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UV LIGHT IRRADIATION OF FIBERS IN TERMOPLASTIC PULTRUSION FOR HIGHER SURFACE ENERGY

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Abstract

Pultrusion is a common way to produce thermoplastic composites reinforced with different kinds of fibers. There are many different opportunities to improve the properties of a thermoplastic material. Different kind of fibers where pultruded in combination with different thermoplastic materials. The fiber content was set to 30wt% comparing the roving strain with the pultruded strain. UV-C light was used in the process to improve the fiber matrix adhesion. The pultruded strain was granulated and injection molded to specimen. The samples were tested in tensile and charpy tests. It could be shown that the concentration of oxygen on the surface of a cellulose fiber can be raised by uv light irradiation. Cellulose fibers show best changes of properties after the uv treatment.

Introduction

Reinforced thermoplastics provide outstanding properties and become more and more popular, especially in automotive industry [1]. There is a high number of fibers available, which steer the properties of the compound in different directions. Cellulose fibers for example are common because of their low density, better recyclability and reduced abrasion to machinery, according to glass fiber reinforced compounds [2, 3]. Glass fiber reinforced compounds are popular where high mechanical properties are required [3]. Carbon fiber is primarily preferred for composites with a very high stiffness and strength. The fibers have an excellent performance to weight ratio and the properties are high even at high temperatures [4, 5].

The interface between the fiber and the matrix is a very important area for the mechanical properties. To make use of the mechanical improvement, the fiber should have a strong adhesion to the thermoplastic [6]. Only a strong connection can transmit the power of the fiber to the matrix. There are several ways to have an influence on the fiber matrix adhesion. Coupling agents show good results on the connection of fiber to matrix. Especially natural fibers and glass fibers show better mechanical properties with an coupling agent, than without. Another opportunity to have an influence on the adhesion is a physical treatment of the fiber. Ultraviolet light has the property to raise the surface energy of a bulk [7].

The surface energy/tension is a addition of the dispersive and polar parts. The dispersive interaction is also called the van der Waals interaction and is caused by temporary fluctuations of the charge distribution in the atoms/molecules. On the other hand the polar part is caused by interaction of permanent dipoles and between permanent and induced dipoles [8, 9].

A pultrusion process at university of kassel is able to impregnate fibers with thermoplastic melt. Part of the process is a extrusion tool to make a strain out of the roving and the melt. Figure 1 shows the pultrusion process with the single stations. An UV irradiation tunnel was built and integrated in the process. Four spotlights with UV-C light and a wavelength of 185nm treat the rovings before they are impregnated with the thermoplastic melt.

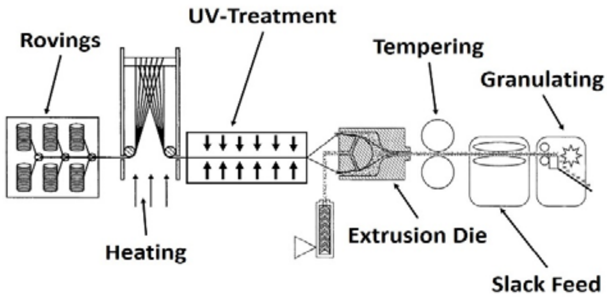

Figure 1. Pultrusion process with integrated uv irradiation

Materials

Thermoplastics

The material used in this study is a polypropylene PP 579S provided by sabic. It has a melt flow rate (230°C, 2.16kg) of 47 g/10min and a density of 0.905 g/cm³. It is used as a material with a low polar surface energy.

On the other hand a polyamide 6 B27E Ultramid by BASF was provided with a higher polar surface energy than the PP. It has a density of 1.12 g/cm³ and a MVR of 130 cm³/10min (275°C/5kg). The granulate was dried for 24 hours at 80°C. Table 1 shows the temperatures of the extruder and the extrusion die in the pultrusion process.

Table 1. Process Temperatures for PP and PA6.

	Temp Extruder			**Temp Die**	
	Zone 1	**Zone 2**	**Zone 3**	**Tool**	**Nozzle**
PP	180°C	190°C	185°C	185°C	190°C
PA6	230°C	240°C	235°C	245°C	250°C

Rovings

Cellulose fiber rovings were provided by cordenka GmbH (Obernburg, Germany). The fiber diameter is 12µm and the roving has 1350 fibers. The density of cellulose is 1.5 g/cm³ and the titer of the roving is 244tex. The roving has to be dried before it gets in contact with the thermoplastic melt. It was dried in process in a heating at 200°C for about 20 sec.

