Experimental Study of Loaded Foams During Free Fall Investigation and Evaluation of Microstructure

Noureddine BOUMDOUHA (✉ boumdouhanoureddine@gmail.com)
Polytechnic Military School (EMP)  https://orcid.org/0000-0002-8070-490X

Zitouni SAFIDINE
Military Polytechnic School

Achraf BOUDIAF
Polytechnic Military School (EMP)

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Experimental study of loaded foams during free fall investigation and evaluation of microstructure

BOUMDOUHA Noureddine*a, SAFIDINE Zitouni b, and BOUDIAF Achraf a

a Materials Engineering Laboratory, Military Polytechnic School, BP 17, Bordj El Bahri, Algeria
b Macromolecular Chemistry Laboratory, Military Polytechnic School, BP 17, Bordj El Bahri, Algeria
E-mail of the corresponding author: boumdouhanoureddine@gmail.com

Abstract

We aim to maintain as much control as possible over the development of the microstructure during the manufacture of polyurethane foam with a certain density. As a result, the finished product may not contain the required characteristics for the shock absorber used. That is why polyurethane foam loaded with zinc oxide and silica must be able to sustain the cellular structure and strengthen it. Mechanical characterization was carried out utilizing a dynamic drop impact test conducted on locally developed and constructed equipment. Polyurethane foams’ mechanical properties are highly reliant on their density, cell structure (size and shape), and the fraction of open or closed cells. Within the cell structure, the foam may be directed preferentially. Following that, Raman spectroscopy and SEM investigation were used to visualize the semi-opened cells of the cellular polymer. The cellular polymer appears to possess permanent, regular cellular structures with a high degree of reversibility in terms of overlap.

Keywords: Polyurethane foams, shock absorber, drop impact, Raman spectroscopy, SEM

1. Introduction

Polymer foam is a two-phase structure with randomly scattered gas bubbles in a polymer matrix. This structure has several advantages, the most essential being base density, as reduced weight is becoming increasingly important in many enterprises due to new environmental constraints.[1][2] Polymer foams also provide excellent thermal and acoustical insulation, along with excellent energy dissipation and impact absorption. [3] For instance, in automobiles, the control panel but moreover,
generally, side panels contain a significant amount of polymeric foam to protect individuals in case of accidents. [4] Packaging is also a significant sector, where substances with sufficient impact dampening ability are necessary to prevent product damage during travel. [5] Aside from the above industries, polymer foam is used in sports equipment such as apparel and sports matting. For instance, polymer foam shoe soles reduce stress on runners’ knee joints,[6][7], and racing protection gear could save lives. Jumping, martial arts, and gymnastics also use polymer foam sports mats to reduce the impact on the player when landing to avoid sports injuries. [8] The most generally used testing for polymeric foam impact damping is dropping testing for the influence of weight, in which an object of a certain mass and form is dropped out of a height around with a test sample. The product's impact energy and impact dampening capabilities may be estimated from the collision force or velocity. [9] A solid support is used when the weight bounces from the sample, whereas assistance with a hole is used when the specimen is penetrated by way of the striker. [10] The decent support test is more relevant in the manufacturing of athletic products and packaging because the pressures on the foams better reflect actual use.

The result of this form of drop weight experimental study is represented on the cushioning curve in use by package designers.[11] Several sport-specific criteria require such a rating. [12] As a result, it's impossible to compare goods for different applications because the conditions for each activity vary. [12] Beyond the test circumstances, the falling weight's form impacts the test outcomes. On closed-cell PMI (Polymethacrylimide) foam with a certain density of 51 and 111 kg/m³, Flores-Johnson et al. [13] Demonstrated this. Gilchrist Mills and 20 observed that various foam shapes give complete protection against diverse items.

Polyurethane foam products are used in a variety of sectors and by researchers throughout the globe. The whole skeleton is made up of strong struts and networks of cells, with gas vacuoles interspersed throughout the structure. A high degree of porosity, low weight, and superior crushability
are characteristics of polyurethane foams. The term "cell" is often used to refer to the smallest building component in a structure. Struts but also walls are used to construct the boundaries and surfaces of foam cells. The distribution of solid material inside the cell walls is influenced by the geometry of the cells and the packing method used to create them. Because of the rising nature of polyurethane foam, cells are more stretched in the foaming rising direction than in the other directions, resulting in mechanical anisotropy in the polyurethane foam [14]. The ultimate characteristics comprising cellular solids that are reinforced are impacted by the type of charge used and the amount of loading applied [15]. The third parameter in Mello & colleagues' approach [16] is the particle size and surface state, followed by dispersion plus filler concentration.

