Characterization of the resistance to abrasive chemical agents of test specimens of thermoplastic elastomeric polyurethane composite materials produced by additive manufacturing

Eva Paz1 | Mariano Jiménez1 | Luis Romero2 | María del Mar Espinosa2 | Manuel Domínguez2

1Department of Mechanical Engineering, Technical School of Engineering – ICAI, Comillas Pontifical University, Madrid, Spain
2Design Engineering Area, National Distance Education University (UNED), Madrid, Spain

Correspondence
Luis Romero, Design Engineering Area – National Distance Education University (UNED), Madrid, Spain.
Email: lromero@ind.uned.es

Abstract
Currently the development of additive manufacturing and the emerging of new materials allows to manufacturing process obtaining functional models with properties and geometries adapted to each particular case with low production times and costs. Specifically, 3D printing by fused deposition modeling (FDM) that operates with polymers, is one of the most widespread and popular techniques. Among the numerous materials available, the elastomeric polymers, whose base composition is polyurethane, are becoming increasingly important since allow to obtain flexible pieces with good mechanical and chemical resistance. The objective of this work is to study the effect of an abrasive fluid (commercial automotive petrol) on test specimens made of two different elastomeric filaments commonly used in 3D printing, thermoplastic polyurethane and thermoplastic elastomers. To do this, some of the main physical and mechanical properties - hardness, weigh variation and tensile and bending tests - of these materials were analyzed after immersion of the samples in petrol for different periods of time. Specimens with different volume of material inside their structure were designed in order to determine the effect of the volume filling on the mechanical properties and the petrol effect.

KEYWORDS
applications, manufacturing, synthesis and processing techniques, thermoplastics

1 | INTRODUCTION
The impressive development of the different additive manufacturing technologies and the wide variety of emerging materials available, have produced a paradigm shift in conventional approaches to industrial production during the last decade, allowing the manufacturing not only of models, but also of functional parts. In particular, fused deposition modeling (FDM) technology has become a highly versatile manufacturing tool that requires low technical knowledge and whose price allows access to a wide audience. Currently there is a wide range of plastic materials available for FDM with very diverse properties, adapted for the manufacturing of 3D models.

Most popular materials used in FDM are hard thermoplastics as polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS). However, the development of
Innovative filaments has opened FDM to new applications, as is the case of the research on flexible filaments that has expanded FDM manufacturing into flexible objects. These objects, which are traditionally made of vulcanized rubber or silicone, can now be made from thermoplastic elastomers (TPE). Among these materials are the flexible filaments made of a thermoplastic polyurethane (TPU) based material, showing certain variety in their elastic and mechanical properties depending on the different types available. In order to respond to some current problems in the industry, using parts obtained through additive manufacturing, it is not only necessary to be able to know the final properties of the parts obtained, based on the different configurable parameters, but it is also crucial to know their behavior under service conditions. In the case of flexible materials, the available literature on their behavior under different aging conditions is still scarce.

Polyurethane has shown good properties against oils, fuels and abrasives, which allows its application in the automotive industry. However, it’s important verify that the filament materials made of TPU and TPE for FDM printing retain these good properties when working under abrasive environments. Consequently, the main objective of this work is to determine the effect of an abrasive chemical (commercial automotive petrol) on the mechanical properties of some elastomeric materials (TPE and TPU) used in FDM. With this purpose, standard tensile, bending and hardness specimens were designed using a 3D solid modeling software (Solid Edge 2020) and subsequently printed to characterize the mechanical properties of materials over time. The selection of a commercial automotive petrol as abrasive chemical has been based on the service conditions of the pieces with medium/high mechanical resistance has been based on the service conditions of the printed pieces for automotive applications.

### 2. MATERIALS AND METHODS

#### 2.1 Materials

The printing materials used were TPE and TPU filaments. Tables 1 and 2 show 3D printing parameters and mechanical and thermal properties of TPE and TPU materials.

The 3D printed parts have two distinct areas, the shell and the infill. The correct parameterization of these two values influences the mechanical performance, the surface finish, the printing time and the cost of the printed pieces.

The shell is the outer walls of the piece in which are included both the layers in contact with the printing base and the upper layers that generate the final surface finish. The lamination programs allow to modify the percentage of infill material from 0% (hollow part) to 100% (whole solid part). The ideal value of the fill percentage depends on the final application of the piece. The most common percentage used is 20%. With this percentage, pieces with medium/high mechanical resistance can be obtained, with low weight and a very efficient printing time, achieving a good resistance/cost ratio.

