Physical Characterization of Material for the Development of Orthopedic Orthosis for Diabetic Foot

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Abstract: The diabetic foot is characterized by the loss of foot ulcerations and sensitivity. The use of orthopedic orthosis can prevent pathological changes in the diabetic foot. The objective of this study was to characterize materials used for producing orthopedic orthosis: silicone; pre-vulcanized latex of Hevea brasiliensis; Evapod, and Podadur. The Hevea brasiliensis latex material is widely indicated in the literature for biomedical purposes. Physical–mechanical properties were determined (properties of elastic deformation, resistance, durability, lightness, energy absorption, resistance to high temperatures, and chemical composition—ASTM International). In the tensile test, the latex reached 6.02 ± 0.33 MPa, having the best performance among the other materials. In the elastic module, the Podadur stood out, with 28.2 ± 0.89 MPa, compared to silicone with 0.42 ± 0.05 MPa. The most excellent Shore A hardness material was Podadur with 58%. As for the resilience, the Podadur presented a minimum value of 22%, while latex had 63%. Silicone was the densest material, with a density of 1.48 g/cm³, and Evapod and Podadur were the lightest, respectively, at 0.22 g/cm³. In the fluorescence test, the presence of metals was observed in the composition of the four materials. In the specimen test, the presence of metal with no empty cells in its structure. In X-ray diffraction, Evapod, Podadur, and silicone materials presented well-defined crystallographic planes, whereas amorphous behavior characterized latex. Thermogravimetry showed weight loss between 240 and 650 °C in the four materials. In the fluorescence test, the presence of metals was observed in the composition of the four materials. Among the materials studied, the Podadur was the material that stood out, with some good properties for the development of orthopedic orthosis.

Keywords: diabetes; orthoses; diabetic foot; silicone; Podadur; Evapod; latex; rubber tree; Hevea brasiliensis

1. Introduction

Diabetes mellitus is a chronic disease considered a growing global public health problem [1]. It is estimated that, in 2019, diabetes affected approximately 463.0 million people worldwide, and this number will grow exponentially to 700.2 million by 2045 [2]. Diabetes is defined as a metabolic disease characterized by persistent hyperglycemia,
arising from the ineffective production of insulin or in its action, or both mechanisms, generating complications [1].

The most common complication of diabetes is diabetic peripheral neuropathy, which usually gives rise to the diabetic foot. According to the International Working Group on Diabetic Foot (2001) [3], a diabetic foot is defined as an infection, ulceration, or destruction of soft tissues that affects the lower limbs, affecting approximately 40 to 60 million people globally [2].

One of the strategies to avoid diabetic foot complications is related to straightforward measures, such as care for the feet and the use of adapted shoes, and the inclusion of orthopedic orthosis [4,5]. In this context, it is essential to choose the appropriate materials for producing the orthosis to ensure that its use is a success, since each material has particularities that can cause foot changes [4,5]. The term “orthosis” is derived from ortho, which means “to straighten” or “correct.” An orthosis is a brace or another wearable device used to achieve one or more of the following goals: improved mobility, immobilization of an injured part of the body to facilitate recovery, prevention of injuries, correction of biomechanical misalignments, pain reduction and weight-bearing, rehabilitation, and correction of a deformity.

Therefore, the materials need to have characteristics that reduce the pressures imposed on the sole to avoid excessive loads and forces [6], and the ability to absorb energy without deforming the material during the step [7].

Other important properties to be observed in an orthosis are the hardness and stress of rupture since the diabetic individual has reduced foot sensitivity. Thus, the greater the hardness of a material, the greater its resistance, leading to more excellent foot protection [4]. Moreover, if the material presents high values of rupture stress, it may offer the orthosis more resistance, contributing directly to the product’s longevity [8].

According to Cordeiro (2010) [8], the density and capacity to absorb the moisture in the feet are attributes that deserve to be highlighted in the choice of materials for producing an orthosis. In the first case, the lower the density of a material, the more lightness it will offer to the orthosis, giving a smoother and more adaptable footstep. The ability to absorb foot moisture, on the other hand, provides the material with an important characteristic, as it prevents the orthosis from facilitating the proliferation of microorganisms, which can result in opportunistic infections.

Therefore, these aspects justify the increase in research on the subject. The physical, mechanical, and chemical properties suggested in the production of an orthopedic orthosis for individuals with diabetic foot are indispensable for the final success and its applicability [7,8]. The objectives of this work included the physical characterization (properties of elastic deformation, resistance, durability, lightness, energy absorption, resistance to high temperatures, and chemical composition) favorable to the physical and mechanical characteristics of four industrial materials, namely silicone, Evapod, Podadur, and latex—a pre-vulcanized latex extracted from the tree trunk of Hevea brasiliensis—to characterize some materials used for producing orthopedic orthoses for diabetic foot.

