DOI: 10.1002/masy.201300140

Investigation of Ageing Mechanisms in Thermoplastic Polyurethanes by Means of IR and Raman Spectroscopy

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Summary: Within the present study FTIR and Raman spectroscopy are evaluated as to specific strengths in terms of analysing deterioration in TPU induced by UV radiation or thermal load. A conventional ester based TPU grade formulated from 4,4'-methylene diphenyl diisocyanate, 1,4-butanediol and polycaprolactone was investigated. Exposure to UV was done in a Suntest CPS+ at different exposure times. Thermal treatment was done in an air circulation oven at 180 °C and different exposure times. Exposed samples were characterized as to changes in molecular structure with complementary methods ATR and Raman spectroscopy. To establish interrelationships between structural changes and macroscopic material characteristics UV/Vis/NIR spectroscopy and DSC were applied.UV/Vis/NIR spectroscopy clearly indicated yellowing, and thus an increase in absorption in the visible wavelength range, of TPU after exposure to UV or to thermal load. Yellowing correlated well with formation of chromophoric groups detected by ATR and Raman spectroscopy. ATR spectroscopy turned out to be very sensitive in detection of changes in chemical structure induced by UV radiation. Raman spectroscopy was found to be very sensitive in detection of changes in chemical structure induced by thermal load. No distinct effect of UV exposure on morphology of TPU was ascertained. In contrast, a strong effect of thermal treatment on (para)crystalline morphology was observed.

Keywords: ageing; infrared spectroscopy; morphology; raman spectroscopy; thermoplastic polyurethanes; UV-vis spectroscopy

Introduction

Thermoplastic Polyurethanes (TPU) are polymeric materials which combine elastomeric properties and thermoplastic processability. These exceptional characteristics are related to a segmented structure made of physically cross-linked hard segments, which are connected by flexible soft segments. To form hard segments diisocyanates and chain extenders, such as low molecular weight diols (glycols), are used. Reaction of diisocyanates and glycols yields in formation of urethane groups. To form long and flexible soft segments polyesters and polyethers are commonly used.[1] By varying formulation and constitution as well as by adding additives, especially mechanical properties, such as modulus, strength, hardness, damping characteristics and tribological performance may be tailored. As a consequence, area of application is wide for TPU: sealings, hoses, shoe soles, cable sheaths, films, foams or automotive interior. In application TPU are frequently exposed to thermal loads and/or ultraviolet (UV) radiation, which may induce ageing and deterioration of performance properties.[2–4] Many authors have investigated ageing of TPU under UV radiation, elevated temperatures, different atmospheres (air, nitrogen,

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ozone), humidity, electron beam irradiation or combinations thereof using different mechanical characterization methods such as Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Nuclear Magnetic Resonance spectroscopy (NMR spectroscopy), UV/Vis/NIR spectroscopy, and Fourier Transform Infrared (FTIR) or Attenuated Total Reflectance (ATR) spectroscopy.[2–13] Changes in molecular and supramolecular structure and in mechanical and optical properties were observed. Thompson et al. reported decrease in molecular weight after hydrolytic ageing of TPU.[14] Additionally, changes in modulus were found. Several authors studied temperature induced alterations of melting and recrystallization characteristics in TPU after thermal exposure.[15–17] Simultaneously, mechanical properties e.g. modulus and stress-strain behaviour were affected.[4] Rosu et al., Wilhelm and Gardette and other authors reported significant yellowing of TPU after exposure to UV radiation or heat.[18,19,3,7]

Nevertheless, degradation mechanisms in TPU have not been fully understood yet. Due to the high chemical diversity in composition of TPU and complex interrelationships with environment (e.g. irradiation, temperature, atmosphere, ambient media) numerous degradation mechanisms and products may occur.[6,8,10–13,18–26] Today, especially FTIR and ATR spectroscopy are well established to study ageing, phase separation, stress relaxation, or formation of hydrogen bonds in TPU.[6,10–13,18–21,23–25,27–31] Raman spectroscopy is another important technique to characterize molecular and supramolecular structure of polymeric materials. However, only few studies dealing with characterization of TPU applying Raman spectroscopy exist. Polymerization kinetics were characterized and principle component regression was performed to predict mole fraction of hard segements in TPU using Raman spectroscopy.[32,33] Futhermore, Ferry et al. investigated the influence of lithium coordination in TPU by FT Raman and FTIR spectroscopy.[28]

Raman and IR spectroscopy are complementary methods and provide supplementary information. Especially combining both methods gives a deeper insight in TPU structure and thus in ageing mechanisms (e.g. [32,34–36]). However, studies applying both, Raman and IR spectroscopy, for analysis of ageing in TPU are not reported so far to the state of knowledge of the authors. Hence, the overall objective of the present study is to apply FTIR and Raman spectroscopy in order to characterize structural changes in TPU caused by UV radiation or thermal load. On the one hand focus is on evaluating and combining information provided by both techniques such as to gain detailed insight in ageing mechanisms. On the other hand specific strengths of each method in terms of analysing deterioration in TPU shall be revealed. To establish interrelationships between structural changes and macroscopic material characteristics UV/Vis/NIR spectroscopy and DSC are applied additionally.

Experimental Part

Material

An ester based TPU grade formulated from 4,4′-methylene diphenyl diisocyanate (MDI), 1,4-butanediol (BD) and polycaprolactone (PCL) was investigated. Injection moulded rectangular technical specimens with an average thickness of 2.3 mm, width of 100 mm and a length of 80 mm were used. Annealing of as-produced samples for 24 h at 100 °C in an air circulation oven resulted in a melting temperature of 156 °C and a melting temperature range from 120 °C to 194 °C.