The usage of functional fillers in polyurethane foams is increasing regularly, fillers allow for the use of a broader range of plastic materials that are often associated with polyurethane foams. Polyurethane has been successful to enhance the polymers sector because of the use of fillers. It is more expensive to produce polyurethane when the availability of oil and gas is in short supply. Fillers minerals are plentiful, resulting in a greater number of polymers. Filling and other additions enable the development of formulas that exceed the competition. Fillers can impact foam in many ways. They can nucleate gas bubbles with polymer crystallization, and they can slow down chemical reactions, including gas production processes. [17][18] Select foam materials with caution. Foam effectiveness is often pursued even if advantages are expected.

Some polymer foam dynamic mechanical studies examine the impact on the foam density is the amount of air contained within the foam cells. It is similar to foams with closed cells in that the gas in cells compresses, enhancing the foam's shock-absorbing ability (Lopez Gonzalez. [19]). (A gas-phase must travel a long distance to traverse a foam.) Their research connected rebounded polyurethane foams' air permeability to shock absorption. According to certain research, non-uniform density functionally
grading foams can increase energy absorption. Uneven foams may absorb more energy. [20][21] Despite significant research, no conclusive findings have been found.

Various publications compared foam densities. They evaluated [22][2][23]. Relative density microcellular polyvinyl chloride foams, as per ASTM D4226. The two correlated linearly. Our prior polyurethane foam research demonstrated a power-law relationship between density with physical characteristics. E. Linul & al. [24] Discovered that foam density affects the mechanical properties more than load direction. These experiments used closed-cell; stiff polyurethane foams available in a variety of densities of 41–160 kg/m$^3$. Foam density is also important, although seldom studied. Briody & Conor [25] researched polymeric foams in various thicknesses, but the samples' densities varied, making conclusions on thickness difficult to make. Our research looks at the relationships between foam thickness also polymer foam impact damping. PU foam densities and mechanical recovery were examined of our laboratories are important in the sports equipment and packaging sectors. [26] The main material in many steel-polymer hybrid sandwich formations [27] is commonly polyurethane foams.

2. Experimental methods

2.1. Polyurethane foam synthesis

Polyurethane foam was fabricated a constant with a polyol weight ratio (50 wt.%). We add different proportions mixture of Catalyst BDMAEE, surfactants Silicone, Dichloromethane, Glycerin, Silicone, and PEG that are mechanically moved for 60 seconds to ensure the full mixing. Then, the PMDI (30 wt. %) was additional in a corresponding NCO/OH ratio of 1.1 (OH calculations accounted for both polyols as well as their water content). The system used to be again mechanical agitated for 15 s and then permitted to rise reinforced and packed foams were obtained, up to 5%, 10%, and 15% by
weight of Silica and Zinc Oxide, the inorganic matter added before MDI. Summary of filler properties used in table 1.

**Table 1: Characteristics of the used filler**

| Fillings      | Density (g/cm³) | Mohs Hardness | Aspect Ratio/Shape | Mean Size (µm) |
|---------------|-----------------|---------------|--------------------|----------------|
| Silica        | 1.9-2.1         | 5.5           | ~1                 | 0.005-0.1      |
| Zinc Oxide    | 5.6             | 4.5           | ~1                 | 0.05-10        |

Manufacturing PU foam in free expansion mode at atmospheric pressure using a 300 ml reactor and mixing the reaction mixture with a mechanical stirrer at 2500 rev/min in figure 1.

**Figure 1.** Production steps for polyurethane foam.

Polyurethane foam is made up of numerous components and two simultaneous processes. The polyurethane synthesis process happens when urethane isocyanate and polyol are mixed, as indicated in equations (1), (2), and (3).

\[
R\cdot\text{NH}_3 + \text{O} = \text{C} - \text{Cl} \xrightarrow{} R\cdot\text{N}=\text{C}=\text{OH}^+ + 2\text{H}\cdot\text{Cl} \tag{1}
\]

\[
R''\text{N}=\text{C} - \text{O} + R\cdot\text{OH} \xrightarrow{} R''\text{NH}\cdot\text{C}=\text{O}\cdot\text{R} \tag{2}
\]
CO$_2$ or supplementary reactive substances evaporate during the process to give extra gases into the liquid polyurethane. They are produced by reacting an isocyanate with mobile hydrogen groups. Because polyurethane is not entirely polymerized, this exothermic process must be combined with gas evolution to create cellular materials.