As a glass fiber roving there were two different kinds provided because of the two thermoplastic materials. The glass fibers have a silane based wax on the surface which indicates a good adhesion to several thermoplastic materials. For the use with the polypropylene, a glass roving JohnsManville 490 with a fiber diameter of 16 µm and a titer of 600tex was provided. The pultrusion with PA6 was done with a roving SE1200 EC17 provided by Lange&Ritter (Gerlingen, Germany) with a fiber diameter of 17µm and a titer of 600tex. This roving has a good adhesion to polyamide.

A polyester roving was pultruded with PA6 and PP. The roving was provided by PHP fibers GmbH (Wuppertal, Germany) and is marked by a low shrinkage. It is the type Diolen 174s. The fiber has a titer of 340tex and the number of fibers is 630. The diameter of the fiber is 23µm.

The carbon fiber was provided by Toho Tenax Europe GmbH (Wuppertal, Germany). It is the type HTS45 P12 with a titer of 800tex and a number of 12000 fibers. The single fiber diameter is 7µm. The roving is made for a good adhesion to thermoplastics, especially to PA6. All rovings were provided in a non-twisted mode.

Table 2. Sizes of rovings.

Roving Type	**Filament diameter (µm)**	**Number of filaments (i)**
Glass fiber JohnsManville 490	16µm	1200
Glass fiber SE1200 EC17	17µm	2000
Cellulose fiber Typ CR 250	12µm	1400
Polyester fiber Diolen 174 S	23µm	630
Carbon fiber HTS45 P12	7µm	12000

Methods

It is expected that the oxygen concentration raises on the surface of the fiber after uv light irradiation. This should be proven by different analysis methods like edx microscopy and FTIR. The UV light was integrated in the pultrusion process and specimen of uv light irradiated and non irradiated fibers were made with two different thermoplastics.

EDX

A single cellulose fiber was tested with EDX to have a look at the oxygen on the surface of the fiber. The fiber was investigated with a CAMSCAN MV2300. The measurement was made with 10kV and a magnification of about 7500. Single fibers were pulled out of a roving before and after a uv irradiation. The treatment was made in the same tunnel than used in pultrusion. The treatment time was 20min.

FTIR

Fourier Transform Infra Red spectroscopy was carried out on a IRAffinity-1S. It measures the wavelength from 350-7800 cm^{-1} and has a resolution of 0.5 cm^{-1}. FTIR was carried out on the roving, because the needle is not able to contact a single fiber.

Pultrusion

A thermoplastic pultrusion process was used to produce the compounds. Figure 1 shows the process and single stations. The extrusion die is made for the impregnation of the rovings with thermoplastic material. A single screw extruder was connected to the extrusion die to melt the polymers. The weight of the pultruded strain was compared to the weight of the roving to set the weight fiber content.

Injection molding

The Arburg Allrounder 320C Golden Edition injection molding machine was used to produce the specimen of the type 1A (DIN EN ISO 527). The machine has a clamping force of 500 kN. The cellulose fiber compounds as well as the PA6 compounds were dried for 24 hours at 80°C to reach a moisture content of <0.2wt%. The injection molding machine was equipped with a standard three-section screw with a diameter of 25 mm. The injection speed was set to 32 cm³/s and the mold temperature was set to 40°C for PP and 100°C for PA6. The inner mold pressure was about 420bar along all compounds. Temperature set along the srew was 160°C to 190°C for PP and 220°C to 240°C for PA6.

To have a good distribution of the fiber in the compound a valve gate nozzle was used to set a high dynamic pressure of 150bar. The nozzle was used for all compounds except the cellulose fiber/PA6 compound. A open machine nozzle was used because of the high pressure in the nozzle.

Characterization

Tensile tests were carried out on a Zwick Z010 universal testing machine according to EN ISO 527. Attention was payed on elongation at break, tensile strength and tensile modulus.

The fiber adhesion to the matrix has a significant effect on the impact properties. Instrumented charpy impact tests were made according to EN ISO 179. The specimen were tested with a 5J hammer in a notched and unnotched mode and the specimen had a size of 80x10x4mm.

Results

The effect of the uv light irradiation was investigated on a cellulose fiber. In FTIR a roving was treated with uv light and tested before and after the treatment.

