Development and characterization of a polymer based on the biomimicry of the intervertebral disc

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Abstract. The development and characterization of a functional graded composite material based on the biomimicry of the human intervertebral disc is reported in this research. The material consists of concentric radial polyurethane layers, synthesized using a condensation polymerization chemical reaction, found on methylene diphenyl diisocyanate, glycerol and castor oil as reagents. The proportions in the components of the polyl, glycerol and castor oil, were modified to generate a change in the degrees of cross-linking in the chains of the material, resulting in slightly rigid layers, as in the structure of the intervertebral disc. Two radial gradations were made through a rotating assembly and the complex modulus of the constituent polyurethane layers was used as the gradation criteria since the complex modulus provides a general description of the mechanical behaviour. After the gradation process, the graded material was characterized by means of a dynamic mechanical analysis that determines its viscoelastic properties, like storage modulus, loss modulus, complex modulus and tan δ. Moreover, with its behavioural pattern to compression and flexion, we performed a comparative analysis of the improvement of the mechanical properties of its constituent materials. The development of this study under biomechanical and chemical guidelines came together with two proposals of graded materials with high versatility and functionality in terms of ruggedness and stability for temperatures changes, as well as absorption and dissipation of mechanical energy. Furthermore, it serves as a tool for the elaboration of machines elements under combined load of compression and flexion at a low cost.

1. Introduction
The result of scientific progress in materials science and the continuing developments of modern industry have given rise to the continual demand for advanced materials that can satisfy the necessary advanced properties and qualities [1]. Recent advances in engineering and the processing of materials have led to a new class of materials called functionally graded materials (FGMs) [2], composites characterized by a gradual variation of the structure and proportions of two or more constituents, to improve the performance of the material in a specific application [3]. These advanced materials with engineered gradients of composition, structure and specific characteristics in the preferred direction are superior to homogeneous material composed of similar constituents [4].

A key focus of current scientific research is the development of bioinspired materials [5]. The biomimicry studies the models, systems, and elements of the nature looking for solution within countless number of problems at all levels [6-7]. The biomimicry of the human body is undoubtedly fascinating;
its diverse configurations and complex structures serve science and engineering as inspiration to solve multiple difficulties [8]. One of its most complex structures is the intervertebral disc (IVD), constituted by a nucleus and a succession of concentric fibrous layers [9], whose obliquity is crossed from one layer to the next. It is located between two vertebral bodies and is subjected to tensile, flexion, compression and torsion stress daily [10-11]; this structure can inspire the design of a functionally graded polyurethane.

Functionally graded polyurethane elastomers (FGPUEs) improve the properties of conventional polyurethane elastomers. Polyurethane elastomers have excellent mechanical properties compared to general-purpose elastomers [12]. The present study sought to show the development of a FGPUEs inspired in the structure of the IVD, characterized by a dynamic mechanical analysis (DMA). The results were compared with the performance of the constituents materials and analyzed to assess the improvement in the new material.

2. Experimental

The process for the development and characterization of the polymer-based on the biomimicry of the IVD is divided into four (4) stages: Pretreatment of the reagents, the synthesis where the constituent polyurethanes are obtained, the gradation and finally the characterization.

2.1. Raw materials

The reagents used are glycerol, castor oil (castor oil - CO) and crude methylene diphenyl diisocyanate (MDI). A color grass powder pigment was added to the CO (17.5 mg / 100 mL CO) and stirred manually until all the pigment powder is dissolved. The pigmented CO and glycerol (each per individual) are dried in a rotary evaporator for 40 min., at a stirring speed of 80 rpm, and a vacuum pressure of 80 mBar. They are stored in a desiccator and, if necessary, the rotary evaporation is repeated every 3 weeks during the tests. We used a rotary evaporator connected to a vacuum pump, Hei-VAP series rotary evaporators by Heidolph.