2. Materials and Methods

The criteria used for choosing the materials were based on information contained in the literature [8]. The following materials were chosen: silicone (Redelease®, São Paulo, SP, Brazil); pre-vulcanized latex of Hevea brasiliensis (Epoxfiber®, Rio de Janeiro, RJ, Brazil); Evapod (Podaly Palmilhas LTDA ME, Brusque, SC, Brazil); ethyl vinyl acetate foam—Podadur (Podaly Palmilhas LTDA ME, Brusque, SC, Brazil). The pre-vulcanized latex of Hevea brasiliensis is extracted from tree trunks and is an Amazon state natural latex rubber with clinical potential for tissue reparation [4,9]. These materials’ benefits for orthosis include standard industrial production, easy obtention, and low cost. Specific ASTM International rules were adopted to standardize all the tests (astm.org) (accessed on 20 April 2022).
2.1. Tensile Testing

The tensile tests (tension and deformation at rupture) were carried out in a universal testing machine, EMIC model DL3000 (Instron Brasil Equipamentos Científicos LTDA, São José dos Pinhais, PR, Brazil). The methodology used was based on the ASTM D882 [10] standard for thin films. The test bodies (C.P.) were cut to dimensions of 12.6 cm × 1.2 cm (approximately) and adjusted to the claws of the equipment, whose initial separation was fixed at 10 cm. The traction speed was 12.5 mm/minute, and the load cell used was 500 N or 50 kgf. Five C.P.s were evaluated for each test. Due to the composition of the material and its specificities, latex used 10 C.P.s for analysis.

2.2. Shore A Hardness Test

Shore A hardness was tested according to the ASTM D 2240 [11] standard with a Shore A LEP006-2 digital durometer (Woltest Indústria, Comércio, Importação e Exportação LTDA, São Paulo, SP, Brazil) and a thickness gauge with a LEP007 dial indicator (ZAAS brand), São Paulo, SP, Brazil). The obtained C.P. had a minimum thickness of 6.0 mm with a flat and smooth surface. The C.P. was supported on a hard, flat, horizontal surface, where the durometer was kept in an upright position and away from the C.P., with the pressure base parallel to its surface. At each C.P., at least three measurements were made at points at least 5 mm apart and, concerning the edges, at least 12 mm. The 1.0 kg mass was used for tests with Shore A in the upper part of the Shore durometer support. The thickness of the C.P. was within 6.00 ± 7.00 mm. The time for which the pressure base was in firm contact with the C.P. was 1 s. The temperature during the analysis was 23 °C, with 56% relative humidity. We used only 1 (one) C.P. for the tests.

2.3. Resilience Testing

Resilience was performed following DIN 53512 [12]. Measurements were made on the brand’s LEP012 impact resilometer (Maqtest® Automação e Controle Industrial L.T.D.A., Franca, SP, Brazil). For the measurement of C.P., an analog LEP010 caliper (Mitutoyo Sul Americana L.T.D.A., Suzano, SP, Brazil) was used. The C.P. had a thickness of 12.5 ± 0.5 mm and a diameter ranging from 29 to 53 mm. After positioning the C.P. on the fixing plate of the device, the pendulum was released from the horizontal position six times in a row to ensure that it fell in the same place each time. Resilience was measured with the last three shocks for each C.P., using three C.P.s for each sample.

2.4. Density Testing

2.4.1. Pycnometry Test

The pycnometry test was carried out according to the ASTM D 297 [13] standard, with an LEP004 analytical balance (Gehaka, São Paulo, SP, Brazil) and LEP004 muffle furnace (Thermo Scientific, Waltham, MA, USA). A 50 mL pycnometer was used to immerse the C.P. in the liquid. The temperature used during the analysis was 23 °C, and the relative humidity was 55%. The fluid used to determine the specific mass was distilled water. The number of C.P.s used to perform the test was two for each material.

2.4.2. Liquid Immersion Test

The liquid immersion test followed the ASTM D 297 [13] standard, with the LEP004 analytical balance (Gehaka, São Paulo, SP, Brazil). A 1 L beaker was used to immerse the C.P. into the liquid. The specific mass of the C.P. was obtained as a function of the dry weight and wet weight measured on the scale and the specific mass of the fluid used. During the experiment, the temperature was 23 °C, and the relative humidity was 55%. The fluid used to determine the specific mass was absolute alcohol. The number of C.P.s used to perform the test was six. The specific mass was obtained using the following formula: specific mass (g/cm$^3$) = \[\text{fluid specific mass (g/cm}^3\text{)} \times \text{dry weight (g)}]/[\text{dry weight (g) − wet weight (g)}].
2.5. Scanning Electron Microscopy

Scanning electron microscopy analyses were performed, and the C.P. were first assembled in stubs for metallization in gold. Metallization was performed in a metallizer (QT150 ES—Quorum®, Laughton, UK), where the samples were exposed to gold for 10 min at 20 nm. After the previous preparation of the C.P., they were analyzed in the SEM microscope (InspectTM 550-FEI Company, Hillsboro, OR, USA) in scans of 30, 100, 300, and 500 µm.

