Polymer Degradation and Stability 252 (2026) 112285

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.journals.elsevier.com/polymer-degradation-and-stability

Recyclability of thermoplastic polyurethane under repeated mechanical reprocessing: degradation mechanisms and volatile emissions

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ARTICLE INFO

Keywords:
Reprocessed thermoplastic polyurethane
Volatile organic compounds
HS-SPME-GC-MS
Py-GC-MS
DSC
GPC
Migration testing

ABSTRACT

Repeated mechanical recycling is a key strategy within circular economy concepts however the accumulation of degradation products and volatile emissions may limit the safe reuse of thermoplastic polyurethanes. This study presents a comprehensive, multi-analytical evaluation of the effects of repeated mechanical reprocessing on thermoplastic polyurethane (TPU), with particular emphasis on structural degradation, the formation of low-molecular-weight compounds and volatile organic compounds (VOCs). TPU samples were subjected to one and two consecutive mechanical reprocessing cycles and systematically characterised using gel permeation chromatography (GPC), differential scanning calorimetry (DSC), rheological analysis, X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS), migration testing, and headspace solid-phase microextraction coupled with gas chromatography–mass spectrometry (HS-SPME-GC-MS). Mechanical reprocessing resulted in a pronounced decrease in molecular weight of the peak maxima (Mp; up to approximately 80%), accompanied by reduced viscosity and a narrower molar mass distribution, indicating extensive polymer chain scission and diminished processability. DSC analysis revealed moderate changes in melting temperature and crystallisation behaviour. Detailed VOC profiling identified several degradation-related compounds, including 1,4-butanediol, methylene diphenyl diisocyanate (MDI) and butylated hydroxytoluene (BHT). Notably, 1-hexadecanol may represent a potential molecular marker of repeated mechanical recycling, as its relative abundance increased consistently with each reprocessing cycle; however, this observation requires further validation, particularly given that it has not been reported in previous studies. Migration testing into water demonstrated limited release of low-molecular-weight compounds, while the persistent presence of 1,6-dioxacyclododecane-7,12-dione across all samples highlights its environmental relevance.

1. Introduction

Global production of plastic in 2018 amounted to 359 million tonnes, of which 61.8 million tonnes were produced in Europe. Just 47% of subsequent plastic waste is collected in Europe, with 32.5% of it being recycled, 42.6% applied in energy recovery and 24.9% going to landfill sites. Polyurethane (PU) is the seventh most widely produced polymer worldwide, and fifth in this regard across Europe, wherein PU consumption equals ca 3 million tons (67% as foam and 6% as elastomers) [1]. Recycling plastics has therefore become increasingly important due to both environmental concerns and EU directives for 2050. Consequently, considerable attention has been devoted to developing effective recycling methods for polyurethane, including physical, mechanical and chemical recycling or energy recovery [2–4].

Thermoplastic polyurethane (TPU) belongs to a group of segmented thermoplastic elastomers composed of hard and soft segments, whose properties depend on intra- and intermolecular interactions within the block copolymer structure. Since it is a modifiable material, different ratios of soft to hard blocks can be produced, lending it a major advantage over standard homopolymers [5–8]. TPU combines the elasticity of rubber with the processability of thermoplastics and is valued for its toughness, abrasion resistance, flexibility and chemical stability [5–8]. Owing to these properties, TPU is widely used in automotive components, electronic devices, wires and cables, sports equipment and consumer products [9–11]. Its broad application range and durability make TPU an attractive material, while simultaneously

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https://doi.org/10.1016/j.polymdegradstab.2026.112285
Received 24 January 2026; Received in revised form 20 May 2026; Accepted 15 June 2026
Available online 16 June 2026
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increasing interest in its recyclability and long-term performance during repeated processing [9–11].

The growing accumulation of plastic waste has motivated the development of efficient recycling strategies for polyurethane materials, including energy recovery [3,12], mechanical or physical recycling [4,13,14] or chemical recycling [15–18]. Mechanical recycling involves the direct reuse of plastic waste without altering its chemical structure, whereas the chemical approach relies on degradation processes to depolymerize such refuse and recover consequent monomers and low-molecular-weight organic compounds [2,19–21]. Due to its cost-effectiveness, environmental friendliness and energy efficiency, mechanical recycling is considered the preferred technique [22]. In this process, plastic waste is crushed and reprocessed using technologies such as extrusion, compression moulding or injection moulding [3,23]. However, repeated reprocessing may compromise the processability and quality of the final products [2]. Recycled polymers are susceptible to thermomechanical and thermo-oxidative degradation during repeated processing or environmental exposure, resulting in inferior properties compared to virgin materials [24–27].

Processing polymers at elevated temperatures induces thermal degradation caused by external or internally generated heat. During repeated recycling cycles, polymers undergo irreversible thermal and mechanical degradation, leading to physical and chemical changes that progressively impair their properties [28–30]. Studies by Calvo-Correas et al. (2022) and Wölfel et al. (2020) confirmed that repeated TPU reprocessing results in reduced molecular weight, deterioration of tensile properties and decreased thermal stability [6,31]. Wölfel et al. (2020) identified two consecutive degradation mechanisms in TPU based on polytetramethylene glycol (PTMG), methylene diphenyl diisocyanate (MDI) and 1,4-Butanediol (BDO): initial degradation of hard segments through urethane bond cleavage (isocyanates and polyols), followed by degradation of soft segments involving cleavage of C–O–C bonds. The thermal stability of TPU strongly depends on the composition of the hard segments [6,32–36].

Mechanical reprocessing was selected in this study due to its economic and environmental advantages [37]. Since repeated processing cycles are known to compromise TPU properties [38], emphasis was placed on determining the maximum number of reprocessing cycles while maintaining acceptable material performance [2,39].

Assessing the potential health risks associated with TPU was also essential. Volatile organic compounds (VOCs), which may pose environmental and health risks, require precise detection for applications such as environmental monitoring and chemical process control [40]. Virgin and reprocessed TPU samples were therefore analysed by HS-SPME-GC-MS together with other characterization techniques including migration testing, differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), X-ray diffraction (XRD) and high-temperature gel permeation chromatography (GPC). The objective was to evaluate the influence of repeated mechanical recycling on TPU degradation and safety.

This study provides a comprehensive assessment of thermoplastic polyurethane after repeated mechanical recycling. The novelty of the work lies in the broad combination of analytical techniques used to evaluate degradation behaviour, VOC formation and material property changes. While Wölfel et al. (2020) investigated changes in TPU properties during recycling, the present study provides a more extensive evaluation of the degradation behaviour of mechanically recycled TPU and its potential environmental and health implications [6]. The obtained results contribute to a better understanding of TPU recyclability and support the sustainable use of polymeric materials within the principles of the circular economy.

2. Materials and methods

2.1. Materials

A sample of thermoplastic polyurethane called Elastollan EB 95 A was obtained from BASF spol. s.r.o., which came in the form of pellets. It has certain advantages over Elastollan® material, whether in aromatic or aliphatic in form, namely that it can be very soft, flame retardant or highly transparent.

Fibrous assemblies of Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS; 50/30 μm), Polyamide (PA; 85 μm) and Polydimethylsiloxane/Divinylbenzene (PDMS/DVB; 65 μm) destined for SPME analysis were provided by Supelco (Bellefonte, USA). Butylated hydroxytoluene and 1,2,4-Trichlorobenzene were purchased from Sigma-Aldrich (Steinheim, Germany). Polystyrene standards (Mp 492500, Mp 990550) and a polystyrene calibration kit (S-M2-10), comprising ten different molecular mass standards (nominal Mp 580 - 300,000 Da, 10 × 0.5 g) were provided by Agilent Technologies (Santa Clara, CA, USA). Filter magazines (1 μm, glass fibre) and clear 20-ml headspace screw-top vials (of type 100PK, Germany) were also obtained from Agilent Technologies. Technical gases required for GC-MS analyses, specifically helium and nitrogen (both of purity 5.5), came from Siad a.s. (Prague, Czech Republic).

2.2. Sample preparation procedures

2.2.1. Mechanical reprocessing of TPU

Samples of Elastollan EB 95 A were produced by injection on a Babyplast 6/10 P-CE microinjection moulding machine (Cronoplast, S. L., Barcelona, Spain). The temperature of all three zones was set to 230 °C. The pressure for the first injection stage equalled 132 bar for 5 s, followed by another at 100 bar for 3.5 s. The second plasticization time was 15.4 s.

When required, the samples were subjected to a controlled cleaning procedure to minimize potential contamination prior to further processing. Specifically, a standard commercial cleaning agent was used, containing (according to the manufacturer's label) 5–15% anionic surfactants for effective degreasing, <5% non-ionic surfactants, as well as additives such as methylisothiazolinone, phenoxyethanol, perfumes, citronellol, and limonene. Cleaning was performed using hot tap water at an approximate temperature of 40 °C. Each sample was washed twice with the detergent solution, followed by thorough rinsing with a large volume of clean hot water without detergent to ensure removal of any residual cleaning agents. This rinsing step was repeated twice to further reduce the risk of contamination.

After washing, the samples were dried at room temperature for 48 h. Once dried, they were cut into small pieces suitable for subsequent reprocessing. The same cleaning and preparation procedure was applied to samples that had undergone two recycling cycles.

Despite initial concerns regarding possible contamination from the cleaning agents, Py-GC-MS analysis did not detect any of the listed surfactant-related compounds. The most structurally similar detected compound was 1,1′-methylenebis(4-isocyanatobenzene) (MDI), which shows some similarity to methylisothiazolinone (2-methyl-1,2-thiazol-3 (2H)-one), although no direct evidence of cleaning agent residues was observed.

A more detailed description of the specimens and the abbreviations for them is provided in Table 1.

2.2.2. Preparation of samples for GPC analysis

Three different sample pieces were cut from each material to create specimens. These sample pieces were dissolved separately in 10 mL of tetrahydrofuran at 40 °C for 8 h, yet did not completely dissolve. The extracts were filtered through PTFE syringe filters (0.45 μm) into 2 mL vials, the final concentration of the analyte in tetrahydrofuran equalling 2–3 mg mL^{-1}. Each sample was extracted and analysed three times.

Table 1
TPU Sample designation.