For the synthesis of the required polyurethanes, we worked with a (NCO/OH) molar ratio of 1:1. As reagents, CO and glycerol were used for the polyol, and crude MDI as isocyanate. In order to obtain a broad spectrum of polyurethanes with these reagents, variations are made in the molar ratios of the polyol Table 1. Exist a degree of immiscibility between the hard urethane segment and the soft polyol segment, which means that although macroscopically polyurethane elastomers (PUEs) are isotropic, microscopically PUEs are not structurally homogeneous [12]. After the gradation we will find scattered soft polyol segments and urethane hard segments.

| Mixture | Polyol | Polyol | Polyol | Polyol | Polyol | Polyol |
|---------|--------|--------|--------|--------|--------|--------|
| 40 – 60 | 40%    | 60%    |        |        |        |        |
| 50 – 50 | 50%    | 50%    |        |        |        |        |
| 60 – 40 | 60%    | 40%    |        |        |        |        |
| 70 – 30 | 70%    | 30%    |        |        |        |        |
| 85 – 15 | 85%    | 15%    |        |        |        |        |
| 100     | 100%   | 0%     |        |        |        |        |

2.2. Preparation of functionally graded polyurethane elastomer

A functionally graded polyurethane is projected radially as the IVD; for this, two gradations will be made by changing the degrees of crosslinking in the chains of the polymer, thus imitating the annulus fibrosus. The process is based on the preparation of metallic materials with a gradient function; the metallurgical process referred to is a fusion process, consisting of sintering in centrifugal casting, in the process particles of different sizes are entered into a casting that is already in rotation. In the case of polyurethane, the particles are the hard urethane segments and the casting would be the soft polyol segments.
2.3. Development of functionally graded polyurethane elastomer
The criterion determined as the basis for the gradation is the complex modulus (E*), taking into account the biomimicry of the IVD were researchers reported that in the radial direction of disc, there are a certain number of fiber layers which mechanical properties of them, such, increase from the innermost layer to the outermost one [13]. The nucleus and the outer layer of the annulus fibrosus have a high E* to preserve their shape. Two (2) types of distribution are designed for the concentric radial layers of the graded material with the E* as criterion and the available spectrum of materials previously characterized, thus generating the gradations, one with polyurethanes ordered from the center to the outside according to the value of its E*, and another descending orderly; leaving in the center and outside of each sample, in turn, the two materials that have a greater E* between the constituents. Figure 1 shows the values of the E* in the multifrequency compression test for the constituent materials and Table 2 the organization of the concentric layers in the gradations.

![Figure 1. Complex modulus E* (MPa) at 40 °C for the constituent materials of the gradations.](image)

| Location | Gradation FGM 70 – 30 | Gradation FGM 60 – 40 |
|----------|-----------------------|-----------------------|
| Centre   | 70-30                 | 60-40                 |
| Layer 2  | 100                   | 40-60                 |
| Layer 3  | 85-15                 | 50-50                 |
| Layer 4  | 50-50                 | 85-15                 |
| Layer 5  | 40-60                 | 100                   |
| Outside (layer 6) | 60-40       | 70-30                 |

2.4. Curing
Previously, the oven was heated to 120 °C. After the reaction was completed and poured in the mold, the material was left in the oven for 10 minutes for curing. The synthesized material is inspected visually for bubbles that may be concentration of stress, if not found, the samples for physical-mechanical characterization are cut and adapted.

2.5. Characterization of functionally graded polyurethane elastomer
The characterization was carried out by means of the multifrequency and creep tests by the DMAQ800 equipment of TA Instruments, allowing to capture an analysis of the improvement in the properties of the polymer in relation to the constituent materials. The DMA was performed on the samples 15 days after the synthesis, giving time to the finalization of the curing in the material.