2.6. Water Absorption Test

According to the ASTM 3575 [14] standard, the water absorption technique was performed. Five C.P.s were used for each material, with dimensions of 50 × 50 mm. Before immersion, the five C.P.s were individually weighed to obtain the dry mass value. Then, the C.P.s were immersed in a container with distilled water. After 24 h of immersion, each C.P. was weighed to quantify the wet mass and dipped again. After 48 h, the test started, and the C.P.s were again removed from the water for subsequent weighing. The water absorption value for either 24 or 48 h was calculated using the following formula: water absorption (kg/m²) = mass (wet) − mass (dry)/surface area of the specimen.

2.7. X-ray Diffraction Test

For configuration in the laboratory, an Xpert Pro M.P.D. (Malvern Panalytical Spectris Company, Almelo, The Netherlands) was used, using CoKα radiation (λ = 0.17889 nm) at 40 kV and 40 mA with parallel beam geometry, and using a hybrid monochromator composed of a mirror and two Ge crystals cut in the direction (220). The height of the beam emerging from the monochromator was 1.2 mm. A 1/4° divergent slot and a Soller slot in the 0.02 rad diffracted beam were used to control axial divergence.

The C.P.s measured in the Xpert Pro M.P.D.—Panalytical were prepared on a zero-background silicon plate whose dimensions were 25 mm in diameter and 2 mm in thickness, containing a cavity with a diameter of 10 mm and depth of 0.2 mm. The diffraction patterns were obtained in the range of 2θ = 10° to 100°, with a step of 0.013° and a total measurement time of 70 min.

Panalytical’s HighScore Plus software [15] (Malvern Panalytical Spectris Company, Almelo, Netherlands) was used to adjust the theoretical curve to the experimental pattern to obtain the width at half height (F.W.H.M.) of the diffraction peaks. This peak width was calculated using the Split-PseudoVoigt function, which considers asymmetries and uses parameters on the left and right sides of the peak. Thus, the width at half height was calculated by the equation F.W.H.M. = F.W.H.M. (left) + F.W.H.M. (right)/2, where F.W.H.M. (left) and F.W.H.M. (right) represent the widths at half height to the left and right of the peak, respectively. In the function of the amorphous structure of latex C.P., it was not possible to perform this quantification by this method. The simulated characteristics of the most intense C.P. peaks were as follows: intensity—Podadur (483), Evapod (610), and silicone (48); position 2θ—Podadur (34.4), Evapod (34.5), and silicone (82.1); F.W.H.M. (degrees)—Podadur (0.32), Evapod (0.27), and silicone (0.43).

According to the Scherrer equation [16], the crystallite sizes are inversely proportional to the width at half the height of the diffraction peaks. Thus, the widths of the most intense peaks presented indicate that the crystallite sizes are of a nanometric order for this family of crystallographic planes, as they are significant peaks.

2.8. Thermogravimetry Test (TGA)

The thermal behavior of the materials was tested using the thermogravimetry method. The tests were performed using the STA 6000 simultaneous thermal analyzer (Perkin Elmer, Waltham, MA, USA) using a heating rate of 25 °C/min to 700 °C under a 50.0 mL/min nitrogen atmosphere.
2.9. X-ray Fluorescence Test

A ZSXMini II X-ray fluorescence spectrometer (Rigaku Corporation, The Woodlands, TX, USA) operating at 40 kV and 1.2 mA with a Palladium (Pd) tube for X-ray fluorescence was used. The analyses were semi-quantitative, with the ability to quantify elements with an atomic number equal to or greater than that of Fluorine to Uranium. The C.P. was placed between two layers of mylar, and this, in turn, was fixed by a cylinder with a diameter of 45 mm and a height of 25 mm. In this way, the C.P. was subjected to radiation.

2.10. Statistical Analysis

The mean ± standard error of the mean was used for the statistical analysis, comparing the four materials. The one-way analysis of variance (ANOVA) was used to analyze the physical and mechanical tests, with the Tukey post-hoc test. The two-way ANOVA was used for the water absorption test, with the Tukey post-hoc test. Statistical significance level of $p < 0.05$ was considered for all tests. The analyses were performed with the GraphPad Prism 7.00 software (GraphPad Software, La Jolla, CA, USA).

3. Results

3.1. Physical and Mechanical Tests

The results of the physical and mechanical tests performed on the different materials are shown in Table 1. Regarding the rupture stress test, latex was statistically different from all materials ($p < 0.0001$) in that it presented a high rupture value. The elastic modulus showed that Evapod and Podadur were significantly different from other materials ($p < 0.0001$). When analyzing the Shore A hardness and resilience, the Podadur demonstrated a high hardness value and a low resilience value. Evapod and Podadur had the lowest values compared to the other materials regarding density.

