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

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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), 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 (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 was identified as a potential molecular marker of repeated mechanical recycling, as its relative abundance increased consistently with each reprocessing cycle. 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. Overall, this work establishes a robust analytical framework for evaluating the recyclability, degradation pathways and emission behaviour of TPU, providing critical insights to support the sustainable use of polyurethane materials in circular material systems.

KEYWORDS

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

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 plastic is deemed more necessary than ever before, through general demand and EU directives set for the year 2050. Hence, the scientific community has been paying great attention to developing appropriate and effective recycling methods, which for polyurethane include physical, mechanical or chemical techniques or energy recovery [2–4].

Various types of polyurethane exist, constituting a group of useful synthetic polymers derived from diisocyanates and diols/polyols via polycondensation reactions within thermosetting or thermoplastic fabrication processes. Introduced in the early nineteenth century, synthetic plastics have become commonplace since they are relatively cheap to produce, with up to 360 million tonnes now being manufactured annually. Thermoplastic polyurethane (TPU) is considered a material that bridges the gap between rubber and plastic, which possesses high levels of elasticity and abrasion resistance. It ranks among a class of combined, thermoplastic elastomers that have desirable elastomeric properties and application temperatures. Their exact characteristics depend on intra- and intermolecular interactions in the block-copolymer chain, the latter consisting of hard and soft segments. 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 was selected for this study for its exceptional versatility and capacity for wide-ranging application. Commonly found in an assortment of everyday products, sports items and decorating materials, it is also deployed by industry in automotive components, electronic devices, wires and cables. TPU has outstanding chemical and physical properties, e.g. toughness, strength, shock absorption and wear resistance, and is highly resistant to acids, alkalis, oil and water. These characteristics mark TPU out as a material suitable for products intended for consumers and industrial applications, while also raising interest in its recyclability and performance under repeated processing [9–11].

The increasing accumulation of plastic waste is a major issue, hence the scientific community has been endeavouring to develop effective methods for reusing and recycling it. Such strategies for polyurethane include energy recovery [3,12] and recycling by mechanical or physical means [4,13,14] or chemically [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, oligomers and low-molecular-weight organic compounds [2,19–21]. The cost-effectiveness, environmental friendliness and energy efficiency of the mechanical method make it the favoured technique [22], wherein plastic is usually crushed and processed through physical processes, e.g. compression moulding [23], extrusion and injection moulding [3]. The processability and quality of resultant products, however, may be comprised by undergoing a high number of reprocessing cycles [2]. When mechanical recycling is carried out effectively, the crushed or melted plastic waste is properly incorporated in polymer materials. Utilizing reprocessed granules in the creation of new products requires that an optimal content of the recycled matter is applied, in order to maintain the desired properties. It is important to note that recycled polymers are susceptible to chemical and mechanical degradation through repeated mechanical processing or exposure to environmental conditions, meaning their properties are often inferior compared to virgin materials [24–27].

Processing polymers at high temperatures tends to induce thermal degradation through exposure to external or internally generated heat via a mechanism of dissipation. Such thermomechanical and thermo-oxidative degradation poses a significant challenge when recycling polymers [28,29]. A complication that arises during mechanical recycling is breakdown in the properties of the polymer each time the procedure is performed due to consequent (thermomechanical) degradation; this is equivalent to (thermo-oxidative) deterioration that occurs during ordinary service life. The given material undergoes irreversible thermal and mechanical degradation with each processing cycle, giving rise to physical and chemical changes which impair its properties. Since polymers cannot withstand extensive reprocessing, just two or three such cycles usually take place [8,30]. This has been confirmed in studies by Calvo-Correas et al. (2022) and Wölfel et al. (2020). They observed deterioration brought on by multiple reprocessing cycles, resulting in loss in the molecular weight of the tested TPU, diminished tensile properties and a heightened rate of thermal degradation. Wölfel et al. (2020) researched methods for recycling and reprocessing types of thermoplastic polyurethane based on polytetramethylene glycol (PTMG), methylene diphenyl diisocyanate (MDI) and 1,4-Butanediol (BDO). They identified two distinct degradation mechanisms for TPU that happen consecutively, i.e. one each for its hard and soft segments [2,6]. The hard segments deteriorate initially, with the cleavage of urethane bonds and compounds such as isocyanates and polyols, giving rise to primary and secondary amines and carbon dioxide [31,32]; the thermal stability of TPU is dependent on the composition of its hard segments. The other stage affects the soft segments, specifically through the cleavage of C-O-C bonds [33–35].

The most advantageous mechanical reprocessing technique for TPU was selected for this study, recognized for its cost-effectiveness, ecological benefits and energy efficiency [36]. Waste plastic was ground up and physical processing methods then conducted, e.g. compression, extrusion and injection moulding [3,23]. Since it was known that repeating the reprocessing cycles would compromise the processability of the material and the quality of the eventual product [37], with each cycle likely to exert irreversible thermal and mechanical degradation and subsequent physical and chemical alterations, emphasis was put on determining the maximum number of such cycles that could occur while still maintaining the properties of the TPU [2,38].

Assessing the potential health risks associated with TPU was also essential. Volatile organic compounds (VOCs), which constitute hazards to the environment and health, require precise detection for applications such as chemical process control and environmental monitoring [39]. Description is given herein of the VOCs present in the TPU and reprocessed samples of it, as analysed by HS-SPME-GC-MS. The material was characterized by migration testing, differential scanning calorimetry (DSC), pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), X-ray diffraction (XRD) analysis and high-temperature gel permeation chromatography (GPC). The objective was to evaluate the influence exerted by repeated performance of mechanical recycling on the safety of the TPU.

This study provides a comprehensive assessment of the state of thermoplastic polyurethane (TPU) after multiple instances of mechanical recycling. The novelty of the research presented here is the number of analyses carried out, namely (i) determination of the volatile organic compounds (VOCs) present, (ii) pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS), (iii) differential scanning calorimetry (DSC), (iv) gel permeation chromatography (GPC), (v) X-ray diffraction (XRD) analysis and (vi) migration testing. Only Wölfel et al. (2020) have attempted anything similar, who focused on changes in the properties of raw materials during recycling, but without taking such a broad analytical approach. The novel and expansive concept applied herein was aimed at discerning the degradation behaviour of mechanically recycled TPU and the associated implications that arise for humans and the environment. Addressing the performance of the given material and such safety aspects produced notable results, which could contribute to furthering the sustainable use of polymers and supporting key principles of the circular economy [6].