Established sample abbreviation	Sample description	Number of processing cycles
TPU	Virgin granulate of Elastollan EB 95 A	0
TPU_1	TPU sample reprocessed once on the Babyplast 6/10 P-CE under defined conditions	1
$rTPU_{n1}$	TPU_1 — washed, cleaned, dried, cut into small pieces and reprocessed	2
$rTPU_{n2}$	TPU_{n1} — washed, cleaned, dried, cut into small pieces and reprocessed	3

2.2.3. Headspace solid-phase microextraction (HS-SPME)

In brief, 1 g (± 0.020 g) of homogenized sample was weighed into 20 mL SPME vials and heated to either 90 °C or 120 °C for 20 min. All samples were produced in duplicate. The targeted low-molecular compounds were analysed via headspace solid phase microextraction (SPME) coupled with gas chromatography quadrupole time-of-flight mass spectrometry (GC-QTOF-MS). As for optimizing the conditions for extraction, two SPME fibres were tested: (i) 100 mm of Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) and (ii) 50/30 mm of Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS). The fibres were prepared in accordance with the recommendations of the manufacturer prior to commencing analysis. With regard to the TPU samples, parameters pertaining to the method that could affect SPME were applied, e.g. the coatings on the fibres, weights of the specimens (1 or 2 g), lengths of time for both extraction (10, 20, 40 and 60 min.) and incubation (5, 10, 15 and 20 min.), extraction temperature (60, 70, 80, 90 and 100 °C) and desorption time (2, 3 and 4 s). Background contamination was performed, with a blank tested prior to each batch of SPME analyses. No significant nuisance species were detected. Residues present on the SPME fibres after four minutes of desorption at the GC inlet were examined, and no apparent carry-over between runs was determined. For analysis of all the TPU samples, the procedure was optimized with the following parameters: an SPME fibre of DVB/CAR/PDMS, a sample weight 1 g, extraction application temperature 90 °C and 120 °C, incubation time 20 min, and extraction time 60 min, respectively, and a 4-minute period of desorption.

2.3. Analysis and characterization

2.3.1. Mechanical properties – hardness

A hardness test was performed according to the EN ISO 868:1997 standard on a Shore A hardness tester (Polymertest, Czech Republic). Three randomly selected specimens from each series (TPU_1, $rTPU_{n1}$ and $rTPU_{n2}$) were investigated, with measurements being taken at five different places.

2.3.2. Gel permeation chromatography (GPC)

Gel permeation chromatography coupled to refractometric detection was conducted to determine the molecular weights of the TPU specimens. GPC analysis occurred on an Agilent PL-GPC 220 chromatographic system fitted with a refractive index and viscometric detector. The volume of the injected sample equalled 100 μL. A series of mixed gel columns was employed and maintained at 160 °C, denoted as PL gel Olexis (300 × 7.5 mm, 10 μm) + MIXED - B (300 × 7.8 mm, 10 μm), with the stabilization of 1,2,4–Trichlorobenzene stabilized using butylated hydroxytoluene. The flow rate was 1 mL min^{-1}. In order to obtain a molecular weight of between 580 and 990 mol^{-1}, the GPC system was calibrated with polystyrene standards. Each sample was extracted and analysed three times, and the corresponding data processed in Cirrus software.

2.3.3. Differential scanning calorimetry (DSC)

The thermal properties of the materials were determined on a DSC1 STARe system (Mettler Toledo, Columbus, USA). TPU samples of ca 5 mg were weighed into aluminium dishes and placed in the measuring cell of the instrument. During the measurement procedure, the nitrogen flow rate equalled 50 mL min^{-1} at a heating/cooling rate of 10 °C min^{-1}. The cycle commenced at the temperature of 25 °C and then dropped to −50 °C, before rising to 240 °C and falling again to −50 °C. The second heating scan increased from −50 °C to 260 °C, following which the sample was cooled from 260 °C to 25 °C.

Values for peak maxima and the linear integration of peaks were applied to calculate the maximal temperatures for exothermic crystallization and melting endotherms (Tc and Tm, respectively), as well as the physical transformation enthalpies (AHc and AHm) of the TPU matrix; values for ΔHc indicate crystallization enthalpy (J g − 1) and ΔHm represents the heat of fusion (J g − 1).

2.3.4. Rheological analysis of TPU samples

Test samples of ca 22 mm in diameter and 1 mm thick were fabricated by injection moulding. The rheological properties of their melts with different thermal histories were measured on a CVO Bohlin Geminy 150 rotational rheometer. This was fitted with a cone-plate system (Ø 25 mm) and operated at 230 °C and across the shear stress range of 2–50 Pa. Viscosity (η_i - shear viscosity, Pa.s) was monitored as a function of temperature.

2.3.5. Gas chromatography-mass spectrometry (GC-MS)

GCMS– measurements were performed on an Agilent 7200 system, consisting of an Agilent 7890B gas chromatograph equipped with a multimode inlet, a PAL RSI 85 arrangement for automated headspace solid-phase microextraction (HS-SPME) and direct injection, in addition to a quadrupole time-of-flight (Q-TOF) mass spectrometer (Agilent Technologies, USA). For the separation of volatile compounds, an Rxi-5 ms capillary column was employed (30 m × 0.25 mm i.d. × 0.25 μm film thickness; Restek, PA, USA). Helium constituted the carrier gas at a flow rate of 1.0 mL min^{-1}.

The DVB/CAR/PDMS fibre was desorbed at the GC inlet in splitless mode at 250 °C for a period of four minutes. The temperature program was as follows: for a rise in temperature from 40 °C (held for 5 min) to 100 °C with an increase at the rate of 10 °C/min^{-1} to 300 °C (maintained for 2 min). A detailed report by Paiva et al. (2021) on a programme for oven temperature informed the research presented herein. The transfer line temperature was set to 280 °C, while the ion and quadrupole source operated at 230 °C and 150 °C, respectively. The mass detector ran in electron ionization (EI) mode at the selected mass range of 40–400 *m/z* with data acquisition in MassHunter GC-MS Acquisition software (B.07.06; Agilent Technologies, Palo Alto, California, USA). The raw data were processed in the programs MassHunter Qualitative Analysis Navigator (version B.08.00) and MassHunter Unknowns Analysis (B.09.00), which incorporated spectral deconvolution. The NIST23 mass spectrum library (National Institute of Standards and Technology, Gaithersburg, Maryland, USA) was applied to identify and verify components by their mass spectra (isotopic pattern, accurate mass; mass error <5 ppm).

2.3.6. Pyrolysis-gas chromatography-mass spectrometry

Such investigation of the TPU took place on a GCMS-QP2010 Plus gas chromatograph with mass spectrometric detection (Shimadzu), equipped with a pyrolysis unit (Frontier Lab). A tested specimen comprised 3 mg of the material in a pyrolysis cup, and a blank cup (without a sample) was analysed after every measurement. Each experiment was conducted in duplicate.

Pyrolysis was performed at 300 °C and 600 °C. The temperature control of the pyrolyzer was set to 300 °C and the ion source operated at 230 °C. Chromatographic separation was carried out using an Ultra Alloy PY2 capillary column (30 m × 0.25 mm × 0.50 μm, Frontier Lab). A quadrupole mass analyzer operated in electron ionization (EI) mode at 70 eV, recording mass spectra across the range of 30–600 *m/z*. Helium

constituted the carrier gas at a constant flow rate of 1.1 mL/min. The sample was injected in split mode (1:20) at 320 °C. The programme for oven temperature commenced at 40 °C (held for 2 min.), then ramped up at 20 °C/min. to 320 °C (maintained for 13 min).

2.3.7. X-Ray diffraction (XRD) analysis

A MiniFlex600 XRD diffractometer (RIGAKU, Japan), a precision instrument, was used to obtain X-ray diffraction measurements based on CoKα radiation (λ = 0.179 nm) at a voltage of 40 kV and a current of 15 mA. X-ray diffractograms were collected from 3° to 120° with a step size of 0.02° 2θ at a scanning rate of 8°/min.

2.3.8. Dynamic mechanical analysis (DMA)

Samples for DMA were prepared by the microtome Leica RM2265 from the original circular samples with final measured dimensions of 10 × 2 × 0.4 mm. Experiments were performed on Dynamic-mechanical analyzer DMA 1 Mettler Toledo, and evaluated using STARe SW 18.0 software. The temperature range of measurement was −75 – 50 °C, amplitude 10 μm, tension clamp (titanium), 1 Hz frequency, 1 N pre-tension. Samples were cooled to the required temperature using liquid nitrogen. Storage modulus (E'), loss modulus (E''), complex modulus (E*), and loss tangent (tan δ) were measured and evaluated. The peak values were determined from the limited section of the curve with specific limits noted inside the appropriate Figures.

2.3.9. Fourier transformed infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectra of TPU samples were recorded using an attenuated total reflectance (ATR) technique on a Nicolet iS5 spectrometer (Thermo Fisher Scientific, USA) equipped with a diamond crystal. Each spectrum was obtained by averaging 64 scans in the wavenumber range of 4000–500 cm^{-1}. Spectral data were processed and analyzed using OMNIC 8 software (Thermo Fisher Scientific, USA).

2.3.10. Migration tests in water

The safety of the TPU material and its reprocessed samples was gauged by conducting tests for migration into water, in accordance with the European standard EN 124572:2002. The containers for the aqueous experiment, wherein determination was made as to the presence of solids, were dried in an oven at 105 °C prior to being placed in a desiccator and weighed. This procedure was repeated until the containers reached a constant weight.

Testing initially focused on the proportion of dry matter in the TPU samples and their moisture content. It commenced with drying to constant weight 2 g of a sample in two replicates in an oven at 105 °C for 24 h. An extension to the experiment involved adding 5 g of the pre-dried sample into 50 ml of distilled water. A ratio of the solid to liquid phase of 10 l/kg was maintained with adherence to the European standard EN 124572:2002. Such samples were then shaken at a temperature of 20 °C for 24 h. All of the TPU was removed from the water afterwards, following which the leachate was dried out at 50 °C and weighed. This experiment was repeated until a constant weight was reached. A blank specimen absent of the TPU material underwent the identical test. The same steps were repeated three times. Concurrently, 2 ml of deionized water was extracted from each sample after allowing the TPU to leach into it. The water was analysed by HS-SPME-GC-MS for the presence of volatile compounds capable of leaching out from the TPU during the migration test.