Table 1. Mechanical and physical tests (mean ± standard error).

| Test                  | Evapod       | Podadur      | Silicone     | Latex         |
|-----------------------|--------------|--------------|--------------|---------------|
| Breaking stress (MPa) | 1.75 ± 0.12  | 2.24 ± 0.13  | 0.52 ± 0.09  | 6.02 ± 0.33  |
| Elatic modulus (MPa)  | 3.15 ± 0.27  | 28.2 ± 0.89  | 0.42 ± 0.05  | 1.35 ± 0.03  |
| Shore A hardness (%)  | 33           | 58           | 40           | NR            |
| Resilience (%)        | 32           | 22           | 43           | 63            |
| Density (g/cm$^3$)    | 0.22         | 0.42         | 1.48         | 0.89          |

* $p = 0.0136$ versus Evapod; ** $p < 0.0001$ versus Evapod; *** $p < 0.0001$ versus Evapod; $¥ p = 0.0007$ versus Podadur; $€ p < 0.0001$ versus Podadur; $£ p < 0.0001$ silicone. One-way ANOVA with Tukey’s post-hoc test. N.R.: no record.

During the test, the specimen was unstable, and each measurement determined a value, while others were not detected, making the tests with latex unfeasible.

3.2. Material Morphology

Figure 1 illustrates the morphology obtained by SEM of the different materials analyzed. Figure 1A,B reveal open and interconnected cells with a well-organized structure. Figure 1C describes poorly delineated and structurally disorganized areas but with the presence of isolated, empty cells. Figure 1D is morphologically characterized by the absence of open cells throughout its structure.
3.3. Water Absorption Test

Table 2 describes the materials’ absorption capacity in water. The measurements at 24 and 48 h showed similar results, where silicone was the material that absorbed the least water compared to the other materials. Evapod and Podadur were the materials with the highest absorption capacity, and Podadur was the material with the most remarkable water absorption capacity concerning Evapod.

Table 2. Water absorption capacity of materials about weight x material.

| Material              | Mean     | 95.00% CI of Diff | p Value |
|-----------------------|----------|-------------------|---------|
| **Initial Weight**    |          |                   |         |
| Silicone vs. Latex    | 207,027  | 182,027 to 232,027| <0.0001 |
| Silicone vs. Evapod   | 265,892  | 239,780 to 292,004| <0.0001 |
| Silicone vs. Podadur  | 267,165  | 241,053 to 293,277| <0.0001 |
| Latex vs. Evapod      | 58,865   | 33,865 to 83,865  | <0.0001 |
| Latex vs. Podadur     | 60,138   | 35,138 to 85,138  | <0.0001 |
| Evapod vs. Podadur    | 1273     | −24,839 to 27,385 | 0.9992  |
| Silicone vs. Latex    | 195,890  | 170,890 to 220,891| <0.0001 |
| Silicone vs. Evapod   | 259,650  | 233,538 to 285,762| <0.0001 |
| Silicone vs. Podadur  | 264,615  | 238,504 to 290,727| <0.0001 |
| Latex vs. Evapod      | 63,760   | 38,759 to 88,760  | <0.0001 |
| Latex vs. Podadur     | 68,725   | 43,725 to 93,725  | <0.0001 |
| Evapod vs. Podadur    | 4965     | −21,146 to 31,077 | 0.9575  |
| **24 h Weight**       |          |                   |         |
| Silicone vs. Latex    | 197,228  | 172,228 to 222,229| <0.0001 |
| Silicone vs. Evapod   | 259,623  | 233,511 to 285,735| <0.0001 |
| Silicone vs. Podadur  | 264,808  | 238,696 to 290,919| <0.0001 |
| Latex vs. Evapod      | 62,395   | 37,395 to 87,395  | <0.0001 |
| Latex vs. Podadur     | 67,579   | 42,579 to 92,579  | <0.0001 |
| Evapod vs. Podadur    | 5184     | −20,927 to 31,296 | 0.9521  |
| **48 h Weight**       |          |                   |         |

* p < 0.0001 versus latex; ** p < 0.0001 versus Evapod; *** p < 0.0001 versus Podadur; £ p < 0.0001 versus Evapod; ¥ p < 0.0001 versus Podadur. Two-way ANOVA with Tukey’s post-hoc test.
3.4. X-ray Diffraction and Thermogravimetry

Figure 2 shows the X-ray diffraction patterns in the different materials. Figure 2A is very similar to Figure 2B, and the amorphous region is present in the range between 20° and 30°, showing three distinct phases: the first of CaCO$_3$, the second of SiO$_2$, and the third of Ca$_2$Ti$_2$O$_5$ and TiO$_2$. This is a phase common to Podadur, CaCO$_3$ (organic phase). Figure 2B shows a CaCO$_3$ phase equal to Figure 2A and two other stages, CaO$_2$ and Ca$_2$Fe(C.N)$_6$. Figure 2C shows two steps, Si$_3$N$_4$ and SiO$_2$. We also observed that the relative intensity between the crystalline peaks and the amorphous behavior is very similar, unlike Evapod and Popadur, where the peaks have a much greater intensity than the amorphous behavior. Figure 2D indicates an amorphous structure. This characteristic is revealed by the projection shown in the profile between 20° and 40°.

