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The Aging Behavior of Polyurethane-based Ureteral Catheters

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Abstract: *Ureteral catheters, commonly known as double j stents according to their specific shape, are largely used worldwide with good results to assure proper renal drainage and to overpass ureteral obstacles successfully. This study deals with the aging behavior of polyurethane-based urinary catheters, explanted at different time intervals: 22 days, 29 days, three months, and eight months respectively. TGA (Thermogravimetric analyses) tests showed significant differences in the thermal behavior of polyurethane-based material, especially at eight months, where a higher thermostability was noticed. Also, the DSC (Differential Scanning Calorimetry) curves presented different shapes for the samples of polyurethane-based urinary catheters after three months and eight months. FTIR (Fourier-Transform Infrared Spectrometry) spectra gave a detailed picture of the chemical transformation which has occurred within the material at eight months. All the analyses gave an overview of the aging process of polyurethane-based urinary catheters and showed insights into the chemical/ physical transformations that the polymeric material suffers from prolonged usage.*

Keywords*: ureteral catheters, polyurethane, double J stent, polyurethane aging behavior*

1.Introduction

Urinary drainage represents an essential step in emergency treatment, and disposable devices to assure this process are largely used worldwide by most practitioners. A urinary obstacle can be easily overpassed depending on its origin, with minimum complications, by placing a urinary bladder catheter, a double J stent, or nephrostomy tube.

Ureteral stents are routinely used with good results to overpass obstacles on the urinary tract and to assure proper renal drainage in order to avoid ureteral-hydronephrosis and its derived complications [1, 2].

Currently used ureteral devices are known as single or double J stents and were described in the 1970s by Thomas Hepperlen and Roy Finney [3].

Advancing technology is continuously changing medical treatment by delivering a new type of equipment to fulfill the clinical demands.

Still searching the ideal device, yet not available, several materials were used to design ureteral stents to achieve better results according to the pathology. Silicone, polyurethane, and metallic devices are most commonly used by urologists based on their particular characteristics to treat ureteral stones, strictures, or malignant pathologies. More recently, some biodegradable stents were developed in order to improve medical treatment and patient's quality of life when dealing with a urologic procedure [4].

Polymeric materials are probably the most largely used based on their features, making them suitable for a vast kind of pathology. The new achievements assured improved stability and reduced friction for polyurethane ureteral stents [5]. Increased biocompatibility, durability, ease of manipulation for different maneuvers such as insertion and extraction or costs are some of the novelties that make it suitable for current use in clinical practice [6].

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Despite the new developments, some inconvenience like encrustation, stone formation, and infections remain challenging as long as they can lead to severe complications which can be hardly controlled [7, 8].

Most of the producers recommend a dwell time of 2 months before extraction for polymeric stents. Still, depending on the pathology, the clinicians can adjust their time usage according to need. Some long-life devices have a prolonged lifetime from 6 to 12 months.

Most of the catheters are required for a short period of time, but there are cases when they are extracted over a more extended period. In these situations, it is crucial to know the behavior of the material-based urinary catheters and to show possible changes of the chemical composition owned to the eventual depositions of other compounds onto the surface of the catheters with time.

Our study aims to reveal the changes in the structural composition in time and thermal behavior of polyurethane-based urinary catheters and explain the differences.

2. Materials and methods

2.1. Materials

Polyurethane urinary catheters extracted from patients at different time intervals were subjected to thermal analyses (TGA and DSC) and were chemically investigated by FTIR. The samples were kindly provided by "Prof. Dr. Theodor Burghele" Clinical Hospital in Bucharest. Samples were collected after 22 days, 29 days, three months, and eight months of usage and allowed to dry before performing the investigations.

2.2. Characterization

Thermogravimetric analyses (TGA) were performed on a TG 209 F1 Libra instrument purchased from Netzsch (Selb, Germany) using a 10°C /min heating rate. Samples of approximately 6.5 mg were analyzed over a 20-700°C temperature interval under 20 mL/min nitrogen gas purging flow.