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, reinforced with glass fibres, 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 x 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*

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 necessary, the samples were cleaned twice with standard washing-up liquid and hot water, then washed thoroughly two times in hot water, prior to being dried for two days at room temperature. Once this time had transpired, they were cut into small pieces for reprocessing. The same procedure was repeated for samples that had been recycled twice. A more detailed description of the specimens and the abbreviations for them is provided in **Table 1**.

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

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 hours, yet did not completely dissolve. The extracts were filtered through PTFE syringe filters (0.45 µm) into 2mL vials, the final concentration of the analyte in tetrahydrofuran equalling 2-3 mg·mL^{-1}. Each sample was extracted and analysed three times.

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 minutes. 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 minutes, respectively, and a 4-minute period of desorption.

2.3. *Analysis and characterization*

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.

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 x 7.5 mm, 10 µm) + MIXED - B (300 x 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.

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).

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.

Gas chromatography-mass spectrometry (GC-MS)

GC-MS 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-5ms 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 minutes) to 100°C with an increase at the rate of 10°C/min^{-1} to 300°C (maintained for 2 minutes). 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).

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 minutes).

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.

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 12457-2:2002. 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 hours. 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 12457-2:2002. Such samples were then shaken at a temperature of 20°C for 24 hours. 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*

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**.

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

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.

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

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

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.

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.

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

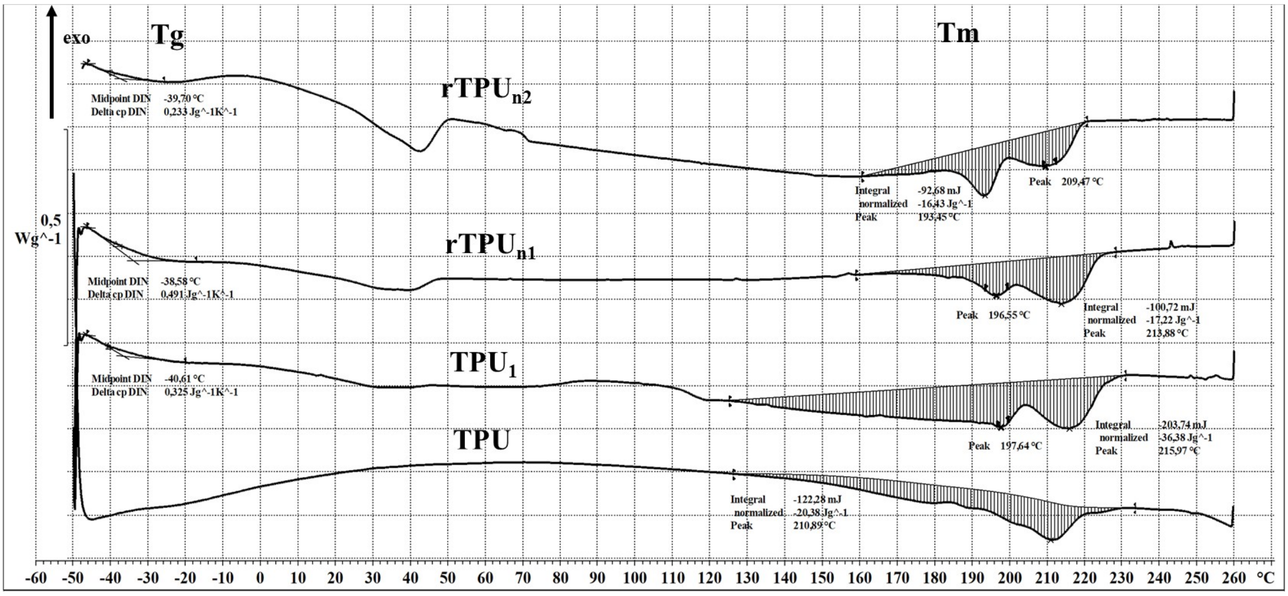

Figure 1: Course of melting (T_m) of the virgin TPU granulate and 1-time and 2-time reprocessed TPU samples.

As detailed in **Figure 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).

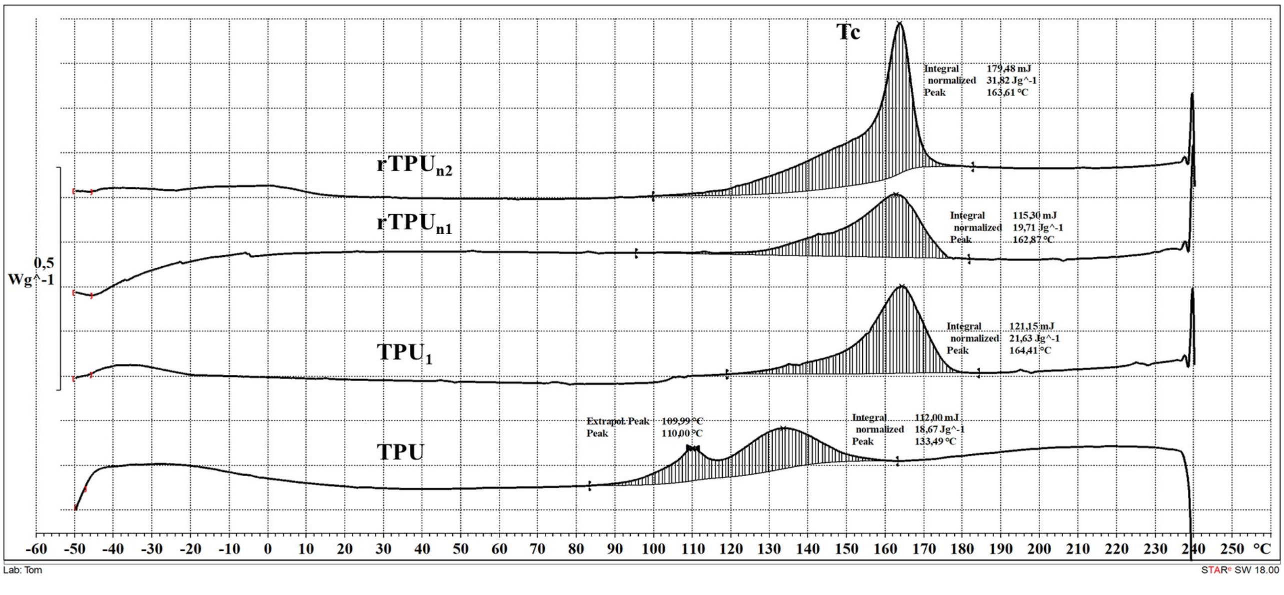

Figure 2: Course of crystallization (T_c) of all the monitored TPU samples.

