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Investigation of Hafnium(IV) Incorporation in Polyurethanes: Structural and Mechanical Properties

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This study investigates the incorporation of hafnium (Hf) into polyurethane foams (PUs), an underexplored area in polymer materials research. The synthesis of Hf-containing PU foams was conducted, and their characterization was performed using Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), optical microscopy (OM), and dynamic mechanical analysis (DMA). The results revealed a significant increase in the stiffness of PU foams due to the potential formation of hafnium isocyanate. Quantitative values obtained through DMA tests demonstrated an approximate increase of 95.97% for PU Hf 0.5% and 342.72% for PU Hf 3%, compared to the sample without Hf. These data highlight the influence of hafnium on enhancing the mechanical properties of polyurethane foams.

Keywords: *polyurethane, hafnium, hybrid material.*

1. Introduction

One of the polymer materials widely used by society is polyurethanes (PUs). These polymers are produced through a chemical reaction between polyol groups, which can come from polyesters or polyethers, and isocyanates, resulting in a final product with a flexible, semi-rigid or rigid foam-like appearance in various densities. They have numerous applications; some examples include coatings, elastomers, adhesives, fibers, thermal and acoustic insulation. Additionally, they are used in the construction industry for structural reinforcement due to their favorable mechanical properties, among others[1-5].

This polymer offers several advantages, including high abrasion resistance, ease of low-temperature molding, wide versatility in molecular structure, the ability to cure under ambient conditions, and reduced costs. However, some notable disadvantages include high flammability and its predominantly petrochemical origin in the main synthesis[1-5].

The first PUs were synthesized in 1848 by Wurtz and in 1884 by Hentschel, with the latter being responsible for the development of PUs. However, it was only in 1937 that Otto Bayer and his collaborators produced PUs on a commercial scale[1,2,6].

One of the properties that has been the subject of investigation in polyurethanes is their rigidity, due to their applications in construction, the transport sector, and related areas. The rigidity of this type of material is determined by the morphology of the foams, being influenced by the type of polyol and isocyanate added to the structure, the crosslink density of the polymer matrix, among other factors[7]. Additionally, the temperature to which the material is exposed affects its mechanical properties, making this variable crucial when selecting the appropriate type of polyurethane for a given application[8].

Various studies in the literature aim to obtain polyurethane foams with greater rigidity by adding different materials to the structure, such as cellulose microfibers[7], aluminum powder[9], aluminum oxide[10], aramid nanofibers[11], polylactic acid[12], graphene[13] and industrial potato protein[14]. These studies indicate the scientific community's interest in investigating alternatives to improve the rigidity properties of polyurethane.

Seeking to alter the properties of polyurethane, numerous studies focus on the incorporation of metal cations into the structure of PU in order to obtain specific characteristics and develop materials with improved properties. For example, Pegoraro et al.[5] identified that in the Web of Science database, approximately 207 studies address the relationship between polyurethane and rare earth elements. Jayakumar et al.[15] explored the inclusion of alkaline-earth elements (Mg and Ca) in polyurethanes, while in a previous work[16], PU structures

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containing Ca, Cd, Pb, Cu, Mn, and Zn were investigated. Hess et al.[17] dedicated their research to the biocompatibility of a nanocomposite of gold and platinum nanoparticles in PU, among other related studies.

However, studies involving the chemical element hafnium and PU in the polymer structure are scarce in the literature, with the primary report being a study on the extraction of zirconium and hafnium thiocyanates using PU foam, as the tetravalent cations of these elements formed complexes with the thiocyanate group[18].

Hf, owing to its distinctive properties, has gained prominence in recent research, both in the medical field due to its favorable electrical characteristics, and in polymeric matrices, contributing to the development of materials with unique properties compared to those involving other metals. In the medical domain, Ding et al.[19] conducted an extensive literature review on Hf applications, highlighting its increasing utilization, particularly in the realm of nanotechnology, where its electrical properties have found substantial use in cancer treatment imaging. In the polymer field, Rodriguez-Lopez et al.[20] investigated the electrical performance of thin hafnium oxide films on flexible polymeric substrates, emphasizing their remarkable stability and mechanical resilience, which opens paths for potential biomedical applications, potentially replacing the currently used hard thin films.