3. Results and discussion

3.1. TPU characterization and analysis

3.1.1. Mechanical properties – hardness

The values discerned for hardness exhibited a relatively high standard deviation, specifically 2–3 on the Shore A scale. Carrying out one-way ANOVA analysis (the post hoc Tukey test at 95% confidence level) revealed that no statistically significant difference existed between the injected and twice-recycled samples. However, the once-recycled samples did differ, albeit marginally. This would suggest that the TPU softened slightly after the first recycling cycle and hardened following the second. In light of the considerable standard deviations manifested, an alternative explanation for such a difference might lie in random errors introduced by various factors. Individual specimens may yield discrete values, hence comparing means for three samples (each measured at five locations) could introduce additional uncertainty. Indeed, it is possible that random errors cause variability of this type, potentially arising through complications in the injection moulding process and inconsistent degradation, as the material is highly sensitive to thermal degradation during recycling. The findings are summarized in **Tables S1** and Table 2.

3.1.2. Gel permeation chromatography

Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC), is capable of determining a mean value for the molecular-weight distribution of a polymer sample, through a method which distinguishes the polymer according to its size or hydrodynamic radius. Applying appropriate detectors and analytical procedures makes it possible to obtain qualitative data on the branching of long chains or the composition distribution of copolymers. The target polymers were detected herein on a differential refractive index detector (RID) suitable for analysing hydrophobic polymers that do not contain functional groups for UV absorbance. The molecular weights of the analytes were evaluated via a calibration curve.

The results of GPC analysis are given in Table 3. As for the comparison of the sample with a higher degree of reprocessing, it showed a high decrease in molecular weight and diminished polydispersity (the degree of "non-uniformity" of distribution). In this regard, the twice reprocessed TPU demonstrated an 80% drop in molecular weight. The TPU chains had degraded to shorter units, affecting the stability of the material and its mechanical properties, potentially rendering it more fragile. In contrast, the polydispersity of TPU decreased each time a reprocessing cycle was repeated, the value for every sample (TPU_1, $rTPU_{n1}$ and $rTPU_{n2}$) approximately equalling 2. By processing, the material in this research can become more uniform with a greater number of shorter chains of the same length. It should be noted that the virgin TPU material is represented in two fractions of the most frequently occurring molecular weights, which introduces a higher polydispersity index in the results for the virgin TPU. Deviation in the experimentally derived values could have been caused by the low weight of the sample granules, as well as the inhomogeneity of the TPU tested under laboratory conditions.

3.1.3. Differential scanning calorimetry (DSC)

DSC is the most widely deployed method of thermal analysis for characterising and verifying the quality of plastic, not only in research and development, but also in industry for the control of inputs and outputs. In the context of this study, TPU samples were exposed to linear heating or cooling, while the rate of heat flow in the sample, which is proportional to the instantaneous specific heat, changing continuously. The technique discerns alterations in the heat absorbed or released by a sample that is exposed to a given temperature programme as a function of temperature and/or time. The consequent data describe the dependence that exists between the thermal properties and molecular structure of the plastic, in addition to its morphology and the conditions in place during production.

Fig. 1 contains data on the melting points of samples, revealing that the virgin TPU and 1x / 2x reprocessed materials showed 210.89 °C and 196.55 / 193.45 °C, respectively. As can be seen, the melting point decreases with the addition of the reprocessing cycle, but it is not a rapid decrease. During reprocessing, the polymer chains are exposed to mechanical and thermal stress, which leads to their cleavage. This was manifested in shortened chain lengths, as indicated by the lower melting

Table 2
Values for hardness of the TPU samples.

Variable	Mean	SE Mean	Standard Deviation	Variance	Coefficient of Variation	Minimum	Median	Maximum
TPU_1	89.53	0.54	2.10	4.41	2.35	87.00	89.00	94.00
$rTPU_{n1}$	87.07	0.54	2.09	4.35	2.40	84.00	87.00	90.00
$rTPU_{n2}$	90.00	0.75	2.90	8.43	3.23	85.00	91.00	94.00

Table 3
Results of GPC/RID analysis of the TPU samples.

Sample	PDI	Mn ($g\ mol^{-1}$)	Mw ($g\ mol^{-1}$)	Mp ($g\ mol^{-1}$)	Mp (%)
TPU	3.01 ± 0.3	77 000 ± 5000	232 000 ± 17 000	124 000 ± 13 000	100
TPU_1	1.93 ± 0	28 000 ± 4000	53 000 ± 5000	53 000 ± 8000	43
$rTPU_{n1}$	1.98 ± 0	18 000 ± 2000	35 000 ± 3000	33 000 ± 3000	27
$rTPU_{n2}$	1.95 ± 0	14 000 ± 600	26 000 ± 1000	25 000 ± 600	20

Definitions: Mp: molecular weight of the peak maxima; Mn: number-average molecular weight; Mw: weight-average molecular weight; PDI: polydispersity index of the polymer; TPU: unprocessed virgin thermoplastic polyurethane; TPU_1: 1 injection of thermoplastic polyurethane; $rTPUn_1$:1-time reprocessed thermoplastic polyurethane; $rTPUn_2$: 2-time reprocessed thermoplastic polyurethane.
Means were calculated from 3 values. Results are shown ± standard deviation.

points, and changes in properties such as reduced thermal stability and the appearance of the polymer (e.g. yellowing).

As detailed in Fig. 2, the virgin TPU exhibited a crystallization value of 133.49 °C, while 163.61 °C was observed for the twice reprocessed sample. The effect of reprocessing results in shortening of the chain lengths and crystallization occurred at higher temperatures (i.e. the shorter chains crystallized faster).

3.1.4. Rheological analysis of TPU

Changes in the material properties during the reprocessing of injection-molded TPU samples were systematically monitored. Rheological measurements provided insight into the extent of degradation they experienced, a phenomenon which directly affected their flow properties. Fig. 3 reveals that the polymer demonstrated pronounced sensitivity to the reprocessing cycles, as evidenced by a significant decrease in viscosity. These changes were accompanied by a visible shift in colour, most likely caused by the combined effects of mechanical shear and thermal degradation.

A more detailed evaluation of the rheological data revealed that the first reprocessing cycle brought about a sharp reduction in melt viscosity (from ≈90 Pa·s to ≈35 Pa·s, corresponding to a ≈ 61% drop), while the second caused a further decrease to ≈12 Pa·s (≈87% compared to the virgin sample). This steep loss in viscosity within such commencing cycles is consistent with previous reports, which indicate that the most pronounced changes in rheological behaviour occur during the initial stages of repeated processing [6,41].

Mechanistically, this reduction in viscosity could be attributed to a combination of degradation pathways. Chain scission of the carbamate and urethane bonds has the effect of lessening molecular weight, thereby diminishing melt viscosity [2,42]. A parallel action transpires, wherein relaxation times and viscoelastic behaviour are altered by disruption of the hydrogen bonding and microphase rearrangements of the hard and soft segments. Oxidative processes also frequently take place in TPU, generating low-molecular-weight by-products and chromophores, and these not only accelerate viscosity loss, but also explain the observed shift in colour [43]. The yellowing of our samples is therefore in accordance with the literature describing thermo-oxidative degradation of TPU after multiple processing cycles.

Numerical comparison showed that the aforementioned losses in relative viscosity (≈60–90%) lay at the upper boundary of typical values. For example, Wölfel et al. demonstrated that molecular weight and viscosity diminished substantially even upon the commencement of processing tests, particularly in systems rather sensitive to thermal and shear stresses [6]. Hernández confirmed experimentally that the rate at which TPU degraded was a function of processing time, temperature and shear intensity, with harsher conditions leading to more severe deterioration [42]. Smorawska et al. and other authors reported that the greatest changes tended to occur within the first few cycles, whereas viscosity often underwent partial stabilization in later ones [41]. However, more a moderate decrease in viscosity (20–50%) has been observed in stabilized TPU systems or under milder processing conditions, suggesting that improved recycling strategies or deploying stabilizers and chain extenders could mitigate degradation [2].

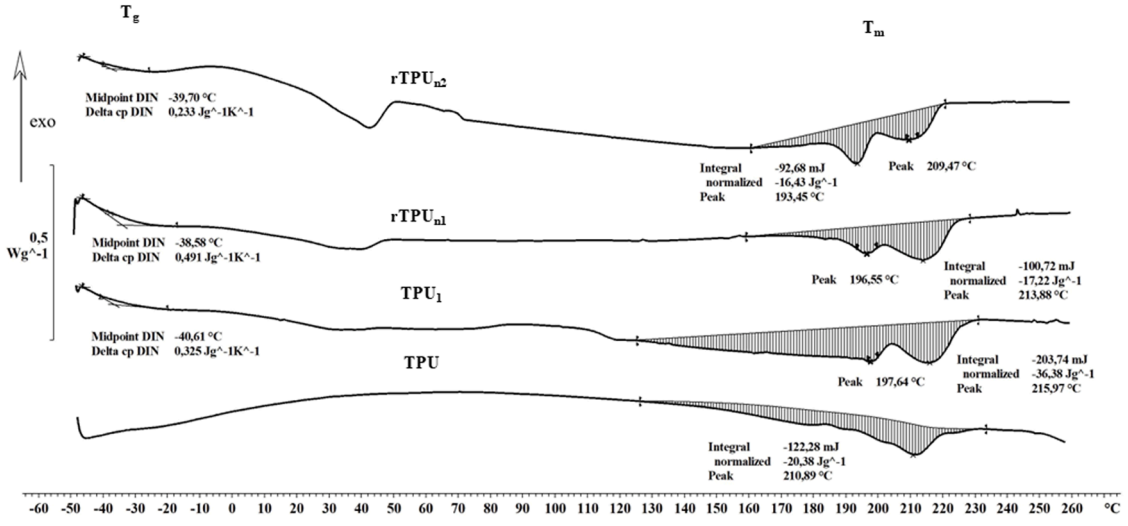


Fig. 1. Course of melting (T_m) of the virgin TPU granulate and 1-time and 2-time reprocessed TPU samples.