Differential Scanning Calorimetry (DSC) data were collected using a DSC 402 F1 instrument from Netzsch (Selb, Germany) using a 10°C / min heating rate. Each analysis was performed on ~4.5 mg sample under nitrogen atmosphere for a 20-300°C temperature interval.

Fourier-Transform Infrared Spectrometry analysis was done via an attenuated total reflection (ATR) accessory using a Bruker Vertex 70 instrument (Bruker, Billerica, MA, USA) 4000-600 cm^{-1} wave-number region. For each measurement, we have performed some 32 scans at a 4 cm^{-1} resolution.

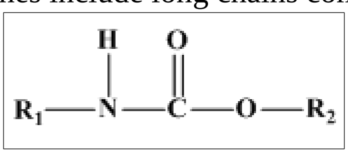
2.3 Type of ureteral stent

Thermoplastic polyurethane Techoflex PU 93A B40 ureteral stents produced by Lubrizol were used to design this study. These are a large family of medical polyethylene TPU devices available in a high range of diameters and colors.

3. Results and discussions

Polyurethanes (PU) represent polymers with various structures and mechanical properties used on a large scale in biomedical applications. They exhibit biodegradability, good biocompatibility against tissues, and average blood compatibility [9]. PU are employed to produce various medical devices like vascular catheters, total artificial heart [10], etc. Due to their high biodegradability, researchers have focused on long-term implants. Thus it was developed an entirely new class of bioresorbable poly-urethanes.

By chemical structure, polyurethanes include long chains composed of urethane groups (1):

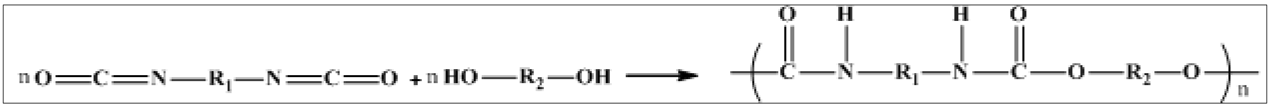


(1)

where: R_1 is an aliphatic or aromatic unit from an isocyanate monomer (R_1-N=C=O);

R_2 is a complex group included in the polyol component and may be a polyester or a polyether.

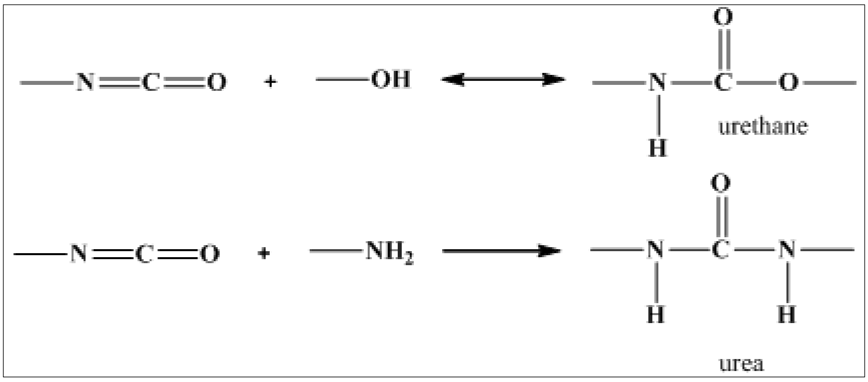
Polyurethanes synthesis (2) requires the reaction between two main components: an isocyanate (usually diisocyanate O=C=N-R_1-N=C=O) and a polyol with two hydroxylic end groups [11]:



(2)

The resulting product will be a thermoplastic polyurethane when the reaction components have only two functional groups. On the other hand, it may develop into a thermoset involving crosslinking if the reactants have more than two functional groups.

