Journal of Applied Polymer Science

Characterization of the resistance to abrasive chemical agents of test specimens of TPE and TPU composite material produced by additive manufacturing

--Manuscript Draft--

Full Title:	Characterization of the resistance to abrasive chemical agents of test specimens of TPE and TPU composite material produced by additive manufacturing
Manuscript Number:	app.20203239
Article Type:	Research Article
Order of Authors:	Eva Paz
	Mariano Jiménez
	Luis Romero
	María del Mar Espinosa
	Manuel Domínguez
Manuscript Classifications:	Applications; Manufacturing; Synthesis and Processing Techniques; Thermoplastics

Manuscript

Type of the Paper: Article

Characterization of the resistance to abrasive chemical agents of test specimens of TPE and TPU composite material produced by additive manufacturing

Eva Paz [1], Mariano Jiménez [1], Luis Romero [2,*], Mª del Mar Espinosa [2] and Manuel Domínguez [2]

[1] Department of Mechanical Engineering, Technical School of Engineering – ICAI, Comillas Pontifical University, Madrid, Spain

[2] Design Engineering Area – National Distance Education University (UNED), Madrid, Spain

* Correspondence: lromero@ind.uned.es; Tel.: (optional; include country code; if there are multiple corresponding authors, add author initials) +34-91-398-9621 (L.R.)

Received: date; Accepted: date; Published: date

Abstract: Currently the development of additive manufacturing and the materials allows the obtaining of functional models with properties and geometries adapted to each case without supposing greater cost or time of manufacture. Specifically, 3D printing by means fused deposition modeling (FDM) that operates with polymers, is one of the most widespread and popular. Among the available materials, the most important ones are the elastomeric polymers, which its base composition is polyurethane, that allows to obtain flexible pieces with good mechanical and chemical resistance. The objective of this work is to verify the effects of this type of fluids on specimens made of two of the elastomeric filaments used in 3D printing, TPU and TPE. To do this, some of the main physical and mechanical properties of these materials will be analyzed, and the test pieces will be subjected to different periods of immersion in a chemical agent. In this process it is necessary to previously deepen the operation of the additive manufacturing, especially the FDM technology with the materials to be studied, considering the different options of configuration of the specimens that exist and how they affect the final properties of the piece.

Keywords: TPU; TPE; FDM; 3D printing; additive manufacturing;

1. Introduction

Currently there is a wide range of materials for 3D printing manufacturing, especially plastics, with many different properties and applications [1-3]. In order to be able to respond to some current problems in the industry using parts obtained through additive manufacturing, it is necessary to be able to know the final properties of the parts obtained based on the different configurable parameters [4].

The development of the different additive manufacturing technologies and the possible materials to be used during the last decade have allowed the manufacture of functional parts and not just models [5]. In particular, FDM technology has become a highly versatile manufacturing tool that requires little technical knowledge and whose price allows access to a wide audience. Fused deposition modeling currently has a wide range of plastic materials with very diverse properties adapted for the manufacture of 3D models [6-8]. Among these materials are the flexible filaments with a polyurethane base material that have a certain variety in their elastic and mechanical properties among the different types available [9].

Polyurethane has good properties against oils, fuels and abrasives which allows its application in the automotive industry. However, it must be verified that materials such as TPU and TPE retain these properties [10-14]. To respond to this situation, this work is carried out. Using 3D CAD software, the specimens are designed and subsequently printed to characterize the materials in accordance with ISO standards [15]. The tests carried out take place for different configurations of the test pieces, as well as before periods of immersion in gasoline that allow us to study the effect it has on materials over time.

The main objective of this work is to determine the effect of a chemical abrasive on the elastomeric materials used in additive manufacturing TPE and TPU. The selection of this abrasive should be based on the chemical and mechanical properties of the study materials and its field of application [16,17]. Other objectives derived from the project are:

• The study of the different additive manufacturing techniques highlighting the FDM technology used in the production of test pieces for work, their operating principle, advantages and disadvantages of each, as well as compatible materials.

• Documentation on polymers, their classification and properties, delving into the elastomers used in this work.

• To know the standardized procedures included in the different international standards, as well as the equipment required to determine the different mechanical properties of the materials and the effect of the chemical used to be studied.

2. Materials and Methods

Designing and manufacturing specimens process.

For the study of the effects of chemical abrasives on the materials under study, it is necessary to establish the scope of the work by selecting the number of chemicals, as well as the properties of the materials studied [16]. Based on the time available and the application in the industry of these materials are analyzed the effects of petrol 98 on the hardness, mass and both traction and bending behavior of the TPE and TPU for three different exposure periods that are compared with the properties of both materials under standard conditions.

In the process of designing the specimens necessary to carry out the study, for those tests in which ISO international standards exist, the established specimen dimensions are used. This is the case of the ISO 527 and ISO 178 bending tests shown [17,18].

