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## Material Properties

## Effects of UV radiation on the friction behavior of thermoplastic polyurethanes



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## ABSTRACT

The effects of weathering exposure on unfilled and filled thermoplastic polyurethanes (TPU) materials are described as performed under different humidity conditions. For this purpose, a weathering device was used with UV-A 340 nm lamps at a constant temperature of 40 °C. The effects of environmental (UV and humidity condition) degradation on the frictional properties of TPU materials are presented along with surface analyses to characterize the chemistry of the degradative process. Photooxidative degradation of unfilled polymer leads to deterioration of physical and mechanical properties, which affects its tribological behavior significantly. Due to crosslinking, the stiffness of the material increases, reducing drastically the friction coefficient of unfilled TPUs. The frictional behavior of glass fiber reinforced TPU is less affected by radiation.

## 1. Introduction

Thermoplastic polyurethanes (TPUs) belong to the group of thermoplastic elastomers that offer the mechanical properties of rubbers with the processability of thermoplastic polymers, making them recyclable. Due to their outstanding toughness, durability and processing ease, TPUs are commonly employed in many fields such as the automotive industry and sports equipment, particularly where slip resistance is required.

Degradation of polymers due to ultraviolet (UV) radiation is a well-known phenomenon that induces physical processes and chemical reactions in polymers. It has been recognized that photooxidative degradation results in breaking of polymer chains, producing free radicals and, subsequently, oxidation products, and reducing molecular weight [1–4], although radical-induced crosslinking can also increase the molecular weight. Many attempts to identify the degradative products of polyurethane based materials have been presented [5–17]. Generally, these structural changes on the molecular level accumulate and ultimately lead to deterioration of macroscopic physical [4] and mechanical properties of polymers [11–13,16]. The effects on the friction and wear behavior have, however, rarely been reported [16,17].

Although radiation-induced crosslinking processes in vacuum are used to improve the properties of some polymers, increasing wear or chemical resistance [18], radiation in air may degrade the performance due to oxidation. Apart from degradation effects due to radiation, it is well known that polymers containing weak bonds like esters are prone

to moisture-induced damage via hydrolysis. Any polymer extraction can lead to a depletion in stabilizers, which in turn increases indirectly degradation.

In this paper, the effects of weathering exposure on unfilled and filled TPU materials are described as performed under different humidity conditions. The effects on friction are presented along with surface analyses to characterize the chemistry of the degradative process.

## 2. Experiments

## 2.1. Materials

As thermoplastic elastomers, TPU materials consist of thermoplastic hard segments and elastomeric soft segments, which are linked by hydrogen bonds. They have the processing advantages of thermoplastics and the material properties of elastomers. In this study, three TPU materials were investigated. A polyether based TPU (TPU1), a polyester based TPU (TPU2) and a glass fiber (20%) filled polyester TPU (TPU3). TPU1 and TPU2 are described in Fig. 1. Some material properties are presented in Table 1. The material properties of TPU 1 and 2 are similar to those of elastomers, while TPU3 has enhanced mechanical properties due to its glass fiber reinforcement.

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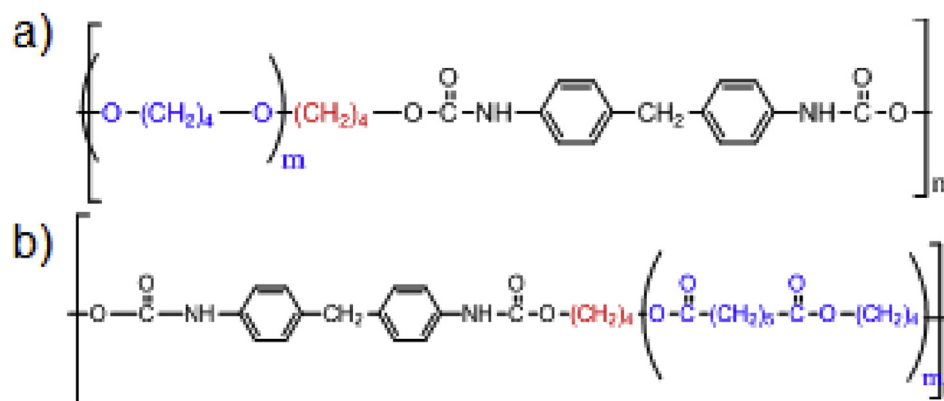


Fig. 1. Structures of a) TPU1 and b) TPU2.