Exposure to UV Radiation

Exposure to UV was done using a xenon arc lamp in a Suntest CPS+ (Atlas Material Testing Technology LLC, Chicago, USA). Wavelength of radiation ranged from 300 nm to 800 nm. Intensity was 600 W/m^2. Black-standard temperature (BST) was 50 °C. Applied exposure times were 10 h,

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50 h, 100 h, 500 h, 750 h and 1000 h. One side of specimen was deposed on a metallic underlay. Specimens were only exposed from one side.

Thermal Treatment

Thermal treatment of TPU was performed using a Heraeus UT6060 circulation air oven (Kendro Laboratory Products, Langenselbold, GER). One side of specimen was deposed on an aluminium underlay. Applied exposure temperature was 180 °C. Exposure times were 5 min, 30 min, 60 min, 120 min and 180 min.

Spectroscopic Investigations

Fourier Transform Infrared spectroscopy (FITR spectroscopy) was performed in Attenuated Total Reflectance (ATR) mode using a Spectrum GX FTIR spectrometer (Perkin Elmer Instruments GmbH, Überlingen, GER) within a wavenumber range from 400 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1} using a diamond crystal (Gladi-ATR Vision, Pike Technologies, Madison, USA). Depending on wavenumber, penetration depth of ATR measurements was approximately between 1 µm and 7 µm. After a background correction one ATR spectrum of each sample surface was measured by using 16 iterations. An automatic baseline correction was performed with Spectrum v.5.3.1 (Perkin Elmer Instruments GmbH, Überlingen, GER). Exposure to UV induced significant changes in ATR spectra of TPU. Thus no normalization was performed for samples exposed to UV radiation. However, ATR spectra of TPU exposed to heat were normalized. The intensity of ATR band at 1596 cm^{-1}, which can be ascribed to aromatic –C=C– stretching vibrations, was used for normalization.

Raman spectroscopy of was performed on a Labram confocal Raman spectrometer (Horiba Jobin Yvon GmbH, Bensheim, GER) equipped with a helium neon laser. The line at 632.8 nm with a power of 6 mW on the sample surface was used for excitation. Furthermore, a diffraction grating with 1800 grooves/mm was applied. Positions of hole and slit were 500 µm and 200 µm, respectively. One Raman spectrum was recorded on each sample surface in the range of 400 cm^{-1} to 3500 cm^{-1} using an integration time of 20 s with 10 iterations and a 100x objective. Due to fluorescence, Raman spectra of some UV exposed TPU were measured with different parameters. Raman spectra of the directly exposed surface after exposure to UV for 500 h were measured with an integration time of 5 s and 31 iterations. Raman spectra of the directly exposed surface after exposure to UV for 750 h were measured with an integration time of 1 s and 201 iterations. Due to high fluorescence measuring the Raman spectra of the directly exposed surface after exposure to UV for 1000 h was not possible. Spectral resolution of 1 cm^{-1} was achieved. Raman spectra were measured within a penetration depth of approximately 3 µm. A baseline correction of Raman spectra was applied using the software LabSpec V.5 (Horiba Jobin Yvon GmbH, Bensheim, GER). Raman spectra were normalized to the intensity of aromatic –C=C– stretching vibration at 1617 cm^{-1}. Smoothing of Raman spectra was performed in Origin 9.0 using a Savitzky-Golay-Filter.

UV/Vis/NIR spectroscopy was performed on a UV/Vis/NIR spectrophotometer (Lambda 950, Perkin Elmer Instruments GmbH, Überlingen, GER) equipped with an Ulbricht sphere (diameter 150 mm). Direct hemispheric transmittance and direct hemispheric reflectance spectra were recorded in the spectral region between 380 nm and 780 nm. Obtained spectra were weighted by the irradiance source function of average daylight (standard illuminant C) in order to obtain integral hemispheric transmittance and integral hemispheric reflectance. Finally, absorption was calculated by subtracting integral hemispheric transmittance and integral hemispheric reflectance from total sum of 1.

Thermal Analysis

Melting characteristics were determined using a differential scanning calorimeter

DSC 821e (Mettler-Toledo AG, Schwerzenbach, CH). Thermograms were recorded under nitrogen atmosphere in a temperature range from 23 °C to 250 °C applying a heating rate of 10 K/min. Two heating cycles were performed for each sample. Sample mass was 6 mg ± 1 mg. Melting temperature and melting enthalpy were evaluated according to ISO11357-3. The presented data were averaged over three measurements.

Results and Discussion

Exposure to UV radiation

In Figure 1a the direct hemispheric transmittance spectra of TPU exposed to UV for different times are presented. In general, the direct hemispheric transmittance decreases with increasing exposure time up to exposure times of 500 h. The direct hemispheric transmittance spectra of 500 h and 1000 h of exposure to UV differ only slightly. The strongest reduction in direct hemispheric transmittance occurs in wavelength region between 400 nm and 500 nm. As this spectral region covers mainly violet and blue light, this indicates significant yellowing of the samples. The loss in direct hemispheric transmittance between 300 nm and 500 nm is attributable to formation of chromophoric groups, which cause absorption.[37,38] Interestingly, the spectrum of the unaged TPU does not fit the spectra of the UV exposed samples. However, a continuous change in curve slope with increasing exposure time is observable starting at the spectrum of the unaged sample.

In Figure 1b absorption of TPU is plotted as a function of UV exposure time. In general, the increase in absorption is correlating with direct hemispheric transmittance spectra. Absorption decreases from 9.8% for the untreated sample to 8.0% for the sample exposed to UV radiation for 10 hours (different shape of spectrum of unaged sample). Afterwards a continuous increase in absorption from 8.0% to 26.4% with increasing exposure time is detectable. Again, absorption barely changes between 500 h and 1000 h of UV exposure. In general, these results indicate significant ageing of TPU due to UV exposure.