Liu et al.[21] explored the use of hafnium oxide in both oxidative and inert environments for the production of thin-film transistors based on poly(3)-(hexylthiophene). Wang et al.[22] observed the excellent catalytic performance of hafnium pyridylamide for the homo- and copolymerizations of ethylene, alpha-olefins, and styren.

Considering the aforementioned, it is evident that Hf has demonstrated significant potential in various research areas, such as medicine, electronics, and polymer chemistry. However, there is a gap in the literature regarding the study of the interaction between the metal and polymer. For these reasons, the present research investigates the properties of a material composed of Hf and PU, due to the wide range of potential applications that high rigidity polyurethanes have.

2. Materials and Methods

2.1. Synthesis of material

Hafnium(IV) oxychloride octahydrate ($HfOCl_2 \cdot 8H_2O$) was obtained by dissolving metallic hafnium (Hf) (99.95%, Chengshuo, China) in sulfuric acid (H_2SO_4) (98%, Synth, Brazil), followed by precipitation with ammonium hydroxide (NH_4OH) (30%, Synth, Brazil). The precipitate was filtered, washed with deionized water and dissolved in hydrochloric acid (HCl) (37.5%, Synth, Brazil), which was then desiccated at room temperature in a desiccator with silica gel to obtain $HfOCl_2 \cdot 8H_2O$ crystals.

Samples of hafnium-containing polyurethane foam (PU Hf) were prepared by reacting a commercial polyol (Redelease, Brazil) with commercial 4,4'-diphenylmethane diisocyanate (MDI) (Redelease, Brazil) in a mass ratio of 1:1, following the manufacturer's instructions.

A specific amount of $HfOCl_2 \cdot 8H_2O$ was added to the MDI and dissolved before mixing it with the polyol, to achieve samples with 0.5% and 3% by mass of $HfOCl_2 \cdot 8H_2O$ relative to the total mass of the polyol and MDI. These samples were denoted as PU Hf 0%, PU Hf 0.5%, and PU Hf 3%, respectively. The samples were allowed to cure for 24 hours at room temperature before characterization.

2.2. Material characterization

Fourier Transform Infrared Spectroscopy (FTIR) were performed in a Perkin Elmer Frontier (Massachusetts, USA) equipment with an Attenuated Total Reflection (ATR) apparatus, from 4000 to 400 cm^{-1} and 4 cm^{-1} of resolution.

X-ray Diffraction (XRD) was performed using a Shimadzu XRD-6100 diffractometer, operating with a copper X-ray tube at 40.0 kV and 30.0 mA. Continuous scans ranged from 10° to 60° for the polyurethane samples and from 10° to 40° for the $HfOCl_2 \cdot 8H_2O$ precursor at 2°min^{-1}.

A Leica EZ4W microscope, connected to a camera and a computer, was used to capture optical microscopy (OM) images of the material.

The dynamic mechanical analysis was conducted on the DMA Q800-TA machine. The samples were cut into a size of 7 mm × 5 mm × 1 mm and tested using the two-point bending method with a film tension clamp at the temperature range of -70 to 200 °C at a heating rate of 5°C min^{-1} in the test frequency of 1 Hz.

3. Results and Discussion

3.1. FTIR

Figure 1 shows FTIR spectra of all samples. Most of the peaks observed are related to the PU matrix, as comprehensively described by the literature[23,24]. In general, all FTIR spectra showed similar bands.

Decreased peaks can be observed at 2270 cm^{-1} region, related to the band of isocyanates (N=C=O), which represents a more rigid PU matrix, as described by others, suggesting that the presence of Hf in different proportions played a role, although not related to the quantity of Hf present in each sample. It can also be inferred by the absence of hydroxyl

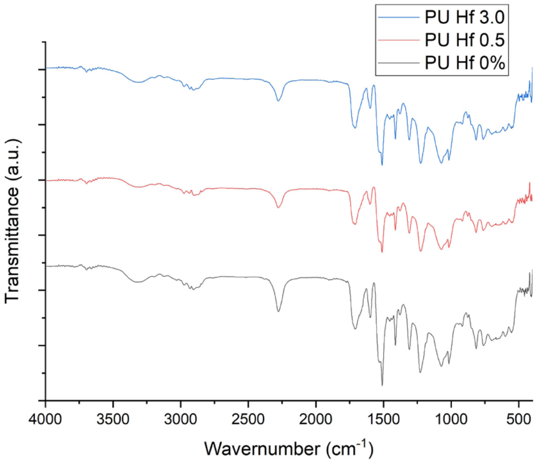


Figure 1. FTIR spectra of all samples.