However, to achieve the maximum tensile strength, pieces must be 100% filled, but this implies higher costs in terms of both time and material consumption, as well as heavier pieces. The ideal infill value should be chosen according to the desired resistance and the printing time, being interesting to take into account that the effect of the infill percentage over the resistance is more pronounced at low percentages. For example, it has been observed that in standard materials, the difference between 25% to 50% of infill can produces a resistance increase by 25%. However, from 50% to 70% of filling variation, increases resistance by only 10%. Depending on the lamination software used, there are different types of fillings configurations, but the four most used are rectangular, triangular (or diagonal), wiggle and honeycomb.

The correct configuration of the filling is important to obtain the desired resistance in the parts made by 3D FDM printing and depends on several parameters. It is

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>TPE</th>
<th>TPU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Printing temperatures (°C)</td>
<td>215–235</td>
<td>220–240</td>
</tr>
<tr>
<td>Printing speed (mm/s)</td>
<td>20–40</td>
<td>15–30</td>
</tr>
<tr>
<td>Hot-Bed temperature (°C)</td>
<td>40</td>
<td>50–60</td>
</tr>
<tr>
<td>Environment temperature (°C)</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Optimal layer height (mm)</td>
<td>0,2</td>
<td>0,2</td>
</tr>
<tr>
<td>Minimal nozzle diameter (mm)</td>
<td>0,4 or higher</td>
<td>0,4 or higher</td>
</tr>
<tr>
<td>Retraction distance (mm)</td>
<td>3,5-6,5</td>
<td>-</td>
</tr>
<tr>
<td>Retraction speed (mm/s)</td>
<td>20–160</td>
<td>-</td>
</tr>
<tr>
<td>Heated bed surface:</td>
<td>No</td>
<td>PEI, mirror / glass</td>
</tr>
<tr>
<td>Adhesive for bed</td>
<td>No</td>
<td>PVA glue stick, Magigoo</td>
</tr>
<tr>
<td>Drying time (h)</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Drying temperature (°C)</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>Fan Speed (%)</td>
<td>50/100</td>
<td>70/100</td>
</tr>
</tbody>
</table>

common to use rectangular filling with 10% density for non-functional parts, models or prototypes, 20% filling for parts with regular use subjected to low / medium loads and 60% for elements that have to support high loads. The type of filling and the percentage values must also be adjusted to each type of 3D printer, and whether the material to be used is rigid (PLA, ABS, PETG, Nylon, etc.) or flexible (Filaflex TPE or TPU).

For each of the tests and aging periods analyzed, specimens with 5%, 20%, 50% and 80% filling by volume (Figure 1), and a solid outer contour of three layers were used (Figure 2). The fill pattern was rectangular.

### 2.2 Design and manufacturing process of specimens

For the study of the effects of chemical abrasives on the materials under study the effects of a commercially available automotive petrol 98 on the hardness, mass variation and both tensile and bending properties of TPE and TPU 3D printed samples were analyzed during three different exposure periods (24 hr, 1 week and 1 month). The results were compared with the properties of both materials under standard conditions without aging. The specimens were designed according to the standard specifications, ISO 527-1:2019 and ISO 178:2019 standards were used for tensile and bending tests respectively (Figure 3). The dimensions for each tensile specimen were length 75 mm, width 5 mm and thickness 3.5 mm, with a gauge length of 25 mm. The dimensions for each bending specimen were 80 mm $\times$ 10 mm $\times$ 4 mm.\textsuperscript{17,21}

In the case of the specimens used for the hardness tests and the study of mass variation, the ISO 868:2003 standard only establishes a minimum thickness of 4 mm, as well as making the hardness measurements in points at least 9 mm away from the edges. The dimensions of the hardness specimens used are shown in Figure 4. The design shown allows the realization of successive measurements in the same specimen in order to guarantee the obtaining of reliable values.\textsuperscript{23}

For the fabrication of the total number of specimens required, five for each filling condition, test, aging and material (TPE and TPU), two FDM technology 3D printers were used: Dynamical Tools DT600 and Prusa i3MK3. The technical characteristics of both printers make it possible to cover a wide range of 3D printing parameters (Table 3).