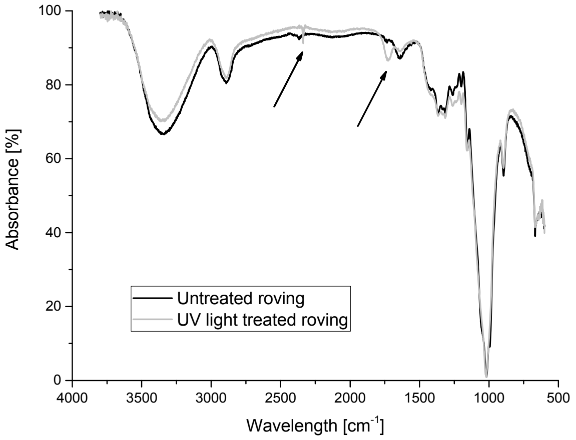

Figure 2. FTIR with uv light irradiated (grey) and untreated (black) cellulose roving

Figure 2 shows the FTIR result of the treated and untreated roving. Special attention should be drawn to the peak at a wavelength of 2500 cm^{-1}. A peak at this wavelength is more pronounced than on the roving before the treatment and shows that O-H groups are built on the surface of this roving. Another change can be seen at a wavelength of about 1700 cm^{-1}. This wavelength shows acid C=O groups and has moved after the uv irradiation [4]. The changes in this graph show that the treatment leads to changes on the surface of the roving.

EDX analysis was made on a single fiber out of a cellulose roving. The fiber was measured before and after uv light irradiation of about 20min. Figure 3 shows the result of the analysis. The peak of oxygen is significantly higher after the uv light treatment. It shows that oxygen was bounded on the surface of the fiber, which leads to a higher polar surface energy.

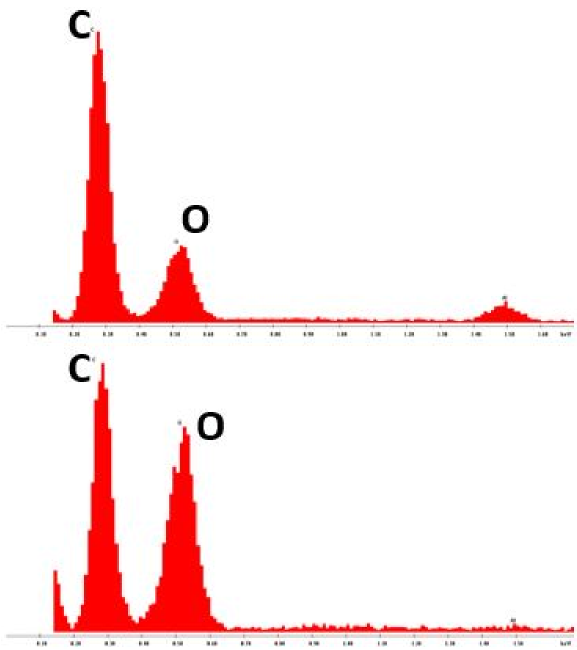

Figure 3. EDX analysis of untreated (above) and uv light treated (below) cellulose fiber

The characterization after the injection molding show very low changes. The treatment time of uv light in the tunnel was about 15sec with a distance of about 4cm to the spotlights. Figure 4 shows the elongation at break and the tensile strength of the specimen with glass fibers and cellulose fibers. At the glass fiber there is no significant change with the described uv light treatment. The cellulose fiber shows a better connection to the polypropylene after the irradiation. The strength increases as the elongation decreases. The benefit is low, which can be caused by the low irradiation time and a rather high distance to the spotlights (4cm). The compounds reinforced with polyester fiber show a lower elongation at break after the uv irradiation. The strength stays about the same.

The results of the fibers pultruded with PA6 matrix show a low increase of the tensile strength along all types of fibers. The elongation at break does not change significantly. The reason for that is a better connection of the fiber to the matrix

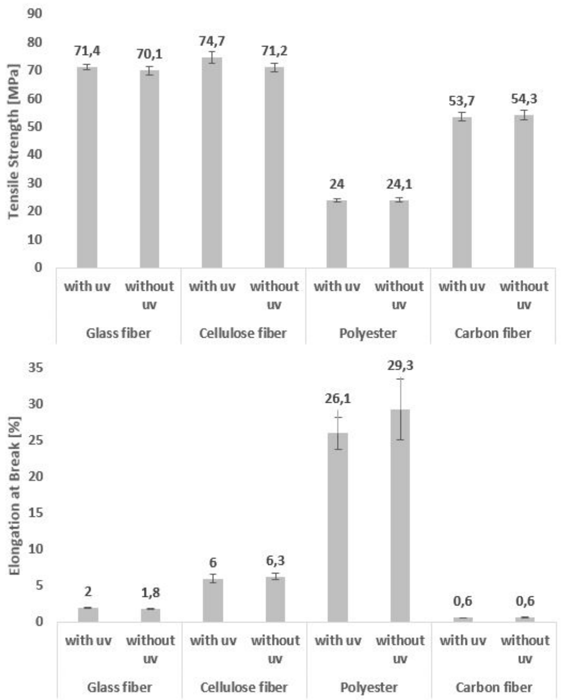

Figure 4. Elongation and strength of compounds with PP/ uv light treated and untreated fibers

