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Studies on UVC Treatment of Polyamide Fibers for Improved Adhesion on TPU and TPA

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Abstract: We report about current work which is aimed to improve the adhesion of melt processable elastomers onto relevant reinforcement materials by means of short wave UVC (ultraviolet C) light. Results of laboratory tests regarding UVC surface activation of polyamide fiber materials in air using low-pressure mercury lamps with 185 nm and 254 nm emissions are shown. The effect of irradiation on fiber strength was studied to find out suitable process parameters for providing the UVC treatment efficient but as gentle as possible to avoid negative effects on reinforcement properties. Application of a laboratory process for UVC pretreatment leads to significantly increased adhesion strength between the fibers and the melt processable elastomers on the base of TPA (polyamide) respectively TPU (polyurethane).

Key words: UVC surface treatment, fiber-TPE (thermoplastic elastomers) composites, surface activation of polyamide fiber.

1. Introduction

Combination of textile reinforcements with melt processable TPE (thermoplastic elastomers) offers an interesting technological approach for efficient manufacturing of composite materials which combine elasticity and high modulus. However, the usage of many new material combinations is often limited by adhesion problems. Thus, it is usually difficult to achieve a firm and permanent bonding of thermoplastic elastomer to synthetic fiber surfaces because most of TPE have no reactive groups which can promote the adhesion as in the case of epoxy or polyurethane matrix materials. The preferred way to enhance the adhesion of TPE is an effective pretreatment of the fibers [1]. Because of certain deficiencies of conventional chemical procedures, such as environmental damages or high specificity, different physical techniques of surface modification are investigated [2]. The UVC treatment of fibers opens an interesting alternative to plasma or corona processes. By irradiation of polymer materials with short wave UVC light different effects of chemical and morphological surface modification were obtained [3-6]. Furthermore enhanced adhesion properties of different polymer materials like polypropylene films or PET fibers by excimer laser irradiation at wavelengths of 193 nm and 258 nm were achieved [3, 12]. But it was also reported that high power of laser radiation effected changes of the surface morphology and polymer degradation. Other authors described that improved wettability and adhesion performances were achieved by UV treatment of vulcanized latex soles or siloxane network films with mercury vapour lamp in the presence of oxygen [7, 8] or by UVC irradiation of polymer surfaces with 172 nm excimer lamp [10]. A major advantage of low-pressure mercury lamps is the continuous emission of UVC light with comparatively low radiation power. Therefore it should be possible to achieve chemical changes at polymer surfaces without thermally induced structuring. This is especially important for UVC treatment of synthetic fibers with small filament diameters.

Subject of the presented studies are investigations on the use of low pressure mercury lamps in activation processes of technical fibers based on PA (polyamide). The basic idea is to generate adhesion promoting functional groups on the surface of

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synthetic fibers by irradiating them with high energy photons of the short-wave UVC range in the presence of atmospheric oxygen. In this way the adhesion abilities of the fiber should be largely improved.

2. Experiments

Focal points of previous experimental work were the assembling of suitable experimental equipment and investigations to evaluate experimental and system parameters for treatment of selected test fibers. Furthermore some test series were carried out to assess the effectiveness of the developed laboratory technique regarding improved adhesion properties in fiber-TPE compounds.

2.1 Materials

In our current investigations, commercial available technical fibers are used. The described irradiation tests were performed with uncoated and untreated continuous monofilaments of polyamide. The fibers were cleaned wet-chemically before further processing in order to produce a comparable surface quality and remove adhered contaminations.

Selected matrix materials for the test compounds were commercially available TPE materials with a suitable working range and without significant adhesion to the untreated fibers on the basis of TPA (polyamide) respectively TPU (polyurethane) of the types UBESTA XPA 9055 or ELASTOLLAN 1195.