2.5.1. Multifrequency compression test. The sample was placed in the clamp at room temperature, closing the equipment for heating to commence in a room temperature up to 40 °C. The constant temperature was kept for 5 min at 40 °C to guarantee the homogeneity of temperature in the sample and then heated to a ramp of 5 °C/min up to 200 °C. A load of 10 N was applied at a frequency of 1 Hz and an amplitude of 10 μm.

2.5.2. Creep compression test. The sample was placed in the clamp at room temperature, the equipment was closed and warming started. The constant temperature was kept for 1 min at 40 °C to guarantee the homogeneity of temperature in the sample and then the load was applied. During the test a stress of 0.052 MPa is applied to the sample and the resulting strain is measured for a period of time, the stress...
is brought to zero and the recovery of the strain is measured as a function of time. The load was applied for 15 min, then the load was removed for 6 min. The loading and unloading cycle were performed 3 times.

2.5.3. Flexion creep test. The sample was placed in the clamp at room temperature, the equipment was closed and heating started. The constant temperature at 40 °C is maintained for 1 min to guarantee the homogeneity of temperature in the sample and then the load is applied. The stress of 1 MPa is applied for 15 min, then the load is removed for 6 min. The loading and unloading cycle were performed 3 times.

3. Analysis and Results

Two (2) functionally graded samples, FGM 70-30 and FGM 60-40 presented in Figure 2, were their names indicating the polyol ratio in the center of the samples. In the samples FGM 70-30 and FGM 60-40 a dynamic mechanical characterization was done by means of compression tests (multifrequency and creep) and flexion (creep).

![Figure 2. Real picture of the gradations carried out. (a) Graded sample FGM 70-30, (b) Graded Sample FGM 60-40.](image)

3.1. Multifrequency compression test

The changes of $E^*$ presented in Figure 3, $E'$ (storage modulus), $E''$ (loss modulus) and $\tan\delta$, for the FGM 70-30 and FGM 60-40 gradations were analyzed. The determination of the modules for the tested material was carried out using the multifrequency test mode, under the parameters referred above in section 2.5.1.

![Figure 3. $E^*$ of the FGPUE and their constituent materials.](image)

The $E^*$ is composed of an elastic and a viscous component. $E'$ is the elastic component and is related to the rigidity of the samples. $E''$ is the viscous component and is related to the ability of the sample to dissipate mechanical energy through molecular motion. It was possible to observe the effect of the gradation of the polymer on $E^*$, generating an increase in the value of it (0.3249 MPa for FGM 70-30 and 0.4541 MPa for FGM 60-40 at 40 °C with greater stability when compared with the constituent materials, indicating that the graded material works better under dynamic loads. By absorbing and dissipating more energy, the lifetime of the material increases.

The $E^*$, Figure 3, of the gradations decreases with its temperature due to changes in the viscosity of the material and the reorganization of the chains, attributable to the prevalence of the viscous state. The maximum drop in values of the $E^*$ is 19% for FGM 70-30 and 12% for FGM 60-40, this gradual decrease...
in the values of the modulus suggests that the structures of the gradations do not degrade so abruptly, increasing, therefore, the working temperature and the performance.

Table 3. Storage modulus, loss modulus and tanδ of FGPUEs.

| Temperature (°C) | Storage modulus E' (MPa) | Loss modulus E'' (MPa) | Tan δ |
|-----------------|--------------------------|------------------------|------|
| 40              | FGM 70-30 | 0.3198 | 0.4490 | 0.0570 | 0.0676 | 0.1781 | 0.1506 |
| 60              | FGM 60-40 | 0.2968 | 0.4349 | 0.0285 | 0.0467 | 0.0959 | 0.1074 |
| 80              | FGM 70-30 | 0.2689 | 0.4068 | 0.0132 | 0.0253 | 0.0491 | 0.0622 |
| 100             | FGM 60-40 | 0.2642 | 0.3996 | 0.0051 | 0.0159 | 0.0192 | 0.0398 |
| 120             | FGM 70-30 | 0.2711 | 0.4004 | 0.0039 | 0.0143 | 0.0143 | 0.0356 |
| 140             | FGM 60-40 | 0.2798 | 0.4025 | 0.0040 | 0.0139 | 0.0142 | 0.0345 |
| 160             | FGM 70-30 | 0.2870 | 0.4050 | 0.0043 | 0.0137 | 0.0151 | 0.0338 |
| 180             | FGM 60-40 | 0.2938 | 0.4105 | 0.0048 | 0.0138 | 0.0164 | 0.0336 |