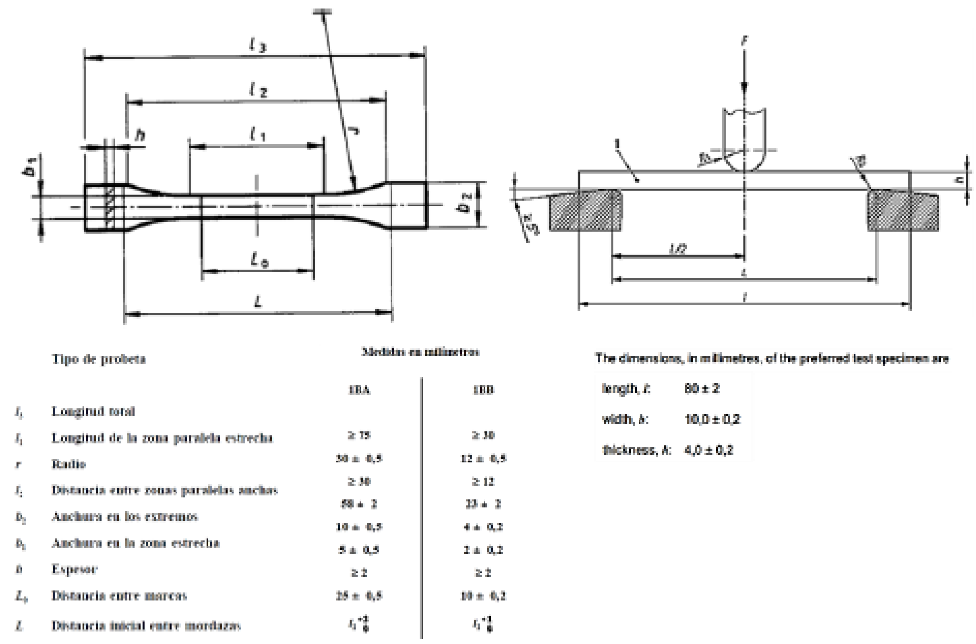

Figure 1. Specimens for tensile and bending test.

In the case of the test specimens used in the tests of hardness and study of the mass, the ISO 868 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 design shown allows the realization of successive measurements in the same specimen in order to guarantee the obtaining of reliable values.

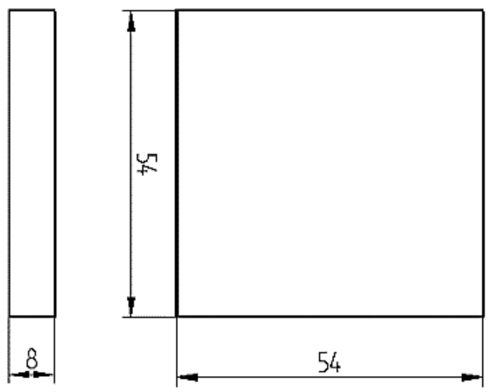

Figure 2. Hardness test specimens.

Once the designs of each of the specimens to be used have been established, it is necessary to determine printing conditions that allow the results of the tests to be extrapolated to any configuration of the printing parameters that are subsequently used in a model. For each of the tests and aging periods studied, specimens with an interline insert of 5%, 20%, 50% and 80% by volume and a solid outer contour of three layers are used.

For the fabrication of the total number of test pieces required, five for the filling condition, the test, the aging time and the material, three different equipment adapted to the FDM printing of flexible materials are used [19].

Figure 3. Results of calibration of printing equipment.

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

Aging process.

When carrying out aging processes, the corresponding ISO 175 standard is used to identify the effects of immersing plastics in chemical fluids. The specimens are placed in sealed containers in which petrol is added until the test pieces are completely submerged. The containers are stored during the aging process in a chamber with temperature control and air extraction to avoid the possible accumulation of vapors from petrol. The established aging periods are 24 hours and a week corresponding to a short and medium period study according to the standard, in addition, another month period aging is carried out. The norm establishes for the long period study an aging period of 16 weeks, however, there is not enough time to carry it out.

Characterization process.

The characterization of mechanical properties for the different filling and aging conditions studied take place in the laboratory of the Universidad Pontificia Comillas - ICAI, using the equipment in each case.

To perform the hardness tests, the Shore A durometer is used to obtain a total of 8 measurements per test piece according to the regulations. Once the surface of the specimen has dried, it is positioned in the test bench and the durometer is dropped on it, preventing it from hitting. After 15 seconds from the contact, the displayed value is taken. Once the measurements have been taken, the test piece is placed on a scale and its mass is noted.

The tensile and bending tests are carried out on the EUROTEST ELIB20 universal test machine with the 2kN load cell, using the tension clamp or bending bridge as required. The control of the parameters in which the test is carried out, as well as the data collection takes place through the Wintest program.

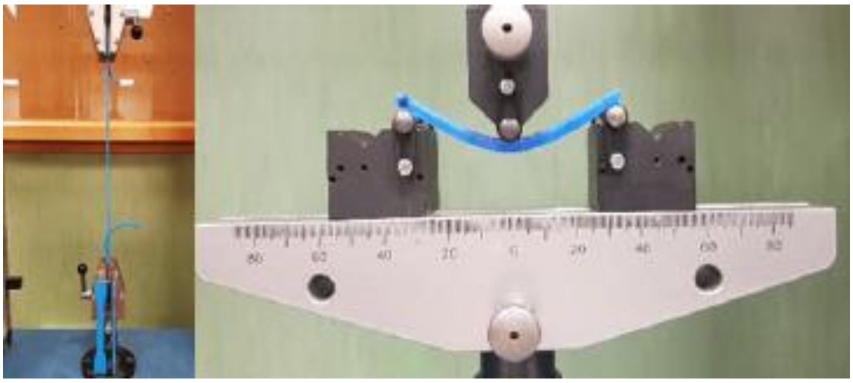

Figure 4. Clamps and bending bridge used during the test.