Figure 2E shows the results of the thermogravimetry analysis of the different materials. It was found that Evapod and Podadur present two regions of mass loss: the first between 300 and 460 °C, probably reflecting the loss of water trapped in the structure, and a second loss of mass in the region between 430 and 500 °C, probably due to the combustion of organic matter eliminated in the form of CO and CO$_2$. This behavior of Evapod and Podadur is quite similar, possibly due to the similarity of the crystalline structures; see Figure 2A,B. Latex, on the other hand, presents a single region of mass loss, between 300 and 460 °C, probably related to the combustion of the organic part. Silicone presents an area with a slight mass gain in the range of 100 to 200 °C, presumably reflecting the oxidation of some of the crystalline phases; after this, it presents a significant region of mass loss between 240 and 650 °C, which could be related to water loss and the combustion of organic matter.

3.5. X-ray Fluorescence Test

Table 3 describes the chemical composition of the analyzed materials. Latex is the material formed by the most significant number of metallic elements, followed by Podadur and Evapod. The presence of semi-metallic and non-metallic elements and gases in the analyzed materials is likely due to the addition of chemical substances during the material handling process.

| Classification | Element | Symbol | Latex % | Silicone % | Evapod % | Podadur % |
|----------------|---------|--------|---------|-----------|----------|-----------|
| **Metals**     | Silver  | Ag     | -       | 0.30      | -        | -         |
|                | Aluminum| Al     | 8.22    | 0.35      | 0.41     | 0.41      |
|                | Calcium | Ca     | 5.02    | 17.12     | 8.08     | 8.08      |
|                | Chrome  | Cr     | 0.81    | -         | -        | -         |
|                | Iron    | Fe     | 29.94   | 0.21      | 7.26     | 7.26      |
|                | Potassium| K     | 3.48    | 0.22      | 76.33    | 76.33     |
|                | Magnesium| Mg   | 14.18   | -         | -        | -         |
|                | Manganese| Mn   | 0.32    | -         | -        | -         |
|                | Nickel  | Ni     | 0.90    | -         | -        | -         |
|                | Titanium| Ti     | 2.10    | 1.16      | 6.58     | 6.58      |
|                | Zinc    | Zn     | 0.08    | 17.78     | 0.37     | 0.37      |
| **Semi-metals**| Silicon | Si     | 34.12   | 97.88     | 6.68     | 0.70      |
| **Non-metals** | Phosphor| P      | -       | 0.10      | 0.04     | 0.04      |
|                | Sulfur  | S      | -       | 0.15      | 0.06     | 0.06      |
| **Gases and non-metals** | Chlorine | Cl | 0.16 | 1.14 | 0.12 |
Figure 2. X-ray diffraction test and thermogravimetry. a.u. = arbitrary units. (A) Diffraction pattern of Evapod, presenting an amorphous and crystalline characteristic. Most intense peak with 610 counts, $2\theta = 34.5^\circ$ and F.W.H.M. = 0.27$^\circ$. $2\theta$ ranging between 10 and 100 degrees. (B) The diffraction pattern of the Podadur presents an amorphous and crystalline characteristic. Most intense peak with 483 counts, $2\theta = 34.4^\circ$ and F.W.H.M. = 0.32$^\circ$. $2\theta$ ranging between 10 and 100 degrees. (C) Diffraction pattern of silicone, with amorphous and crystalline characteristics. Most intense peak with 48 counts, $2\theta = 82.1^\circ$ and F.W.H.M. = 0.43$^\circ$. $2\theta$ ranging from 10 to 100 degrees. (D) Diffraction pattern of latex, showing its amorphous characteristic. $2\theta$ from 10 to 100 degrees. (E) Thermogravimetry pattern of the analyzed materials.

3.6. Recommendation of Materials for the Development of Orthopedic Orthosis for Diabetic Foot

Table 4 describes the degree of recommendation of the materials for producing orthopedic orthoses based on the physical, mechanical, and chemical analyses. Podadur was the material that stood out the most compared to other materials, having excellent potential to
produce orthopedic orthoses, followed by Evapod and latex. On the other hand, silicone had few positive attributes; thus, it is not recommended.

Table 4. Degree of recommendation for the development of orthopedic orthosis.

|                             | Evapod | Podadur | Silicone | Latex |
|-----------------------------|--------|---------|----------|-------|
| Breaking stress             | *      | **      | *        | ***   |
| Elastic modulus             | **     | ***     | *        |       |
| Shore A hardness            | *      | ***     | **       | NR    |
| Resilience                  | **     | ***     | *        |       |
| Density                     | ***    | ***     | *        |       |
| Morphology                  | *      | *       | ***      |       |
| Water absorption            | **     | ***     | *        |       |
| X-ray diffraction           | ***    | ***     | ***      |       |
| Thermogravimetry            | ***    | ***     | ***      | ***   |
| X-ray fluorescence          | **     |        | *        | ***   |

Degree of recommendation: * Poor; ** Moderate; *** Strong; NR: No record. During the test, the specimen was unstable; each measurement determined a value, and others were not detected, making the tests with latex unfeasible.

