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Photochemical surface modification of PP for abrasion resistance

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ABSTRACT

The potential of a photo-chemical approach to increase the surface hardness of polypropylene (PP) has been studied. Using a 222 nm excimer lamp, fibers and film were irradiated in the presence of multi-functional substances diallylphthalate (DAP), tetraallyloxyethane (TAE), and pentaerithritoltriacylate (PETA) and characterized with regard to the resulting effect on abrasion resistance. AFM-based methods were employed to analyze thermo-mechanical surface properties. Nanoindentation and microthermal analyses of the outermost surface layers of UV treated fibers gave clear indications of an effective cross-linking of reactive substances present during irradiation. One may assume that the reactive media polymerize on top of the surface of the PP substrate and form a thin-layer. The abrasion resistance of the PP fibers was tested by applying stress through a rotating and axially oscillating roller of defined roughness and measuring the mass loss as a function of time. The abrasion resistance was found to be remarkably improved compared to the untreated fiber. Best effects were achieved using PETA as reactive substance. The experiments clearly showed the influence of processing conditions, namely with regard to homogeneous coverage of the substrate surface with the reactive medium.

1. Introduction

The commonly available synthetic polymer and natural fibers are widely used in various fields such as biocompatible materials, textile and composite industries, although most of these fibers are not suitable for uses under hostile conditions including acids, bases, organic solvents, high temperature, and various kinds of radiations. Polypropylene (PP) fibers and monofilaments have been rapidly developed and increased in application recently. The relevance of the PP fibers in high-performance products and composites has been discussed by Adams and Eby [1] and Wampler et al. [2]. Main advantages of these fibers are specific surface area, strength, chemical environment resistance and low price. Considerations of structural parameters such as orientation and chain stiffness and their influence on fiber properties have been published by Mark [3] and Raab and Nedzbedova [4]. For many applications, however, PP fibers show insufficient abrasion resistance. Therefore, surface damages arising from weaving and processing result in reduction of fiber mechanical properties. Several ways to increase the hardness of the fiber surfaces to a similar level as polyamide have been studied, examples being cross-linking by ionizing radiation such as, e.g., electron beam [5–7], plasma treatment (e.g., [8]), and deposition of highly cross-linked thin-layers by plasma-polymerization (e.g., [9]). Most approaches were disadvantageous with regard to the durability of the thin-layers to washing and certain mechanical stresses, e.g., flexural fatigue [10,11].

The potential of a photo-chemical approach to increase surface hardness of polymer fiber and film has been studied by the authors [11–14]. The interaction of UV light with strongly absorbing polymers allows to generate a large number of radicals at the substrate surface, which can react with neighboring molecules (cross-linking of the substrate surface) or with suitable multi-functional substances in the environment (grafting or thin-layer growth). The general condition to achieve such reactions is a significant difference in the absorbance of a low or non-absorbing atmosphere and a strongly absorbing substrate. The actual radical generation and the ensuing reactions only take place at the outermost surface of the substrate which forms the boundary between the atmosphere and the activated substrate. Basically, four different types of reactions are possible (Table 1): (I) recombination of radicals, (II) cross-linking of polymer chains, (III) addition of radicals from the reactive atmosphere, and (IV) addition of bi-functional molecules resulting in cross-linking between the functional groups. It has been shown that reactions III and IV could result in photo-induced grafting of functional groups and thus could be used to increase both wettability and fluid repellence with regard to water or oil [11,13]. In addition, the

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Table 1
Possible reactions following UV lamp irradiation. PET molecules are denoted as A_i, and the reactive substance as Z.

Type	Reaction type	Reaction scheme	Effect
I	Recombination	$A_1{}^* + {}^*A_1 \rightarrow A_1\text{–}A_1$	None
II	Reaction with radical (s) of a neighboring chain	$A_1{}^* + {}^*A_2 \rightarrow A_1\text{–}A_2$	Cross-linking
III	Reaction with reactive atmosphere	$A_1{}^* + Z \rightarrow A_1\text{–}Z^*$	Addition
IV	Reaction with bi-functional substance	$A_1{}^* + Z \rightarrow A_1\text{–}Z^*\ A_1\text{–}Z^* + {}^*A_2 \rightarrow A_1\text{–}Z\text{–}A_2$	Cross-linking, thin-layer deposition

modifications are extremely durable because of covalent bonding to a certain degree. It is, therefore, possible to establish durable thin-layers following reaction schemes II and IV which significantly increase the polymer's resistance to alkaline hydrolysis, e.g., in the case of poly(ethyleneterephthalate) (PET) [15]. The effect is attributed to either superficial cross-linking of the polymer by bridging macromolecules with multi-functional species such as diallylphthalate (DAP), or by generating of a network of the multi-functional species on top of the substrate surface (thin-layer cross-linking) (cf. [14]).