<table>
<thead>
<tr>
<th>Property</th>
<th>Standard</th>
<th>TPE</th>
<th>TPU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>DIN EN ISO 1183-1-A</td>
<td>1.08</td>
<td>1.23</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>DIN ISO 7619-1 (3 s)</td>
<td>710</td>
<td>98</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>DIN 53504-S2</td>
<td>32</td>
<td>53.7</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>DIN 53504-S2</td>
<td>900</td>
<td>318</td>
</tr>
<tr>
<td>Stress at 10% elongation (MPa)</td>
<td>DIN 53504-S2</td>
<td>-</td>
<td>12.1 (200 mm/min.)</td>
</tr>
<tr>
<td>Stress at 20% elongation (MPa)</td>
<td>DIN 53504-S2</td>
<td>1.7</td>
<td>-</td>
</tr>
<tr>
<td>Stress at 50% elongation (MPa)</td>
<td>DIN 53504-S2</td>
<td>-</td>
<td>22.1 (200 mm/min.)</td>
</tr>
<tr>
<td>Stress at 100% elongation (MPa)</td>
<td>DIN 53504-S2</td>
<td>3.6</td>
<td>28.4 (200 mm/min.)</td>
</tr>
<tr>
<td>Stress at 300% elongation (MPa)</td>
<td>DIN 53504-S2</td>
<td>6.6</td>
<td>37.8 (200 mm/min.)</td>
</tr>
<tr>
<td>Tear strength (N/mm²)</td>
<td>DIN ISO 34-1Bb</td>
<td>47</td>
<td>170</td>
</tr>
<tr>
<td>Abrasion loss (mm³)</td>
<td>DIN ISO 4649-A</td>
<td>46</td>
<td>23</td>
</tr>
<tr>
<td>Compression set 23°C / 72 hr(%)</td>
<td>DIN ISO 815</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>Compression set 70°C / 24 hr(%)</td>
<td>DIN ISO 815</td>
<td>39</td>
<td>-</td>
</tr>
<tr>
<td>Tensile strength after storage in water at 80°C for 42 days (MPa)</td>
<td>DIN 53504-S2</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>Elongation at break after storage in water at 80°C for 42 days (%)</td>
<td>DIN 53504-S2</td>
<td>900</td>
<td>-</td>
</tr>
<tr>
<td>Notched impact strength (Charpy) at +23°C (kJ/m²)</td>
<td>DIN EN ISO 179-1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Notched impact strength (Charpy) at +23°C (kJ/m²)</td>
<td>DIN EN ISO 179-1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Once the specimen designs have been established, it was necessary to determine the optimum printing conditions that allow the extrapolation of the printing parameters from the tests to the printing of models. For each of the tests and aging periods studied, specimens with an interline insert of 5%, 20%, 50% and 80% filling by volume and a solid outer contour of three layers were used (Figure 5).

The printers used have a pre-set configuration to work with these materials so by a small adjustment of the temperature parameter, satisfactory results were obtained.

### 2.3 Aging process

When aging processes were carried out, the corresponding ISO 175:2010 standard was used to identify the effects of immersing plastics in chemical fluids. The specimens were placed in sealed containers in which petrol was added until the test pieces were completely submerged. The containers were then stored during the different aging periods in a chamber with temperature control and air extraction to avoid the possible accumulation of vapors from petrol. The established aging periods were 24 hr and a week corresponding to a short and medium period study according to the standard, in addition, an aging period of 1 month was also used.

### 2.4 Characterization

Hardness measurements were done using a Shore A durometer Bareiss® Durometer (Bareiss®, Neurtek, Eibar, Spain) to obtain a total of eight measurements per specimens according standard specification. The hardness was calculated as the mean value of the eight measurements. Previous to the hardness measurement, the specimen was dried with a paper in order to eliminate the superficial petrol. Once the measurement was taken, the mass variation was determined with a scale.

The tensile and bending tests were carried out using an Universal Testing Machine EUROTEST ELIB20 (Ibertest®, Madrid, Spain) with a 2kN load cell operating at a crosshead speed of 5 mm/min and using the tensile clamp or bending bridge as required (Figure 6). The Wintest Software (Ibertest®, Madrid, Spain) was used for control of the test parameters and data collection.

During the tests the force (N) versus displacement (mm) were registered tensile until the breakage of the specimens occurs. To obtain the stress–strain curves and the modulus of tensile and bending modulus of each specimen, the equations Equation 1, Equation 2 and Equation 3 were used, where \( \sigma \) is the stress in MPa, \( F \) the force in N, \( S \) the surface in \( \text{mm}^2 \), \( L \) the distance between loading points in mm and \( b \) and \( h \) are the thickness and height of bending specimens in mm.

\[
\text{Tensile stress } : \sigma = \frac{F}{S} \quad (1)
\]
\[
\text{Deformation } : \varepsilon = \frac{\Delta L}{L_0} \quad (2)
\]
The tensile tests were carried out using a contact extensometer (Epsilon 3542, Epsilon Tech, Jackson, USA) that provides the exact deformation.