groups (O-H) in excess, which may perform crosslinking between PU chains[23]. At 1730 cm^{-1}, carbonyl (C=O) bands showed some alterations in intensity, more marked at PU Hf 0.5% sample, with a smaller peak. The band located at 1600 cm^{-1} is related to the carbamate group (C-N), and at 1510 cm^{-1} is related to C=C bonds of urethanes, followed by the band located at 1220 cm^{-1}, from C-O-C groups. Symmetric and non-symmetric stretching of C-H bonds are slightly present at 2900 cm^{-1} [23,24]. The formation of hafnium isocyanate is indicated in FTIR by the displacement of bands in the region around 3410, 2150, and 1280 cm^{-1} [25]. However, this was not observed for Hf containing samples in Figure 1 when compared to PU Hf 0%. Nevertheless, this does not imply that hafnium isocyanate was not formed, as the polyurethane matrix may have masked this displacement, although additional characterizations must be performed to confirm such statement.

3.2. XRD

XRD diffraction patterns are shown in Figure 2 for pure and all Hf containing PU samples, along with the diffractogram for the $HfOCl_2$ used as the Hf precursor. After conducting classical gravimetry with $HfOCl_2$, the hydration of the material was quantified at 8. Furthermore, the peaks in the diffractogram of $HfOCl_2$ were similar to JCPDS card 47-0816, to which, according to Barraud et al.[26], $HfOCl_2 \cdot 8H_2O$ can be attributed.

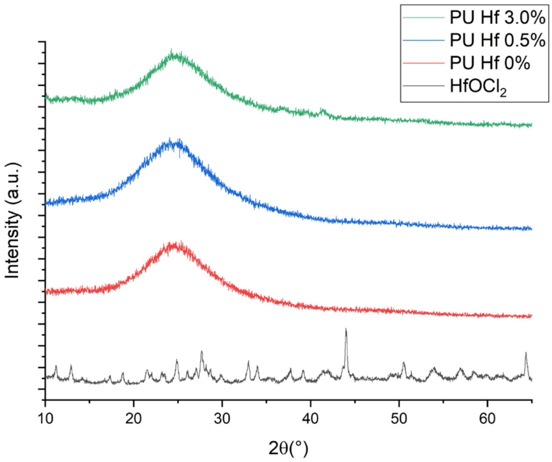


Figure 2. X-ray diffractograms of PU foams containing 0%, 0.5% and 3% Hf and the $HfOCl_2$ precursor.

All the PU diffractograms were very similar and showed characteristic soft PU broad peaks centered on 19º, whereas no other peaks appeared on 8º, 11º and 43º, which would be attributed to more crystalline rigid or semi rigid PUs. The absence of these peaks indicates partial crystallinity in all samples. The formation of less crystalline soft PU can be justified by the reduction of urethane crosslinking in the PU foams, which is affected by the hydroxy groups from the polyol. Since a fixed proportion of polyol to isocyanate was used for all foam samples during the synthesis, the similarities between all diffraction patterns indicate that the addition of Hf in varying quantities up to 3% had no noticeable effect on the diffraction patterns[23].

The addition of Hf^{4+} to a polyurethane matrix may not be directly comparable to existing studies, since most of the previous research focuses on loading the polymer with compounds, metal nanoparticles or oxide nanoparticles instead of using salt precursors. However, the presence of XRD patterns showing the same type of PU in samples with different loading amounts, as is the case in the current work, has been observed multiple times for different compounds. Graphene[27], reduced graphene oxide[28], iron(III) oxide nanoparticles[29], nickel oxide nanoparticles[30] and silver nanoparticles[31] are a few examples in which the only noticeable difference was a change in intensity of the PU broad peaks with different amounts of compound loading in the polymer matrix.