Commonly, polyurethanes containing MDI are susceptible to UV induced yellowing.[21,22] Figure 2 illustrates photooxidative degradation mechanisms which are proposed in literature. According to mechanism a, the central methylene unit yields in formation of highly conjugated mono- and diquinone structures. Mechanism b suggests a Photo-Fries rearrangement. Both

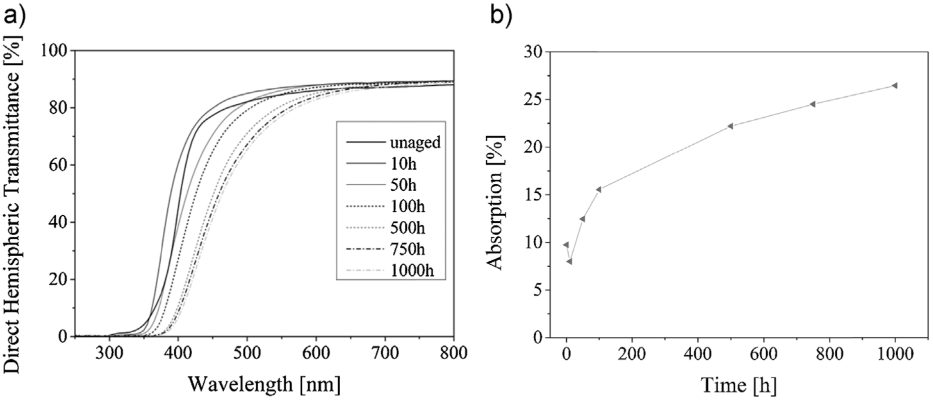

Figure 1.
(a) Direct hemispheric transmittance spectra of TPU exposed to UV for different times (b) Absorption of TPU exposed to UV for different times.

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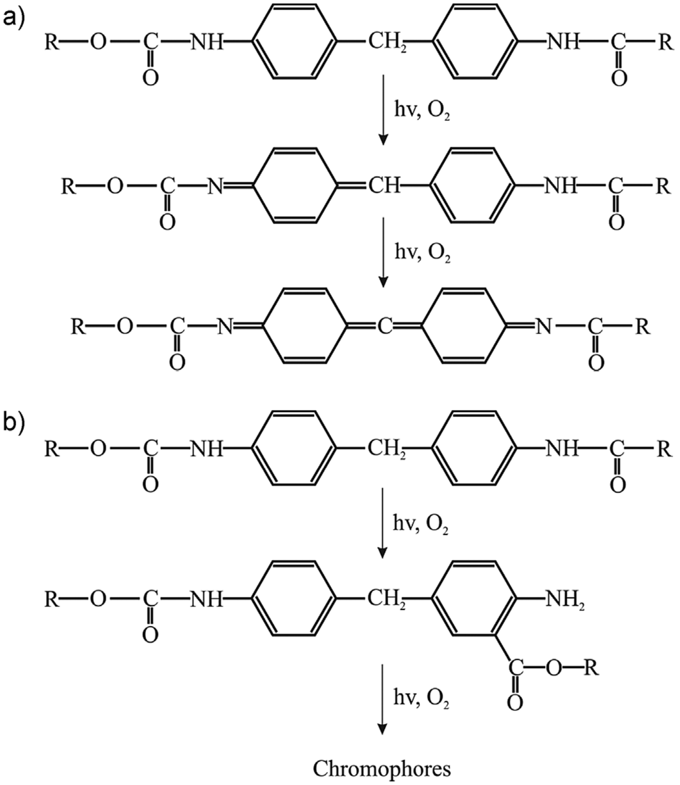

Figure 2.
(a) Formation of mono- and diquinone structures (b) Formation of chromophores via Photo-Fries rearrangement.

photooxidative degradation mechanisms result in the formation of chromophoric groups.[19,39,21]

In Figure 3 ATR spectra of TPU exposed to UV for various times are compared. At the top ATR spectra of the directly exposed surface are shown. At the bottom ATR spectra of the samples bottom side (not directly exposed) are presented. The ATR spectra of the directly exposed surface (top) change systematically with increasing exposure time, indicating UV induced degradation of TPU. Most significant changes in ATR spectra can be recorded between 100 h and 500 h of exposure to UV radiation, which is in agreement with results from UV/Vis/NIR spectroscopy (cf. Figure 1). The band at 3328 cm^{-1} is caused by the stretching vibration of the N-H bond of the urethane unit. The intensity decreases with increasing exposure time. This can be ascribed to a reduction of the urethane structures due to UV radiation.[18,22] In the surroundings of the stretching vibration of the N-H group a broad ATR band superimposes after 750 h and 1000 h of exposure. Rosu et al. also found a broadening around 3328 cm^{-1} in the FTIR spectra of UV aged polyurethane.[18] However, deconvoluted bands differ from those observed within this study. According to Rosu et al. the emerging broadening could be attributed to the formation of primary amines as suggested in Figure 2b.[18] The asymmetric and symmetric N-H stretching vibration of primary amines is located between 3550 cm^{-1} and 3250 cm^{-1}.[40] Similar broadening of the ATR spectrum between 3580 cm^{-1} and 3200 cm^{-1} can be observed