During the tensile and bending tests, the program provides the data corresponding to the force exerted and the displacement until the breakage of the test pieces occurs. To obtain the stress-strain curves and the modulus of elasticity of each of the test pieces, the equations included in the standard must be applied.

The tests are carried out in a customary manner using an extensometer that provides the exact deformation in a section of the specimen. Due to the high flexibility and deformation that these materials present, it is not possible to use extensometers until reaching the breaking point. Failing this, one of the specimens corresponding to each case is subjected to tensile testing with an extensometer as far as it is permitted.

3. Results

For each of the tests carried out, the results obtained in both materials are analyzed in a comparative manner under standard conditions (without having been exposed to petrol) in order to be able to determine the differences they present. Subsequently, the effects of the aging process are analyzed for each one of them in the different filling conditions.

In the graph below (Figure 5), the hardness curves for the different exposure periods in both materials are shown. They have been obtained from the measurements made under the filling conditions studied. First, both materials have very different hardness values.

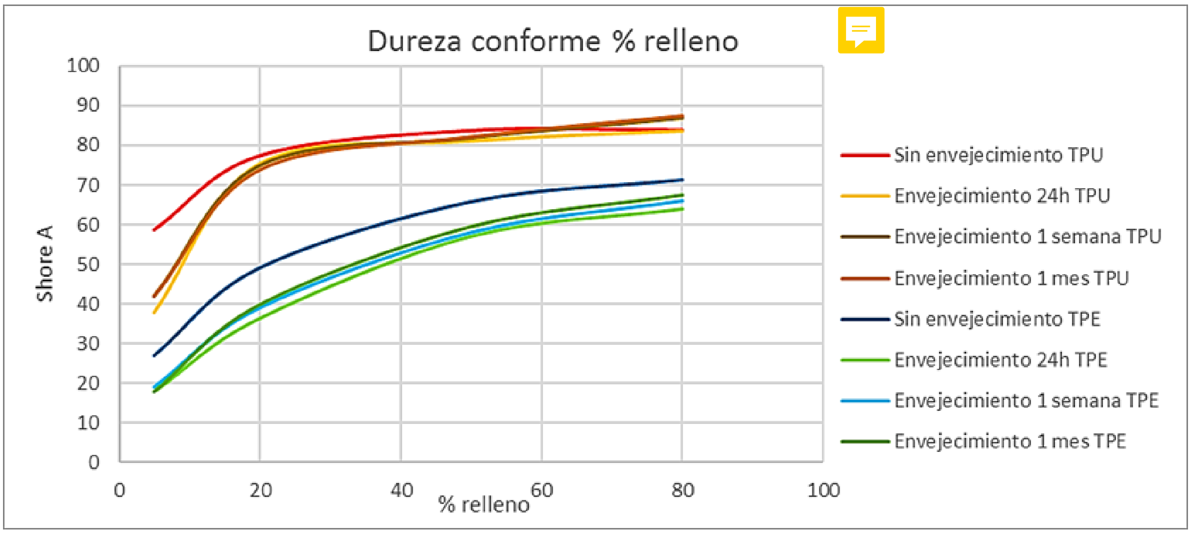

Figure 5. Hardness test results.

According to the hardness shown by the TPU specimens, those that contain 80% filler have the highest values. However, there are no major differences with lower filling conditions above 20%. Likewise, the exposure to petrol during the different periods does not significantly affect the hardness of the material when it exceeds 20% filling in the specimens.

The TPE specimens show a progressive increase in hardness as the filling of the specimens increases, which seems to be stabilized from a 70% filler. Unlike the TPU, the exposure to petrol produces a sharp drop in hardness values in the first 24 hours that does not increase as the exposure time is extended.