As previously stated, density affects foam expansion after gas release [28]. Slowly, it decreases, accumulating mass towards the block's base. The particles of Zinc Oxide act as colloidal particles, encouraging the creation of additional bubbles, and this appears to rise with filler content. Increasing viscosity appears to impede cell growth [19,20], lower concentration foams allow for easier cell growth, resulting in a lower final foam density [29]. The vacancy percentage and filling content impact foam density [30]. With its higher density than ordinary polyurethane, zinc oxide could enhance final foam density. The ultrasonic cavitation disperses the small particles into a polyurethane, as this technique has been demonstrated to be successful in creating a homogenous dispersed of tiny particles [21]. The amalgamation was then exposed to ultrasonic cavities by use of an ultrasonic horn with a high-intensity (20 kHz, Ti-horn, 100 W/cm$^2$) mixing 40 minutes at 60 percent amplitude to achieve a homogenous dispersion. To minimize overheating throughout sonication, outside cooling is used by immersing the mixed flask in a thermostat solution at around 1 °C for the length of the ultrasonic applications. In step 02, component A is mixed with part B at a rate of 47-50 to use a mechanical drive at 2500 rpm for roughly 30 seconds. An aluminium mold is warmed on the inside of the oven to around 50 °C before the combination is poured, and then in step 03, in the mold, the substance is poured, as well as maintained inside the ovens at 38.7 °C for 24 hours for healing. Finally, the foam is pulled out of the mold to prepare the sample for testing.
The density of foams was calculated as the weight-to-volume ratio of a cylinder sample polyurethane foam. The sample weight was the preciseness of about 0.001 g, as well as the linear dimensions, which had been 10 cm in diameter, and ~1 cm in height. Each sample has at least six replicated specimens. As previously stated, density affects foam expansion after gas release [17]. Slowly, it decreases, accumulating mass towards the block's base. The particles Zinc Oxide act as colloidal particles, encouraging the creation of additional bubbles. Furthermore, this appears to rise with filler content. Increasing viscosity appears to impede cell growth. Lower concentration foams allow for easier cell growth, resulting in lower final polyurethane foam density [31]. The vacancy percentage and filling content impact foam density [32]. With its higher density than ordinary polyurethane, zinc oxide could enhance final polyurethane foam density. Additives, stabilizers, and adjuvants modify the property of PU foam. The following table 2 lists polyurethane foam additives:

Table 2. Quantity of charges of polyurethane foams formulation (in wt. %)

| Material         | PU_01 | PU_02 | PU_03 | PU_04 | PU_05 | PU_06 |
|------------------|-------|-------|-------|-------|-------|-------|
| Polyol (wt. %)   | 50    | 50    | 50    | 50    | 50    | 50    |
| Glycerin (wt. %) | 4.36  | 2.22  | 2.14  | 4.23  | 2.28  | 1.06  |
| Dichloromethane (wt. %) | 1.3 | 1.28 | 0.32 | 1.06 | 1.31 | 0.90 |
| Silicone (wt. %) | 3.83  | 2.07  | 1.02  | 4.54  | 2.24  | 1.16  |
| PEG (wt. %)      | 3.25  | 1.16  | 0.22  | 3.57  | 2.39  | 1.11  |
| Catalyst BDMAEE (wt. %) | 2.26 | 3.27 | 1.3 | 1.6 | 1.78 | 0.77 |
| Silica (wt. %)   | 5     | 10    | 15    | 0     | 0     | 0     |
| Zinc Oxide (wt. %) | 0   | 0     | 0     | 5     | 10    | 15    |
| PMDI (wt. %)     | 30    | 30    | 30    | 30    | 30    | 30    |

2.2. Drop weight tests

Impact testing was conducted according to the recommendations of the NF EN ISO 6603-2 standard. For these dynamic tests, the free drop weight of weight is used without initial velocity on a specimen placed at its base. It is equipped with a steel impactor having a square shape. The weight's total mass drop weight is 5 kg and the maximum drop weight height is 1.20 m. The latter is equipped
with a sensor piezoelectric force type PCB 203B, with an acquisition card whose role is to bind the sensor with the digital oscilloscope with a bandwidth of 200 MHz, which is sufficient given the test time and a screen color and a USB input for data backup, to recover the forces exerted during the impact tests as a function of time. These measures are used in the analysis of the evolution of the strength and duration of impact. The configuration of the test is illustrated in figures 7, and 8 in supporting information (SI).