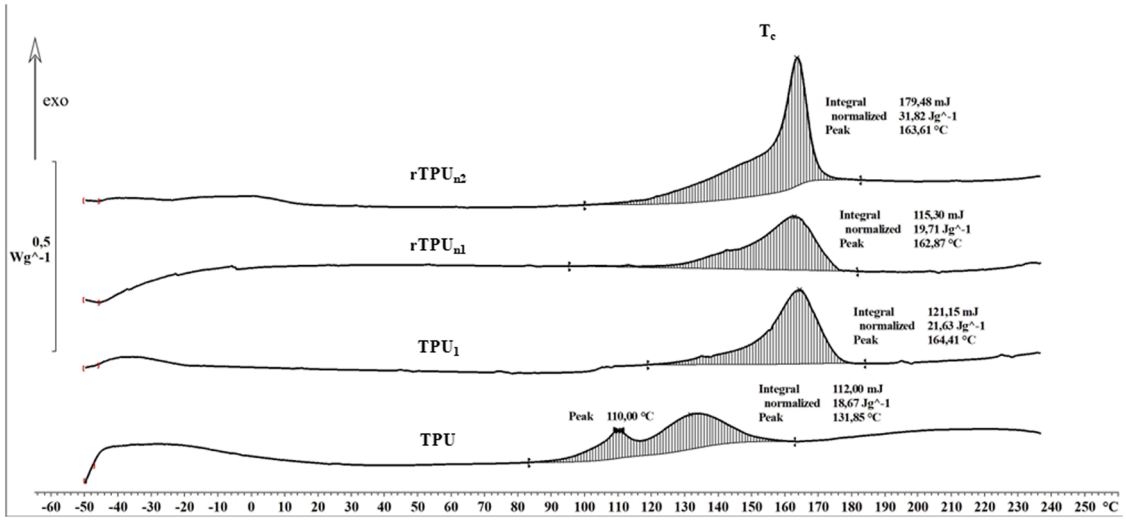


Fig. 2. Course of crystallization (T_c) of all the monitored TPU samples.

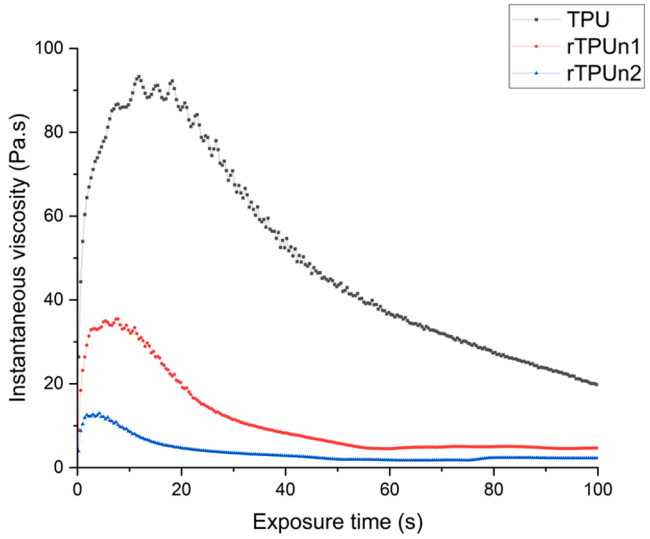


Fig. 3. Rheological properties of TPU samples: virgin, once and twice reprocessed; as per the dependence of viscosity on temperature (230 °C) under specific processing parameters.

The results given herein denote relatively intense degradation, in comparison to the findings mentioned above. This phenomenon might stem from the intrinsic susceptibility of the TPU investigated (e.g. a higher content of ester soft segments or the absence of stabilizers) or the severity of the processing conditions applied. In this context, a recent study by Yıldırım et al. reported similarly steep drops in viscosity, attributed therein to predominant chain scission in combination with stabilizing additives of limited efficiency [43].

The findings stated in this article qualitatively confirm the general trend of TPU degradation upon repeated processing, while quantitatively demonstrating an unusually strong loss in viscosity as early as within the first two reprocessing cycles.

3.1.5. Pyrolysis-GC-MS analysis

Various types of poly(ether urethane) exist, synthesized through the chain extension of diols and hydroxyl-terminated polyols. Hydrogen bonding within the hard segments results in virtual or reversible cross-linking in these polymers. The relative proportions of hard and soft segments, degree of phase separation (or miscibility) and extent of hydrogen bonding in it are influenced by the nature and relative concentrations of isocyanates, chain extenders and polyols used in their formulation. Critical factors that affect the thermal degradation of polyurethane (PU) include the types of isocyanates, polyols and chain extenders employed, since a variety of thermal dissociation temperatures are exhibited by different chemical bonds in the polymer backbone. Aromatic diisocyanate-based thermoplastic polyurethanes (TPUs) are generally recognized for their superior thermal stability. Aliphatic hydrocarbon units in diisocyanates are considered vulnerable sites for thermo-oxidative degradation in a similar manner to polyols. It is notable that TPU formulated from 4,4′-methylenebis(phenyl isocyanate) (MDI) has the capacity to form quinonoid structures at the onset of thermo-oxidative degradation, which potentially inhibit further decomposition. In contrast, MDI-based TPU has been found to be less thermally stable than TPU synthesized from toluene-2,4-diisocyanate (TDI), likely due to the presence of benzylic carbon atoms that can be stabilized through the action of aromatic units and converted into benzophenone structures during radical-mediated degradation processes [44].

Pyrolysis-gas chromatography/mass spectrometry (Py-GC-MS) is a common way to identify thermoplastic elastomers based on poly(ether urethane) (PEU). In a study by Hiltz et al. (2015), which examined the polymer in this manner, three reaction mechanisms were proposed to investigate the degradation products that form within thermal or pyrolytic breakdown of PEU segments. The first mechanism involved dissociation of the urethane bond to form an alcohol and isocyanate. The second mechanism leads to the generation of an olefin, a primary amine and carbon dioxide (CO_2) via a six-membered transition state. Decarboxylation transpired in the third, whereby a secondary amine was produced. It is important to note that the distribution of polyurethane pyrolysates is influenced by the analytical parameters of ether moieties, and proves highly dependent on the temperature of pyrolysis [45,46].

As confirmed in related studies (Hiltz et al., (2015); Zeller et al., (2023)), high-temperature pyrolytic degradation of TPU gives rise to MDI and 1,4-Butanediol. The primary degradation products of TPU identified by Py-GC-MS, are detailed in pyrograms (**Figures S1** and **S2**) and Table 4. Commonly employed in the synthesis of poly(ether urethanes) as chain extenders and diisocyanates, these compounds are released during the thermal decomposition of urethane-rich hard segments. As shown in Table 4, conducting a greater number of reprocessing cycles and applying a higher pyrolysis temperature of 600 °C resulted in the generation of the following: 2H-pyran-2-one and tetrahydro-3,6-dimethyl, with a slight increase in relative abundance (this trend was observed for most analytes); in addition to 2-

Table 4
Primary degradation compounds of TPU as analytically characterized by Py-GC-MS.

Sample	Retention time (min.)	CAS number	Target compound	Area	Relative representation of substances (%)
TPU 300 °C	0.537	460-13-9	n-Propyl fluoride	624,677,675	38.93
	1.525	302-01-2	Hydrazine	168,549,564	10.50
	9.098	110-64-5	1,4-Butanediol	298,498,454	18.60
	16.755	101-68-8	1,1′-Methylenebis(4-isocyanatobenzene) (MDI)	389,791,929	24.29
TPU 600 °C	0.428	57-56-7	Hydrazinecarboxamide	1698,837,383	20.15
	3.439	107-89-1	Butanal, 3-hydroxy-	526,050,008	6.24
	3.728	858971-43-4	Palladium, bis[(1,2,3-.eta.)-2-butenyl]-	421,982,408	5.01
	5.005	96-47-9	Furan, tetrahydro-2-methyl-	443,821,660	5.26
	5.144	20201-24-5	Ethyl 3-methyl-2-oxobutyrate	565,995,155	6.71
	6.976	638-28-8	Hexane, 2-chloro-	564,878,743	6.70
	9.858	110-63-4	1,4-Butanediol	1706,188,260	20.24
	17.102	19471-12-6	3,3′-Diaminodiphenylmethane	833,781,933	9.89
TPU_1 300 °C	0.630	302-01-2	Hydrazine	178,075,184	17.89
	1.093	7782-44-7	Oxygen	65,095,069	6.54
	9.232	110-63-4	1,4-Butanediol	276,025,840	27.74
	16.887	101-68-8	1,1′-Methylenebis(4-isocyanatobenzene) (MDI)	336,561,653	33.82
	22.500	777-95-7	1,6-Dioxacyclododecane-7,12-dione	55,988,528	5.63
TPU_1 600 °C	3.485	1489-69-6	Cyclopropanecarboxaldehyde	383,180,720	10.27
	3.676	157-33-5	Bicyclo[1.1.0]butane	292,714,997	7.85
	5.132	96-47-9	Furan, tetrahydro-2-methyl-	412,836,269	11.07
	7.106	3720-22-7	2H-Pyran-2-one, tetrahydro-3,6-dimethyl-	479,288,937	12.85
	9.564	110-63-4	1,4-Butanediol	937,737,523	25.14
	16.873	101-68-8	1,1′-Methylenebis(4-isocyanatobenzene) (MDI)	525,645,753	14.09
Sample	**Retention time (min.)**	**CAS number**	**Target compound**	**Area**	**Relative representation of substances (%)**
$rTPU_{n1}$ 300 °C	0.875	4114-31-2	Hydrazinecarboxylic acid, ethyl ester	468,072,012	33.24
	1.854	1972-28-7	Diethyl azodicarboxylate	267,421,795	18.99
	9.172	110-63-4	1,4-Butanediol	251,390,428	17.85
	16.877	101-68-8	1,1′-Methylenebis(4-isocyanatobenzene) (MDI)	342,834,912	24.35
$rTPU_{n1}$ 600 °C	3.456	1489-69-6	Cyclopropanecarboxaldehyde	350,642,374	14.27
	3.653	157-33-5	Bicyclo[1.1.0]butane	220,350,447	8.97
	5.112	96-47-9	Furan, tetrahydro-2-methyl-	368,791,248	15.01
	7.089	3720-22-7	2H-Pyran-2-one, tetrahydro-3,6-dimethyl-	366,380,878	14.91
	7.140	110-82-7	Cyclohexane	184,223,726	7.50
	9.463	110-63-4	1,4-Butanediol	722,191,376	29.40
$rTPU_{n2}$ 300 °C	0.565	302-01-2	Hydrazine	960,705,306	43.86
	1.892	1972-28-7	Diethyl azodicarboxylate	239,229,368	10.92
	9.325	110-63-4	1,4-Butanediol	523,933,930	23.92
	16.869	101-68-8	1,1′-Methylenebis(4-isocyanatobenzene) (MDI)	300,075,940	13.70
$rTPU_{n2}$ 600 °C	3.425	1489-69-6	Cyclopropanecarboxaldehyde	389,622,731	13.90
	3.617	157-33-5	Bicyclo[1.1.0]butane	266,728,494	9.51
	5.076	7319-16-6	1-Propene, 1-methoxy-	417,562,623	14.89
	7.088	3720-22-7	2H-Pyran-2-one, tetrahydro-3,6-dimethyl-	429,965,356	15.33
	7.137	110-82-7	Cyclohexane	134,277,439	4.79
	9.467	110-63-4	1,4-Butanediol	746,802,185	26.64

*Most frequently occurring substances with a relative representation of substances in excess of.
*Most frequently occurring substances with a relative representation of substances in excess of 5%.