3 | RESULTS

For each test, the results obtained in both materials were compared with the results under standard conditions (without aging in petrol) in order determine the effect of the petrol environment on the different mechanical properties.

In Figure 7, it is represented the hardness versus the filling content for the different exposure periods (aging time) in both materials, TPE and TPU. It can be observed that both materials have remarkably different hardness values, being the hardness of TPU material higher than TPE in all cases; for example, shore D hardness of TPU (5%) without aging is by 59 and in the case of TPE (5%) is by 27.

Regarding the variation of TPU hardness depending on the filling content, it was noted that those samples that contain 80% of filler showed the highest values. However, no major differences were observed when the filling was above 20%. Likewise, the exposure to petrol during the different periods did not significantly affect the hardness of the material when it exceeds 20% filling in the specimens. These results demonstrated that the effect of the petrol on the TPU hardness is more notable when the filling content is lower than (20%) where it can be noted a significant decrease of hardness. This indicate that the TPE material is more sensitive to the effect of the abrasive chemical than the material of the filling.

The results of TPE specimens show a progressive increase in hardness as the filling of the specimens increases, which seems to be stabilized from a 70% of filler. Unlike the TPU, the exposure to petrol produces a sharp drop in hardness values, regardless of filler content (Figure 8).

Regarding the variation of the mass of the specimens with the aging time, in Figure 8 can be observed that the specimens weigh increased with the exposure time to petrol. This was due to the absorption capacity of the material and the chemical interaction of the polymer chains with the fluid. It was noted that the petrol uptake was more markedly in TPE samples than in TPU, being
specially notable the differences during the first week of aging. This higher absorption is according with the higher decrease on the hardness observed for the TPE materials.

In Figure 9 some examples of representative graphs obtained from the tensile tests of TPU and TPE with different filling contents and without aging are represented. As was observed in the hardness results TPU and TPE showed very different stress and strain curves for the different conditions studied.

It can be observed that the tensile strength and tensile modulus was higher for the TPU specimens than for those of TPE, additionally it was noted that as higher was the filling content, greater was the Strength and Modulus of both materials, being this increase especially noticeable in TPU samples.

The TPU showed a higher tensile strength and was able to withstand stress values much higher than the TPE before breaking. Otherwise, the TPE specimens demonstrated a much higher deformation capacity. In line with the hardness results obtained, the specimens with the higher filler content, reached the maximum tension values. However, the maximum deformation of the TPU was reduced as the filling of the specimens was increased, with the exception of those with 80% filler whose deformation was contrary to this tendency. This can be attributed to the ability of printed samples to orient the internal fibers of the specimen during the test. The smaller the filling, the easier it is to align the fibers without interfering with one another. In the case of the specimens with 80% filling, the union between fibers is practically absolute, causing the specimen to behave like a single fiber23 and hampering the alignment, which can be noted as a reduction on the deformation.

The effects of aging in petrol over TPU during the times studied for the different fillings are shown in Figure 10. A general trend was observed in all cases because of the leakage of petrol into the test specimens, during the first 24 hr the specimens showed a drastic reduction in the tensile stress and tensile modulus but keeping very similar maximum deformation values. Subsequently, in the results corresponding to 1 week and
1 month of aging there is a partial recovery of the properties and an increase in the capacity of deformation of the material in comparison with the material without aging. However, some differences can be noted depending on the filling content, probably because the presence of the filler can affect to the aging rate of the material,
hampering the absorption of petrol. In the case of specimens with 80% filling, given the impossibility of infiltration of petrol, the deterioration of the properties is minimal, as well as the increase in the maximum deformation showed.

In TPE specimens the observed trend was very similar to TPU (Figure 11). The short-term aging results showed a maximum achievable resistance and a lower modulus of elasticity. However, for the higher exposure periods studied, the properties of the material were not only recovered, but also higher voltage values were achieved. Consequently, these results suggest that the interaction between petrol and polymers consists on two phases: initially, petrol weakens the structures and bonds present...
in the specimens, and subsequently leads to the appearance of new unions that allow recovering or improving the properties.

In the case of bending test results (Figure 12), the observed trends were similar tensile tests. According to the obtained stress - deformations curves, as well as the bending modulus and strength, it is observed that the values are lower than the obtained from tensile tests. Analogously, the values showed by the TPU were much higher than those of the TPE. The force and displacement values collected during the TPE tests did not enjoy the desired precision. Due to the high flexibility of the material, during the beginning of the test, the equipment used did not detect force opposing the movement of the crossbar, so that the data collection did not start until a later time.