2.2 UVC Irradiation Experiments

The UVC treatment of the fibers was carried out using an experimental station designed and manufactured in-house. The modular concept of the irradiation equipment allows the application of different irradiation sources, the variation of several parameters for the investigation of influence factors, as well as the installation of additional components and test chambers. Here, we present the results of the treatment tests on synthetic polyamide fibers applying UVC (ultraviolet C)-light from low pressure mercury lamps emitting line spectra at 185 nm and 254 nm. For the test series a height adjustable irradiation unit with an irradiation area of 380 mm by 400 mm was used, equipped with 11 single switchable low pressure mercury lamps (HG-LP classic lamp) of the type NIQ 60/35XL of the company Heraeus Noblelight. The irradiation of the fibers was performed in continuous mode and under atmospheric conditions, using an especially adapted conveyor belt system. For the UVC treatment the cleaned fibers were clamped in a frame with a window of 210 mm by 120 mm and treated as plane specimens on both sides, so that the whole fiber circumference could be irradiated.

The experimental setup allowed to record temperature, irradiance at 185 nm and 254 nm as well as the ozone concentration locally and directly on the treated surface while UVC treatment is in progress.

The experiments were performed in a parameter range which was adapted from previously determined technological and material specific demands (Table 1).

Time and intensity of irradiation were controlled by varying the conveyor speed or the distance from lamp to treated surface.

2.3 Evaluation of Irradiation Effects

To evaluate irradiation effects, the wetting behavior, fiber strength and adhesion properties of irradiated fibers in comparision to untreated fibers were determined.

Table 1 Parameters of the irradiation experiments.

Parameter	Unit	Range
Time of irradiation	s	30-120
Distance of irradiated fiber to UVC-source	mm	40-150
Intensity of irradiation at 185 nm on fiber surface	mW/cm^2	1.6-7.5
Maximum temperature at fiber surface (measured next to specimen while test was running)	°C	32-36

After UVC-treatment of fibers the dynamic contact angles of the fiber surfaces towards water and polyethylene glycol were measured to characterize the wetting behaviour. The measurement was performed with a tensiometer (Dataphysics, DCAT 21) in an atmospheric environment at a temperature of 298 K. The respective contact angle (advancing angle) was calculated as the average value of at least five separate fiber samples.

Tensile tests using a tensile test machine (INSTRON 4400) were carried out to prove strengths of irradiated monofiles as well as compound strengths.

Test compounds of the pretreated fibers with the above mentioned TPE were produced to evaluate the pretreatment effect of the particular irradiation experiment in relation to the adhesion abilities. The fabrication of the compounds was made via hot pressing by using a specific compression mould device and by means of a heated plate press of the company RUCKS GmbH, Glauchau (Germany).

The bonding strength between fiber and matrix was statically tested by single fiber pullout test [12, 13] using a self made test setup following the example of the so called T-test which is commonly used for adhesion tests of conventional rubber-fiber composites (Fig. 1). In this method the single fiber is embedded in the TPE matrix and the maximal thread pullout-strength of the embedded fiber is determined by modified tensile test. Experimental results of these tests, which are shown in 3.2, were obtained for samples with an embedded length of 10 mm.

3. Results and Discussion

3.1 Effect of UVC-Irradiation in the Presence of Air

Regarding the application of mercury low pressure lamps for treatment of synthetic fibers, it must be noted, that especially the energy of photons at 185 nm is sufficient to break most of organic bonds. Degradation reactions can result, if the fiber material absorbs irradiation energy in the range of polymer