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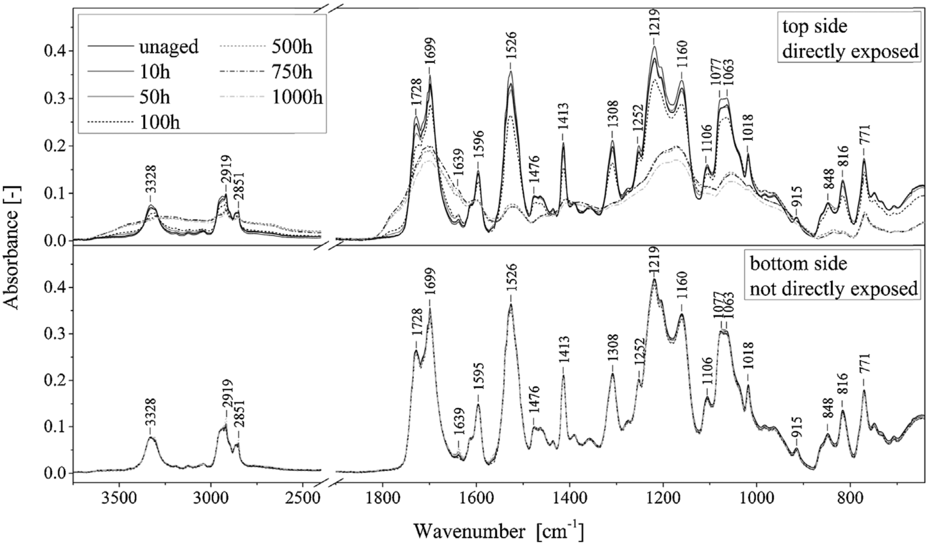

Figure 3.
ATR spectra of TPU exposed to UV for different times.

after formation of hydroxyl groups.[19,40,41] The ATR bands between 3000 cm^{-1} and 2800 cm^{-1} can be ascribed to CH_2 stretching vibrations. A loss in band intensity with increasing exposure time is observable. Thus, CH_2 groups of the TPU might also be affected by degradation. The ATR bands at 1728 cm^{-1}and 1699 cm^{-1} represent stretching vibrations of the carbonyl groups, whereas the bands can be attributed to the ester and to urethane carbonyls, respectively.[12,18,41] Both carbonyl bands are getting weaker with increasing exposure time along with formation of new bands between 1835 cm^{-1} and 1745 cm^{-1}. These changes indicate degradation of the urethane and ester groups and formation of new carbonyl groups. Formation of new carbonyl groups along with hydroxyl groups, which are observable between 3580 cm^{-1} and 3200 cm^{-1}, suggests the formation of carboxyl groups induced by UV radiation. The increasing band intensity at approximately 1639 cm^{-1} indicates N-H deformation vibrations of primary amines which are typically found between 1650 cm^{-1} and 1580 cm^{-1}. Additionally, alkene groups occur in spectral region between 1680 cm^{-1} and 1620 cm^{-1}.[10,40] Furthermore, C=O stretching vibrations of oxidized methylene bridge show ATR bands between 1652 cm^{-1} and 1638 cm^{-1}.[12] Also the ATR band at 1596 cm^{-1}, which can be ascribed to −C=C− stretching vibration of aromatic ring, loses intensity with increasing exposure time. Similar loss of intensity is detectable for the aromatic =C−H out of plane deformation vibration at 848 cm^{-1}. This implies chemical changes and degradation of aromatic structure. This is probably attributable to photooxidation of central methylene unit according Figure 2a.[18] The ATR band at 1526 cm^{-1} represents a combination of N-H deformation and C−N stretching vibration (amide II band) of the urethane group.[40] A decrease in intensity with increasing exposure time is also detectable for this peak. This is correlating with degradation mechanisms given in Figure 2. Moreover, strong reduction of intensity of ATR bands in the region between 1300 cm^{-1} and 1100 cm^{-1} are observable with increasing exposure time. This spectral region is assigned in literature to C−O stretching vibrations of urethane units or C−O stretching vibrations of esters.[18,41] Identical, but

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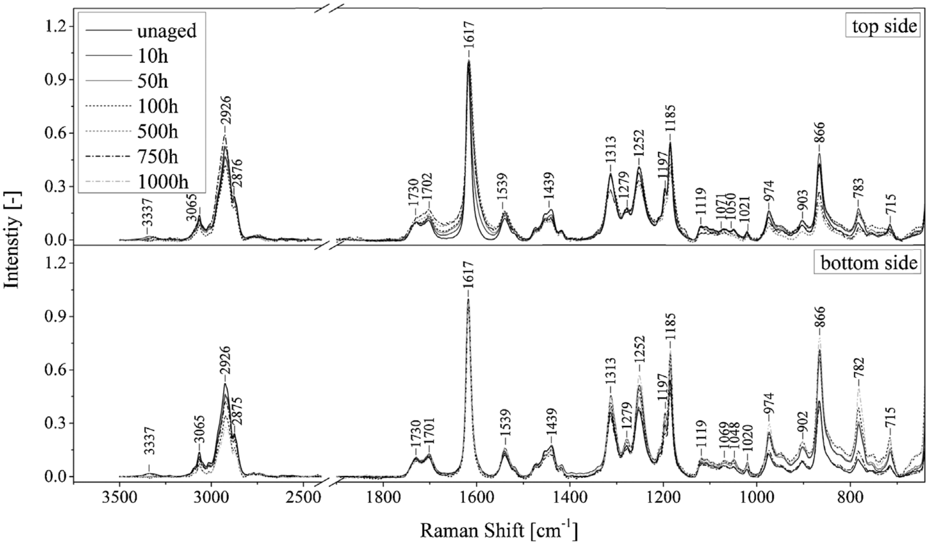

Figure 4.
Raman spectra of TPU exposed to UV for different times.