The cylindrical specimen is about 10 mm long and 10 cm diameter prepared by a special mold for preparing different dimensions of the samples to drop weight tests, to maximize the free drop weight contact area. The specimen is free during an impact, according to Standard AITM 1-0010 (Table 3).

Table 3. Characteristics of drop weight tests.

| Test  | Thickness (mm) | Density (g/mm³) | Impact velocity (ms⁻¹) | Deformation speed (s⁻¹) |
|-------|----------------|-----------------|------------------------|------------------------|
| PU_1  | 14             | 0.40            | 0.87                   | 0.23                   |
| PU_2  | 12             | 0.15            | 1.9                    | 0.23                   |
| PU_3  | 10             | 0.20            | 2.4                    | 0.24                   |
| PU_4  | 15             | 0.30            | 3.2                    | 0.25                   |
| PU_5  | 13             | 0.25            | 3.4                    | 0.24                   |
| PU_6  | 11             | 0.35            | 3.8                    | 0.24                   |

After the preparation, we cut the samples by the rotation of the cutting tool, on the one hand, and the advance of the workpiece on the other hand. The machine is equipped with numerical control, to realize all types of even complex forms. The impact strength and shape of the falling weights were varied during the test (Table 4). We concentrated on the three following mechanical factors while evaluating the results: Energy absorbed during an impact E by %, force maximal mostly on weight F by kN, foam deformation maximum p by mm, as well as impact time t by ms.

Table 4. Conditions for the impact tests with falling weights

| Property                  | Parameters for testing |
|---------------------------|------------------------|
| Falling weights' geometry | Cylinder               |
| Weight loss mass          | 5 kg                   |
| Diameter of falling weight | 50 mm |
|---------------------------|-------|
| The kinetic energy of impact | 20.26 to 41.46 J |
| Height of the drop | 1.20 m |
| The temperature used in testing | 24 °C |

The free drop weight test is used for fillings impact with a stacking sequence. To obtain some impact energy $E_{\text{impact}}$, the potential energy of the impactor is transformed into kinetic energy. The initial distance "H" between the specimen's top surface and the end of the impactor is calculated by the equation (4):

$$H = 1.1 \frac{E_{\text{impact}}}{g \cdot M_{\text{impact}}}$$  \hspace{1cm} (4)

Where $g$ is gravity = 9.81 m/s². The mass of the impactor "$M_{\text{impact}}$" is 5 kg while factor 1.1 is used to compensate for the losses occurring during the test, such as the friction between the guide tube and the assembly of drop weight.

For the acquisition of signals, a digital oscilloscope is used (Figure 8 in SI). For each input signal, a particular voltage range is set. The test is very fast, it has a broad frequency range. Thus, the frequency range of the acquisition system is set at its maximum of 200 kHz and with each $\Delta t = 0.005$ ms the values are recorded. This interval is very short (a few milliseconds), so a trigger, associated with the signal of the force, is used for signal recording. When a certain threshold is exceeded, the data backup is performed. The acquisition system is also able to save pre-trigger data, so all relevant data is available.

The test can be analyzed with the data collected during the impact. The first parameter to be determined is the impact force acting simultaneously on the impactor and the specimen. The force sensor delivers a voltage that is equal to the force in KN, $1V = 1KN$.

2.3. Raman spectroscopy
Raman spectroscopy is used in conjunction with other techniques, to infrared spectrometry and is utilized for the organic and inorganic characterization of polymers and pigments [33][34]. The Raman spectrum generally shows peaks whose Raman offsets by the wavelength differences with the laser excitation light, which characterize the vibration frequencies of the atoms in the molecules present.

Raman spectroscopy is caused by the absorption of photons at a certain frequency and the subsequent emission of photons at a different frequency by a diffusion phenomenon at a frequency that is greater or lesser. The variation of scattered photon scattering either by gaining or losing energy results from the vibratory and rotational movement of the molecules in the sample [35][36].

For the Raman characterization, we have used a foreman 685-2 Foster and freeman model spectrometer, driven by the Form 685-2 software, with a laser diode emitting red light with a wavelength of 685 nm. Raman offsets are determined in the range 400-2000 cm\(^{-1}\). The acquisition parameters used are as follows: 532 nm green laser with a power of 1 %, the objective of the x50 microscope, spectral range in wavenumber from 100 to 3200 cm\(^{-1}\), exposure time 10 sec, 3 accumulations for each spectrum.