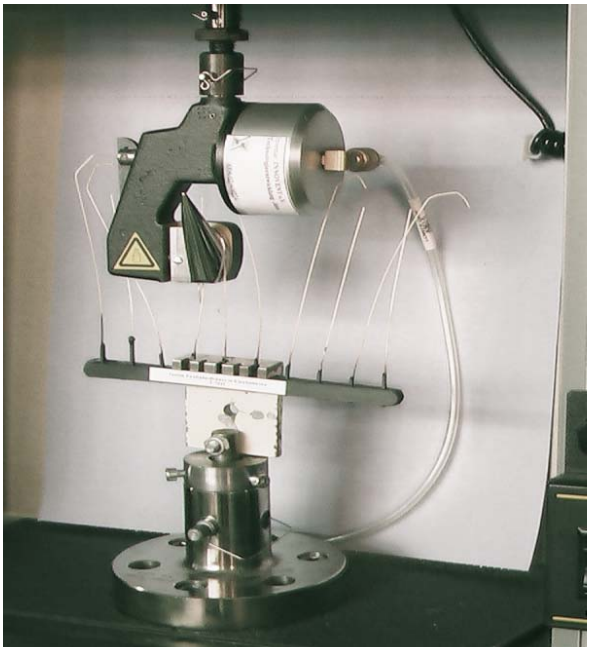

Fig. 1 Experimental setup of testing the maximal thread pullout-strength (T-test).

bonding energy. The use of short-wave UVC light for treatment of reinforcing synthetic fibers can only be successful, if the surface activation can be performed with preservation of fiber properties. Therefore, it is necessary to investigate the effects of short-wave UVC irradiation of synthetic fibers on their material properties.

From various publications and our own studies it is known that attacks of photochemical activated oxygen species can induce additional surface reactions if the vacuum ultraviolet irradiation takes place in air, i.e. in the presence of oxygen [4, 8, 10, 11]. Oxygen functional groups containing C=O or C-O components can be generated on the polymer surface in result of photolytic induced oxidation processes. The generated oxygen containing structures through 185 nm/254 nm UVC irradiation of PP (polypropylene) in the presence of air were studied by means of FTIR-Spectroscopy (Fourier Transform Infrared Spectroscopy) and XPS (X-ray Photoelectron Spectroscopy) [11]. Analyses of polypropylene foil before and after the UVC treatment showed an increase of carbonyl bonds on the polypropylene surface (Fig. 2, Table 2).

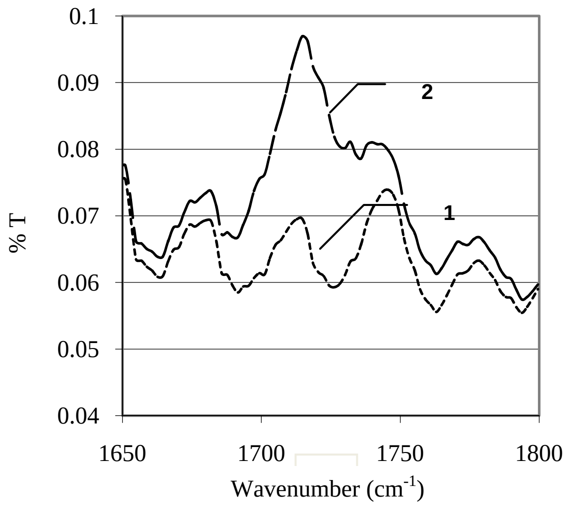

Fig. 2 Comparative FTIR transmission analysis of polypropylene foil (spectrum detail: increase of C=O signal) before (1) and after (2) 185 nm/254 nm UVC treatment in presence of air.

Table 2 XPS results of the PP surface analysis before and after 185 nm/254 nm UVC treatment in presence of air (20 min).

Pretreatment of PP foil	(Atom %)	
	C1s	O1s
Without	99.6	0.4
UVC irradiation/air $I_{185\ nm}$ = 1.4 mW/cm² $I_{254\ nm}$ = 8.9 mW/cm²	93.4	6.6

These results correspond with described effects of chemical surface modification of polymers by irradiation using other UVC light sources with emissions in VUV range in presence of oxygen or air [3, 6-10].

The described UVC induced generation of oxygen containing stuctures on polymer fiber surfaces could effect improved adhesion behavior. Therefore, the surface analytical results support development regarding the use of short-wave UVC light for pretreatment of fiber materials, especially of synthetic materials based on non polar polymers.