less pronounced changes are discernible at the bottom of the specimens (Figure 3 bottom). Intensity of radiation decreases with increasing sample thickness, due to absorption and scattering according to Lambert Beer law. Therefore, the bottom surface is less susceptible to UV induced ageing. In Figure 4 Raman spectra of TPU exposed to UV for various times are compared. At the top Raman spectra of the directly exposed surface are shown. At the bottom Raman spectra of the samples bottom side (not directly exposed) are presented. The weak Raman band at 3337 cm^{-1} can be attributed to urethane N–H stretching vibrations.[40] Due to weak intensity of this broad bond and increasing noise of Raman spectrum with increasing exposure time, this bond was excluded from interpretation. The Raman band at 3065 cm^{-1} represents =C–H stretching vibrations of the aromatic ring.[40] The Raman bands with a maximum at 2928 cm^{-1} and 2875 cm^{-1} can be attributed to asymmetric and symmetric C–H stretching vibrations of CH_2 groups.[40] C=O stretching vibrations of ester and urethane groups can be seen at 1730 cm^{-1} and 1702 cm^{-1}.[32,33] However, Raman spectra between 3150 cm^{-1} and 1680 cm^{-1} are not significantly affected by exposure time. The intense band between 1660 cm^{-1} and 1570 cm^{-1} with a maximum at 1617 cm^{-1} can be ascribed to –C=C– stretching vibrations of aromatic ring.[32,33] Figure 5 shows this peak for various exposure times in detail for the directly exposed surface. A broadening with increasing exposure time is observable. This indicates chemical degradation of aromatic rings. The Raman spectra of the back side of the TPU specimen don't

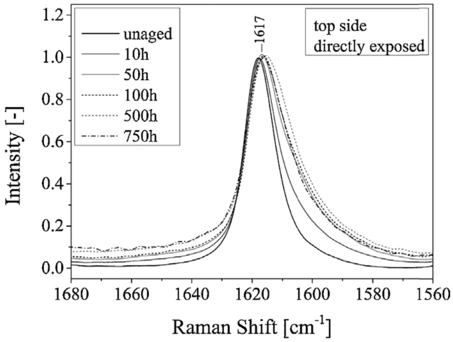

Figure 5.
Detail of Raman spectra of TPU exposed to UV for different times between 1680 cm^{-1} and 1560 cm^{-1}.

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show the broadening around 1617 cm^{-1} (Figure 4). Combined N–H deformation and C–N stretching vibrations (amid II band) are ascribable to the Raman band at 1539 cm^{-1}.[33,40] The band between 1400 cm^{-1} and 1500 cm^{-1} with a maximum at 1439 cm^{-1} can be ascribed to C–H deformation vibrations of CH_2 groups.[33,40] None of these bands is affected by UV exposure. Around 1251 cm^{-1} coupled C–N and C–O vibrations of urethane group (urethane amid IV band) are discernible.[40] The Raman band at 1185 cm^{-1} may be attributed to aromatic =C–H in plane deformation vibrations.[40] Generally, intensities of different bands detected by Raman spectroscopy between 3100 cm^{-1} and 2810 cm^{-1} and between 1400 cm^{-1} and 700 cm^{-1} varied with varying exposure time. Nevertheless, no distinct correlations between band intensity and exposure time are discernible.

In general, ATR and Raman spectra were measured at TPU surface including a volume with few microns penetration depth. Although depth of measurement is similar, compared to ATR spectroscopy, Raman spectroscopy is less sensitive to UV induced changes in TPU structure under investigated conditions. ATR spectroscopy indicates formation of chromophores. This is consistent with increasing yellowing detected by UV/Vis/NIR spectroscopy between 400 nm and 500 nm and increasing absorption induced by UV radiation.

Figure 6 shows the melting enthalpy of TPU exposed to UV for different times along with melting temperature and corresponding on-set and end-set temperatures. Samples for DSC measurements covered a volume including directly exposed and bottom side of TPU. Therefore, melting enthalpy presented hereafter reflects a mean value of the samples. Melting enthalpy slightly increases with increasing exposure time (Figure 6a). Melting enthalpy ranges between 17.5 J/g for the as-produced TPU and 19.9 J/g for the TPU exposed to UV for 1000 hours. The strongest increase of melting enthalpy from 17.6 J/g to 18.5 J/g is found between 0 and 10 h of UV exposure. On the one hand, the increase in melting enthalpy may be ascribed to annealing of the samples due to radiation induced temperature increase within the suntest instrument. Annealing allows the crystals to reorganize and to increase or decrease order.[1] On the other hand, melting enthalpy may be affected by photooxidative changes in morphology. As deducible from Figure 3, photooxidation is stronger on directly exposed surface than on bottom side of the samples. Therefore, the detected changes in melting enthalpy reflect most likely a superimposition of annealing effect and changes in

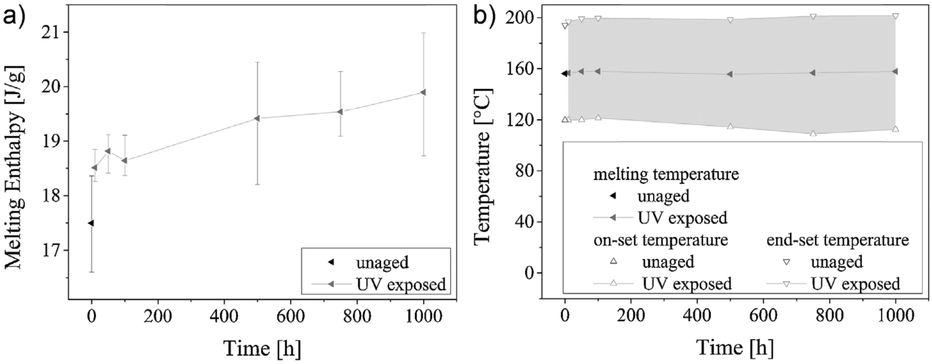

Figure 6.
(a) Melting enthalpy of TPU exposed to UV for different times (b) Melting temperature and corresponding on-/end-set temperature of TPU exposed to UV for different times.