2.4. Scanning Electron Microscopy (SEM)

SEM was utilized to image reinforced and unreinforced foams. Small foam samples (average height) were cut with a small blade and cryo-fractured (fragile) in nitrogen gas. Gold sputter-coated samples Philips type JEOL JSM 5800 scanning electron microscopes operating at 15 kV put to utilize. We calculated relative densities in (formula 5) and also the extent of the expansion using SEM images. Additionally, sample density (formula 6). Our next steps were to compute cell density (formula 7), nucleation (formula 8), then average thicknesses (formula 9) [37].
\[
\rho_{rel} = \frac{\rho_{foam}}{\rho_{solid}} (-) \tag{5}
\]

\[
\phi = \frac{1}{\rho_{rel} (-)} \tag{6}
\]

\[
N_C = \left(\frac{n}{A}\right)^3 \text{ (cells/cm}^3\text{)} \tag{7}
\]

\[
N = N_C \times \phi \text{ (cells/cm}^3\text{)} \tag{8}
\]

\[
\delta = \left(\sqrt[3]{\phi} - 1\right) \times l \text{ (\mu m)} \tag{9}
\]

\[
l = \sqrt[3]{\frac{\phi - 1}{N}} \times 10^4 \text{ (\mu m)} \tag{10}
\]

Where the proportional density is denoted by \(\rho_{rel}\). The polyurethane foam’s density sample is given by \(\rho_{foam} \text{ (kg/m}^3\text{)}\). The density of that strong substance \(\rho_{solid}\) to foaming is 916 (kg/m\(^3\)). The magnitude of the expansion is represented by \(\phi\). The density of cells is denoted by \(N_C \text{ (cell/cm}^3\text{)}\). The quantity of cells between SEM pictures is denoted by \(n \text{ (cells)}\). \(A \text{ (cm}^2\text{)}\) denotes the area of the specimen that has been examined. \(N \text{ (cells/cm}^3\text{)}\) is the density of nucleation. \(\delta \text{ (\mu m)}\) is indeed the mean average thickness of a specific material of the cell wall, also \(l \text{ (m)}\) is the cell size average.

The density of cells indicates the number of cells contained in a particular volume cube, as measured by the cell count identified in the identical region of the scanning electron microscope picture. The thickness of the cell wall we required to know the mean average cell size (formula 10), which is
estimated in two ways: with SEM images, utilizing picture analysis software, also from Chul34, presumptuous a homogenous cell structure and treating the cells cubes.

3. Results

III.1. Characterization of a Polyurethane Foam by drop weight test

The drop-weight experiment is a dynamic validation test, particularly about the material behavior laws. The stress results curves measured as a function of the crushing of the sample (obtained by processing the impactor displacement signal). For a better reading, the data are presented in absolute value. The piezoelectric sensor has a sensitivity of 56.2 mv per 1 KN, hence the need to process the results obtained from the oscilloscope by Excel to obtain the data. The actual curves of the force's development as a function of time.

Figure 2 represents the time-dependent evolution of the impact force for six impact energies, obtained on six samples of the polyurethane foams. It can be seen that for impact energies lower than 15 J, these curves can be assimilated to a sinusoidal shape, two critical points can be distinguished, $F_0$, the second is the maximum force of the impact recorded by the force sensor noted $F_{max}$ is proportional to the initial potential energy or we find a value of 15196 N as the maximum value for the energy of the PU drop weight test PU_03 and 13959 N for PU_06, and about 13252 N for the energy drop weight test PU_02, and about 10425 N for the energy test PU_05, and about 9011 N for the energy test, and 4594 N for PU_01, this is explained by the high kinetic energy during the impact which generates a significant impact force compared to the low energies. We note that the strength of samples adsorption to the result is connected to the number of fillers in the polyurethane foam matrix, where it was found that samples PU_03 and PU_06 (15 in wt.%) have the largest energy. We also note that the effect of silica fillers is greater than that of zinc oxide fillers.
The variation of the force of impact is shown as a function of the displacement. Until a displacement at the beginning of the application of the force on the sample, the force increases linearly with the displacement of the impactor. The stiffness of the polyurethane foam is high. The rigidity of the specimens decreased to around 1500 N/ms. The temporal evolution of the energy transmitted by the impactor to the polyurethane foams, during the impact test, is illustrated in figure 2. We can note that the energy of the foam increases to a maximum value equals to the kinetic energy. Based on the first results of the impact tests (force-time curves) associated with the visual inspection of the impacted samples. The different energy and the corresponding velocities are presented in table 5.