The results of the tensile tests in TPU showed in the previous figure allow to determine the effect of the aging periods in the different filling conditions. The trend showed in the different cases was similar. Exposure to
petrol caused short-term deterioration of the specimens, which was reflected in a lower resistance to bending and a lower deformation capacity (something that did not happen in tensile tests). The results provided by the samples subjected to an aging of 1 week showed a greater reduction of the maximum tension and the modulus of resistance to flexion, increasing in this case the deformation shown by the specimens. Finally, observing the results for a one-month petrol exposure, the value of the maximum tension obtained was similar to that previously obtained, the deformation having increased. This effect was noticeable to a lesser extent for the test pieces with 80% filler in which petrol only affects the outer surface.

The curves obtained in the tests of TPE specimens despite not having great precision allow the study and comparison of the effects of petrol for different cases. For the different filling conditions studied as the period of exposure to petrol increases, the TPE has a lower maximum tension and modulus of flexural strength. The variation of the deformation shown by the specimens shows a process identical to that observed in the TPU. After the first 24 hr, the specimens show greater rigidity than before being submerged. In the results corresponding to the subsequent aging periods, the specimens show a higher deformation capacity with according to the originals, which are very similar to each other. This seems to indicate a stabilization in the behavior of the material.

4 | DISCUSSION AND CONCLUSIONS

The main purpose of this project is to validate the effect of petrol 98 as a chemical abrasive on parts manufactured in TPE and TPU by additive manufacturing in order to establish the effects of this abrasive chemical on the main mechanical properties of both materials before different periods of exposure. Chemicals can affect mechanical, dimensional and visual properties. Therefore, properties such as weight variation and surface appearance, elongation at breakpoint, Young’s modulus and tensile strength. Should be analyzed in order to evaluate chemical attacks.

It has been analyzed the viability of these materials in the industry, specifically, in the development of automotive components intended to operate in those service conditions in which could be exposed to petrol, as the most important fluids found in the automotive industry, which requires the characterization of the technical feasibility of these materials in applications with this fluid.

According to the properties shown by the filaments of both materials, a considerable reduction of the maximum tension, the capacity of deformation (in the case of the TPE it was not possible to check the elongation at break) and the hardness. This difference is bigger when the infill is lower in the samples studied, showing properties somewhat like the original material those with a filling of 80% in volume.

The results of short-time aging show a considerable variation of the properties in the different tests; The hardness, the maximum tension and the modulus of elasticity are greatly reduced. Likewise, the weight of the studied samples are lower than the ones shown before being subjected to this process. Once the established aging periods have elapsed, a recovery of these is observed, obtaining values similar to those registered by test specimens that had not been exposed to the action of petrol. In some cases, the TPE specimens showed better properties after the maximum aging studied than before being subjected to it.

Due to this repeated behavior for the different fillings studied, the hypothesis is contemplated in which the interaction between gasoline and these polymers that have a polyurethane base consists of two phases. First, gasoline causes the rupture of some of the chains that make up the polymer, causing the loss of mass and the deterioration of the properties it presents. After this process, these chains tend to join again or to form new chains that allow to reinforce the structure of the specimens again, partially recovering their properties. Taking place in a shorter time in the case of the TPE. This has not been possible to confirm given the lack of means and time, nevertheless, it is a crucial aspect to be able to understand the reason why the properties of these materials describe this behavior.

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CONFLICT OF INTEREST

“The authors declare no conflict of interest.”

AUTHOR CONTRIBUTIONS

“Conceptualization, Eva Paz, Mariano Jiménez, Luis Romero, Ma del Mar Espinosa and Manuel Domínguez; methodology, Eva Paz and MJ; software, Mariano Jiménez and Luis Romero; validation, Ma del Mar Espinosa and Manuel Domínguez; formal analysis, Eva Paz, Mariano Jiménez and Luis Romero; investigation, Mariano Jiménez and Luis Romero; resources, Luis Romero; data curation, Mariano Jiménez; writing—original draft preparation, Eva Paz and Luis Romero.
writing—review and editing, Mariano Jiménez, Ma del Mar Espinosa and Manuel Domínguez; visualization, Eva Paz and Mariano Jiménez; supervision, Mariano Jiménez and Manuel Domínguez; project administration, Eva Paz and Ma del Mar Espinosa All authors have read and agreed to the published version of the manuscript”.

**ORCID**

Luis Romero [https://orcid.org/0000-0002-8597-3084](https://orcid.org/0000-0002-8597-3084)

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