourier transformed infrared spectroscopy (FTIR), which provides a measure of changes in molecular structures through molecular vibrational excitations. The FTIR spectra of reinforced and unreinforced waste polymers as a function of the reprocessing cycles are shown in *Figs.6A* and *6B*. By this method, modifications in the molecular structures of polymers could be observed as a result of changes in their chemical bonds. A typical spectrum of polyamide can be described as follows:

- stretching vibration of -CH$_2$- and -CH$_3$ groups between 2800–3000 cm^{-1}

- symmetric and asymmetric deformation stretching of -CH$_3$ groups between 1430 and 1470 cm^{-1} and 1365 and 1395 cm^{-1}

- $\beta_{asymmetric}$CH$_2$ of -CH$_2$- groups at 720 cm^{-1}

- bands at 3350, 1730 cm^{-1}, and 630 cm^{-1} as well referring to the N–H and C=O bonds from –NH– and –CO functional groups.

The methyl/methylene group (–CH$_3$/–CH$_2$–) ratio in an average molecule was calculated based on the FTIR peak intensities in the range of 2800–3000 cm^{-1}. Results are summarised in *Fig.7*. As shown, the ratio of methyl and methylene groups slowly decreased in both cases as a function of reprocessing cycles. This suggests that the numbers of methyl groups increased, while the methylene groups decreased in an average molecule. This is a consequence of polymer degradation, when the C-C bonds of main polymer chains are cleaved, which resulted in shorter chains containing less methylene groups.
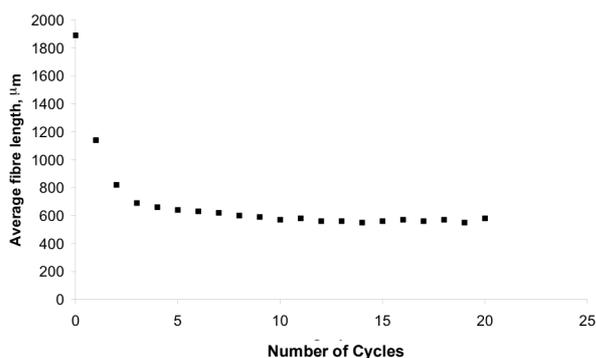
Figure 8: The average length of glass fibre reinforcements
as a function of reprocessing cycles

Scanning Electron Microscope Graphs

As the polyamide matrix covered the fibres, it was difficult to determine their average length. Therefore to investigate the average length of the reinforcements and thus gain insights into their degree of degradation, the samples were burned and the remaining glass fibres were investigated by SEM techniques. The results are shown in *Fig.8*. As shown, the average length of the glass fibre reinforcements decreased as a function of the reusing cycle number. The length of glass fibres suddenly decreased from 1890 μm to 660 μm during the first four cycles of reprocessing. Then the average length exhibited a relatively constant value between 550 and 640 μm. The mean and standard deviation were 581 μm and 28 μm between the fifth and twentieth cycles, respectively. The cause for the degradation of the reinforcement fibres was the mechanical stress caused by the rotating screw and plasticising cylinder.

Conclusions

We investigated the reprocessing of waste glass fibre reinforced and unreinforced polyamide 6.6 materials. It was found that the mechanical properties of both wastes deteriorated as a function of reprocessing. For example, the tensile strengths of reinforced and unreinforced polyamide 6.6 wastes were 84.2 MPa and 165.2 MPa, respectively, which decreased to 38.0 MPa and 97.0 MPa after the twentieth reprocessing cycle. On the other hand, the trend lines of the changes were significantly different in the case of reinforced and unreinforced wastes. More gradually decreasing ratios could be measured regarding unreinforced plastics until the tenth cycle. Based on infrared spectra, it was concluded that the deterioration in mechanical properties presumably was the consequence of polymer degradation. The C-C bonds of the main polymer chains were broken and resulted in the formation of shorter polymer chains. The lengths of glass fibres suddenly decreased from 660 μm to 1890 μm during the first four cycles of reprocessing. Then, the average length exhibited a relatively constant value between 550 and 640 μm. The coefficients of

linear heat extension changed randomly in both cases between 2.05 and 2.27 ºC^{-1}. The average value was 2.18 ºC^{-1} for both reinforced and unreinforced samples within 0.01 ºC^{-1}.

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