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. **Figure 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 [6,35].

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 [2,40]. 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 [41]. 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. (2020) 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 (2008) 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 [40]. Smorawska et al. (2023) 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 [35]. 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].

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. (2024) reported similarly steep drops in viscosity, attributed therein to predominant chain scission in combination with stabilizing additives of limited efficiency [41].

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.

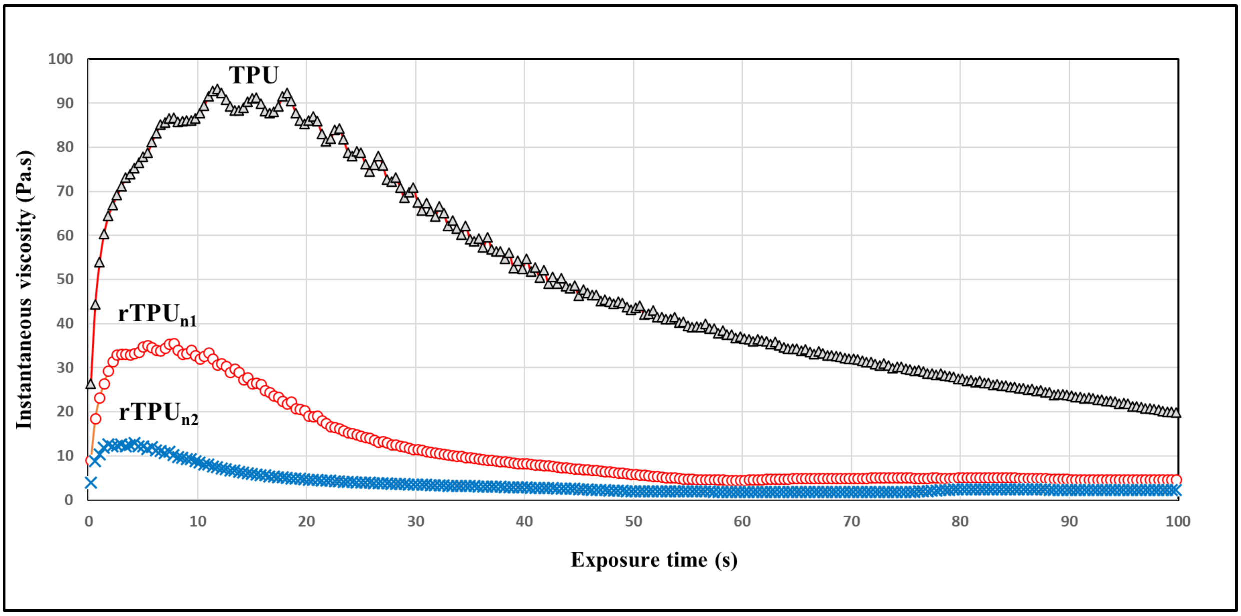

Figure 3: Rheological properties of TPU samples: virgin, once and twice reprocessed; as per the dependence of viscosity on temperature (230°C) under specific processing parameters.

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 [42].

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 [43,44].

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-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 [43,45].

Sample	Retention time (min.)	CAS number	Target compound	Area	Rel represe substa
TPU 300°C	0.537	460-13-9	n-Propyl fluoride	624677675	38
	1.525	302-01-2	Hydrazine	168549564	10
	9.098	110-64-5	1,4-Butanediol	298498454	18
	16.755	101-68-8	1,1′-Methylenebis(4-isocyanatobenzene) (MDI)	389791929	24
TPU 600°C	0.428	57-56-7	Hydrazinecarboxamide	1698837383	20
	3.439	107-89-1	Butanal, 3-hydroxy-	526050008	6.
	3.728	858971-43-4	Palladium, bis[(1,2,3-.eta.)-2-butenyl]-	421982408	5.
	5.005	96-47-9	Furan, tetrahydro-2-methyl-	443821660	5.
	5.144	20201-24-5	Ethyl 3-methyl-2-oxobutyrate	565995155	6.
	6.976	638-28-8	Hexane, 2-chloro-	564878743	6.
	9.858	110-63-4	1,4-Butanediol	1706188260	20
	17.102	19471-12-6	3,3'-Diaminodiphenylmethane	833781933	9.
TPU_1 300°C	0.630	302-01-2	Hydrazine	178075184	17
	1.093	7782-44-7	Oxygen	65095069	6.
	9.232	110-63-4	1,4-Butanediol	276025840	27
	16.887	101-68-8	1,1′-Methylenebis(4-isocyanatobenzene) (MDI)	336561653	33
	22.500	777-95-7	1,6-Dioxacyclododecane-7,12-dione	55988528	5.
TPU_1 600°C	3.485	1489-69-6	Cyclopropanecarboxaldehyde	383180720	10
	3.676	157-33-5	Bicyclo[1.1.0]butane	292714997	7.
	5.132	96-47-9	Furan, tetrahydro-2-methyl-	412836269	11
	7.106	3720-22-7	2H-Pyran-2-one, tetrahydro-3,6-dimethyl-	479288937	12
	9.564	110-63-4	1,4-Butanediol	937737523	25
	16.873	101-68-8	1,1′-Methylenebis(4-isocyanatobenzene) (MDI)	525645753	14