Furthermore, the UVC induced surface modification was reflected by changes of contact angles against representative liquids. It was established that the irradiation effects a significant decrease in water contact angle, the fiber surface became more hydrophylic. For example, the water contact angle of PA6 fibers decreased from 74° to 46° if the samples are treated with UVC light of mercury low pressure lamps for two minutes with a 185 nm intensity of 7.1 mW/cm². This result is in accordance with the observed generation of oxygen functional groups due to VUV-irradiation in the presence of oxygen. The wettability against polyethylene glycol was determined to have a model for interaction of fiber surfaces with molecule structures of TPU. Comparing the contact angles of fiber surfaces against polyethylene glycol without and after UVC-treatment of 39° and 26°, it is also observed a significant improved wettability. This may suggest that the UVC irradiation in air is a promising approach to improve the adhesion properties of polyamide fibers in compounds with TPU.

However, it could be possible that the influence of high photonic energy causes undesirable damages of fiber material because of thermal stress or photolytic cleavage of chemical bonds in polymer chains even inside the fiber. Such effects were observed in experimental treatments of synthetic polyester fibers or polypropylene foils using short-wave UVC laser sources [3, 6] and also in the treatment of polymer material using mercury vapour lamp [7]. Realizing a gently irradiation of synthetic fibers is particularly challenging because most of the products have very small diameters in the range of only a few micrometers. That’s why the treatment effects must be surface active, but a small depth effect is also required to save the quality of the bulk material, especially its mechanical properties. The effects which are induced by UVC irradiation depend on the emission spectrum of the UV light source and on the absorption properties of the irradiated system. Previous research work we found was only focused onto effects of chemical and morphological surface modification by UVC irradiation. Reviews which include investigations of the influence of short wave UVC irradiation in air on fiber strength were not found. Our current studies regarding the use of mercury low pressure lamps with 185 nm and 254 nm emission wavelength consider the influence of important treatment parameters like duration or intensity of UVC irradiation on tensile strength of selected fiber types.

Some results of corresponding test series with monofilaments of PA 6 (polyamide 6) and PA66 (polyamide 66) are listed in Table 3. In these experiments, the UVC irrradiation was modified by varying the radiation time and the distance of UV light source from the treated fiber surfaces.

In the test series we applied parameter ranges which combine material related, technical and economic aspects because of the application-oriented work. Experimental results show that the duration and intensity of UVC irradiation can influence the tensile strength of tested filaments. However, parameter sets of UVC treatment without any loss of tensile strength were also obtained. The test results allow deducing the preferred parameters for exploratory tests regarding UVC pre-treatment of synthetic fibers to get improved adhesion properties.

3.2 Adhesion Tests

The described laboratory process (2.2) was used to perform exploratory trials regarding UVC pretreatment of fiber materials to improve their adhesion in fiber reinforced thermoplastic elastomers. First results of tests with treated filaments for compounds with polyamide thermoplastic elastomer (TPA) and polyurethane thermoplastic elastomer (TPU) as matrix materials are shown below.

The T-test results of first laboratory tests show that the UVC irradiation of polyamide fibers according to the developed process causes improved adhesion of fibers in the TPA matrix material. While untreated fibers had no adhesion in the used TPA type UBESTA (pull out strength < 1 N), the pull out strength which was gauged in tests with UVC treated fiber samples was significantly higher (more than 13 N). With the applied T-test method most of the samples show cohesive fractures of fiber material because of

Table 3 Influence of irradiation time (*t*) and distance of mercury low pressure radiation source (*h*) on tensile strength of UVC treated 160 µm PA66-monofilaments and 700 µm PA6-monofilaments. Average value of 15 samples in relation to untreated fiber (100%): PA66 (160 µm 14.1 N); PA6 (700 µm 194 N).

t (s)	h (mm)	I_{max} (mW/cm²)	Tensile strength (%)	
			PA66	PA6
0	-	0	100	100
30	40	7.1	100	100
30	80	4.3	100	100
60	40	7.1	100	100
60	80	4.3	100	100
90	40	7.1	98	99
90	60	6.4	99	100
90	80	4.3	98	100
120	80	7.1	94	97
120	60	6.4	98	98
120	80	4.3	98	99

Table 4 T-test results of exploratory tests on UVC pretreatment of 160 µm PA66 monofilaments for improved adhesion on TPA (type UBESTA).