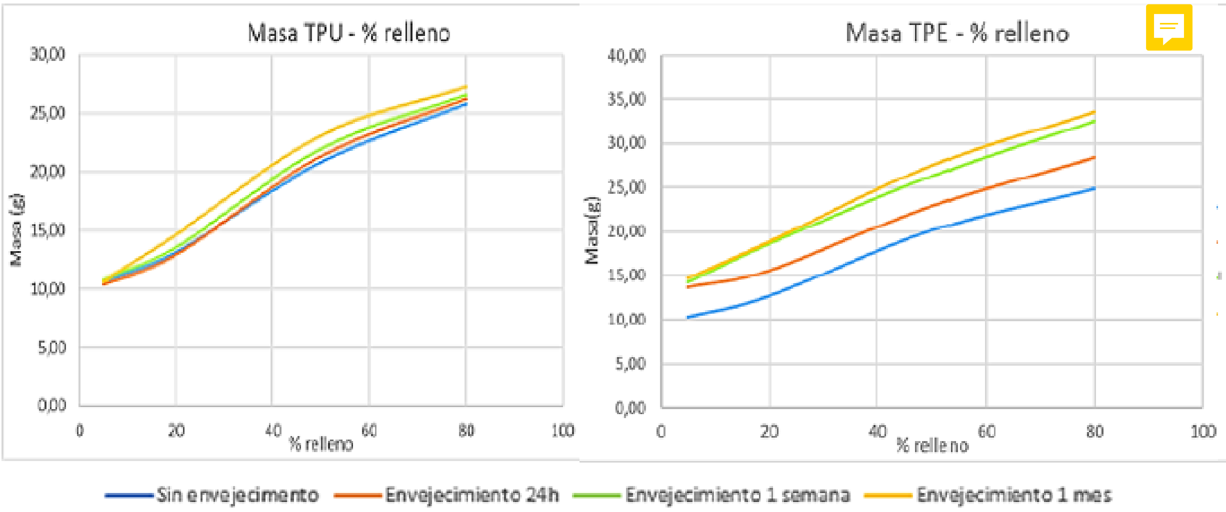

Figure 6. Mass variation results.

Regarding the variation of the mass of the specimens after the different periods of aging, it is observed that the specimens have a greater weight as the exposure to petrol is prolonged. This is due to the absorption capacity of the material and the chemical interaction of the polymer chains with the fluid. This phenomenon occurs more markedly in the TPE, there being considerable differences during the first week of aging.

As mentioned above, during the performance of the tensile tests it was only possible to achieve breakage in the specimens made of TPU. Additionally, the break in the test pieces manufactured by 3D printing does not occur uniformly throughout the section. Instead the fibers break successively as shown in the graph below. The break of the piece is considered when the first step is generated in the graph.

Figure 7. Composite materials break behavior.

Similar to what happens in the hardness results obtained, TPU and TPE have very different stress and strain values for the different conditions studied.

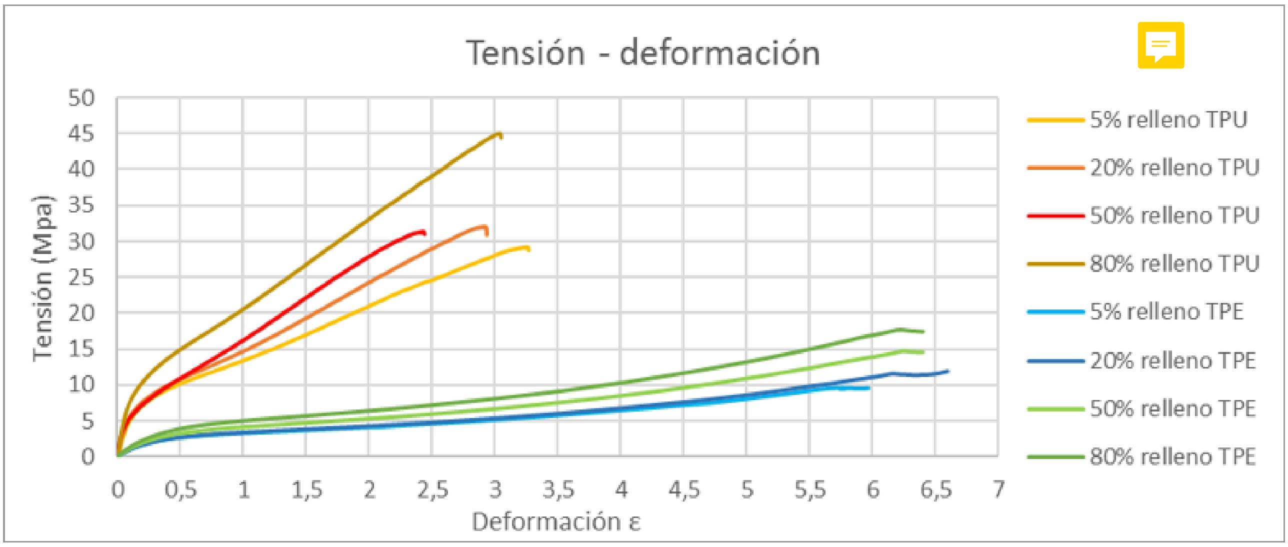

Figure 8. Tensile test results comparison for TPE and TPU.

The TPU has a higher tensile strength and is able to withstand stress values much higher than the TPE before breaking. On the other hand, the TPE has a much higher deformation capacity, which, as it is remembered, could not be measured in its entirety. In line with the hardness results obtained, the maximum values of tension reached correspond to the specimens that present a higher% fill. However, the maximum deformation of the TPU is reduced as the filling of the specimens increases, with the exception of those with 80% filler whose deformation is contrary to this tendency. This is due to the ability to orient the internal fibers of the specimen. The smaller the filling, the easier it is to align the fibers without interfering with one another. In the case of the specimen with 80% filling, the union between fibers is practically absolute, causing the specimen to behave like a single fiber.

Analyzing the effects of aging in petrol during the times studied for the different fillings shown in the graphs below, a common trend is observed. Because of the leakage of petrol into the test specimens, during the first 24 hours the specimens show a drastic reduction in the tensile stress and modulus of elasticity, 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 with according to that shown before being exposed to petrol. In the case of test tubes 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 shown.