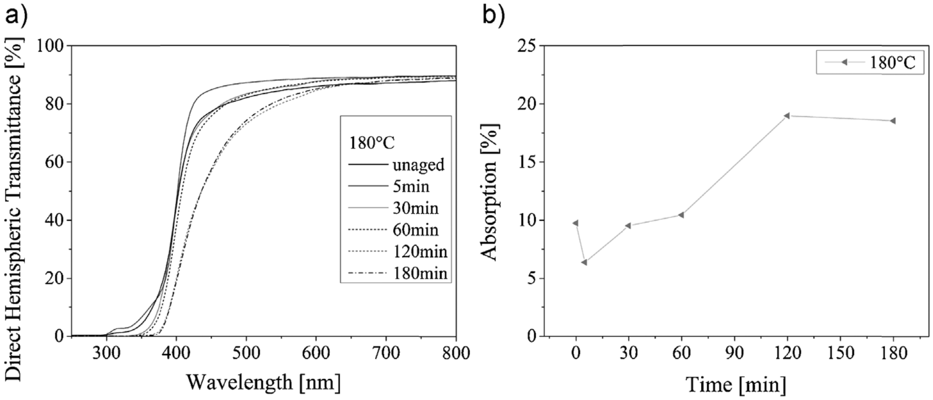

Figure 7.
(a) Direct hemispheric transmittance spectra of TPU exposed to 180 °C for different times (b) Absorption of TPU exposed to 180 °C for different times weighted by illuminant C.

morphology due to photooxidation. Melting temperature, on-set and end-set temperatures are not affected by UV exposure conditions applied within this study (Figure 6b).

Thermal Treatment

In Figure 7a the direct hemispheric transmittance spectra of TPU exposed to 180 °C for different times are presented. The direct hemispheric transmittance spectra for exposure times of 120 min and 180 min differ only slightly. The strongest reduction in the direct hemispheric transmittance occurs in the wavelength region between 400 nm and 500 nm. This is an indication for yellowing of the samples. As already discussed above, yellowing may be ascribed to the formation of chromophoric groups. As for the UV exposed samples (Figure 1a) the spectrum of the unaged TPU does not fit the spectra of the exposed samples. This may be caused by changes in morphology after thermal treatment. Influence of local thickness and local chemical structure could also be possible. However, slope of the spectra of the unaged and the sample exposed for 5 min show similarities. Further increase in exposure time yields in a continuous change in slope of the spectra.

In Figure 7b absorption of TPU is plotted as a function of treatment time. In general, absorption characteristics are correlating with direct hemispheric transmittance spectra. Absorption decreases from 9.8% for the untreated sample to 6.4% for the sample treated for 5 min according to the different shape of the spectra for both samples. Afterwards, an increase in absorption with increasing treatment time is detectable. For exposure times of 30 min and 60 min absorption is 9.5% and 10.4%, respectively. The biggest increase in absorption from 10.4% to 19.0% occurs for treatment times between 60 min and 120 min. After a treatment time of 120 min absorption decreases again slightly from 19.0% to 18.5%. In general, these results indicate significant ageing of TPU due to thermal treatment.

In Figure 8 ATR spectra of TPU exposed to 180°C for various times are compared. At the top ATR spectra of the directly exposed top side are shown. At the bottom ATR spectra of the samples bottom side are presented. ATR spectroscopy reveals only marginal differences between unaged and heat exposed samples. Minor differences between the ATR spectra of unaged and heat exposed TPU can be observed around the asymmetric and symmetric CH_2 stretching vibrations between $3000\,cm^{-1}$ and $2800\,cm^{-1}$: the untreated material shows more pronounced shoulders at $2918\,cm^{-1}$ and $2851\,cm^{-1}$. Another difference is a band with weak

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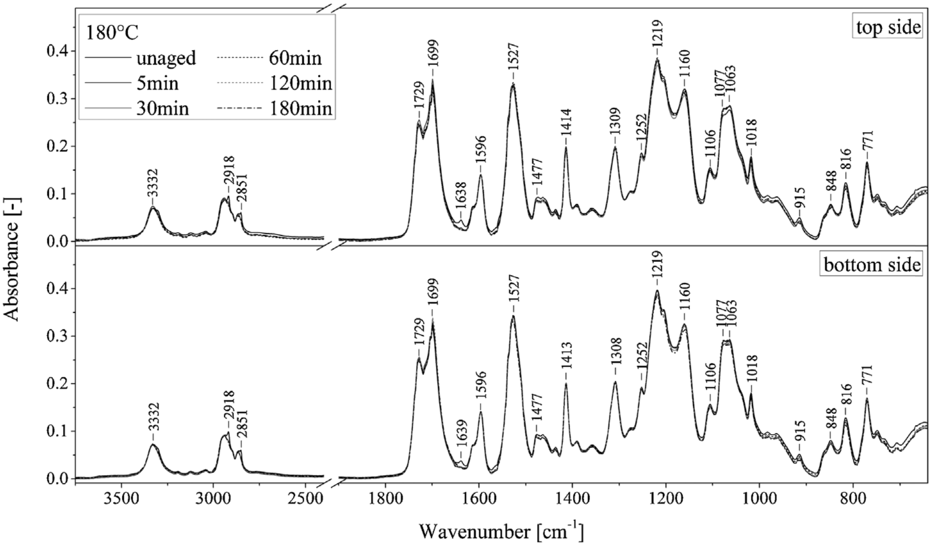

Figure 8.
ATR spectra of TPU exposed to 180 °C for different times.

intensity at 1638 cm^{-1}, which is only discernible for the untreated sample. This ATR band is located in spectral region where typically N-H deformation vibrations of primary amines (between 1650 cm^{-1} and 1580 cm^{-1}) and alkene C=C stretching vibrations occur (between 1680 cm^{-1} and 1620 cm^{-1}).[40] Servay et al., who investigated heat ageing of an ester based TPU by NMR and ATR spectroscopy, found a new band formed after heat exposure at 1645 cm^{-1}, which was not present in the unaged material.[12] According to Servay et al., ATR bands between 1652 cm^{-1} and 1638 cm^{-1} can be attributed to C=O stretching vibration of oxidized methylene bridge. The presented ATR spectra show the opposite trend: a band at 1638 cm^{-1} decomposes after heat exposure. No differences between top and bottom surface are observable.