4. Discussion

Diabetic foot is an abnormal foot condition that can cause the loss of neural skin tissue, ulcerations, and even lower-limb amputations [2]. Depending on the peculiarities of the patient, the materials may have advantages and disadvantages in specific properties. However, all physical, mechanical, and chemical characteristics present in the materials used in selecting the orthosis are indispensable for their applicability [17]. In this context, the present study analyzed four different materials used to produce orthopedic orthoses for diabetic foot.

The latex composite material presented the highest rupture stress value among all materials—see Table 1—providing the orthosis with high resistance to wear and durability, resisting the demands imposed on the material, a characteristic that directly influences the product’s longevity [7].

Evapod and Podadur were the materials that stood out in terms of the elastic modulus, as presented in Table 1, emphasizing Podadur, which showed a significant difference from the other materials. This property gives the material a greater capacity for elastic deformation, quickly adapting to changes in the environment, which helps in the oscillation changes that the foot undergoes during the step. It is important to note that Evapod and Podadur are materials with the same composition (ethylene vinyl acetate—EVA). The difference between these materials is found in their compaction. Podadur is a more compact material, while Evapod is a non-compact material with perforations throughout its plate, influencing its physical and mechanical properties.

The hardness of the material is a relevant parameter to be analyzed to offer the individual superior foot protection. Podadur showed the highest hardness value—see Table 1—compared to the other materials. The higher the hardness, the greater the product’s ability to resist external damage such as perforation since the diabetic individual has a significant reduction in their foot sensitivity [4]. The combinations of plastazote foam (PLZ), silicone gel (SG), and ethyl vinyl acetate foam (EVA) layers (from top to bottom) are recognized as the best among three-layer insoles. Moreover, the best three-layer insole is more effective in promoting a favorable stress and strain distribution than single-layer insoles, especially in dynamic mode [18].

The decrease in the foot sensitivity of the diabetic individual may result in the absence of the perception of loads imposed on the feet, establishing an overload of localized energy in certain areas. Thus, material resilience plays an essential role in absorbing the energy generated during the step. The lower the resilience values, the greater the capacity of a material to absorb energy [5]. In the present study, it was observed that Podadur was the...
material with the lowest resilience value—see Table 1—with a higher capacity for absorbing energy, which can result in decreased plantar pressure.

The density parameter is another fundamental property to be analyzed when choosing a material for an orthopedic orthosis. The material density depends significantly on its chemical composition, the additives used, and the type of cell present in its structure [8]. This property is directly related to the lightness of the product. The lower the value, the lighter the material. The density values found in the analyzed materials ranged from 0.9 to 1.5 g/cm$^3$ (Table 1). Evapod and Podadur showed the lowest density values, respectively, demonstrating that these materials can give the orthosis more lightness.

According to the International Working Group on Diabetic Foot (2001) [3], autonomic neuropathy, standard in diabetic conditions, leads to a decrease or the total absence of sweat secretion. Foss-Freitas, Marques Júnior, and Foss (2008) [19] report that distal anhidrosis mainly affects the extremities of the lower limbs, which are dried out, creating cracks and fissures, associated with a reduction in thermoregulatory capacity and vasomotor abnormalities.

Suppose that there is no effective perspiration (sweat) in the feet. A material with open cells, such as Evapod (Figure 1A), Podadur (Figure 1B), or latex (Figure 1C), does not show advantages in removing moisture from the feet. However, this characteristic makes these materials favorable in liquid absorption, corroborating the findings in Table 2. It is worth noting that a material that absorbs many liquid types in its structure is more likely to have increased dimensions and weight, with a greater probability of causing surface microfractures and damage, compromising its mechanical properties [20]. As shown in Figure 1D, silicone, on the other hand, has an advantage in its morphological structure concerning the other materials due to the absence of open cells, which favors the absorption of liquid, corroborating the findings in Table 2 and making it a better choice in orthosis production.

The atoms’ spatial ordering in each type of material also directly influences the morphological characteristics of the material. In the present study, it was found through the X-ray diffraction findings that the Evapod, Podadur, and silicone materials (Figure 2A–C) present well-defined crystallographic planes, corroborating their morphological structures, and this may be one of the reasons that some materials have such favorable performance in physical and mechanical tests, as is the case of Evapod and Podadur [21].

Regarding thermogravimetry (Figure 2E), it is observed that the analyzed materials can withstand high temperatures before beginning their loss of mass or water; this is not a problem when producing an orthosis since the materials on the market present the characteristic of becoming moldable at temperatures between 50 and 80 °C, which gives these materials the ability to become resistant to ambient temperatures. Thus, the four analyzed materials have thermal characteristics favorable to their clinical applicability [22].

The standard quality for a processed product is necessary to observe a material’s chemical composition, especially the verification of the heavy metal content [23]. It can be seen in Table 3 that all analyzed materials have many metals in their composition. Metals are widely used as a structural element to replace, reinforce, or stabilize rigid fabrics, which are generally subjected to tensile and compression loads [24].