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

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

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	468072012	33.24
	1.854	1972-28-7	Diethyl azodicarboxylate	267421795	18.99
	9.172	110-63-4	1,4-Butanediol	251390428	17.85
	16.877	101-68-8	1,1′-Methylenebis(4-isocyanatobenzene) (MDI)	342834912	24.35
rTPU$_{n1}$ 600°C	3.456	1489-69-6	Cyclopropanecarboxaldehyde	350642374	14.27
	3.653	157-33-5	Bicyclo[1.1.0]butane	220350447	8.97
	5.112	96-47-9	Furan, tetrahydro-2-methyl-	368791248	15.01
	7.089	3720-22-7	2H-Pyran-2-one, tetrahydro-3,6-dimethyl-	366380878	14.91
	7.140	110-82-7	Cyclohexane	184223726	7.50
	9.463	110-63-4	1,4-Butanediol	722191376	29.40
rTPU$_{n2}$ 300°C	0.565	302-01-2	Hydrazine	960705306	43.86
	1.892	1972-28-7	Diethyl azodicarboxylate	239229368	10.92
	9.325	110-63-4	1,4-Butanediol	523933930	23.92
	16.869	101-68-8	1,1′-Methylenebis(4-isocyanatobenzene) (MDI)	300075940	13.70
rTPU$_{n2}$ 600°C	3.425	1489-69-6	Cyclopropanecarboxaldehyde	389622731	13.90
	3.617	157-33-5	Bicyclo[1.1.0]butane	266728494	9.51
	5.076	7319-16-6	1-Propene, 1-methoxy-	417562623	14.89
	7.088	3720-22-7	2H-Pyran-2-one, tetrahydro-3,6-dimethyl-	429965356	15.33
	7.137	110-82-7	Cyclohexane	134277439	4.79
	9.467	110-63-4	1,4-Butanediol	746802185	26.64

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

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., 2025) [46].

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 minutes) and incubation (5, 10, 15 and 20 minutes). It was found that the most effective durations were 4 minutes for desorption and 20 minutes for incubation.

Further tests focused on extraction durations (10, 20, 40 and 60 minutes) 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 minutes. **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 minutes 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 minutes; extraction for 60 minutes; and desorption for 4 minutes. 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.

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 [47]. The thermo-oxidative degradation pathways of polyether, polyester, and polycarbonate polyols in PU are well established [48–57]. 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 [57]. 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 [48,50,55]. It is well known that polyester-based PU is more resistant to thermo-oxidative degradation than polyether-based PU [58,59]. The possibility exists that polyol chain scission and subsequent radical rearrangements could give rise to volatile organic compounds (VOC), including aldehydes, acetates and formats [2,38,42].

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 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 [44,60–62]. 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 [63]. 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) [42]. 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) [63,64].

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 [65,66]. The formation of them in polymers is primarily caused by thermal or thermo-oxidative degradation [47,69,70]. Concerns over air quality and human health have led to stricter regulations on their emission [67,68]. 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 [48–51,71,72]. 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 [73].

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.

XRD analysis of TPU

X-ray diffraction (XRD) diffractograms were acquired to elucidate the degradation process, as illustrated in **Figure 4**. TPU is a segmented copolymer made up of alternating segments of soft polyester and hard polyurethane-urea. As illustrated in the **Figure 4**, XRD is capable of analysing the course of TPU degradation through the broadening and shifting of diffraction peaks that denote alterations in molecular ordering and crystallite size [74,75]. Post-processing the samples of TPU caused a drop in crystallinity, as evidenced by data depicted in **Figure 4c** on the one-time recycled specimen, reflected in moderate decreases in the intensities of specific peaks in the XRD patterns, as extensively documented in numerous studies [76,77]. When undergoing degradation, the intensities of the crystalline peaks diminished (see **Figure 4d)**, attributed to consequent disruption to the crystalline structure. This potentially culminated in a more amorphous state as the molecular integrity of the TPU deteriorated [78]. These processes were influenced by the structure of the polymer, specifically its hard and soft segments, their composition and the selection of diisocyanates. 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 leads to the formation of broader amorphous halos [79].

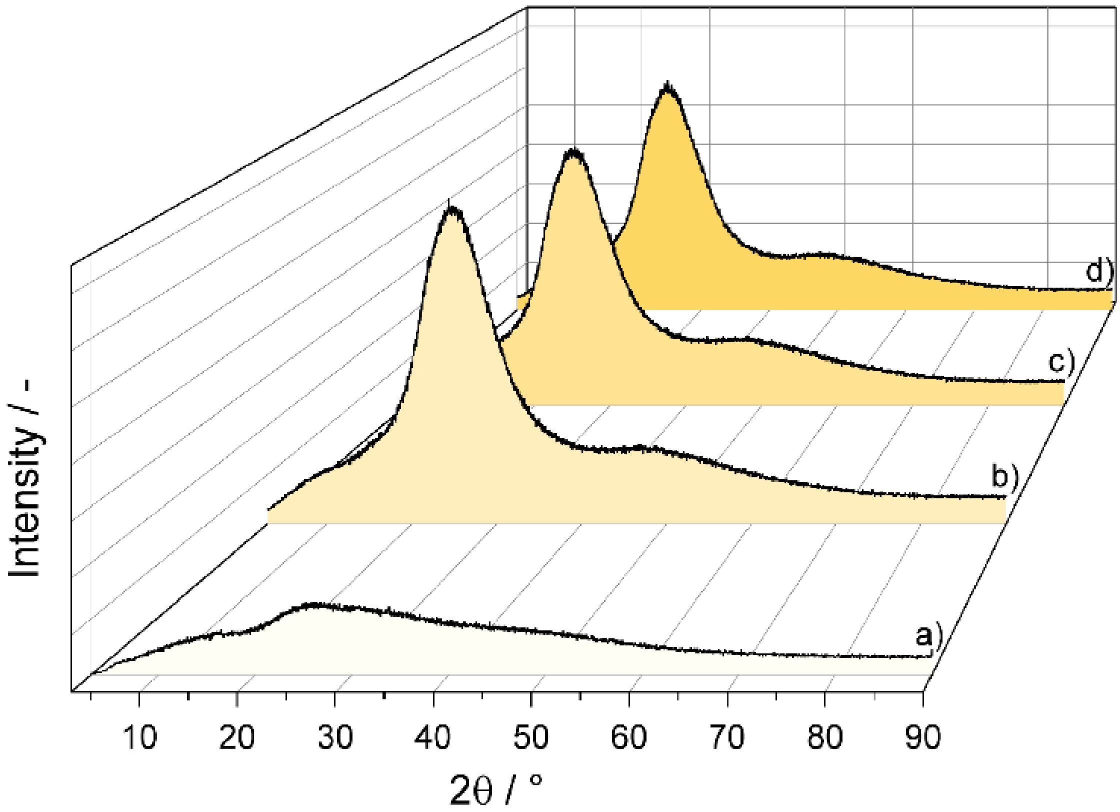

Figure 4 Diffractograms of the measured samples: a) TPU; b) TPU_1; c) $rTPU_{n1}$; and d) $rTPU_{n2.}$

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 less than 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 S4**).