The synthesized polyurethane exhibits low mechanical strength if the direct reaction between a diisocyanate and a long chain diol occurs. Therefore, to increase the mechanical resistance, some so-called "chain extenders" are added, typically a diol (HO-R-OH) or a diamine (H_2N-R-NH_2), which presents a much shorter chain in comparison with the longer chains of polyurethanes [11,12]. Thus, the following reactions occur (3) between the chain extender and the polyurethane main chain resulting in newly added segments of urethane or urea to the polyurethane chain:



(3)

These new-formed extended chains act as rigid segments, which will finally increase the material's mechanical strength.

When the isocyanate monomer contains an aromatic R_1 segment, a peculiar structural behavior may be noticed. The rigid aromatic rings from the isocyanate units exhibit a high tendency to form aggregated by stacking through the π-bonding of the benzene rings. Thus, polyurethanes will suffer a micro-phase separation, creating hard segments of chain extender, diisocyanate, and soft amorphous parts.

As the chemical and physical integrity of the material is very important for long-term applications of PU-based urinary catheters, we have performed several analyses on the provided samples designed to give insight into the aging process of the material.

3.1. TGA analysis

Table 1. The TGA data for the polyurethane-based urinary catheters explanted at different times

Sample	Weight Change (%)	Weight loss temperature (°C)		
		3%	5%	10%
PU	76.33	294.2	302.2	314.5
PU 22 days	59.11	317.2	322.0	329.0
PU 29 days	54.29	316.7	321.5	328.3
PU 3 months	59.97	324.9	332.8	343.9
PU 8 months	72.76	340.7	351.7	374.0

TGA data may be used as an indirect assessment for changes in the polyurethane-based urinary catheters in time. Thus, from Table 1, one may observe that in time, the thermal stability increases since the temperature at which the weight loss is 3%, 5%, and 10% respectively increases sharply from 22 days to 8 months. Also, it can be noticed that the weight change slightly varies from the initial moment of implanting the polyurethane-based urinary catheters up to 8 months of use. The weight change at eight months is vital since it is almost of the same value as it was at time zero. However, during the exploitation at 22 days, 29 days, and three months, the weight change of the sample is smaller than the one at the initial time.