**Table 5:** Impact forces and corresponding velocities for specimens

| Samples     | PU_1 | PU_2 | PU_3 | PU_4 | PU_5 | PU_6 |
|-------------|------|------|------|------|------|------|
| Thickness (mm) | 14   | 12   | 10   | 15   | 13   | 11   |
| Max Force (N)   | 9011 | 13252| 15196| 4594 | 10425| 13959|
| Max Deformation (mm) | 13.1 | 11.08| 9.02 | 14.06| 12.07| 10.11|
| Absorbed energy % | 64   | 66   | 69   | 62   | 63   | 65   |
| Duration of impact (ms) | 14.05| 12.08| 10.07| 15.06| 13.04| 11.09|
Table 5 shows that the test piece PU_3 has better resistance to impacts concerning the rest of the samples. From the impact velocity values, it is possible to estimate that, theoretically, the initial deformation velocities localized under the impactor (here we consider the rate of deformation of the initial point the extent to which the impactor comes into touch with the sample, thus located on the axis of symmetry of the impactor) are $\dot{\varepsilon}_0 = 175 \text{ s}^{-1}$ for a drop height of 333 mm.

Figure 2 shows that, for the tests carried out, the impact velocities had only a small influence on the stress/crush curves obtained, a consistent result has given their re-strewed variation range. However, the results presented are to be taken with great care for crushing greater than 10 mm, i.e. More than 33 % of crushing. Indeed, given the variability observed in the results, it seems that the relevance of the proposed curves is no longer acquired.

The results indicate that the time of impact differed about the sample thickness, with the influence of density, becoming more important above 10 mm, as greater density foams are much less distorted in comparison to their thickness, resulting in a shorter period of impact. It can also be said that the thickness of the foam greatly affects the shock-absorbing capacity, because in the case of foam with a thickness of 10 mm, the maximum force is 15196 N with a density of the foam material 0.2, while for foam with a thickness of 15 mm this value has decreased to 4594 N.

The maximum force data are summarized in figure 3, the energy absorbed, maximum stress, and impact's duration. Since the findings from the 10-15 mm-thick specimens were already approaching the accelerometer measurement limit, we examined foams of different thicknesses as we performed four tests per sample.
Figure 3. The results of the drop weight effect test are based on thickness. Energy absorbed (a); Maximum strength (b); Maximum deformity (c); The impact's duration (d).

The shock test results showed that the shock absorption capacity is principally affected by the thickness of the foam, whereas the absorbing of energy is mainly affected by the density of the foam.

The varied cell architectures and deformation rates of the various foam densities explain the variations in impact damping capabilities. These foams smaller cells with thicker walls making them stiffer and more load resistant foams of lower density. As a result, the foam slowed the striker down before the cell walls joined. This reduced the energy burden on the compressed “solid” structure, reducing the force at its maximum. In the 14, and 15 mm samples, the percentage maximum distortion...
of the foam dropped. As a consequence, no solid structure was produced, and the impact dampening of foam was eliminated. Unlike maximal force, absorbed energy by foam thickness, various foams have equal energy absorption capabilities. Although thicker foams deform more, the maximum force is reduced as thickness increases.

The figures support our prediction that severe thinner foam deformation caused cell wall collisions, resulting in a significant rise in force in the curve's second stage. Consequently, whenever the condensed “solid” architecture is attained, the striker is slower, reducing the maximum force.

The first hit generated the greatest force differential; subsequent drops caused less mechanical degradation. The first impact dampening effectiveness decreased with foam thickness. Cell deformation explains this. The thinner foams deform more, causing cell compaction, irreversible damage, with microcracks throughout the cell membranes. The level of damage presumably relies on deformation, thus thicker foams have less of an impact.

The difference in maximum forces in zinc oxide-filled foams surpassed 100 N, whereas in silica-filled foams it reached 200 N. As a result of the aforementioned incident, we must calculate the appropriate foam thickness to avoid compacting the environment during operation, which would permanently damage the product's mechanical characteristics. The optimum thickness for a given density of such a product may be calculated using the acquired data and the application's maximum load.