Treatment fluence 185 nm	Extraction-force in N	Fracture
Untreated 0 J/cm²	< 1	100% adhesive
UVC Option 1 1.8 J/cm²	> 12	80% cohesive (fiber)
UVC Option 2 3.4 J/cm²	> 13	100% cohesive (fiber)

Table 5 T-test results of exploratory tests on UVC pretreatment of 1.2 mm PA6 monofilaments for improved adhesion on TPA (type UBESTA).

Treatment Fluence 185 nm	Extraction force in N	Compound strength in MPa
Untreated 0 J/cm²	65	1.7
UVC Option 1 1.8 J/cm²	148	3.9
UVC Option 2 3.4 J/cm²	218	5.8

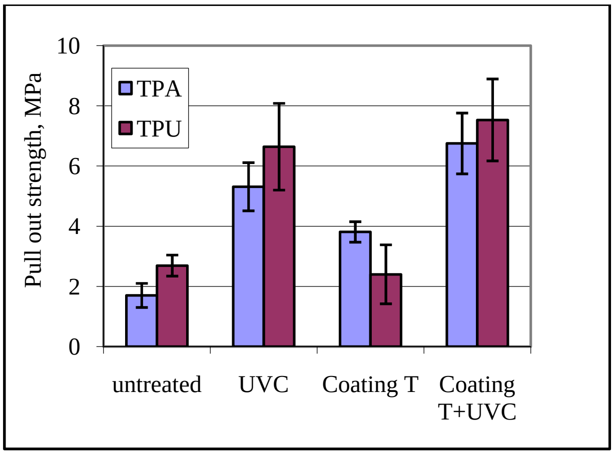

Fig. 3 T-test results of pull out strength of test composites of PA6 fiber (diameter 700 µm) with TPU type Elastollan 1195 or with TPA type UBESTA XPA 9055 using various pretreatment methods without UVC (untreated, Coating T) or with 185 nm/ 254 nm UVC irradiation ($I_{185\ nm}$ = 7.1 mW/cm²).

increased pull out strength that is higher than tensile strength of embedded 160 µm PA 66 fibers. Therefore, in further test series fibers with larger diameters were used to prevent cohesive fracture of fibers in strength tests (Table 5).

UVC irradiation tests showed improved adhesion properties of the UVC pretreated fibers on TPE matrix materials based on polyamide (Elastollan) as well as polyamide (UBESTA).

Fig. 3 presents several results of test series with technical PA 6 fibers and compares the effect of UVC irradiation of fibers with other methods of fiber treatment. The fibers were processed into composite samples immediately after the specific pretreatment procedure. It can be seen that through application of treatment processes using the 185 nm/254 nm UVC radiation significantly higher adhesion strengths in the T-test samples were achieved. Additionally, the experimental results suggest promising possibilities of a combination of UVC treatment and chemical coatings.

4. Conclusions

Evaluating the results of irradiation test series it can be concluded that it may be a promising approach to use short-wave UVC light of mercury low pressure lamps to develop efficient methods for pretreatment of technical textiles to improve their adhesion properties in composites with TPE. Application of the developed laboratory procedure for UVC pretreatment of synthetic fiber materials resulted in significantly increased adhesion strength of fiber-TPE test composites. Suitable parameter ranges could be found in the result of exploratory analyses about the effect of UVC irradiation process on fiber tensile strength by performing the UVC test series on these materials. With ongoing research we will continue and expand the developments for using of short-wave UVC light in surface treatment of synthetic technical fibers to enhance adhesion strength.

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