In TPE specimens the trend shown is very similar to that previously seen. The short-term aging results show a maximum achievable resistance and a lower modulus of elasticity. However, for the higher exposure periods studied, the properties of the material are not only recovered, but also higher voltage values are achieved.

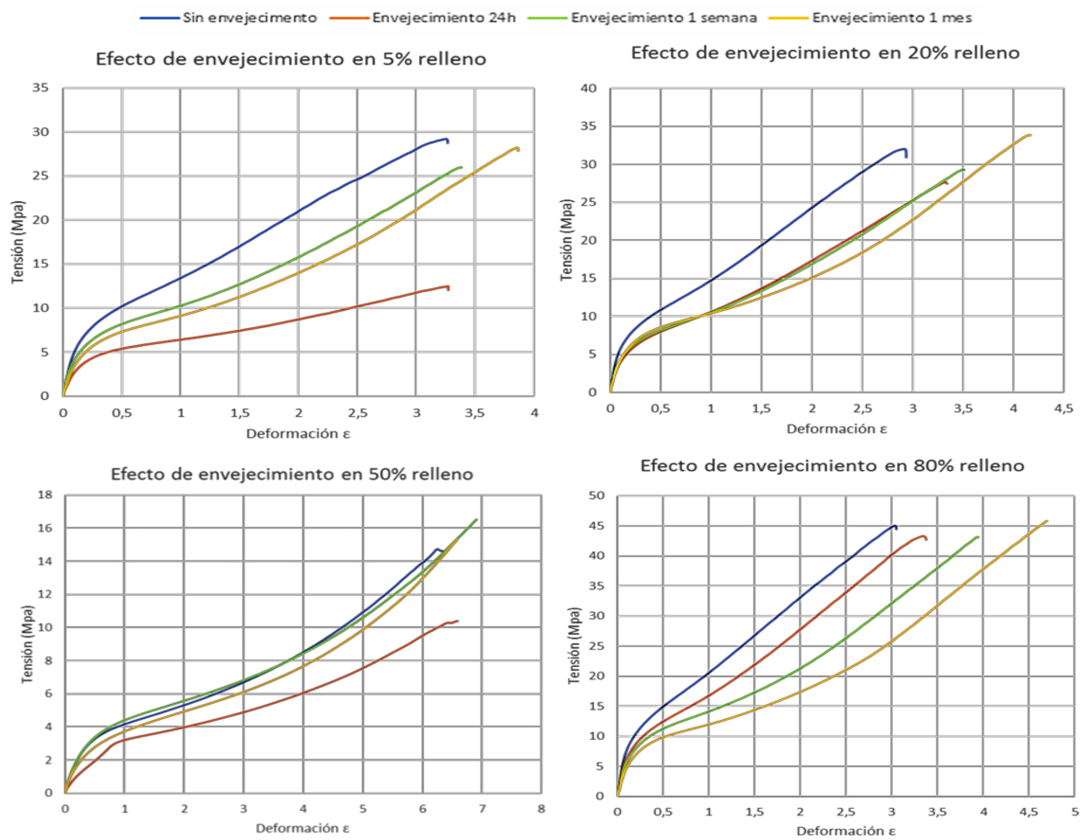

Figure 9. Tensile test result from TPU with different infill and aging.