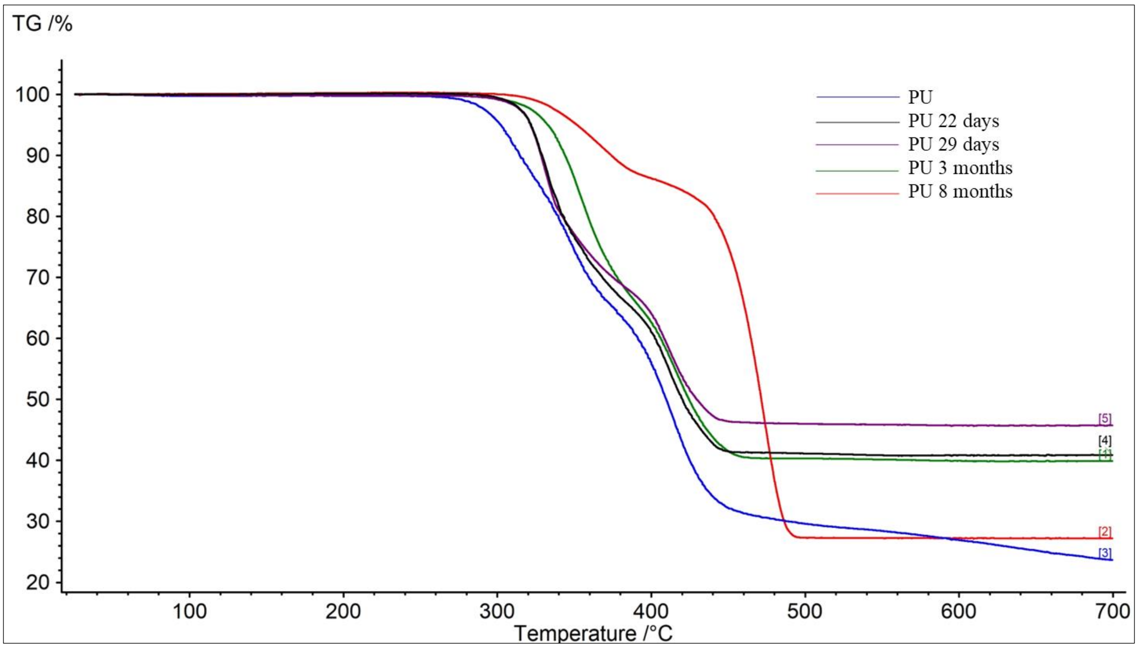


Figure 1. The TGA curves of different samples of polyurethane-based urinary catheters explanted at various time intervals: 0 days; 22 days; 29 days; 3 months; 8 months

The TGA curves (Figure 1) present the main steps of polyurethane decomposition, which is in good agreement with similar data reported in the literature [13]. The first stage of decomposition is characteristic for the degradation of urethane hard chain segments [14], and it occurs between 200 and 280°C. The second degradation stage occurs between 290 and 370°C, absent for the polyurethane-based urinary catheters extracted at longer times (3 months and eight months). This particularity is for sure related to the deposition of various components onto the polyurethane samples, occurring in time through the contact of the polyurethane surface with the urine compounds. A similar effect was reported in the literature [13, 15,16] for various biocomposites based on polyurethane. The onset temperature was much higher for polyurethane-based biocomposites than pure polyurethane [13, 15, 16]. These measurements evidently support that the structure of the polyurethane-based urinary catheters will be close to a composite one after a prolonged time of use (3 to 8 months). In time different compounds resulting from the adsorption onto the polyurethane surface will increase the overall thermal stability of the catheters.

3.2. DSC analysis

Table 2. The DSC data for the polyurethane-based urinary catheters explanted at different times

Sample	**Peak Value**					
	Temperature, (°C)	DSC, (mW/mg)	Temperature, (°C)	DSC,(mW/mg)	Temperature, (°C)	DSC, (mW/mg)
PU	27.9 (endo)	0.1985	32.5 (exo)	0.1589		
PU 22 days	53.6 (exo)	0.1053	65.0 (endo)	0.2402	122.8 (endo)	0.2365
PU 29 days	30.9 (endo)	0.4352	122.9 (endo)	0.4216		

PU 3 months	52.2 (exo)	0.4052	60.8 (endo)	0.9333	125.7 (endo)	0.7485
PU 8 months	54.3 (exo)	0.4934	63.8 (endo)	1.309	88.0 (endo)	1.198

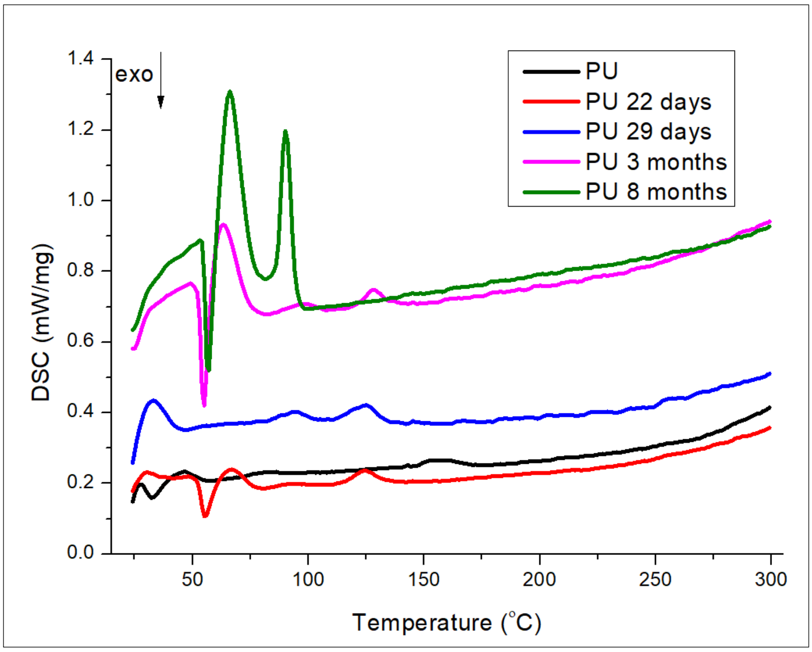


Figure 2. The DSC curves for various polyurethane-based urinary catheters explanted at different times