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.

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), migration testing and X-ray diffraction (XRD), permitted systematic investigation of the effects of one and two reprocessing cycles on the behaviour of TPU.

GPC analysis revealed a substantial reduction in molecular weight of up to ca 80% had occurred after two reprocessing cycles, accompanied by decreases in polydispersity and viscosity, indicative of extensive 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 emerged as a potential indicator of repeated reprocessing, based on the VOCs measured by HS-SPME-GC-MS. Detected exclusively at 120°C, it exhibited a marked increase in relative abundance from the first to the second cycle. In contrast, the antioxidant butylated hydroxytoluene (BHT) showed a substantial decline, highlighting a progressive loss in 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.

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.

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.

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.

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Data availability

Data will be made available on request.

References

[1] H.M.C.C. Somarathna, S.N. Raman, D. Mohotti, A.A. Mutalib, K.H. Badri, The use of polyurethane for structural and infrastructural engineering applications: A state-of-the-art review, Constr Build Mater 190 (2018) 995–1014. https://doi.org/10.1016/J.CONBUILDMAT.2018.09.166.

[2] T. Calvo-Correas, M. Benitez, I. Larraza, L. Ugarte, C. Peña-Rodríguez, A. Eceiza, Advanced and traditional processing of thermoplastic polyurethane waste, Polym Degrad Stab 198 (2022) 109880. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2022.109880.

[3] K.M. Zia, H.N. Bhatti, I. Ahmad Bhatti, Methods for polyurethane and polyurethane composites, recycling and recovery: A review, React Funct Polym 67 (2007) 675–692. https://doi.org/10.1016/J.REACTFUNCTPOLYM.2007.05.004.

[4] K. Ragaert, L. Delva, K. Van Geem, Mechanical and chemical recycling of solid plastic waste, Waste Management 69 (2017) 24–58. https://doi.org/10.1016/J.WASMAN.2017.07.044.

[5] A. Boubakri, K. Elleuch, N. Guermazi, H.F. Ayedi, Investigations on hygrothermal aging of thermoplastic polyurethane material, Mater Des 30 (2009) 3958–3965. https://doi.org/10.1016/J.MATDES.2009.05.038.

[6] B. Wölfel, A. Seefried, V. Allen, J. Kaschta, C. Holmes, D.W. Schubert, Recycling and Reprocessing of Thermoplastic Polyurethane Materials towards Nonwoven Processing, Polymers 2020, Vol. 12, Page 1917 12 (2020) 1917. https://doi.org/10.3390/POLYM12091917.

[7] A. Kemona, M. Piotrowska, Polyurethane Recycling and Disposal: Methods and Prospects, Polymers 2020, Vol. 12, Page 1752 12 (2020) 1752. https://doi.org/10.3390/POLYM12081752.

[8] G. Rossignolo, G. Malucelli, A. Lorenzetti, Recycling of polyurethanes: where we are and where we are going, Green Chemistry 26 (2024) 1132–1152. https://doi.org/10.1039/D3GC02091F.

[9] J. Wang, D. Zhang, Y. Zhang, W. Cai, C. Yao, Y. Hu, W. Hu, Construction of multifunctional boron nitride nanosheet towards reducing toxic volatiles (CO and HCN) generation and fire hazard of thermoplastic polyurethane, J Hazard Mater 362 (2019) 482–494. https://doi.org/10.1016/J.JHAZMAT.2018.09.009.

[10] L. Wan, C. Deng, H. Chen, Z.Y. Zhao, S.C. Huang, W.C. Wei, A.H. Yang, H.B. Zhao, Y.Z. Wang, Flame-retarded thermoplastic polyurethane elastomer: From organic materials to nanocomposites and new prospects, Chemical Engineering Journal 417 (2021) 129314. https://doi.org/10.1016/J.CEJ.2021.129314.

[11] C. Jiao, H. Jiang, X. Chen, Reutilization of abandoned molecular sieve as flame retardant and smoke suppressant for thermoplastic polyurethane elastomer, J Therm Anal Calorim 138 (2019) 3905–3913. https://doi.org/10.1007/S10973-019-08328-Z/FIGURES/11.

[12] D.A. Hicks, M. Krommenhoek, D.J. Soderberg, J.F.G. Hopper, Polyurethanes Recycling and Waste Management*, Cellular Polymers 13 (1994) 259–276. https://doi.org/10.1177/026248939401300401.

[13] O. Grigoryeva, A. Fainleib, L. Stepanenko, L. Sergeeva, P. Pissis, Recycling of PVC/PU waste and reuse in PVC formulations: Structure-property relationship, Polym Eng Sci 45 (2005) 801–808. https://doi.org/10.1002/PEN.20343;PAGE:STRING:ARTICLE/CHAPTER.

[14] A.J. Hulme, T.C. Goodhead, Cost effective reprocessing of polyurethane by hot compression moulding, J Mater Process Technol 139 (2003) 322–326. https://doi.org/10.1016/S0924-0136(03)00548-X.

[15] Z. Dai, B. Hatano, J.I. Kadokawa, H. Tagaya, Effect of diaminotoluene on the decomposition of polyurethane foam waste in superheated water, Polym Degrad Stab 76 (2002) 179–184. https://doi.org/10.1016/S0141-3910(02)00010-1.

[16] M. Murai, M. Sanou, T. Fujimoto, F. Baba, Glycolysis of rigid polyurethane foam under various reaction conditions, Journal of Cellular Plastics 39 (2003) 15–27. https://doi.org/10.1177/002195503031021.