Given this background, the irradiation of monofilaments made of PP in the presence of multi-functional substances was studied in this work, with regard to the resulting effect on abrasion resistance. In contrast to the situation given in the sketched treatment of PET, a fundamental difference is the low absorption of PP in the spectral range above 200 nm. Accordingly, reactive substances absorbing the incident UV radiation have been chosen for the experiments reported here. In this paper atomic force microscope (AFM) nanoindentation and microthermal analysis were applied to measure the effects of UV radiation on mechanical and thermal behavior of polymer surfaces.

2. Experimental

2.1. Materials

An industrially manufactured continuous PP fiber (monofilament) having a diameter of 165 μm was used as the standard sample material. The samples were extracted before use (Soxhlet, ethanol/petroleum ether, 3 h at 40 °C). The cross-linking agents were the multi-functional substances diallylphthalate (DAP) (Acros), tetraallyloxyethane (TAE) (Highlink TA), and pentaerithritoltriacylate (PETA) (Aldrich). These substances were chosen based on their different absorption properties to UV as shown in the relevant spectra (Fig. 1). The samples to be treated were dipped in the substances, which were solved in ethanol under variation of concentration.

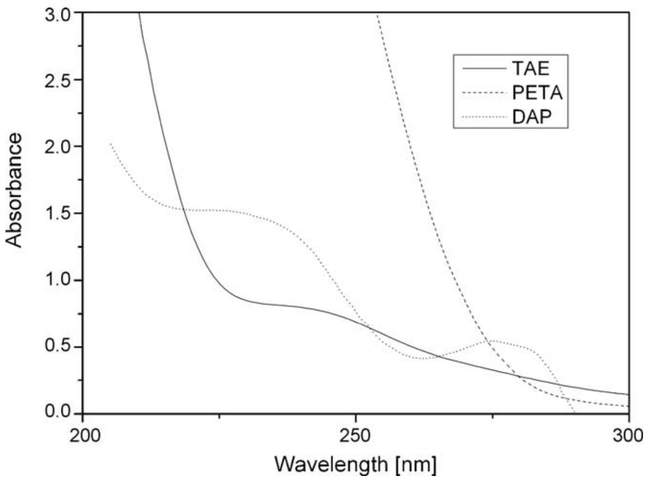

Fig. 1. Absorption spectra of the studied reactive substances in ethanol in the UV. *Note*: The irradiation of the finished samples was executed with 222 nm.

2.2. Irradiation

The irradiation was applied immediately after the dipping process (cf. Fig. 2), using a KrCl* excimer lamp (Heraeus, Germany). The lamp emits at 222 ± 5 nm and operated at constant power throughout. The irradiation was performed at a constant distance of 8 cm from the samples under inert atmosphere in order to prohibit competitive reactions with oxygen and ozone radicals. Inert conditions were realized by flooding the irradiation zone with argon at a pressure slightly above normal.

Besides the concentration of the substances in ethanol, varied process parameters were the irradiation time and the amount of finishing agent, i.e. reactive substance in ethanol, applied to the monofilaments. In addition, some treatments were carried out in separate steps, i.e. dipping of a certain length of monofilament (23 cm), drying and ensuing irradiation. The effective amount of the finishing agent was defined by a capillary through which the monofilaments were guided. In most cases, the finishing and irradiation were performed in a continuous online process at processing speeds between 0.3 and 1 m/min, accordingly, the exposure times varied between 0.33 and 1.1 min.

Following irradiation, the samples were extracted again according to the procedure described before.

2.3. Characterization

Atomic force microscope (AFM) nanoindentation was applied to measure the effects of UV radiation on mechanical behavior of polymer surfaces. The AFM-based nanoindentation has become an increasingly popular tool for characterizing polymer surfaces and thin films with widely different properties [16–20]. During operation of the AFM nanoindentation in force mode, the probe tip is first lowered into contact with the sample, then indented into the surface, and finally lifted off the sample surface. A measurement of the probe tip deflection is produced through an optical lever detection system, which continuously records the indentation force, *F*, and penetration depth, *h*, during one complete cycle of loading and unloading with a loading rate of 1 Hz (cf. Fig. 3). The contact stiffness, *k*, is the slope of the initial elastic unloading curve, d*F*/d*h*. It can be taken from the graphs given in Fig. 3 that *k*

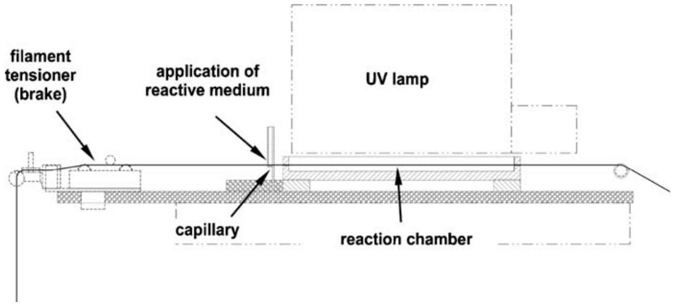

Fig. 2. Experimental setup for the continuous treatment of monofilaments.