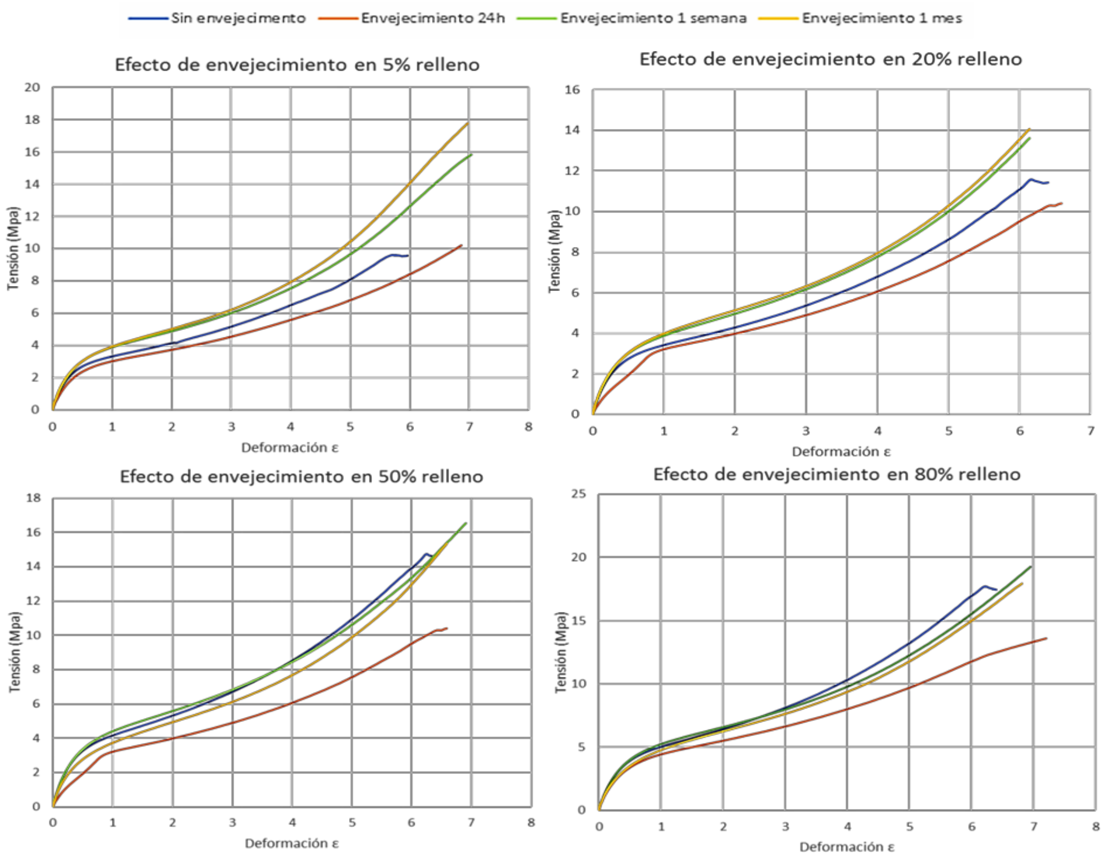

Figure 10. Tensile test result from TPE with different infill and aging.

These results therefore suggest that the interaction between petrol and polymers consists of 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 shown by the petrol. material.

Bending test results obtained show a similar variation of the properties to that observed in the tensile tests. First, the behavior of both materials is analyzed comparatively.

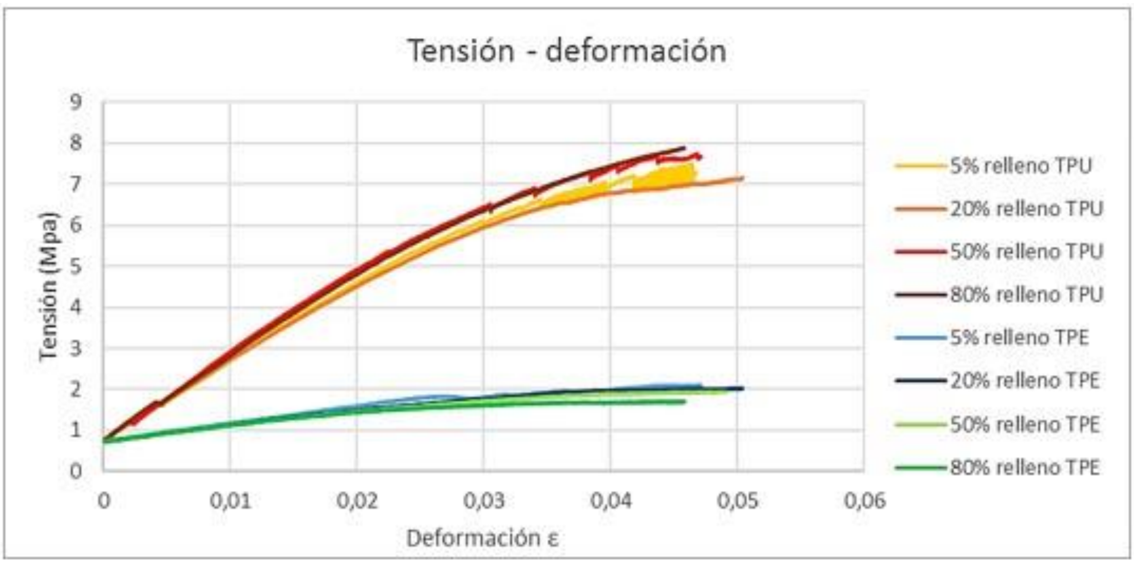

Figure 11. Bending test results comparison for TPE and TPU.

According to the values obtained, the stresses and deformations recorded, as well as the modulus of flexural strength shown by both materials are 10% of those observed in tensile tests. Analogously, the values shown by the TPU are much higher than those of the elastomer thermoplastic. The force and displacement values collected during the TPE tests do 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 does not start until a later time.