[17] C.H. Wu, C.Y. Chang, C.M. Cheng, H.C. Huang, Glycolysis of waste flexible polyurethane foam, Polym Degrad Stab 80 (2003) 103–111. https://doi.org/10.1016/S0141-3910(02)00390-7.

[18] X. Wang, H. Chen, C. Chen, H. Li, Chemical degradation of thermoplastic polyurethane for recycling polyether polyol, Fibers and Polymers 12 (2011) 857–863. https://doi.org/10.1007/S12221-011-0857-Y/METRICS.

[19] W. Yang, Q. Dong, S. Liu, H. Xie, L. Liu, J. Li, Recycling and Disposal Methods for Polyurethane Foam Wastes, Procedia Environ Sci 16 (2012) 167–175. https://doi.org/10.1016/J.PROENV.2012.10.023.

[20] T. Calvo-Correas, L. Ugarte, P.J. Trzebiatowska, R. Sanzberro, J. Datta, M.Á. Corcuera, A. Eceiza, Thermoplastic polyurethanes with glycolysate intermediates from polyurethane waste recycling, Polym Degrad Stab 144 (2017) 411–419. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2017.09.001.

[21] D. Simón, A.M. Borreguero, A. de Lucas, J.F. Rodríguez, Recycling of polyurethanes from laboratory to industry, a journey towards the sustainability, Waste Management 76 (2018) 147–171. https://doi.org/10.1016/J.WASMAN.2018.03.041.

[22] J. Maris, S. Bourdon, J.M. Brossard, L. Cauret, L. Fontaine, V. Montembault, Mechanical recycling: Compatibilization of mixed thermoplastic wastes, Polym Degrad Stab 147 (2018) 245–266. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2017.11.001.

[23] É. Léger, B. Landry, G. LaPlante, High flow compression molding for recycling discontinuous long fiber thermoplastic composites, J Compos Mater 54 (2020) 3343–3350. https://doi.org/10.1177/0021998320913625;PAGE:STRING:ARTICLE/CHAPTER.

[24] J. Datta, M. Włoch, Morphology and properties of recycled polyethylene/ground tyre rubber/thermoplastic poly(ester-urethane) blends, Macromol Res 23 (2015) 1117–1125. https://doi.org/10.1007/S13233-015-3155-5/METRICS.

[25] S.M. Al-Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): A review, Waste Management 29 (2009) 2625–2643. https://doi.org/10.1016/J.WASMAN.2009.06.004.

[26] D. Carta, G. Cao, C. D'Angeli, Chemical Recycling of Poly(ethylene terephthalate) (PET) by Hydrolysis and Glycolysis, Environmental Science and Pollution Research 10 (2003) 390–394. https://doi.org/10.1065/ESPR2001.12.104.8/METRICS.

[27] N. George, T. Kurian, Recent developments in the chemical recycling of postconsumer poly(ethylene terephthalate) Waste, Ind Eng Chem Res 53 (2014) 14185–14198. https://doi.org/10.1021/IE501995M/ASSET/IMAGES/LARGE/IE-2014-01995M_0008.JPEG.

[28] H.S. Kim, E.M. White, G. Crane, K. Patel, M.H. Noh, M.A. Rahman, A.M. Feist, J.J. Locklin, J.K. Pokorski, Scalable fabrication of a tough and recyclable spore-bearing biocomposite thermoplastic polyurethane, Chemical Engineering Journal 505 (2025) 159863. https://doi.org/10.1016/J.CEJ.2025.159863.

[29] D.V.A. Ceretti, M. Edeleva, L. Cardon, D.R. D'hooge, Molecular Pathways for Polymer Degradation during Conventional Processing, Additive Manufacturing, and Mechanical Recycling, Molecules 2023, Vol. 28, Page 2344 28 (2023) 2344. https://doi.org/10.3390/MOLECULES28052344.

[30] F. Paolo, L. Mantia, Basic Concepts on the Recycling of Homogeneous and Heterogeneous Plastics, (n.d.).

[31] M. Szlachta, K. Ordon, K. Nowicka, K. Pielichowska, Thermal properties of polyurethane-based composites modified with chitosan for biomedical applications, J Therm Anal Calorim 143 (2021) 3471–3478. https://doi.org/10.1007/S10973-020-09283-W/TABLES/4.

[32] L. Jiao, H. Xiao, Q. Wang, J. Sun, Thermal degradation characteristics of rigid polyurethane foam and the volatile products analysis with TG-FTIR-MS, Polym Degrad Stab 98 (2013) 2687–2696. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2013.09.032.

[33] E. Głowińska, J. Datta, J.F. Rodríguez Romero, D. Simón Herrero, M. Carmona, Novel cast polyetherurethanes based on dispersed polymeric polyols, Polym Test 68 (2018) 340–349. https://doi.org/10.1016/J.POLYMERTESTING.2018.04.034.

[34] Y.T. Shieh, H.T. Chen, K.H. Liu, Y.K. Twu, Thermal degradation of MDI-based segmented polyurethanes, J Polym Sci A Polym Chem 37 (1999) 4126–4134. https://doi.org/10.1002/(SICI)1099-0518(19991115)37:22<4126::AID-POLA11>3.0.CO;2-A.

[35] J. Smorawska, M. Włoch, E. Głowińska, Structure–Property Relationship and Multiple Processing Studies of Novel Bio-Based Thermoplastic Polyurethane Elastomers, Materials 2023, Vol. 16, Page 6246 16 (2023) 6246. https://doi.org/10.3390/MA16186246.

[36] J. Maris, S. Bourdon, J.M. Brossard, L. Cauret, L. Fontaine, V. Montembault, Mechanical recycling: Compatibilization of mixed thermoplastic wastes, Polym Degrad Stab 147 (2018) 245–266. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2017.11.001.

[37] P. Oblak, J. Gonzalez-Gutierrez, B. Zupančič, A. Aulova, I. Emri, Processability and mechanical properties of extensively recycled high density polyethylene, Polym Degrad Stab 114 (2015) 133–145. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2015.01.012.

[38] I. Goitisolo, J.I. Eguiazábal, J. Nazábal, Effects of reprocessing on the structure and properties of polyamide 6 nanocomposites, Polym Degrad Stab 93 (2008) 1747–1752. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2008.07.030.