When performing the DSC analyses of the samples from polyurethane-based urinary catheters (Table 2), various peaks with different intensities were noticed on the curves. The peaks observed in the DSC curves are totally distinct with the increase of usage time. Two extremes are seen for the initial PU-based sample: the first one representing an endothermal peak around 30°C and a very close exothermal one around 32°C, similar to the reported data [17]. As the time of explanting increases (3 months and eight months), more endothermal peaks occur in the DSC curves, which are very prominent and may be attributed to the change of aggregation of the hard segments from the polyurethane chains. Some authors have reported only one large peak in this respect, but two very sharp endothermal peaks appeared in our study, well defined mainly at eight months (Figure 2).

3.3.FT-IR analysis

Figure 3 reveals that the spectra exhibit the leading characteristic bands for polyurethanes: ~3324 cm^{-1} assigned to –NH vibration, ~1600 and ~1700 cm^{-1} attributed to C=O, ~1230 cm^{-1} assigned to C-N, and on a secondary scale, the signals at ~2856 and ~2928 cm^{-1} characteristic to aliphatic C-H bends. Analyzing the signal differences between spectra of samples taken at different usage times (22 days, 29 days, three months, and eight months respectively), one may observe a significant difference in the signal at ~1100 cm^{-1}, absent for the sample at eight months. This signal is usually assigned to C-O-C stretching vibration. The disappearance of this signal means that the chemical process of destroying the C-O-C segments occurs in time, which leads to structural changes of the material.