According to Groover (2014) [25], metals are characterized by their properties of ductility, malleability, and good electrical and thermal conductivity. Latex was the material formed by the most significant number of metallic elements, which is the reason that this material performed well in the tensile test; see Table 1. This was followed by Podadur and Evapod, which performed well in the hardness tests, Shore A test, and traction test. The presence of semi-metallic and non-metallic elements and gases is due to the addition of chemical substances during the material handling process.

The diabetic foot requires special attention. The proper distribution of weight on the feet is essential in preventing and treating injuries. Orthoses are useful tools in the care and rehabilitation of these patients, as indicated by the American Diabetes Association, in the presence of neuropathy, regardless of the degree of involvement. Therefore, changes in the
processes allow the better distribution of the plantar load, relieve pressure points, which are especially harmful to diabetic feet, reduce the likelihood of pressure ulcers forming, and aid in wound healing by clearing wounded areas in cases of injured patients [14–18]. The chosen materials were individually studied and characterized. However, using material multilayers could improve the cited advantages instead of a single monolayer orthosis.

The results showed that each material has its specificities (Table 4), demonstrating its indication for different situations. Material characterization under the International Standard Test Methods is essential for optimizing orthopedic orthoses. The minimum material requirements and the professional’s expertise can produce a better product, tailored to the diabetic patient’s particularities.

5. Conclusions

Podadur was the material that presented the best properties of elastic deformation, resistance, durability, lightness, energy absorption, resistance to high temperatures, and chemical composition favorable to its physical and mechanical characteristics. Podadur was the material that stood out the most compared to the other materials, with good potential for the production of an orthopedic orthosis, followed by Evapod and latex. The Hevea brasiliensis latex material is widely used in the literature for biomedical purposes. The work perspectives include diabetic human tests for future clinical possibilities.

As demonstrated throughout the present study, certain materials are indicated for a particular environment and medical purpose. Thus, even if no material demonstrated the desired characteristics, this study reveals relevant properties throughout the selection and characterization of materials that can all be useful in orthopedic orthoses.

Author Contributions: Conceptualization, F.F.U.S.J. and V.M.C.; methodology, A.M.d.L.B., E.B.D. and J.E.R.M.; validation, A.N.M.F., J.W.G.D., D.F.D., M.d.F.R. and R.M.d.F.; writing—original draft preparation, R.M.d.F. and S.M.d.S.F.; writing—review and editing, K.C.L.d.S., F.F.U.S.J. and V.M.C.; supervision, F.F.U.S.J. and V.M.C. All authors have read and agreed to the published version of the manuscript.

Funding: The A.P.C. was funded by the Coordination of Superior Level Staff Improvement—Renorbio Proap/Capes.

Acknowledgments: Biomass Technology Laboratory at EMBRAPA—Brazilian Agricultural Research Corporation; Polymer Testing Laboratory at SENAI/FIEMG—National Service for Industrial Learning/Federation of Industries of the State of Minas Gerais; Analytical Center of the Federal University of Ceará; X-ray Laboratory of the Physics Department of the Federal University of Ceará; FUNCAP—Cearense Foundation to Support Scientific and Technological Development; CAPES—Coordination for the Improvement of Higher Education Personnel; CNPQ—National Council for Scientific and Technological Development.

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

References

1. Sociedade Brasileira de Diabetes. Diretrizes da Sociedade Brasileira de Diabetes 2019–2020. 2019. Available online: https://www.diabetes.org.br/profissionais/images/DIRETRIZES-COMPLETA-2019-2020.pdf (accessed on 20 April 2022).
2. International Diabetes Federation. Diabetes Atlas de La FID. 9th ed. 2019. Available online: https://diabetesatlas.org/upload/resources/material/20200302_133352_2406-IDF-ATLAS-SPAN-BOOK.pdf (accessed on 20 April 2022).
3. Ministério da Saúde. Manual do Pé Diabético. Estratégias Para o Cuidado da Pessoa com Doença Crônica. Brasília-DF, Brasil. 2016. Available online: http://www.as.saude.ms.gov.br/wp-content/uploads/2016/06/manual_do_pe_diabetico.pdf (accessed on 20 April 2022).
4. Guerra, N.B.; Pegorin, G.S.A.; Boratto, M.H.; Barros, N.R.; Graeff, C.F.O.; Herculano, R.D. Biomedical applications of natural rubber latex from the rubber tree Hevea brasiliensis. Mat. Sci. Eng. C 2020, 126, 112126. [CrossRef] [PubMed]
5. Oliveira, A.P. Avaliação e Seleção de Materiais para Ortóteses Plantares. 2013. 96f. Master’s Thesis, Mestrado em Engenharia de Materiais—Universidade do Minho, Escola de Engenharia, Campus de Azurém, Guimarães, Portugal, 2013.
6. Faulí, A.C.; Andrés, C.L.; Rosas, N.P.; Fernández, M.J.; Parreño, E.M.; Barceló, C.O. Physical Evaluation of Insole Materials Used to Treat the Diabetic Foot. J. Am. Podiatr. Med. Assoc. 2008, 98, 229–238. [CrossRef] [PubMed]

7. Callister Júnior, W.D. Fundamentos da Ciência e Engenharia de Materiais, 2nd ed.; Gen, LTC: Rio de Janeiro, Brazil, 2006; p. 160.