[39] Q. Fan, Z. Qin, T. Villmow, J. Pionteck, P. Pötschke, Y. Wu, B. Voit, M. Zhu, Vapor sensing properties of thermoplastic polyurethane multifilament covered with carbon nanotube networks, Sens Actuators B Chem 156 (2011) 63–70. https://doi.org/10.1016/J.SNB.2011.03.073.

[40] E. Hernández, Effect of Degradation During Processing on the Melt Viscosity of a Thermoplastic Polyurethane, (n.d.).

[41] R. Yıldırım, O. Mert, G. Özkoç, M. Kodal, Enhanced Recyclability of Thermoplastic Elastomer Toughened Polyamide 6 via Tri- and Multi-epoxy-Terminated POSS Hybrid Additives, ACS Omega 9 (2024) 45467–45486. https://doi.org/10.1021/ACSOMEGA.4C07547/SUPPL_FILE/AO4C07547_SI_001.PDF.

[42] T. Servay, R. Voelkel, H. Schmiedberger, S. Lehmann, Thermal oxidation of the methylene diphenylene unit in MDI-TPU, Polymer (Guildf) 41 (2000) 5247–5256. https://doi.org/10.1016/S0032-3861(99)00743-0.

[43] J.A. Hiltz, Analytical pyrolysis gas chromatography/mass spectrometry (py-GC/MS) of poly(ether urethane)s, poly(ether urea)s and poly(ether urethane-urea)s, J Anal Appl Pyrolysis 113 (2015) 248–258. https://doi.org/10.1016/J.JAAP.2015.01.013.

[44] A. Lattuati-Derieux, S. Thao-Heu, B. Lavédrine, Assessment of the degradation of polyurethane foams after artificial and natural ageing by using pyrolysis-gas chromatography/mass spectrometry and headspace-solid phase microextraction-gas chromatography/mass spectrometry, J Chromatogr A 1218 (2011) 4498–4508. https://doi.org/10.1016/J.CHROMA.2011.05.013.

[45] M. Zeller, K. Garbev, L. Weigel, T. Saatzer, D. Merz, S. Tavakkol, D. Stapf, Thermogravimetric studies, kinetic modeling and product analysis of the pyrolysis of model polymers for technical polyurethane applications, J Anal Appl Pyrolysis 171 (2023) 105976. https://doi.org/10.1016/J.JAAP.2023.105976.

[46] A. Polachova, J. Cisar, M. Novak, M. Dusankova, V. Sedlarik, Effect of repeated thermoplastic processing of polypropylene matrix on the generation of low-molecular-weight compounds, Polym Degrad Stab 238 (2025) 111337. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2025.111337.

[47] M. Herrera, G. Matuschek, A. Kettrup, Thermal degradation of thermoplastic polyurethane elastomers (TPU) based on MDI, Polym Degrad Stab 78 (2002) 323–331. https://doi.org/10.1016/S0141-3910(02)00181-7.

[48] D. Allan, J. Daly, J.J. Liggat, Thermal volatilisation analysis of TDI-based flexible polyurethane foam, Polym Degrad Stab 98 (2013) 535–541. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2012.12.002.

[49] J.P. Lewicki, K. Pielichowski, P.T. De La Croix, B. Janowski, D. Todd, J.J. Liggat, Thermal degradation studies of polyurethane/POSS nanohybrid elastomers, Polym Degrad Stab 95 (2010) 1099–1105. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2010.02.021.

[50] J.L. Fan, J.C.W. Chien, Thermal degradation studies of segmented thermoplastic elastomers, Polym Degrad Stab 12 (1985) 43–63. https://doi.org/10.1016/0141-3910(85)90056-4.

[51] N. Grassie, G.A. Perdomo Mendoza, Thermal degradation of polyether-urethanes: Part 1—Thermal degradation of poly(ethylene glycols) used in the preparation of polyurethanes, Polym Degrad Stab 9 (1984) 155–165. https://doi.org/10.1016/0141-3910(84)90063-6.

[52] D.K. Chattopadhyay, D.C. Webster, Thermal stability and flame retardancy of polyurethanes, Prog Polym Sci 34 (2009) 1068–1133. https://doi.org/10.1016/J.PROGPOLYMSCI.2009.06.002.

[53] O. Phillips, J.M. Schwartz, P.A. Kohl, Thermal decomposition of poly(propylene carbonate): End-capping, additives, and solvent effects, Polym Degrad Stab 125 (2016) 129–139. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2016.01.004.

[54] P. Król, Synthesis methods, chemical structures and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers, Prog Mater Sci 52 (2007) 915–1015. https://doi.org/10.1016/J.PMATSCI.2006.11.001.

[55] L. Shufen, J. Zhi, Y. Kaijun, Y. Shuqin, W.K. Chow, Studies on the thermal behavior of polyurethanes, Polymer - Plastics Technology and Engineering 45 (2006) 95–108. https://doi.org/10.1080/03602550500373634;JOURNAL:JOURNAL:LPTE19;PAGE:STRING:ARTICLE/CHAPTER.

[56] X.H. Li, Y.Z. Meng, Q. Zhu, S.C. Tjong, Thermal decomposition characteristics of poly(propylene carbonate) using TG/IR and Py-GC/MS techniques, Polym Degrad Stab 81 (2003) 157–165. https://doi.org/10.1016/S0141-3910(03)00085-5.

[57] Z.S. Petrović, Z. Zavargo, J.H. Flyn, W.J. Macknight, Thermal degradation of segmented polyurethanes, J Appl Polym Sci 51 (1994) 1087–1095. https://doi.org/10.1002/app.1994.070510615.

[58] F. Bellucci, G. Camino, A. Frache, A. Sarra, Catalytic charring–volatilization competition in organoclay nanocomposites, Polym Degrad Stab 92 (2007) 425–436. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2006.11.006.

[59] Z. Wang, E. Han, W. Ke, Effect of acrylic polymer and nanocomposite with nano-SiO2 on thermal degradation and fire resistance of APP–DPER–MEL coating, Polym Degrad Stab 91 (2006) 1937–1947. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2006.03.001.