3.2. **Raman spectroscopy**

The purpose of Raman spectroscopy analysis is to confirm that the addition of additives always gives rise to a PU and to affirm, at the same time, the non-existence of side reactions leading to other undesired products as shown in the diagram next (Figure 4).
From figure 5, it becomes clear that the addition of the additives does not in any way change the basic formulation (PU) and does not give secondary reactions detected by these two spectral techniques. The peak at 1530 is attributed by some [38] to the 4,4'-para-MDI isomers in the MPDI. Others say that it accounts for 1/3 of the C-C elongation vibrations in monosubstituted benzenes (The aromatic rings of PMDI) [39].

To assess the rate of polymerization process for this particular PU formulation, the intensity of the isocyanate's Raman scattering (stretch that is asymmetrical at 2275 cm$^{-1}$), urethane, and hydroxyl (amide I at 1732 cm$^{-1}$, N–H stretch, amide II at 1530 cm$^{-1}$, amide III at 1303 cm$^{-1}$) functional groups can be utilized. However, the N–H bending vibration bands of hydroxyl and urethane are too narrow or beyond the Raman shift spectrum region (300–3300 cm$^{-1}$) to be utilized for the quantitative kinetic study. Quantitative investigation of the amide I vibrational in urethane generated during PU polymerization. Quantitative studies of urethane amide I vibration bands are challenging due to S/N ratios are low due to H-bonding. The Amido II and III vibration bands are suitable for quantitative investigations, but suffer
from multi-peak overlapping and/or low signal-to-noise ratios. As demonstrated in figure 4, the intensity of a band during 1530 cm$^{-1}$ diminishes with an increase in the time required for polymerization. This band is visible in both the pure MDI Raman spectra at ambient temperature. According to research, this band is caused by para (4,4'-isomer) MDI vibrations of substituted phenylene rings [40]. The vibrational modes of C–C stretching associated with the monosubstituted benzene phenyl groups is thirty, as determined by Raman spectroscopy[41].

3.3. Scanning Electron Microscopy (SEM)

The findings of microstructural characterization of the polyurethane foams used as reference material are presented (Figure 5). The image obtained by Raman microscope shows a partially open-cell foam not completely closed by its wall and communicating with other cells or with the outside. Cell membranes are visible between the walls of some cells. However, the majority of cells show the absence of membranes. Foam with open or partially open cells is generally a soft or semi-flexible foam. In our case, the partially open cell structure is consistent with the soft nature of the foam.

Figure 5 shows a scanning electron microscope image of the 5, 10, and 15% filled foams. The interior anatomy of samples shows closed and open cells, with closed cells making up the majority of the empty sample. The empty foam photos showed cells with identical sizes and shapes, practically irrespective of the directions of testing. Anisotropic geometry is observed in the reinforcing foam 15 wt. %, with longer cells and a wider shape/size dispersion than the foam 5, 10 wt. The full sample had some smaller cells, which may imply that the scattered silica and zinc oxide particles worked as nucleating locations for cell structure [42][43].
Figure 5. SEM images of the 5, 10, and 15 (wt.%) filled foams.
Formula (10) was used to compute the mean cell size, which assumes a homogenous distribution. Taking into consideration deviation fields, the computed values were nearly identical to the mean cell diameters determined using image analysis tools. Thus, the studied foams' cell structure may be termed homogenous and regular, confirming the validity of formulas (7), (8), and (9). Table 6 shows that foams with a greater density have smaller cells, considering that cell sizes to an average of various density foams are considerable. A study of variance with a single factor was confirmed (with a 96% confidence level). This is a three-order-of-magnitude analysis below 0.05. Foams' cell density implies that as density increases, smaller cells make up the structure, construction that is more load-resistance, the result of increased thickness of the cell wall and higher cell wall stiffness.

**Table 6:** The cell morphology, characteristics of the polyurethane foams that were examined.

| Sample | \( N_c \) (cells/cm\(^3\)) | \( N \) (cells/cm\(^3\)) | \( l_m \) (μm) | \( l \) (μm) | \( \delta_m \) (μm) | \( \delta \) (μm) |
|--------|----------------------------|-----------------------------|----------------|-----------|----------------|-----------|
| PU_1   | 4195                       | 93598                       | 568 ± 160       | 610       | 8.8           | 9.5       |
| PU_2   | 6959                       | 92149                       | 467 ± 156       | 513       | 13            | 14.2      |
| PU_3   | 7126                       | 93125                       | 690 ± 168       | 680       | 15            | 16.8      |
| PU_4   | 2811                       | 88833                       | 620 ± 152       | 700       | 6.8           | 7.8       |
| PU_5   | 4840                       | 92235                       | 500 ± 137       | 582       | 9             | 10.2      |
| PU_6   | 6950                       | 92130                       | 465 ± 107       | 512       | 12.5          | 13.7      |

The "m" refers to the findings obtained by the picture analysis program.