In Figure 9 Raman spectra of TPU exposed to 180 °C for various times are compared. At the top Raman spectra of the directly exposed top side are shown. At the bottom Raman spectra of the samples bottom side are presented. The weak Raman band at 3337 cm^{-1} can be attributed to hydrogen bonded urethane N-H stretching vibrations. As already discussed above, the Raman bands between 2800 cm^{-1} and 3150 cm^{-1} with peaks at 3065 cm^{-1}, 2926 cm^{-1} and 2875 cm^{-1} can be ascribed to =C–H stretching vibrations of the aromatic ring and asymmetric and symmetric C-H stretching vibrations of CH_2 groups.[40] For none of these bands systematic correlations between peak intensity and exposure time are discernible. Similar observations can be made for C=O stretching vibrations of ester and urethane groups at 1730 cm^{-1} and 1703 cm^{-1}. Significant changes in Raman spectra as a function of exposure time occur in the region between 1680 cm^{-1}and 1560 cm^{-1}, which is mainly determined by aromatic –C=C– stretching vibration with a peak at 1617 cm^{-1}.[32,33] Thus in Figure 10a this spectral region is zoomed out. With increasing exposure time increasing broadening of the Raman band around 1617 cm^{-1} can be observed. The asymmetric broadening of this band is caused by an emerging hidden band around 1605 cm^{-1}. The Raman band at 1605 cm^{-1} can be assigned to aromatic –C=C– stretching vibrations.[40] This additional Raman band indicates modifications of aromates, which yield in a slight decrease

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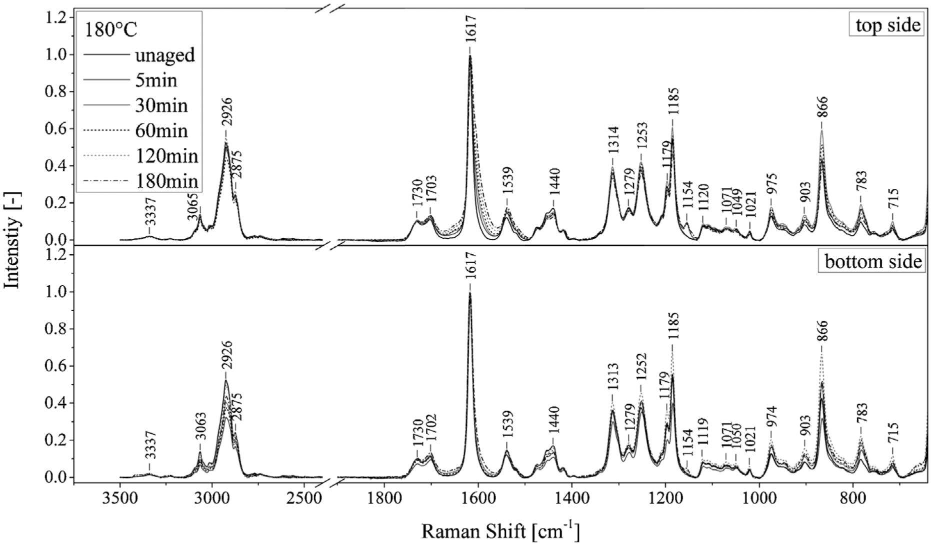

Figure 9.
Raman spectra of TPU exposed to 180 °C for different times.

of wavenumber. Further significant changes in Raman spectra with increasing exposure time can be detected at 1154 cm^{-1}. A new band emerges after an exposure time of 30 min. This is presented in Figure 10b in more detail. Currently, the chemical identity of this band is not clear. However, these results clearly indicate temperature induced changes in chemical structure in TPU. Most likely aromatic structure is affected. Servay et al. reported similar findings.[12] Interestingly, the observed changes are less pronounced at the bottom side of specimen, though TPU was equally tempered on both sides (Figure 9). Experiments conducted in nitrogen atmosphere yielded similar results. Thus, this phenomenon may not be ascribed to effects induced by oxygen.

Although depth of measurements is similar, compared to ATR spectroscopy, Raman spectroscopy is more sensitive to changes in TPU structure induced by

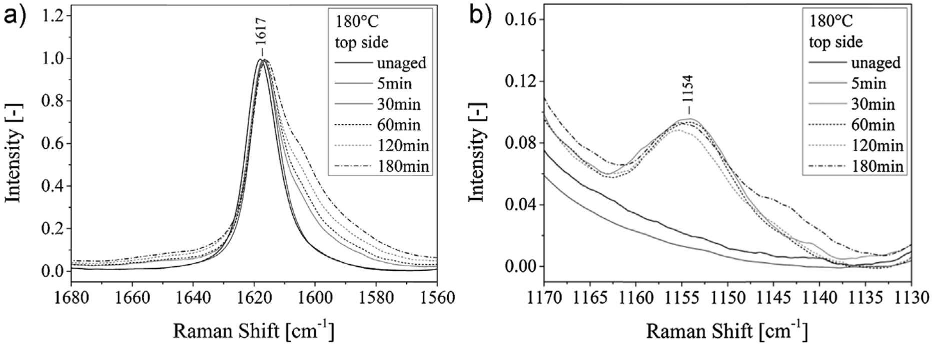

Figure 10.
(a) Detail of Raman spectra of TPU exposed to 180 °C for different times between 1680 cm^{-1} and 1560 cm^{-1}.
(b) Detail of Raman spectra of TPU exposed to 180 °C for different times between 1170 cm^{-1} and 1130 cm^{-1}.