8. Cordeiro, G.G. Caracterização Físico-Mecânica de Materiais Utilizados em Palmilhas para Diabéticos. 2010. 59f. Master’s Thesis, Mestrado em Engenharia Biomédica—Pós-Graduação em Bioengenharia, Universidade do Vale do Paraíba, São José dos Campos, São Paulo, Brazil, 2010.

9. Cunha, J.A.; Carneiro, M.R.A.; Souza, K.C.L.; Santos Júnior, F.F.U.; Cecatto, V.M. Biomaterials Characterization for Orthopedic Orthoses: A Systematic Review. J. Mater. Sci. Nanotechnol. 2019, 7, 101.

10. Rosa, S.S.R.F.; Rosa, M.F.F.; Marques, M.P.; Guimarães, G.A.; Motta, B.C.; Macedo, Y.C.L.; Inazawa, P.; Dominguez, A.; Macedo, F.S.; Lopes, C.A.P.; et al. Regeneration of diabetic foot ulcers based on therapy with red L.E.D. light and a natural latex biomembrane. Ann. Biomed. Eng. 2019, 47, 1153–1164. [CrossRef] [PubMed]

11. ASTM D 882. Standard Test Method for Tensile Properties of Thin Plastic Sheeting. Available online: https://www.astm.org/d0882-18.html (accessed on 20 April 2022).

12. ASTM D 2240. Standard Test Method for Rubber Property—Durometer Hardness. Available online: https://www.astm.org/d2240-15r2.html (accessed on 20 April 2022).

13. DIN 53512. Determining the Rebound Resilience of Rubber Using the Schob Pendulum. Available online: http://www.ydtest.com/uploadfile/DIN%2053512-2000.pdf (accessed on 20 April 2022).

14. ASTM D 297. Standard Test Methods for Rubber Products—Chemical Analysis. Available online: https://www.astm.org/d0297-21.html (accessed on 20 April 2022).

15. ASTM D 3575. Standard Test Methods for Flexible Cellular Materials Made from Olefin Polymers. Available online: https://www.astm.org/d3575-20.html (accessed on 20 April 2022).

16. Degen, T.; Sadki, M.; Bron, E.; König, U.; Nénert, G. The Hidhscore Suite. Powder Diffraction; Cambridge University Press: Cambridge, UK, 2014; Volume 29, pp. S13–S18.

17. Holzwarth, U.; Gibson, N. The Scherrer Equation versus the ‘Debye-Scherrer equation’. Nat. Nanotechnol. 2011, 6, 534. [CrossRef] [PubMed]

18. Ghassemi, A.; Mossayebi, A.R.; Jamshidi, N.; Naemi, R.; Karimi, M.T. Manufacturing and finite element assessment of a novel pressure reducing insole for Diabetic Neuropathic patients. Australas. Phys. Eng. Sci. Med. 2015, 38, 63–70. [CrossRef] [PubMed]

19. Foss-Freita, M.C.; Marques Júnior, W.; Foss, M. Neuropatia Autonômica: Uma Complicação de Alto Risco no Diabetes Melito Tip. Arq. Bras. Endocrinol. Metabol. 2008, 52, 398–406. [CrossRef] [PubMed]

20. Raymundo, E.A.; Ribeiro, R.B.; Carvalho, E.F.; Domingues, B.S.M. Analysis of water absorption in polymeric composites reinforced with natural fibers. Cadernos UniFOA 2012, 7, 23–28.

21. Melo, M.E.R.; Rivera, M.H. Estructura de sólidos amorfos. Ingenierías 2000, 3, 7–14.

22. Wang, S.; Mark, J.E.; Erman, B.; Fakirov, S. Mechanical properties of thermoplastic elastomers of poly (butylene terephthalate) and poly (ethylene glycol) in a bending deformation. J. Appl. Polym. Sci. 1994, 51, 141–145. [CrossRef]

23. Note for Guidance on Specifications: Test Procedures and Acceptance Criteria for Biotechnological/Biological Products (Cmpn/Ich/365/96). Available online: https://www.ema.europa.eu/en/human-regulatory/research-development/scientific-guidelines (accessed on 20 April 2022).

24. Poinern, G.E.J.; Brundavanam, S.; Fawcett, D. Biomedical Magnesium Alloys: A Review of Material Properties, Surface Modifications and Potential as a Biodegradable Orthopaedic Implant. Am. J. Biomed. Eng. 2012, 2, 218–240. [CrossRef]

25. Groover, M.P. Introdução aos Processos de Fabricação; Editora LTC: Rio de Janeiro, Brazil, 2014; 758p.