The highest value of the E' at 40 °C, Table 3, for the sample FGM 60-40 tells us that it is more rigid, has greater capacity to store energy and a better elastic response to larger strains when it is subjected to dynamic loads. The little variation in the values of the modulus for the graded samples reflects that its elastic behavior is stable in a wide range of temperatures, this range could be defined between 40 °C to 80 °C. Despite the fact that after the inflection in the curve at 80 °C the gradations are in the elastic zone, this precedes the degradation of the material, which is why the working range between 40 °C – 80 °C is recommended for safety.

The speed in the decrease of the value of E'' in Table 3 indicates that they come from a kinetic transition corresponding to an accommodation of the chains that precede the elastic zone in the material. It is an indication that the phase shift between the applied stress and the strain is decreasing, concordant with a primarily elastic behavior, therefore the gradations are dissipating less energy.

The damping factor tanδ, Table 3 shows a decrease in it value for both samples in the section from 40 °C to 100 °C, this decline indicates that the material is less viscous, dissipates less and store more energy. Values close to zero (0), for the damping factor, classify the material as a good buffer for dynamic loads.

3.2. Creep compression test

The compressive creep of the material was analyzed by the creep compression test mode Figure 4, when analyzing each cycle, the recovery percentage for the gradations is approximately 100%, referring to the low values presented in the strain during discharging.

![Figure 4. Percentage of strain in multiple loading and unloading cycles of FGM 70-30 and FGM 60-40.](image-url)

The strain percentage is higher for the FGM 60-40 but the recovery percentage is also higher than the other sample, implying that FGM 60-40 can works better in solicitations for loading and unloading.
charges. The deformation in both samples is exponential as in the IVD suggesting that total recovery of samples thickness requires some time. If these loads and unloads are repeated too often, the IVD does not have time to recover its initial thickness \[10\], showed in the percentage of strain in Table 4.

### Table 4. Strain and recovery percentages for the samples in the multiple creep compression test.

| Sample   | % Strain | % Recovery | Cycle |
|----------|----------|------------|-------|
| FGM 70-30 | 1.02     | 102.10     | 1     |
|          | 1.07     | 98.66      | 2     |
|          | 1.08     | 97.44      | 3     |
| FGM 60-40 | 2.04     | 102.30     | 1     |
|          | 2.13     | 100.30     | 2     |
|          | 2.14     | 99.99      | 3     |

In theory, the creep test is the most direct way to measure the elasticity of a material; however, in practice it is impossible to isolate the sample in such a way that the only energy storage mechanisms in the material are the conduction in the sample during the recovery, thus explaining the disturbance in the recovery phase of the first cycles of each samples with values of 102% or negative strains, Table 4 although values in these ranges imply that the gradations are optimal for static load and discharge cycles.

#### 3.3. Flexion Creep test

The compressive creep of the material was analyzed by the flexion creep test mode. When analyzing each cycle of loading and unloading, Figure 5, the recovery percentage of the gradations is approximately 80%. Gradations are good for static loading and unloading cycles, but not as highly as in compression cycles, perhaps it is related to the shape of the sample.

![Figure 5. Percentage of strain in multiple loading and unloading cycles of FGM 70-30 and FGM 60-40.](image)

The changes in the percentages of recovery, Table 5, are due to the fact that the samples, after their initial strain, do not recover completely and therefore before the same load in the next cycle, the strain is less. In addition, creep phenomena of the first cycle are still present, reflected in the fact that in the last load cycles the recovery is 96% on average.