3.3. OM

The optical microscopy images of the samples of PU foams containing Hf are shown in Figure 3. It is possible to notice that the control sample, PU 0%, (a) presents hexagonal shaped cells, with similar size distribution, which indicates that the control foam demonstrates an open-type cell structure[32]. The 0.5% Hf PU sample (b) exhibited a certain morphological difference compared to the control foam, with a more rounded and homogeneous shape, which may have occurred due to the fact that the addition of 0.5% hafnium oxychloride provided greater nucleation, and consequently, a greater generation of bubbles. The addition of this element

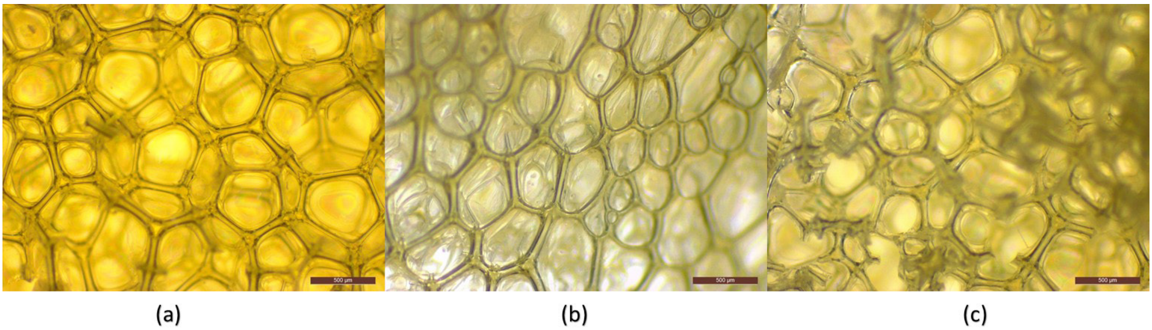


Figure 3. Optical microscopy of PU foams containing (a) 0%, (b) 0.5% and (c) 3% $HfOCl_2$.

may also have contributed to the bubbles present in the foam avoiding the phenomenon of coalescence, thus explaining the reduction in the size of the cells[33].

However, 3% (c) sample showed a significant difference in their respective morphologies when compared with the control foam and the PU Hf 0.5%. These foams exhibited irregular morphology, which indicates that the addition of 3% hafnium oxychloride caused a probable rupture of the cell wall during the expansion of the samples, causing coalescence and, consequently, the formation of tears, probably due to the agglomeration of hafnium oxychloride in the structure. However, it did not significantly change the size and shape of the polymer cells when compared to the control foam[32,34,35].

3.4. DMA

DMA tests were conducted on the polyurethane foams with hafnium and the control sample (without hafnium) to assess the viscoelastic behavior and thermomechanical properties. DMA analysis is a precise technique that provides information on viscoelastic properties such as stiffness and energy dissipation in both soft and hard materials[32]. The storage modulus (E') is associated with the amount of mechanical energy stored by the sample in the form of recoverable elastic energy after deformation and is linked to the material's stiffness. The loss modulus (E") is a parameter related to the viscous component of the material and the energy dissipated/lost and not recoverable during deformation. Tan delta is the dimensionless ratio between the loss modulus and the storage modulus, establishing the internal damping or internal friction of the polymer macromolecules. The peak maximum of tan delta corresponds to the glass transition temperature (T_g)[36,37].

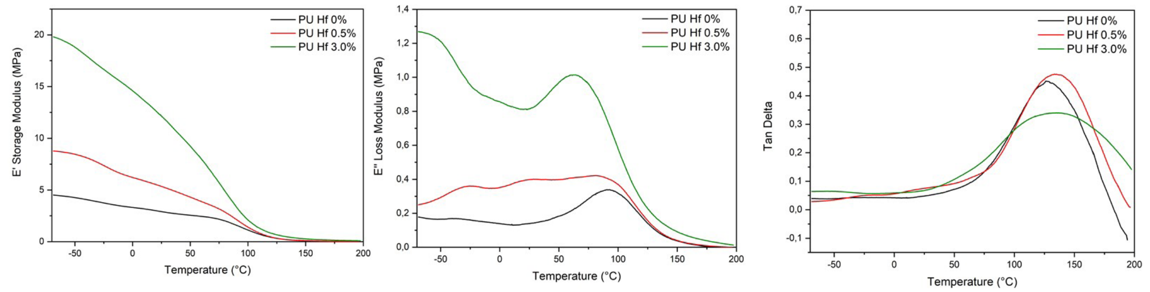
Figure 4 displays the curves of storage modulus (E'), loss modulus (E"), and tan delta for polyurethane foam samples with hafnium at various concentrations. Table 1 lists the values obtained for E', E", and glass transition temperature (Tg) obtained from the peak of the tan delta for the analyzed samples.