[60] B. Thiébaut, A. Lattuati-Derieux, M. Hocevar, L.B. Vilmont, Application of headspace SPME-GC-MS in characterisation of odorous volatile organic compounds emitted from magnetic tape coatings based on poly(urethane-ester) after natural and artificial ageing, Polym Test 26 (2007) 243–256. https://doi.org/10.1016/J.POLYMERTESTING.2006.10.006.

[61] M. Watanabe, C. Nakata, W. Wu, K. Kawamoto, Y. Noma, Characterization of semi-volatile organic compounds emitted during heating of nitrogen-containing plastics at low temperature, Chemosphere 68 (2007) 2063–2072. https://doi.org/10.1016/J.CHEMOSPHERE.2007.02.022.

[62] M. Hakkarainen, Solid Phase Microextraction for Analysis of Polymer Degradation Products and Additives, Advances in Polymer Science 211 (2007) 23–50. https://doi.org/10.1007/12_2007_118.

[63] D.K. Chattopadhyay, D.C. Webster, Thermal stability and flame retardancy of polyurethanes, Prog Polym Sci 34 (2009) 1068–1133. https://doi.org/10.1016/J.PROGPOLYMSCI.2009.06.002.

[64] Y.J. Choi, P. Alagi, J.H. Jang, S.J. Lee, H. young Yoon, S.C. Hong, Compositional elements of thermoplastic polyurethanes for reducing the generation of acetaldehyde during thermo-oxidative degradation, Polym Test 68 (2018) 279–286. https://doi.org/10.1016/J.POLYMERTESTING.2018.04.025.

[65] J. Dewulf, H. Van Langenhove, Anthropogenic volatile organic compounds in ambient air and natural waters: a review on recent developments of analytical methodology, performance and interpretation of field measurements, J Chromatogr A 843 (1999) 163–177. https://doi.org/10.1016/S0021-9673(99)00225-3.

[66] E. Uhde, T. Salthammer, Impact of reaction products from building materials and furnishings on indoor air quality—A review of recent advances in indoor chemistry, Atmos Environ 41 (2007) 3111–3128. https://doi.org/10.1016/J.ATMOSENV.2006.05.082.

[67] I.N. Einhorn, Physiological and toxicological aspects of smoke produced during the combustion of polymeric materials, Environ Health Perspect vol (1975) 163–189. https://doi.org/10.1289/ehp.7511163.

[68] C. Bach, X. Dauchy, M.C. Chagnon, S. Etienne, Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: A source of controversy reviewed, Water Res 46 (2012) 571–583. https://doi.org/10.1016/J.WATRES.2011.11.062.

[69] M. Dzięciol, Studies of volatile compounds emitted during thermo-xidative degradation of poly(butylene terephthalate), Int J Environ Anal Chem 89 (2009) 881–889. https://doi.org/10.1080/03067310902999124;CTYPE:STRING:JOURNAL.

[70] K.C. Khemani, A novel approach for studying the thermal degradation, and for estimating the rate of acetaldehyde generation by the chain scission mechanism in ethylene glycol based polyesters and copolyesters, Polym Degrad Stab 67 (2000) 91–99. https://doi.org/10.1016/S0141-3910(99)00097-X.

[71] D. Rosu, N. Tudorachi, L. Rosu, Investigations on the thermal stability of a MDI based polyurethane elastomer, J Anal Appl Pyrolysis 89 (2010) 152–158. https://doi.org/10.1016/J.JAAP.2010.07.004.

[72] B. Singh, N. Sharma, Mechanistic implications of plastic degradation, Polym Degrad Stab 93 (2008) 561–584. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2007.11.008.

[73] Y.J. Choi, P. Alagi, J.H. Jang, S.J. Lee, H. young Yoon, S.C. Hong, Compositional elements of thermoplastic polyurethanes for reducing the generation of acetaldehyde during thermo-oxidative degradation, Polym Test 68 (2018) 279–286. https://doi.org/10.1016/J.POLYMERTESTING.2018.04.025.

[74] C. Fang, R. Yang, Z. Zhang, X. Zhou, W. Lei, Y. Cheng, W. Zhang, D. Wang, Effect of multi-walled carbon nanotubes on the physical properties and crystallisation of recycled PET/TPU composites, RSC Adv 8 (2018) 8920–8928. https://doi.org/10.1039/C7RA13634J.

[75] M. Fuensanta, A. Khoshnood, J.M. Martín-Martínez, Structure–Properties Relationship in Waterborne Poly(Urethane-Urea)s Synthesized with Dimethylolpropionic Acid (DMPA) Internal Emulsifier Added before, during and after Prepolymer Formation, Polymers 2020, Vol. 12, Page 2478 12 (2020) 2478. https://doi.org/10.3390/POLYM12112478.

[76] E. McMullin, H.T. Rebar, P.T. Mather, Biodegradable Thermoplastic Elastomers Incorporating POSS: Synthesis, Microstructure, and Mechanical Properties, Macromolecules 49 (2016) 3769–3779. https://doi.org/10.1021/ACS.MACROMOL.6B00470/ASSET/IMAGES/LARGE/MA-2016-00470H_0007.JPEG.

[77] F.G. Ornaghi, V. Pistor, R.V.B. De Oliveira, Thermoplastic polyurethane synthesis with modified montmorillonite prepared by torque rheometry: Investigation of morphological, thermal, chemical, and physical properties, J Appl Polym Sci 132 (2015) 42640. https://doi.org/10.1002/APP.42640.

[78] S. Aiswarya, S.S. Banerjee, Shape Memory Behavior and Self-Healing Effects of Dynamically Vulcanized TPU/ENR Thermoplastic Elastomeric Blends, ACS Appl Polym Mater 5 (2023) 10446–10457. https://doi.org/10.1021/ACSAPM.3C02280/ASSET/IMAGES/LARGE/AP3C02280_0008.JPEG.

[79] B.D. Akkoyun, A.A. Wis, R. Yıldırım, Ü. Makal, G. Özkoç, M. Kodal, Enhanced Crystallinity Through Melt Annealing of Thermoplastic Polyurethanes, J Appl Polym Sci 142 (2024) e56593. https://doi.org/10.1002/APP.56593;PAGEGROUP:STRING:PUBLICATION.