**3.3.1. Particle size distribution**
Figure 6. Histogram of the distribution of the mean pore diameter of the various produced PU.

3.3.2. Descriptive Statistics
We summarize the distribution of the polyurethane foam cells as well as the filler in the corresponding table 7.

Table 7. Calculation of radii values of polyurethane foam cells, and filler material.

| Microstructural characteristic | Foams | Dimensions | Minimum      | Maximum       | Mean (average) |
|-------------------------------|-------|------------|--------------|---------------|---------------|
|                               | PU_01 | Diameter (µm) | 2.85727     | 318.14691    | 46.34821      |
|                               |       | Area (µm²)   | 6.412        | 79496.003    | 4206.20428    |
|                               | PU_02 | Diameter (µm) | 2.84074     | 366.65483    | 22.99048      |
|                               |       | Area (µm²)   | 6.338        | 105585.601   | 1860.57841    |
|                               | PU_03 | Diameter (µm) | 2.84051     | 380.23445    | 30.60873      |
|                               |       | Area (µm²)   | 6.337        | 113551.481   | 2813.78705    |
|                               | PU_04 | Diameter (µm) | 2.86573     | 225.85698    | 33.70228      |
|                               |       | Area (µm²)   | 6.45         | 40064.24     | 1914.38362    |
|                               | PU_05 | Diameter (µm) | 2.86573     | 520.80741    | 31.17384      |
|                               |       | Area (µm²)   | 6.45         | 213031.682   | 3290.74094    |
|                               | PU_06 | Diameter (µm) | 2.84074     | 264.34972    | 27.24901      |
|                               |       | Area (µm²)   | 6.338        | 54884.232    | 1937.46993    |

4. Conclusions

The study's goal was to see how polymer foam thickness affected impact damping characteristics. In this study, closed-cell polyurethane foams containing silica and zinc oxide were tested dynamically at 0.15–0.40 g/m³ density and 10–15 mm thickness. An SEM was utilized to analyze the foam's cell structure.

Our findings demonstrate that foam thickness affects impact damping characteristics, whereas energy absorption is influenced by cellular structure and density. We also demonstrated that increasing the density of foam does not enhance its impact damping capabilities, and so the maximum load may be determined for an application to help decide the appropriate thickness. This thickness restriction is measured by the typical cell size and thickness of the foam's cell walls.
In addition, excessive cell compaction leads to permanent microstructural changes, reducing the foams' impact damping and energy absorption capabilities. Our results may be used in various industries, including sports and packaging. A location where items made of polymer foam are sold is assessed using our falling weight impact testing. A polymer foam with a predetermined density may be layered to enhance impact absorption and decrease material requirements in these applications.

**Conflicts of interest**

According to the authors, the study was done independently of any commercial or financial interests, the relationship that might be seen as a potential conflict of interest.

**Goals**

This project intends to research the physical and mechanical characteristics of flexible polyurethane foam by determining the dynamic mechanical properties and evaluating the microstructure, and also the extremely fascinating behavior of polyurethane foam, utilizing our free-falling and solid wall machine. Because of this, in the foam business, we work to manage the settings of dynamic variables to ensure that the resulting products have the necessary application characteristics.

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AUTHOR INFORMATION

E-mail
boumdouhanoureddine@gmail.com
safidine18@gmail.com
achraf.boudiaf@emp.mdn.dz

ORCID
PhD. BOUMDOUHA Noureddine https://orcid.org/0000-0002-8070-490X
HDR. HSAFIDINE Zitouni https://orcid.org/0000-0002-0569-2523
HDR. BOUDIAF Achraf https://orcid.org/0000-0003-3519-2404

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Supporting Information

The arrangement of equipment needed for impact testing is shown in the corresponding figure 7:

**Figure 7:** Diagram of the drop weight test.

**Figure 8:** Arrangement of equipment for an impact test.
In what follows, the elements of the drop weight test and their respective functionalities are described. The components are shown in (Figure 10)

**Figure 9:** Mixer Types.

**Figure 10:** Components of Solid Wall Elements for Drop Weight Test.
Figure 11: Images generated by the oscilloscope during dynamic tests of actual curves of force evolution as a function of time.
Figure 12: Laser striking sites for Raman spectroscopy for different PU samples.