Upon analyzing the E' curves presented in Figure 4a and the data provided in Table 1, it was observed that the incorporation of hafnium led to a significant increase in the stiffness of polyurethane foams at concentrations of 0.5% and 3% hafnium. The remarkable increase showcases the potential of hafnium incorporation at concentrations of 0.5% and 3%, hafnium boosted stiffness by approximately 95.97% and 342.72%, compared to PU Hf 0%. This enhancement likely stems from the formation of hafnium isocyanate, which complexes with the polymeric matrix, resulting in a significantly stiffer structure. This interaction restricts polymer chain mobility, producing a material less prone to plastic deformation. These findings highlight hafnium's role in elevating the mechanical properties of polyurethane foams, paving the way for advanced materials with superior rigidity and performance.

In the loss modulus (E") curves presented in Figure 4b, a reduction in the peak temperature was observed, indicating a more viscous behavior of the material. This peak is distinctive of the transition from the glassy region to the elastomeric region. This observation was anticipated, given the increase in the stiffness of foams containing hafnium, which hinders the movement of polymeric chains. However, the values of the loss modulus underwent few changes, except for the PU Hf 3% sample, which exhibited a significant increase of 306%.

The stronger the interaction between the additive and the matrix, the greater the dissipation of energy, leading to a higher peak in tan delta. This is because the release of energy in polymeric matrices occurs through the interface[38]. There was an increase in the peak height of the tan delta curve (Figure 4c) with the addition of Hf to polyurethane, indicating interaction between the two materials.

Through the maximum peak of the tan delta (Figure 4c), a slight shift to the right of the curve was observed, indicating



(a) (b) (c)

Figure 4. DMA curves for PU foams with different concentrations of Hf, where (a) is E', (b) is E", and (c) is tan delta.

Table 1. Results obtained from DMA analysis for PU foams with different concentrations of Hf.

Sample	E' max	E' onset	Peak E'		Peak tan delta
	MPa	°C	MPa	°C	°C
PU Hf 0%	4.47	78.3	0.33	92.24	127.29
PU Hf 0.5%	8.76	73.40	0.38	84.90	135.97
PU Hf 3.0%	19.79	52.58	1.01	62.84	135.37

an increase in the glass transition temperature (T_g) in all samples. The presence of Hf in the polyurethane foam resulted in a restriction of chains, requiring more energy for their mobility. The material with T_g above room temperature is in a glassy state; in this case, the polyurethane foam with Hf is rigid and less susceptible to plastic deformations[37].

4. Conclusion

One of the polymer materials widely used by society is In this study, successful synthesis of polyurethane foam samples containing hafnium in different proportions, ranging from 0%, 0.5% and 3.0% in relation to the sum of the masses of polyol and MDI, was achieved. Through a detailed analysis of the samples, it was possible to observe changes in the physical and morphological properties of the polyurethane foams with the addition of hafnium.

FTIR analyses revealed that the presence of hafnium affects the isocyanate (N=C=O) and carbamate (C-N) bands in the polyurethane samples, indicating a potential alteration in the PU matrix. XRD analyses demonstrated that the addition of hafnium did not have a significant impact on the diffraction patterns of the polyurethane samples, indicating that the crystallinity of the PU foams remained similar, regardless of the amount of hafnium added. MO images showed that the addition of 0.5% hafnium resulted in a slightly different morphology, with more rounded and uniform cells. However, the addition of 0.5% to 3% hafnium caused more significant changes in morphology, with the formation of irregular structures and cell ruptures.

The significant increase in stiffness observed in polyurethane foams (PU Hf) can be attributed to the formation of hafnium isocyanate. The incorporation of hafnium at varying concentrations resulted in substantial stiffness gains, indicating complexation with the polymeric matrix. This interaction restricts the mobility of polymer chains, yielding a stiffer material less prone to plastic deformation. DMA tests showed stiffness increases the viscoelastic behavior demonstrated a stronger interaction between the additive and the polymer matrix, resulting in greater energy dissipation and an increased glass transition temperature (Tg). These findings underscore the role of hafnium in enhancing the mechanical properties of polyurethane foams, paving the way for the development of materials with tailored stiffness and superior performance in applications demanding higher rigidity and resistance.

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