Table 1

Material properties.

|                                 | TPU1 | TPU2 | TPU3 |
|---------------------------------|------|------|------|
| Density $d$ , g/cm <sup>3</sup> | 1.12 | 1.19 | 1.38 |
| Tg °C                           | -41  | -38  |      |
| Hardness Shore D                | 36   | 36   | 73   |
| Tensile strength MPa            | 45   | 50   | 80   |
| Young's modulus MPa             | 20   | 20   | 2800 |

## 2.2. Weathering exposure

Weathering exposure tests on TPU materials were carried out in “Global UV-Test 200” fluorescent lamp devices from Weiss Umwelttechnik GmbH, Germany. The UV-A 340 nm lamps produce a continuous spectrum with a maximum near 340 nm and do not show spectral contributions below the solar cut-off of about 290 nm. Constant UV irradiance of 40 W/m<sup>2</sup> at a constant temperature of 40 °C was applied. The samples were exposed up to 1000 h. Three different zones were prepared to produce a dry (15 %RH), humid (90 %RH) and wet areas (immersed in water) in parallel in the same weathering device using microclimatic sub-chambers. All exposure parameters were chosen as maximum parameters actually occurring under natural weathering conditions.

## 2.3. Surface analyses

The FTIR investigations of solids were performed using attenuated total reflection (ATR, Smart Orbit Accessory) in a Nicolet 6700 FTIR spectrometer (Thermo Scientific) with a DTGS KBr detector. To obtain a spectrum, 32 scans were taken at an optical resolution of 4 cm<sup>-1</sup>. For the ATR-FTIR investigations, the materials were pressed on the diamond cell to achieve surface sensitive test results. The spectra presented here are recorded from the directly exposed to UV side. An ATR correction as well as atmospheric correction were applied.

Optical, Scanning Electron and Atomic Force Microscopy were performed with a Keyence VHX-500, a Zeiss Supra™40 and an Asylum Research Cypher microscope, respectively, to detect any changes in the polymer surface following UV exposure and friction tests.

## 2.4. Friction and wear tests

The friction properties were characterized by 2 mm thick polymer samples against an aluminum disc ( $R_a = 0.16\text{--}0.2$ ) in a 3-pin arrangement with a reversing movement for 10 cycles (Fig. 2a). The contact pressure was 0.5 MPa, the maximal velocity 0.4 mm/s and the stroke 10 mm. The experiments were performed in air at about 30–40% RH. The friction contact was the UV-irradiated side. Wear rate

measurements were performed against a bearing steel disk (52100) with a pin-on-disk arrangement (Fig. 2b) by continuous sliding for 1000 m at 0.1 m/s and 1 MPa.

## 3. Results and discussion

### 3.1. Surface and chemical degradation effects

Surface properties were investigated as, especially, UV radiation first causes degradation on the surface and, in this way, degradation can be detected more sensitively than for the characterization of bulk properties. The influence of weathering on the color and surface morphology is illustrated in Fig. 3. Optical microscopy images of TPU samples are presented before and after radiation for 1000 h in dry, humid and wet conditions. Under all three conditions, the samples become yellowish, particularly TPU1. Under humid conditions, cracks appear, especially for TPU1 and TPU2.

Chemical changes on the surface of TPUs were confirmed by ATR-IR spectroscopy, performed before and after irradiation. Fig. 4 shows the bulk absorption spectra in the UV/VIS range of the unfilled polyether (TPU1) and polyester (TPU2) based materials at various times of radiation and dry conditions. The ATR spectra of the exposed surface change systematically with increasing exposure time, indicating UV induced degradation of TPUs.

For both unfilled materials, the most significant change appears between 3650 cm<sup>-1</sup> and 3000 cm<sup>-1</sup>, where the signal at 3328 cm<sup>-1</sup>, characteristic of stretching vibration of H-bonded N–H group, broadens with two maxima at 3451 cm<sup>-1</sup> and 3200 cm<sup>-1</sup> respectively, suggesting the formation of hydroxyl groups (–OH) induced by UV radiation. However, these two bands could also be characterized as a stretching vibration of N–H group in primary amine. The 3451 cm<sup>-1</sup> band has been attributed to hydroperoxidation of the methylene bridge [9].

ATR-IR spectra of both TPUs show a significant decrease of the N–H deformation band and C–N stretching vibration band of the urethane group (1534 cm<sup>-1</sup>). Also, both carbonyl regions 1734 cm<sup>-1</sup> - 1700 cm<sup>-1</sup>, corresponding to free and H-bonded respectively, became weaker with increasing exposure time, along with the formation of new carbonyl groups. Peaks between 1652 cm<sup>-1</sup> and 1638 cm<sup>-1</sup> were attributed to C=O stretching vibrations of oxidized methylene bridge [8]. Furthermore, it can be seen in Fig. 4a that the intensity of the peak at 1110 cm<sup>-1</sup>, attributed to the C–O–C vibrations of the ether groups, strongly reduces on irradiation. Also, the peak at 1597 cm<sup>-1</sup>, which can be ascribed to –C=C– stretching vibration of aromatic ring, loses intensity with increasing exposure time. Similar decrease is detectable for the aromatic = C–H out of plane deformation vibration at 817 cm<sup>-1</sup>.

The ATR bands between 3000 cm<sup>-1</sup> and 2800 cm<sup>-1</sup>, which are ascribed to CH<sub>2</sub> stretching vibrations, is particularly affected in the

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