Methyltetrahydrofuran, a compound that primarily substitutes for tetrahydrofuran (THF), which is occasionally derived from sugar-based furfural and marketed as a biofuel. Another compound detected in our study, predominantly at the lower pyrolysis temperature of 300 °C, was hydrazine. This is a colourless liquid with a faint ammonia-like odour, highly toxic and corrosive, primarily utilized as a rocket propellant. At the same temperature, 1-Fluoropropane was also identified as a pyrolysis product of TPU. In summary, the degradation products identified in the course of this research may serve as potential markers for TPU reprocessing cycles, constituting a notable and valuable finding [45,47].

3.1.6. Testing method – SPME parameters

For the purpose of optimizing the technique, an unprocessed virgin TPU sample was selected, as it was expected to contain the highest number of peaks and potential odorous compounds, albeit with relatively small peak areas. When developing the HS-SPME-GC-MS method, various parameters were tested, including the weights of samples, type of SPME fibre, times for incubation and extraction, and duration and temperature of desorption. The gas chromatography method was also optimized by applying different column heating rates to identify conditions that yielded the best separation. As effective extraction conditions are known to enhance VOC peak intensities in the chromatogram, the efficiency of each setup was evaluated by comparing the relative peak areas of the identified volatile compounds. The methodology adopted was based on that applied to polypropylene in a previous study by the authors Polachova et al. [48].

Selecting the appropriate SPME fibre is critical due to differences in extraction selectivity among coatings. Two types were evaluated for VOC extraction from TPU - polydimethylsiloxane/divinylbenzene (100 μm; PDMS/DVB) and divinylbenzene/carboxen/polydimethylsiloxane (50/30 μm; DVB/CAR/PDMS); the experiments for both were performed under identical conditions. The DVB/CAR/PDMS fibre demonstrated superior performance in the number and intensity of peaks for volatile compounds, hence it was selected for subsequent tests.

Two samples of 1 g and 2 g in mass were investigated to determine which provided the best chromatographic resolution. The 1 g samples yielded a greater number of peaks of higher intensity. Parameters for optimization included the time allowed for desorption (2, 3 and 4 min) and incubation (5, 10, 15 and 20 min). It was found that the most effective durations were 4 min for desorption and 20 min for incubation.

Further tests focused on extraction durations (10, 20, 40 and 60 min) and temperature (60, 70, 80, 90 and 100 °C). These parameters proved critical to headspace extraction and significantly affected the reproducibility of findings. When evaluating the methodology, 14 prominent

peaks recorded for most of the TPU samples were chosen for extra characterization, including reprocessed variants. These peaks demonstrated retention times that ranged from ca 6 to 25 min. Table 5 summarizes key analytical data, such as the compound name, match factor, CAS number, presence in a specimen and relative abundance.

With respect to selecting the final parameters, differences that existed in peak responses across those tested were not statistically significant, i.e. the weight of a sample, type of SPME fibre, incubation and extraction times, and desorption conditions. Extending the period of extraction to 60 min proved suitable for capturing compounds with shorter retention times, while still maintaining consistent quality in peaks for compounds which eluted later. Ultimately, prioritization was given to sharp peaks and the high-resolution separation of VOCs (particularly ones of low molecular weight) when it came to selecting the final conditions.

The final optimized parameters applied to all the TPU samples in this study comprised the following: the DVB/CAR/PDMS SPME fibre; sample weight of 1 g; extraction temperatures of 90 °C and 120 °C; incubation for 20 min; extraction for 60 min; and desorption for 4 min. An additional extraction temperature of 120 °C was included to simulate elevated outdoor conditions, allowing for a broader VOC profile to be captured under a realistic scenario of environmental exposure.

3.1.7. Characterization of volatile compounds and the degradation process of TPU

In 1972, Wooley proposed a general degradation process for variants of polyurethane, classifying two types of combustion products based on the polyols used, namely polyethers and polyesters [49]. The thermo-oxidative degradation pathways of polyether, polyester, and polycarbonate polyols in PU are well established [50–59]The ether bond in PU is considered weak in terms of thermo-oxidative degradation, as thermal stress causes the α-carbon of the ether group to experience hydrogen abstraction [59]. In the presence of oxygen, hydroperoxide groups can form on aliphatic hydrocarbon units, and even mild heat might induce hydroperoxide decomposition, generating radicals that further facilitate PU chain scission. Regarding polyols, poly(propylene glycol) (PPG) exhibits greater sensitivity to oxygen than other polyether polyols, likely due to the presence of reactive tertiary carbon atoms, which serve as initiation sites for oxidative degradation [50,52,57]. It is well known that polyester-based PU is more resistant to thermo-oxidative degradation than polyether-based PU [60,61]. The possibility exists that polyol chain scission and subsequent radical rearrangements could give rise to volatile organic compounds (VOC), including aldehydes, acetates and formats [2,39,44].

Table 5 lists the volatile compounds most frequently identified volatile compounds present in TPU materials, while **Figure S3** contains the VOC profile of every TPU sample measured by HS-SPME-GC-MS at both extraction temperatures. The compounds are classified in order of elution and further specified by relevant details. The abbreviations adopted for the volatile compounds are as follows: TPU represents the reference sample of virgin thermoplastic polyurethane; n denotes the number of reprocessing cycles the TPU specimen underwent, specifically once reprocessed TPU ($rTPU_{n1}$), twice reprocessed TPU ($rTPU_{n2}$), and TPU_1 standing for the material from the initial injection-moulding stage. Table 5 outlines the preliminary results of the most prominent and common VOCs, these being degradation products of TPU which include

Table 5
Volatile compounds tentatively identified in the virgin and reprocessed TPU analysed by HS-SPME-GC-MS.

Order of compounds	Target compound	CAS number	Retention time (min.)	Match factor (%)	Description of odour / note	Sample	Estimated average relative representation of substances (%) Ratio TPU/TPU_1/ $rTPU_{n1}$/$rTPU_{n2}$
Extraction temperature of 90 °C / 120 °C							
1	Cyclopentanone	120-92-3	6.1183	97.3	Odour: peppermint-like; applied in fragrances (derived from jasmone), pesticides, etc.	TPU	9(8)
2	3-Nonen-1-ol, (Z)-	10340-23-5	13.2042	91	Odour: vegetal, waxy, melon, cucumber	TPU_1-$rTPU_{n1}$	1/0.2
3	Cyclooctyl alcohol	696-71-9	13.3689	88	-	$rTPU_{n2}$	3
4	1-Dodecyne	765-03-7	14.8307	94	Colourless liquid with a mild, pleasant odour. useful for a number of applications, e.g. in detergents.	TPU-$rTPU_{n2}$	0.4/2/0.2/2
5	Geranylacetone	3796-70-1	18.2738	91	Component of essential oils (geranyl group) from various plants (Nelumbo nucifera); applied as a flavouring agent, fragrance, volatile oil component and plant metabolite.	TPU_1-$rTPU_{n2}$	8/2/4
6	Cyclododecane	294-62-2	18.5148	94	Musty odour and an unpleasant smell	TPU_1-$rTPU_{n2}$	3/1/5
7	4-Methoxy-3-(isopenten-2-yl) acetophenone	26931-99-7	18.7004	83	-	TPU-$rTPU_{n1}$	11(6)/6/1
8	Butylated Hydroxytoluene	128-37-0	19.1043	94.5	Odour: faint musty, cresylic, phenolic (for pure white to off-white crystalline powder); BHT: an antioxidant deployed in perfumes	TPU-$rTPU_{n2}$	73(68)/62(1)/18(0.4)/ 26(0.4)
9	2-Acetyl-2-Methyltetrahydrofuran*	32318-87-9	19.6768	85	-	TPU_1	9
10	2-Butenoic acid, 2-methyl-, 2-methylpropyl ester, (E)-	61692-84-0	19.7121	83	Odour: herbal, pungent	$rTPU_{n1}$	73
11	1-Pentanol, 4-methyl-2-propyl-	54004-41-0	20.7723	90.5	-	TPU-$rTPU_{n2}$	1(5)/9(2)/3(0.5)/1
12	1-Octanol, 2-butyl-	3913-02-8	21.1578	95	Odour: mild, floral or fruity; used in fragrances and flavourings	TPU-$rTPU_{n1}$	2(5)/4(18)/2
13	Hexadecane	544-76-3	22.2384	95.1	Gasoline-like to odourless	TPU-$rTPU_{n2}$	1/2/2(5)/22
14	1-Hexadecanol*	36653-82-4	25.0547	92.6	Odour: waxy, clean, greasy, floral, oily	TPU_1-$rTPU_{n2}$	65/92/94

* Substances occurring only when using the extraction temperature of 120 °C; the analytes detected at both extraction temperatures (90 and 120 °C) are highlighted in grey.

linear and branched alkanes and alkenes, hexadecane, cyclopentanone, cyclododecane, alcohols and esters. The broadest spectrum of VOCs was detected in the virgin TPU and the initial injection-moulded specimen (TPU_1), though the differences between them were marginal. The twice-reprocessed sample ($rTPU_{n2}$) possessed the least number of VOCs, implying that each reprocessing cycle led to a drop in the concentration of such volatiles. This suggests that repeating the high-temperature treatment, i.e. protracted thermal exposure, may have removed or degraded many of the original volatile analytes.

The most abundant compound in all the samples was butylated hydroxytoluene (BHT), a common antioxidant in perfumes, with a faint musty and cresylic phenolic smell. Its relative abundance decreased as the number of reprocessing cycles rose, from 73% in the virgin TPU to 26% in the twice-reprocessed sample. Only the once-reprocessed sample ($rTPU_{n1}$) contained 2-butenoic acid, characterized by a pungent, herbaceous aroma, at a high estimate of relative abundance of 73%. Cyclopentanone was also found in low relative amounts in the virgin TPU.