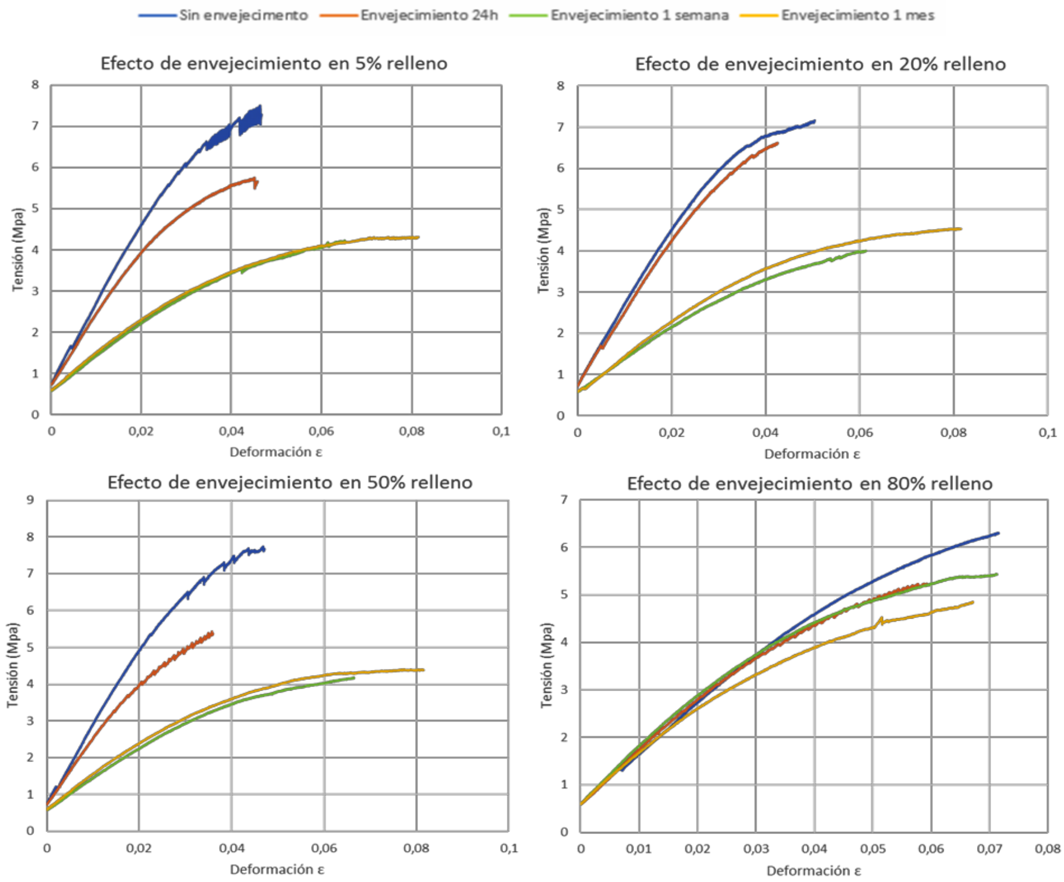

Figure 12. Bending test result from TPU with different infill and aging.

The results of the tensile tests in TPU shown in the previous figure allow to determine the effect of the aging periods in the different filling conditions. The trend shown in the different cases is similar. Exposure to petrol causes short-term deterioration of the specimens, which is reflected in a lower resistance to bending and a lower deformation capacity (something that does not happen in tensile tests). The results provided by the samples subjected to an aging of one week show 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 is similar to that previously obtained, the deformation having increased. This effect is 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.

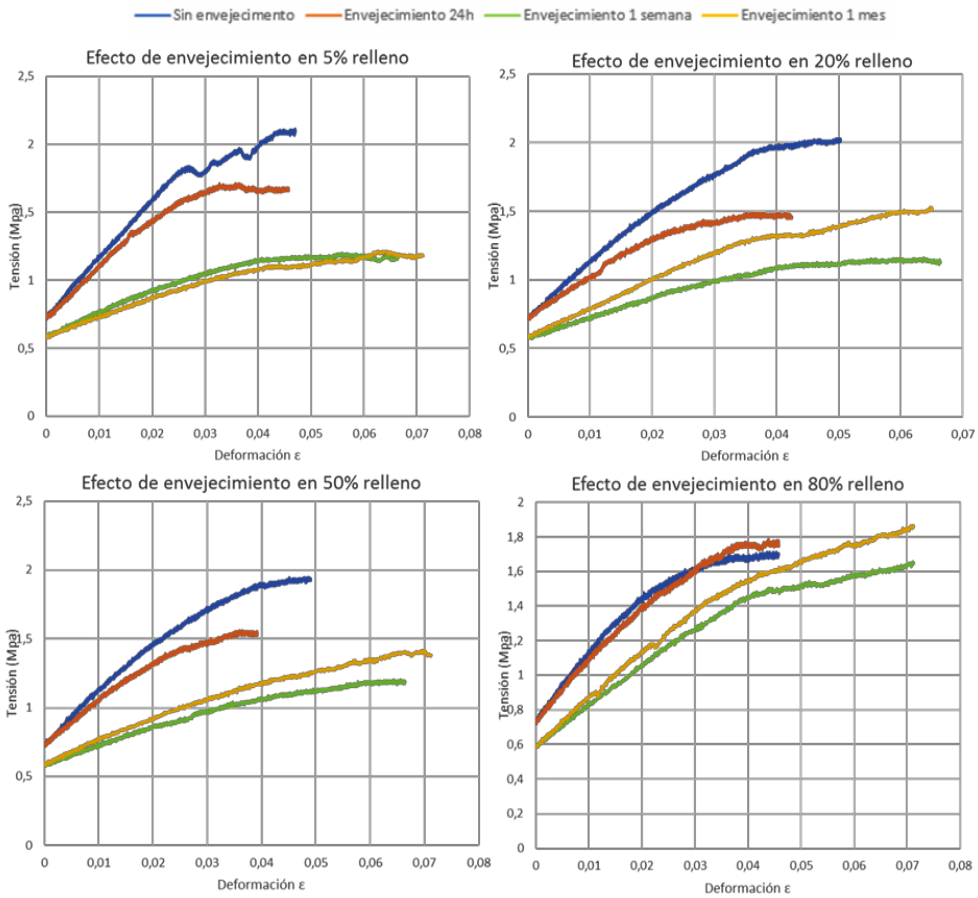

Figure 13. Bending test result from TPE with different infill and aging.