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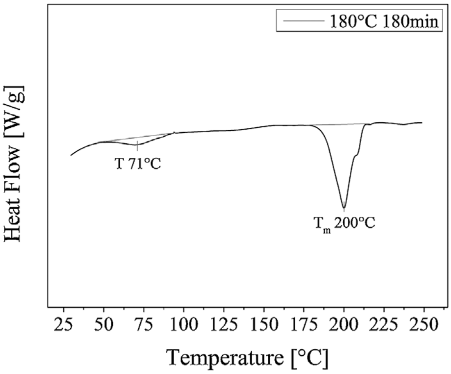

Figure 11.
Exemplary thermogram of heat exposed TPU.

thermal loads investigated within the present study. Diversifications in Raman spectra indicate formation of heat induced degradation products. Results are correlating with results from UV/Vis/NIR spectroscopy, indicating the formation of chromophoric degradation products.

A typical thermogram of TPU after heat ageing at 180 °C for 180 min is presented in Figure 11. A melting peak with melting temperature of 200 °C and melting enthalpy of 11.5 J/g is discernible. Moreover, a small endotherm peak with a peak temperature of 71 °C and an enthalpy of 1.4 J/g is observable. This weak endotherm peak stays nearly unaffected by thermal exposure. Therefore, it is probably not associated with changes in degree of crystallinity. Thus, for the following discussion only the main peak at higher temperatures is evaluated.

In Figure 12 melting enthalpy of heat exposed TPU is presented along with melting temperature and corresponding on-set and end-set temperatures. Compared to melting enthalpy of 17.5 J/g of unaged TPU, the melting enthalpy is reduced after heat exposure (Fig. 13a). Melting enthalpy of thermally treated samples ranges from 4.8 J/g (5 min) to 11.5 J/g (180 min). From exposure times of 5 min to 120 min a continuous increase in melting enthalpy is detectable, which can be attributed to crystallisation. Afterwards the melting enthalpy remains nearly constant. As it can be seen in Figure 12b, on-set and end-set temperatures of heat exposed samples are higher than those of unaged TPU. The unaged TPU exhibits a melting temperature of 156 °C with an on-set and end-set temperature of 120 °C and 194 °C, respectively. TPU exposed to 180 °C for 5 min exhibits two melting regions: a first broad melting peak between 100 °C and 175 °C and a second more pronounced and narrow melting peak between 175 °C and 196 °C (on-set and end-set temperatures). Sum enthalpy of 4.8 J/g was measured. Further rising of exposure time yields in a narrow single melting peak indicated by on-set and end-set temperatures. Similar

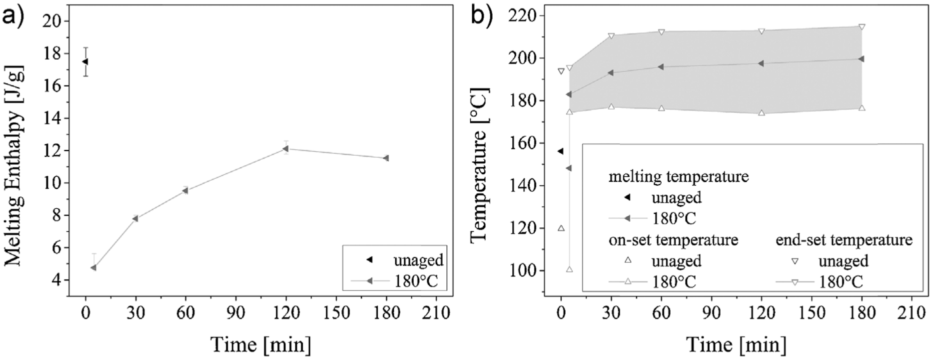

Figure 12.
(a) Melting enthalpy of TPU exposed to 180 °C for different times (b) Melting temperature and corresponding on-/end-set temperature of TPU exposed to 180 °C for different times.

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observations were made in literature and can be ascribed to a higher order of (para) crystalline structure after heat exposure.[1] These results clearly indicate a strong influence of time and temperature on morphology in TPU.

Conclusion

Within this paper the effects of exposure to UV radiation and thermal load on chemical and supramolecular structure of TPU were studied applying UV/Vis/NIR spectroscopy, ATR spectroscopy, Raman spectroscopy and DSC. UV/Vis/NIR spectroscopy clearly indicated yellowing and thus an increase in absorption in the visible wavelength range, of TPU after exposure to UV or to thermal load. A distinct correlation between degree of yellowing and exposure time was ascertained.

For samples exposed to UV, yellowing was in good agreement with results from ATR spectroscopy. ATR spectra showed systematic formation of chromophores, such as quinones and coloured products formed after Photo-Fries rearrangement, with increasing exposure time. Additionally, formation of carboxyl groups, alkene groups and primary amines was indicated. In general, changes in chemical structure were more pronounced on the sample surface exposed to UV directly. In contrast to ATR spectroscopy, Raman spectroscopy did not reveal any significant differences between TPU exposed to UV for various times. DSC did not reveal any distinct effect of UV exposure on morphology of TPU.

For samples exposed to thermal load, yellowing was in good agreement with results from Raman spectroscopy. Interestingly, ATR spectroscopy turned out to be less sensitive in detection of chemical changes induced by the thermal loads investigated within in this study. However, Raman spectra showed systematic formation of chromophores with increasing exposure time. Changes in Raman spectra were detectable around the aromatic $-C=C-$ stretching vibration at $1617\,cm^{-1}$. Moreover, formation of an additional Raman band at $1154\,cm^{-1}$ was observed. DSC revealed a strong effect of thermal treatment on (para)crystalline morphology.

Acknowledgement: The research work of this paper was performed at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Austrian Ministry of Traffic, Innovation and Technology with contributions by the Chair of Materials Science and Testing of Polymers at the University of Leoben and SKF Sealing Solutions Austria GmbH. The PCCL is funded by the Austrian Government and the State Governments of Styria and Upper Austria. The authors wish to express their acknowledgement to A. Rauschenbach for support during spectroscopic measurements and for helpful discussions.

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