Two extraction temperatures were assessed, the lower being 90 °C to simulate a typical maximum temperature of TPU indoors, and the other 120 °C to test a potential elevated outdoor temperature (see Table 5). The higher extraction temperature (120 °C) led to the detection of additional degradation products not previously observed at 90 °C, including 2-acetyl-2-Methyltetrahydrofuran and 1-Hexadecanol. Compounds detected at both extraction temperatures comprised: cyclopentanone, 4-methoxy-3-(isopenten-2-yl) acetophenone, butylated hydroxytoluene, 2-butenoic acid, 4-methyl-2-propylpentan-1-ol and 2-butyl-1-octanol; the remaining VOCs were only identified at 90 °C. Notably, 1-Hexadecanol, a compound with a waxy, clean, fatty, floral odour, emerged as a potential reprocessing marker. It was detected exclusively in the reprocessed TPU samples at 120 °C and showed a clear trend of increase in relative abundance with rise in the number of reprocessing cycles—65%, 92% and 94% for TPU_1, $rTPU_{n1}$ and $rTPU_{n2}$, respectively. This observation was verified by repeated SPME tests under varying polypropylene conditions, confirming the relevance of the analyte as a potential indicator of degradation for recycled TPU.

Volatile organic compounds (VOCs) have become a topic of concern in the polymer industry for their potential environmental and health-related impacts. As far as the authors are aware, no studies directly comparable to the one presented here have been published, hence evaluating the occurrence of VOCs in reprocessed TPU samples by HS-SPME-GC-MS is a relatively novel contribution. Only a few papers of a different nature have assessed volatile organic compounds emitted by polyurethanes [46,62–64]. Some related research does exist, though. For example, Ye Jin Choi et al. (2018) investigated the effects of compositional factors of TPU on the generation of acetaldehyde (AA) during thermal processing in air.

The thermal degradation of polyurethanes under inert atmospheres usually commences with the cleavage of urethane bonds, followed by recombination, isomerization and dehydrogenation reactions, that result in the formation of carbon oxides, amines, olefins and various VOCs [65]. It has been reported that thermal degradation primarily occurs at elevated temperatures (>200 °C), while thermo-oxidative degradation in the presence of air can occur at significantly lower processing temperatures (60–130 °C) [44]. Above their melting point, polyurethanes not incorporated with antioxidants are highly susceptible to oxidative degradation. The literature states that the soft segment of TPU, i.e. the polyol component, is generally more prone to oxidative degradation than the hard segment (urethane) [65,66].

Greater attention is now being paid to VOCs, which are characterized by relatively high vapour pressure at ambient temperature. VOCs rank among the most common air pollutants and are often released from polymers in the gas phase, posing potential environmental and health hazards [67,68]. The formation of them in polymers is primarily caused by thermal or thermo-oxidative degradation [49,69,70]. Concerns over air quality and human health have led to stricter regulations on their emission [71,72]. Among the most dangerous VOCs emitted from polymers is acetaldehyde (AA), classified as a Group 1 carcinogen and considered a major pollutant, also engendered through thermal or thermo-oxidative degradation [50–53,73,74]. Due to its low boiling point (20.2 °C), AA readily diffuses from polymers, potentially contributing to environmental contamination and health risks. Fortunately, acetaldehyde was not released from any of the materials tested herein [75].

3.1.8. Formation of 1-hexadecanol as a potential marker of TPU reprocessing

In the context of polymer recycling, the formation of specific low- and high-molecular-weight compounds as indicators of degradation history has been reported across several polymer systems, although such markers are strongly dependent on the chemical structure and degradation pathways involved. In polyolefins, thermo-oxidative degradation during repeated processing leads to the formation of oxidation products such as aldehydes (e.g., hexanal, nonanal), ketones, and alcohols, which have been widely used as indicators of degradation extent [76,77]. These species originate from radical-driven chain scission followed by oxygen incorporation and β-scission reactions.

In polyethylene terephthalate (PET), acetaldehyde is a well-established degradation marker formed via thermal decomposition of the ester backbone and has been extensively correlated with processing history and material [78,79]. Similarly, in polyamides, the release of caprolactam and related low-molecular-weight amides has been shown to increase with repeated thermal processing, reflecting chain scission and depolymerisation processes [80].

For polyurethane systems, previous studies have predominantly identified general degradation products such as amines, alcohols, olefins, and carbonyl-containing compounds formed via urethane bond dissociation and subsequent radical reactions [65,77]. However, unlike in polyolefins or PET, the identification of a compound that systematically correlates with the number of reprocessing cycles has not been clearly established for TPU materials.

The formation of long-chain aliphatic alcohols, such as 1-hexadecanol observed in this study, can be rationalized by thermo-oxidative degradation of soft segments, particularly those derived from polyether or polyester polyols. Oxidative chain scission of aliphatic segments followed by radical recombination or termination reactions may yield higher molecular weight alcohols and wax-like compounds [77]. Such products are typically less volatile and therefore less frequently reported in VOC-focused studies, which tend to emphasize low-molecular-weight species.

The detection of 1-hexadecanol exclusively in reprocessed TPU samples, together with its increasing abundance during successive reprocessing cycles, may indicate an association with cumulative thermo-oxidative degradation processes. In contrast to more commonly reported volatile degradation products such as aldehydes or ketones, the occurrence of this higher molecular weight alcohol could reflect degradation phenomena related to the soft-segment structure of TPU. To the best of the authors' knowledge, the occurrence of 1-hexadecanol has not been widely discussed as a possible indicator of TPU degradation or recycling history in the currently available literature. Therefore, although the present observation should still be regarded as preliminary and requires further validation using additional TPU systems and complementary analytical approaches, it may represent an interesting contribution to future studies focused on identifying degradation-related markers in polyurethane recycling systems.

3.1.9. XRD Analysis of TPU

X-ray diffraction (XRD) diffractograms were acquired to elucidate the structural evolution of the material, with particular emphasis on identifying structural alterations that could indicate the release, redistribution, or formation of secondary phases during processing and ageing, as shown in Fig. 4. Thermoplastic polyurethane (TPU) is a

segmented copolymer composed of alternating soft polyester segments and hard polyurethane–urea domains, whose microphase-separated morphology governs its structural response. In this context, XRD represents a powerful tool for probing changes in structural organization, including potential phase separation phenomena or the emergence of additional crystalline contributions [81,82]. Notably, the diffractogram presented in Fig. 4a indicates that the investigated system consists of a neat TPU matrix without additional inorganic fillers or other crystalline additives. Accordingly, the diffraction response can be attributed solely to the intrinsic microstructure of TPU. Any observed modifications, such as peak broadening or positional shifts, therefore reflect changes in molecular ordering and crystallite size associated with degradation-induced alterations within the polymer matrix, rather than the evolution of extrinsic phases [83]. Post-processing of the TPU samples is associated with subtle modifications in the diffraction response, which may indicate slight changes in structural organization rather than unequivocal evidence of advanced degradation. Evidence of these changes can be observed in Fig. 4**c** for the one-time recycled specimen, where a moderate decrease in the intensity of the diffraction peak at 2θ ≈ 24.8°, corresponding to the (110) lattice plane, is apparent [84–86]. A further reduction in crystalline peak intensities (Fig. 4**d**) may be associated with partial disruption of the crystalline domains. This may indicate a shift towards a more amorphous-like structure as the molecular integrity of the TPU deteriorated [87]. These processes were influenced by the structure of the polymer, specifically its hard and soft segments, their composition and the type of diisocyanates employed. The trend is for methylene diphenyl diisocyanate to form crystalline segments rather than aliphatic diisocyanates. Hard segments tend to associate into ordered domains that exhibit a crystalline or semi-crystalline structure, while the soft segments remain amorphous. The degradation process has a cumulative impact on crystallinity, continually affecting the previously more ordered structure of the material. While specific effects may vary, the ongoing diffusion of the soft segments, in conjunction with the disintegration of more complex crystalline domains, potentially contributing to the development of broader amorphous halos [88,89].

3.1.10. Behavior of segmented TPU: relationship between hard and soft domains and structural effects of reprocessing

Based on Py-GC-MS analysis, the studied TPU consists of methylene diphenyl diisocyanate (MDI) forming with 1,4 butanediol chain extender the hard segments, and polytetrahydrofuran (polyTHF) as the soft segment. In segmented TPUs, it is well established that soft segments (polyether domains) exhibit lower thermal transitions and begin to melt first, while the hard segments, stabilized by hydrogen bonding and capable of forming ordered domains, melt at higher temperatures [90,91].

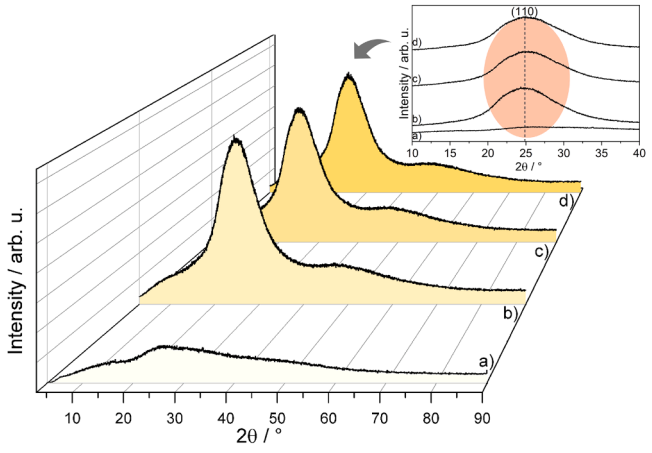


Fig. 4. Diffractograms of the measured samples: a) TPU; b) TPU_1; c) $rTPU_{n1}$; and d) $rTPU_{n2}$.

The decrease in melting temperature with increasing number of reprocessing cycles can be attributed primarily to chain scission, as also confirmed by GPC analysis showing a significant reduction in molecular weight (up to ~80%). Shorter polymer chains reduce the stability and perfection of hard-segment domains, leading to lower T_m values. Additionally, disruption of hydrogen bonding and microphase separation contributes to reduced thermal stability of these domains. Similar behavior has been reported for MDI-based TPUs subjected to thermomechanical degradation [2].