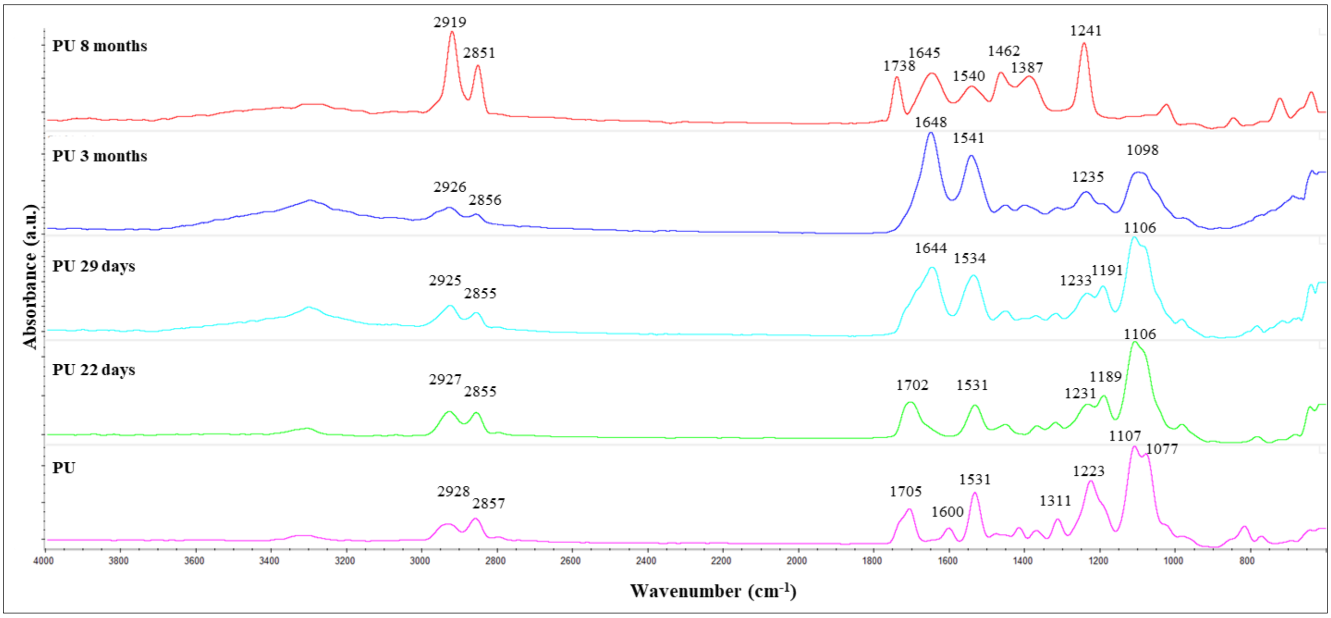


Figure 3. FT-IR spectra of polyurethane-based urinary catheters samples at various usage times

3.4. Clinical aspects of ureteral stents

The advantages of employing polymeric catheters to realize proper renal drainage were tested over time. Their use in treating different kinds of urologic pathologies represents a standard solution for nowadays options.

Besides their potential benefits, they also present several inconveniences which may be improved as technology advances. The perfect material or type of ureteral stent does not yet exist. Thus, urologists have to deal with ureteral stent complications like infections, pain, drainage failure, or encrustations.

The more time a stent is maintained, the more increases the risk of developing associated complications.

Using a ureteral catheter for a prolonged time as part of nephrolithiasis treatment and associated infections may lead to encrustations on the stent exterior part. Finally, the device cannot be extracted by standard techniques, and an endourological approach becomes necessary. Several methods according to the level of encrustation are described in the attempt to remove an altered catheter. These methods include extracorporeal lithotripsy, percutaneous nephrolithotomy, retrograde intrarenal surgery, or open surgery [18-20].

Biofilm formation after insertion is intensely discussed as different types of molecules adhere to the stent surface [21]. Attaching bacteria to the external layer of the catheter is considered essential in developing struvite and hydroxyapatite deposits [22].

Recent studies demonstrated that bacterial presence is not mandatory for developing mineral crystals, and urinary *p*H represents a more critical factor in this process of encrustation [23]. In order to diminish this inevitable fact, the actual EAU Guidelines recommend L-methionine and phytin administration to prevent crystallization and control urinary *p*H. L-methionine is an essential amino acid with high properties in modulating and controlling urinary acidity while using a ureteral catheter [24], while phytin presents inhibitory properties for calcium-developed stones [25].

Impaired urinary flow as the encrustation process develops until complete occlusion may lead to high mortality rates by causing renal infections or severe sepsis [26].

Urinary tract infections are commonly associated with ureteral stent placement. The principal known risk factors for developing bacteria are related to diabetes and dwell time over 90 days [27]. The triclosan-loaded stent represents one of the proposed solutions in the attempt to avoid bacterial development as long as it is pharmacologically incorporated with active agents [28].

For over 20 years, most studies recommend a frequent replacement of ureteral stents when used for a long period in treating chronical diseases to avoid or diminish morbidity and mortality associated rates [29].

4. Conclusions

The polyurethane-based urinary catheters suffer in time of use different/various processes that may be physical and/or chemical. These changes may lead to structural modifications in the polyurethane mass, and the addition by adsorption of new compounds may actually influence the overall behavior of the polyurethane material.

The overall thermal stability of the urinary catheters is increased in time, compared with the initial polyurethane-based material, probably due to the adsorption of some compounds onto the polyurethane surface. The change was observed through TGA and DSC, and the FT-IR analysis gave insight into the cause of these transformations.

The polyurethane as a base material for producing urinary catheters may suffer even structural changes over time which was proved by the disappearance of the C-O-C FT-IR signal at a longer usage time (8 months), meaning that the chemical structure was affected. The overall modifications of the urinary catheters based on polyurethane were proven. Our results might be the base for later studies on the eventual development of long-term polyurethane-based implantable devices.

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