### Table 5. Strain and recovery percentages for the samples in the multiple creep compression test.

| Sample   | % Strain | % Recovery | Cycle |
|----------|----------|------------|-------|
| FGM 70-30 | 13.01    | 77.55      | 1     |
|          | 10.38    | 96.18      | 2     |
|          | 10.97    | 93.45      | 3     |
| FGM 60-40 | 22.50    | 75.22      | 1     |
|          | 17.44    | 96.38      | 2     |
|          | 16.97    | 98.79      | 3     |
4. Conclusions
The FGPUE developed with two (2) types of radial distribution FGM 70-30 and FGM 60-40, generated a rise effect in the values of the E* and the E’, being these greater values in the gradations than in the constituent materials; in addition to obtain greater stability with the increase of the temperature. It was also observed that the values of the E ” and the damping factor tan δ, classify the material as highly elastic and versatile.

It can be concluded that the gradation by layers based on the biomimicry of the IVD, represented with six (6) layers of polyurethane with different Complex modulus and cross-links, permitted to obtain a material for disc-shaped machines elements without introducing bi-material interfaces, which reduces stress and failure concentrators, being very advantageous in industrial applications involving damping and isolation of vibrations, emulating in some mechanical aspects of the human IVD.

References
[1] González-Estrada O A, Leal Enciso J and Reyes Herrera J D 2016 Análisis de integridad estructural de tuberías de material compuesto para el transporte de hidrocarburos por elementos finitos Rev. UIS Ing. 15 105
[2] Besisa D H A and Ewais E M M 2016 Advances in functionally graded ceramics processing, sintering properties and applications Advances in Functionally Graded Materials and Structures (London: InTech)
[3] Valizadeh N, Natarajan S, González-Estrada O A, Rabczuk T, Quoc Bui T, Bordas S P A and Bui T Q 2013 NURBS-based finite element analysis of functionally graded plates: static bending, vibration, buckling and flutter Compos. Struct. 99 309
[4] Bhatnagar N and Srivatsan T 2008 Processing and fabrication of advanced materials- XXII vol 1 (India: I.K. International Pub. House) p 475
[5] Trask R S, Williams H R and Bond I P 2007 Self-healing polymer composites: mimicking nature to enhance performance Bioinspir. Biomim. 2 1
[6] Benyus J M 2002 Biomimicry: Innovation inspired by nature (New Jersey: William Morrow & Company)
[7] Maglic M J 2012 Biomimicry: Using nature as a model for design (Amherst: University of Massachusetts Amherst)
[8] Newell N, Little J, Christou A, Adams M, Adam C and Masouros S 2017 Biomechanics of the human intervertebral disc: A review of testing techniques and results J. Mech. Behav. Biomed. Mater. 69 420
[9] Zhou Z, Gao M, Wei F, Liang J, Deng W, Dai X, Zhou G and Zou X 2014 Shock absorbing function study on denucleated intervertebral disc with or without hydrogel injection through static and dynamic biomechanical tests in vitro Biomed Res. Int. 2014 1
[10] Rodas A 2009 Valores umbrales límite - Techo para levantamiento de cargas (Quito: Universidad San Francisco de Quito)
[11] Campana S, Charpail E, de Guise J A, Rillardon L, Skalli W and Mitton D 2011 Relationships between viscoelastic properties of lumbar intervertebral disc and degeneration grade assessed by MRI J. Mech. Behav. Biomed. Mater. 4 593
[12] Kongpun T and Furukawa M 2014 Characterization of functionally graded polyurethane elastomers Energy Procedia 56 157
[13] Asgharzadeh Shirazi H and Ayatollahi M R 2014 Biomechanical analysis of functionally graded biomaterial disc in terms of motion and stress distribution in lumbar spine International Journal of Engineering Science 84 62