Conversely, the increase in crystallization temperature (T*c*) with reprocessing is attributed to enhanced chain mobility of shorter segments, which facilitates faster crystallization kinetics. As the molecular weight decreases, the mobility of both soft and partially degraded hard segments increases, allowing the material to reorganize and crystallize at higher temperatures during cooling. This effect is consistent with literature reports describing accelerated crystallization in degraded or low-molecular-weight TPU systems [92].

Importantly, the observed shifts in DSC peaks are relatively moderate, suggesting that, in addition to chain scission, supramolecular rearrangements of hard-segment domains play a significant role. Reprocessing induces partial reorganization of these domains, altering their size, distribution, and degree of phase separation. Such morphological changes are known to influence thermal transitions without necessarily causing dramatic shifts in peak positions, as also supported by XRD results showing decreased crystallinity and disruption of ordered structures [93].

Furthermore, the two-stage degradation mechanism of TPU, initial degradation of hard segments followed by soft segment cleavage, has been well documented in the literature, and provides additional support for the interpretation of the DSC behavior observed in this study[65].

In addition to chain scission, the potential contribution of branching or cross-linking reactions was also considered. In polyurethanes, the formation of allophanate and biuret linkages may occur at elevated temperatures (typically above ~130 °C), leading to branching or partial network formation. However, these reactions require the presence of residual free isocyanate (–NCO) groups. In the investigated TPU system, no free –NCO groups are expected due to complete conversion during synthesis, making such reactions unlikely under the applied reprocessing conditions.

Moreover, the DSC results do not indicate the formation of a cross-linked structure. Extensive cross-linking would significantly restrict molecular mobility and typically manifest as suppression or broadening of melting and crystallization transitions. In contrast, only minor shifts in DSC peak positions were observed, suggesting that the dominant mechanism is not network formation but rather chain scission combined with supramolecular rearrangement.

Therefore, the observed thermal behavior is more consistently explained by a reduction in molecular weight caused by splitting of PU chains and a concurrent reorganization of hard- and soft-segment domains. Small temperature shifts are attributed to changes in the supramolecular architecture, particularly the redistribution and partial disruption of hard-segment domains, rather than the formation of new covalent cross-links. This interpretation is in agreement with previous studies on thermomechanically degraded TPUs, where structural rearrangements dominate over cross-linking processes [2].

3.1.11. DMA Analysis of TPU

DMA was utilized to determine the difference between the mechanical performance of repeatedly recycled samples. As observed in **Figure S4**, the storage modulus E' at low temperatures has a tendency to oscillate with the as-injected sample, providing a significantly smoother curve. At higher temperatures (above approx.−5 °C), differences between individual samples are very minor.

Alternatively, **Figure S5** hinted at a linear relation between the number of recycling cycles and the glass transition temperature (Tg) of

the samples with peaks at −35.71, −38.72, and −40.87 °C for as-injected, 1x reprocessed, and 2x reprocessed samples, respectively. However, the Tg values as determined from tan δ measurements and seen in **Figure S6** show that the lowest Tg in this case belongs to the 1x reprocessed sample.

The most important observation is that the peak values of tan δ are decreasing with an increase in the number of recycling cycles, which suggests accumulation of errors within the material's structure and therefore the different mode of energy loss under the repeated load, where at lower temperatures (−45 to −30 °C) loss is higher but afterward tends to be less than that of as-injected samples. Overall, the curves are shifting towards lower temperatures (including Tg) as the number of recycling cycles is increased. Additionally, the 2x reprocessed sample has local minima of tan δ at approx. 20 °C, after which it starts to increase again, while this minimum is between 35 and 40 °C for the injected and 1x reprocessed sample. Complex modulus E* is provided in **Figure S7** to illustrate the similarity between it and E', which shows that the sample is highly elastic with relatively low E'' values.

Although DMA analysis provided valuable insight into viscoelastic behaviour and segmental mobility, conventional tensile testing was not included in the present study due to processing limitations associated with the highly elastic behaviour, dimensional instability, and foaming tendency of repeatedly reprocessed TPU specimens during sample preparation. In addition, the relatively small differences observed in Shore A hardness suggested that only limited variations in conventional tensile parameters could be expected. Nevertheless, complementary tensile testing may provide additional information regarding the practical mechanical performance of recycled TPU materials in future studies.

3.1.12. FTIR-ATR Analysis of TPU

The FTIR spectra of the virgin TPU (Elastollan) and materials subjected to successive recycling cycles are presented in Fig. 5.

The spectrum of the original sample (neat Elastollan) corresponds well to the characteristic spectral profile of thermoplastic polyurethane (TPU), as shown in Fig. 5. A broad absorption band around 3300 cm^{-1} is attributed to the stretching vibrations of N–H bonds in urethane groups. The bands observed in the region of 2850–2940 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of $–CH_2$ groups. The absorption band located between 1700 and 1735 cm^{-1} is assigned to the stretching vibration of the carbonyl (C═O) group in urethane linkages. The region around 1530–1540 cm^{-1} is associated with the amide II band, arising from a combination of N–H bending and C–N stretching vibrations. Furthermore, the band in the range of 1220–1250 cm^{-1} is attributed to coupled C–N stretching and N–H bending vibrations [94].

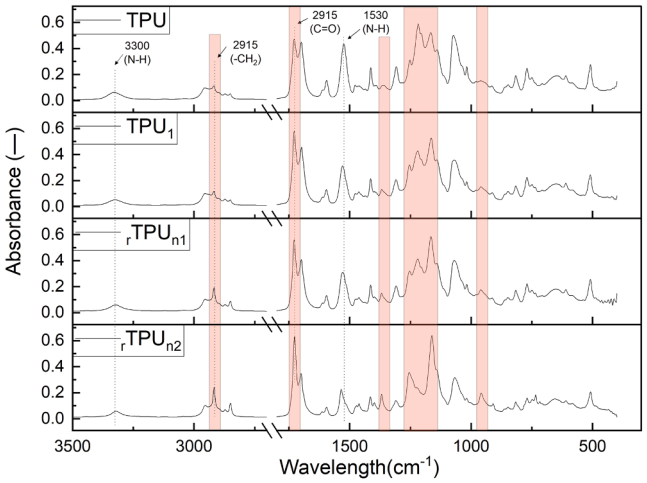


Fig. 5. FTIR spectra of TPU samples during repeated recycling cycles.

Compared to the spectrum of neat TPU, the injection-molded sample (TPU_1) exhibits only moderate changes in the intensity of selected characteristic bands (Fig. 5). An increase in absorbance at 1727 cm^{-1}, corresponding to the C═O stretching vibration of urethane groups, suggests a modification in the ratio of free to hydrogen-bonded carbonyl groups, which is commonly associated with thermal and pressure-induced effects during injection molding. Concurrently, a decrease in the intensity of the amide II band at 1531 cm^{-1} indicates changes in the local environment of N–H groups. A more pronounced band at 1367 cm^{-1} is also observed, which appeared only as a weak shoulder in the original sample. Additionally, a newly emerging peak at 956 cm^{-1} may reflect the formation of additional vibrational modes in the lower wavenumber region, potentially linked to chain rearrangement phenomena [95].

A comparison of FTIR spectra across successive recycling cycles ($rTPU_{n1}$ and $rTPU_{n2}$) shown in Fig. 5 reveals a consistent evolution of several characteristic bands. The intensity of the band at 2917 cm^{-1}, assigned to $–CH_2$ stretching vibrations, gradually increases with the number of recycling cycles. A similar trend is observed for the bands at 1727 cm^{-1} (C═O stretching of urethane groups) and 1367 cm^{-1}. These changes may be related to alterations in the proportion of free and hydrogen-bonded carbonyl groups, as well as conformational adjustments of TPU segments induced by repeated thermal and mechanical stress. In contrast, the band at 1216 cm^{-1} progressively decreases in intensity and becomes indistinguishable after the second recycling cycle. A general reduction in intensity is also evident for other bands associated with C–O–C and C–N vibrations. Notably, the band at 956 cm^{-1} becomes increasingly prominent with recycling, indicating structural rearrangements within the polymer matrix [41,96].

3.1.13. Integrated interpretation of molecular degradation and structural rearrangements

The pronounced decrease in molecular weight observed by GPC, together with the substantial reduction in melt viscosity, indicates that repeated thermomechanical processing induces extensive chain scission within the TPU matrix. Simultaneously, FTIR and DMA analyses suggest that these chemical degradation processes are closely associated with structural rearrangements occurring at the level of the segmented morphology. The limited changes observed in the FTIR spectra imply that degradation does not lead to the formation of entirely new dominant chemical functionalities, but rather to progressive cleavage of existing urethane and soft-segment bonds accompanied by modifications in hydrogen bonding interactions. The DMA results further support this interpretation, as changes in storage modulus and tan δ behaviour indicate increased segmental mobility and partial rearrangement of hard and soft domains. These observations collectively suggest that the substantial molecular weight decrease primarily reflects progressive depolymerisation and reduction of chain length, while the FTIR and DMA responses predominantly capture the accompanying physical and morphological consequences of this degradation process [74,97,98].

3.1.14. Migration test of TPU into water

Samples of thermoplastic polyurethane were examined with respect to overall migration into water, specifically regarding their migration behaviour and the organic and inorganic substances released. Tests were conducted on commercial-grade TPU and mechanically reprocessed samples (virgin TPU granules, the initial injection-moulded specimen, and 1 × and 2 × reprocessed materials). This assessment of partial leaching into water was relevant to understanding the environmental impacts of TPU.

Investigation was made of a commercially available thermoplastic polyurethane, respectively Elastollan EB 95 A from BASF. The purpose of the leaching experiment was to determine what substances might migrate from the TPU into an aqueous environment. A novel aspect of the research concerned how multiple mechanical reprocessing cycles would influence the behaviour of the polymer in water. This aligns with

current trends and evolving regulatory frameworks that increasingly mandate the use of recycled materials in products, heightening the content of such reprocessed materials in plastic manufactured industrially.

No solid fraction of <4 mm (with a moisture threshold set at 0.03%) was detected as having leached from either the virgin or reprocessed TPU samples. A complementary experiment identified any volatile organic compounds (VOCs) additionally released into the water, as determined via a devised HS-SPME-GC-MS method. This procedure was carried out under the same conditions as the migration test, except that direct analysis of the VOCs was performed rather than evaporation to dryness of the aqueous phase.