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 hours, 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

In this project has been studied 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 product on the main mechanical properties of both materials before different periods of exposure. The purpose of this study is to analyze the viability of these materials in the industry, specifically, in the development of automotive components intended to operate with said fluid.

In view of the means and the time available for carrying out such analysis, it has been necessary to determine, in the first place, those trials that could provide more information in this regard. Therefore, it is decided to perform tensile, bending and hardness tests. For the adequate printing of the test pieces it was necessary to make several modifications in the printing parameters in both materials.

For the analysis of the effects of aging in petrol of the materials, the study has been carried out in the short and medium term, according to ISO-175, carrying out a third aging period of 1 month in order to predict in any way the long-term behavior of the properties studied in both materials. After carrying out the established tests and analyzing the results provided by each of them, it has been possible to establish the following:

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 more 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 lowers 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. Firstly, 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.

Author Contributions: "Conceptualization, E.P., M.J., L.R., M.M.E. and M.D.; methodology, E.P. and M.J; software, M.J. and L.R.; validation, M.M.E. and M.D.; formal analysis, E.P., M.J. and L.R.; investigation, M.J. and L.R..; resources, L.R.; data curation, M.J.; writing—original draft preparation, E.P. and L.R. writing—review and editing, M.J., M.M.E. and M.D.; visualization, E.P. and M.J.; supervision, M.J. and M.D.; project administration, E.P. and M.M.E. All authors have read and agreed to the published version of the manuscript".

Funding: "This research received no external funding"

Acknowledgments: The authors would like to express their gratitude for their support to the Universidad Pontificia Comillas ICAI, the company Lupeon S.L. and the Escuela Técnica Superior de Ingenieros Industriales of UNED (in the frame of the proyect ICF06-2019).

Conflicts of Interest: "The authors declare no conflict of interest."

References

1. Kruth J.P., Mercelis P., Van Vaerenbergh J., Froyen L., Rombouts M. (2005). Binding mechanisms in selective laser sintering and selective laser melting. Rapid prototyping journal, 11(1), 26-36.
2. Murr L.E., Gaytan S.M., Ramirez D.A., Martínez E., Hernández J., Amato, K.N., Shindo P.W., Medina F.R., Wicker R.B. (2012). Metal fabrication by additive manufacturing using laser and electron beam melting technologies. Journal of Materials Science & Technology, 28(1), 1-14.
3. Wong K.V., Hernández A. (2012). A review of additive manufacturing. International scholarly research notices.
4. Srinivasan V., Bassan J. (2012). 3D printing and the future of manufacturing. Leading Edge Forum Technology Program, CSC USA.
5. Kearney A.T. (2015). 3D printing: A manufacturing revolution. Korea.
6. Finnes T. (2015). High definition 3d printing–comparing SLA and FDM printing technologies. The Journal of Undergraduate Research, 13(1), 3.
7. Hiemenz J., Stratasys I. (2014). LA IMPRESION 3D CON FDM: ¿Cómo funciona?. Pixel Sist.
8. Ukar E., Lamikiz A. (2015). Fabricación aditiva: qué es cada tecnología. Plásticos Universales, (197), 90-99.
9. Arán Aís F. (2000). Síntesis y caracterización de poliuretanos termoplásticos que contienen resinas de colofonia y su aplicación como adhesivos. Doctoral dissertation, Universidad de Alicante.

10. Brydson J.A. (1999). Plastics materials. Elsevier.
11. García S. (2009). Referencias históricas y evolución de los plásticos. Revista Iberoamericana de polímeros, 10(1), 71-80.
12. Cantrell J., Rohde S., Damiani D., Gurnani R., DiSandro L., Anton J., Young A., Jerez A., Steinbach D., Kroese C., Ifju P. (2017). Experimental characterization of the mechanical properties of 3D-printed ABS and polycarbonate parts. Rapid Prototyping Journal, 23(4), 811-824.
13. Patton S.T., Chen C., Hu J., Grazulis L., Schrand A.M., Roy A.K. (2017). Characterization of thermoplastic polyurethane (TPU) and Ag-carbon black TPU nanocomposite for potential application in additive manufacturing. Polymers, 9(1), 6.
14. Wang X., Jiang M., Zhou Z., Gou J., Hui D. (2017). 3D printing of polymer matrix composites: A review and prospective. Composites Part B: Engineering, 110, 442-458.
15. Szilvśi-Nagy M., Matyasi G.Y. (2003). Analysis of STL files. Mathematical and computer modelling, 38(7-9), 945-960.
16. Ojados Sánchez, G. (2013). Resistencia al desgaste y a la abrasión de polímeros técnicos y nanocomposites. Proyecto Fin de Período Formativo de Doctorado. UPCT.
17. Osswald T.A., Menges G. (2012). Materials science of polymers for engineers. Carl Hanser Verlag GmbH Co KG.
18. Juárez D., Ferrándiz S., Balart R.A., García D. (2012). Estudio, análisis y clasificación de elastómeros termoplásticos. 3c Tecnología: glosas de innovación aplicadas a la pyme, 1(2), 2.
19. Núñez M.H. (2013). Tecnologías de impresión de polímeros-procesos y aplicaciones. REVISTA DE PLÁSTICOS MODERNOS, 105(677).

Graphical Abstract Image