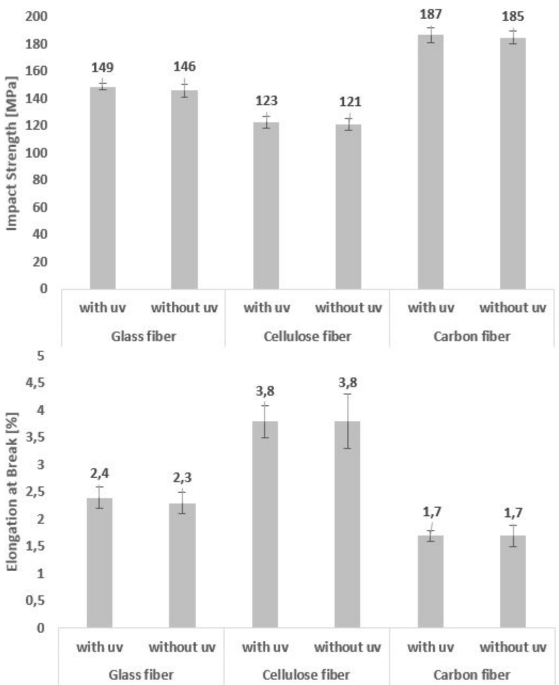

Figure 5. Elongation and strength of compounds with PA6/ uv light treated and untreated fibers

The impact strength was investigated in charpy impact tests. As the aim of the uv irradiation is a stronger connection of the fiber to the matrix, the charpy impact strength can be influenced in both directions. The main reason of a high impact strength is a high number of fiber pull outs, which absorb more energy than fiber cracks [10]. If the connection of the fiber to the matrix is weak, the raise of the adhesion leads to more absorbed energy, as long as the fiber pulls out. On the other hand, a very high adhesion between the fiber and the matrix leads to fiber cracks, which decreases the impact strength, because of less absorbed energy.

Figure 6 shows the results of the impact strength on notched specimen. The compounds are made of PA6 reinforced with glass, cellulose or carbon fiber. It can be recognized, that the cellulose fiber reinforced compounds show 10% less impact strength after the uv irradiation, compared to the value before. This indicates more fiber cracks due to a better connection of the fiber to the matrix.

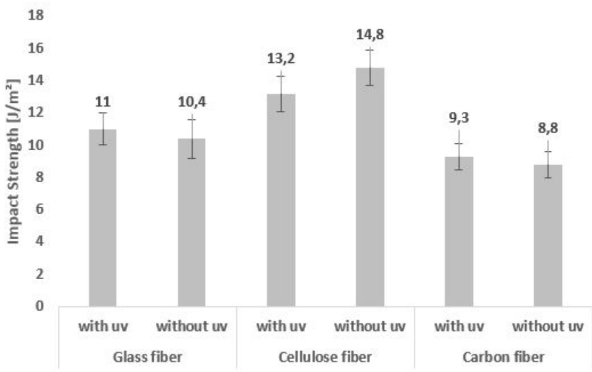

Figure 6. Impact strength of notched specimen at PA6 compounds

Conclusions

The study was made to investigate the influence of uv light irradiated rovings in the thermoplastic pultrusion process. In the process the rovings were treated for 15sec with spotlight at a wavelength of 185nm. The rovings reinforced PA6 with a high polar surface energy character and a low polar surface energy of a PP. The investigations lead to the following conclusions:

- The change of the polar part of the surface energy was shown on cellulose fibers in FTIR and EDX. The oxygen raises significantly after the uv irradiation.
- The treatment of the fibers showed best results on the cellulose fiber reinforced compounds. The PP reinforced compounds reinforced with cellulose fibers showed better adhesion of the fiber leading

to higher tensile strength and lower elongation at break.

- The PA6 matrix with a high polar surface energy shows a strong connection to the fiber. The tensile results were not significantly influenced by the uv irradiation. The notched impact strength shows a better adhesion of the fiber to the matrix leading to more fiber cracks. This results in a lower impact strength.
- The low changes of the tensile and charpy impact results are caused by a low irradiation time and a high distance to the spotlights. The irradiation time was limited by the length of the uv tunnel and the pulling speed of the process.

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