The predominant compound detected in every TPU sample was 1,6-dioxacyclododecane-7,12-dione, a substance utilized in the production of polyurethane adhesive, especially in multilayered packaging. It was consistently present in samples with estimated relative abundances of 98% (TPU), 91% (TPU_1), 97% ($rTPU_{n1}$) and 94% ($rTPU_{n2}$). Other compounds were detected merely in trace amounts, such as 2,5-bis(1,1-dimethylethyl)-phenol and dimethylsilanediol, the latter appearing sporadically in the leachates of TPU_1 and $rTPU_{n2}$ at relative abundances of ca 2–4% (see **Figure S8**).

Analysing the VOCs that leached into the water from the TPU samples revealed that performing a higher number of mechanical reprocessing cycles did not cause a rise in their emission, which is a favourable outcome from an environmental and health-related perspective.

Especially, the occurrence of 1,6-dioxacyclododecane-7,12-dione did not show any systematic dependence on the number of reprocessing cycles, suggesting that it is not primarily formed during thermomechanical degradation. This compound belongs to the class of cyclic diesters (lactones), which are well documented as non-intentionally added substances (NIAS) formed during polyester and polyurethane synthesis via condensation reactions of diols and dicarboxylic acids. For example, cyclic polyester oligomers have been widely reported to originate during polymerization and persist in the final material as residual species [99]. Similarly, studies on food packaging materials containing polyurethane adhesives have demonstrated that cyclic ester oligomers formed during manufacturing can migrate into surrounding media, independent of subsequent processing history [100].

Furthermore, 1,6-dioxacyclododecane-7,12-dione has been specifically identified in polyester-based systems such as PBAT, where it is formed during polymerization from 1,4-butanediol and adipic acid and classified as a typical NIAS present already in the virgin material (Lin et al.; Canellas et al.; Ubeda et al., as summarized in recent migration studies). More generally, cyclic oligomers are known to coexist with linear chains in polyester materials and may migrate or “bloom” to the surface without requiring additional degradation processes [101].

Based on these findings and the absence of any increasing trend with reprocessing cycles, 1,6-dioxacyclododecane-7,12-dione is therefore interpreted as a residual oligomer originating from the polyester-based raw material or TPU manufacturing process rather than a degradation product formed during repeated mechanical recycling. This behaviour is consistent with the established understanding of cyclic oligomers in polyester-containing polymer systems, which are typically present irrespective of processing history and may be released during migration experiments.

4. Conclusions

This study provides a comprehensive assessment of the effects of mechanical reprocessing on the structural, thermal and chemical properties of thermoplastic polyurethane (TPU), with particular emphasis on the formation of low-molecular-weight degradation products and volatile organic compounds (VOCs). Carrying out multiple forms of analysis, namely gel permeation chromatography (GPC), differential scanning calorimetry (DSC), rheological analysis, pyrolysis-gas chromatography/mass spectrometry (Py-GC-MS), headspace solid-phase microextraction coupled with GC-MS (HS-SPME-GC-MS), Fourier transformed infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), migration testing and X-ray diffraction (XRD), permitted systematic investigation of the effects of one and two reprocessing cycles on the behaviour of TPU. Due to the processing limitations associated with the highly elastic and partially unstable nature of repeatedly reprocessed TPU specimens, conventional tensile testing was not included in the present study; however, future investigations may benefit from complementary mechanical characterization.

GPC analysis revealed a substantial reduction in molecular weight of the peak maxima of up to ca 80% had occurred after two reprocessing cycles, accompanied by decreases in polydispersity and viscosity, indicative of chain scission and diminished processability. DSC data showed a drop in melting temperature and shift in crystallization behaviour, consistent with morphological changes and thermal degradation. Rheological analysis confirmed these structural alterations, demonstrating a significant loss in melt strength.

The profile of degradation products during TPU pyrolysis evolved in parallel with molecular degradation. Several degradation products were consistently detected in all samples, including 1,4-butanediol and MDI, while others (e.g. 2-methyltetrahydrofuran and 2H-pyran-2-one) increased in abundance with higher pyrolysis temperatures and repeated processing, serving as markers of thermomechanical degradation. Notably, 1-hexadecanol was observed as a compound whose relative abundance increased with repeated reprocessing, based on VOC analysis by HS-SPME-GC-MS. Detected exclusively at 120 °C, it exhibited a noticeable increase from the first to the second reprocessing cycle. While this trend suggests that 1-hexadecanol may be associated with degradation processes occurring during repeated thermal treatment, its identification as a potential marker of reprocessing should be considered preliminary. Further validation using complementary analytical techniques and investigation across different TPU systems would be necessary to confirm its suitability as a reliable indicator. In contrast, the antioxidant butylated hydroxytoluene (BHT) showed a substantial decline, highlighting a progressive loss of stabilizing additives under thermal stress.

X-ray diffraction (XRD) analysis further supported the evidence of structural degradation. A progressive broadening and reduction in the intensities of characteristic crystalline peaks was observed in parallel with additional reprocessing cycles, indicating a decline in long-range molecular order and reduced crystallinity. These changes were attributed to the disruption of hard segment domains and the heightened amorphous character of the material, aligning with the chain scission and morphological transformations identified by GPC and DSC. Results suggest that such reprocessing induces cumulative structural rearrangements in the hard and soft segments, ultimately leading to diminished structural coherence.

Dynamic mechanical analysis reveals that repeated recycling of TPU induces only moderate changes in viscoelastic behavior, without evidence of extensive chemical degradation. The shift of the glass transition temperature (Tg) toward lower values indicates increased segmental mobility, which is consistent with the following FTIR results showing modifications in hydrogen bonding and redistribution of carbonyl groups rather than chain scission. The progressive decrease in tan δ peak intensity suggests reduced energy dissipation, likely associated with structural reorganization and changes in microphase separation between hard and soft segments. The relatively stable storage modulus (E′) and its close correspondence with the complex modulus (E) further confirm that the elastic integrity of the polymer network is largely preserved.

The FTIR analysis indicates that repeated recycling of TPU does not result in significant chemical degradation of the polymer backbone, as no new characteristic absorption bands associated with chain scission or oxidative by-products are observed. Instead, the spectral evolution is characterized by gradual changes in the carbonyl (C═O) and N–H regions, reflecting modifications in hydrogen bonding within the hard

segments. The increase in intensity of the carbonyl band at ~1727 cm^{-1}, accompanied by a decrease in the amide II band, suggests a redistribution between free and hydrogen-bonded urethane groups. Concurrent changes in the –CH_2 stretching region, together with the intensification of bands at lower wavenumbers (notably around ~956 cm^{-1}), point to conformational rearrangements of the polymer chains. The progressive decrease in bands associated with C–O–C and C–N vibrations further support alterations in segmental organization. Overall, these findings indicate that thermo-mechanical reprocessing primarily induces structural reorganization and partial disruption of intermolecular interactions rather than extensive chain scission. This behavior is consistent with the relative stability of urethane linkages under the applied processing conditions, while highlighting the sensitivity of hydrogen-bonded domains to repeated thermal and mechanical stress. Overall, both DMA and FTIR results consistently indicate that thermo-mechanical recycling leads primarily to physical reorganization and partial disruption of intermolecular interactions, rather than significant degradation of the TPU backbone.

Migration testing confirmed minimal leaching of solids and VOCs into water, even after multiple reprocessing cycles, with 1,6-dioxacyclododecane-7,12-dione consistently present in all leachates.

Finally, an integrated conceptual framework describing the possible relationships between degradation processes and VOC formation during repeated TPU reprocessing was developed based on the combined Py-GC-MS and HS-SPME-GC-MS results (Tables 4 and 5). The results consistently demonstrate that thermo-mechanical and thermo-oxidative degradation is dominated by chain scission processes, particularly urethane bond cleavage in hard segments, leading to the formation of key structural compounds such as 1,4-butanediol and methylene diphenyl diisocyanate (MDI), along with nitrogen-containing species including hydrazine derivatives and diethyl azodicarboxylate. At elevated temperatures, secondary degradation pathways involving radical reactions, fragmentation, and cyclization result in the formation of low-molecular-weight compounds such as cyclopropanecarboxaldehyde, tetrahydro-2-methylfuran, and 2H-pyran-2-one derivatives. Under milder conditions, VOC evolution appears to be predominantly associated with thermo-oxidative degradation of soft segments, which is consistent with the detection of oxygenated compounds such as cyclopentanone, 3-nonen-1-ol, geranylacetone, and various alcohols, together with hydrocarbons including hexadecane and additive-related compounds such as butylated hydroxytoluene. The increasing abundance of long-chain oxidation products, particularly 1-hexadecanol, observed with repeated reprocessing cycles may reflect cumulative degradation effects and could indicate its possible relevance as a tentative marker of material ageing; however, this interpretation would require further validation using additional TPU systems and complementary analytical approaches. Overall, the proposed conceptual interpretation associates the observed VOC profile with progressive structural degradation occurring during repeated TPU reprocessing and contributes to a better understanding of the potential recyclability limitations and environmental aspects of thermoplastic polyurethane materials.

Overall, the findings of this study establish a clear correlation between molecular degradation and the evolving structural and volatility profiles of TPU. As polymer chains become shorter and more uniform through repeated reprocessing, a shift is seen in emission characteristics and crystalline structure, emphasizing the importance of monitoring subsequent physical and chemical transformations. This study offers novel insights into the course of degradation of TPU and provides a robust analytical framework that could aid the development of sustainable, circular-economy recycling strategies for thermoplastic elastomers.

CRediT authorship contribution statement

Andrea Polachova: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Martin Novak:** Methodology, Investigation, Formal analysis. **Jaroslav Cisar:** Methodology, Investigation, Formal analysis. **Milan Masar:** Methodology, Investigation, Formal analysis. **Vladimir Sedlarik:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the European Just Transition Fund within an Operational Programme entitled “Just Transition” under the aegis of the Ministry of the Environment of the Czech Republic, project CirkArena number CZ.10.03.01/00/22_003/0000045; and the Ministry of Education Youth and Sports of the Czech Republic, through the Operational Programme Johannes Amos Comenius OP JAC – “Application potential development in the field of polymer materials in the context of circular economy compliance (POCEK)”, number CZ.02.01.01/00/23_021/0009004.

The authors are also grateful for co-funding from the development process of the Centre of Polymer Systems, Tomas Bata University in Zlin, via the programme DKRVO (RP/CPS/2024-28/002 and RP/CPS/2024-28/007) supported by the Ministry of Education Youth and Sports of the Czech Republic.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2026.112285.

Data availability

Data will be made available on request.

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