Mechanical and chemical characterizations of filled polyurethane foams used for non-lethal projectiles

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Mechanical and chemical characterizations of filled polyurethane foams used for non-lethal projectiles

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ABSTRACT

Non-Lethal Weapons are made and designed proportionately and developed to hinder or expel individuals, with a low probability of fatality or permanent injury, with minimal undesired damage or impact on the natural world. Many real cases show that non-lethal projectiles can lead to severe lesions and sometimes to death. Consequently, there is a necessity to develop and control the manufacturing of the projectile materials to ensure good effectiveness with a lower injury level. In the present paper, a methodology of elaboration and characterization of filled polyurethane foams is proposed. The proposed methodology tends to control the development of the microstructure leading to the final product with desired properties for the non-lethal application. The mechanical characterization was carried out using dynamic tests. A homemade pneumatic launcher and a rigid wall are used for the dynamic characterization. Moreover, physicochemical characterization of the developed foams was carried out: spectroscopy and XRD analysis, to highlight the opened-cell morphology and chemical irregularities, respectively.

Keywords: non-lethal projectiles, Polyurethane foam, Pneumatic launcher, rigid wall, Raman spectroscopy, XRD analysis.

1. INTRODUCTION

Non-lethal kinetic energy uses weapons to transfer sufficient influence to a person to deter their dangerous and illegal behavior without causing permanent harm to them. Non-lethal projectiles are used to neutralize and incapacitate people in situations such as riots, crowd control, and the interception of suspicious marine craft. They offer an alternative for an adequate response by guaranteeing neutralization without causing permanent injuries to the targeted targets. There is a wide range of products on the market. Nevertheless, the study focuses on the characterization of different degrees of foam for the nose removed [1]. There are several reported cases of serious injuries or even death following the use of this type of projectile. It is therefore essential to associate the manufacturing process with the assessment of the lesion risk of these projectiles to avoid any situation that would be contrary to the doctrine of the use of non-lethal projectile weapons. Various materials are used to ensure the soft use of non-lethal projectile weapons, in which modified polyurethane foams are generally used.

That, for the elaboration of polyurethane foam within a certain density; we seek to control as much as possible the formation of a microstructure so that the final product has the desired properties for non-lethal projectiles. They must be able to incapacitate a target without causing a permanent injury or a fatal outcome. This work aims at the elaboration and the mechanical characterization of different polyurethane foams elaborated by the optimal formulation. Mechanical characterization is about dynamic testing a homemade pneumatic launcher and a rigid wall is used. Also, an x-ray diffraction XRD and spectroscopy analysis has been performed to confirm the open cell structure of the elaborate foam.

2. EXPERIMENTAL METHOD

From a synthesis point of view, the alveolar polyurethanes are obtained by the reaction between poly(isocyanate) and polyols, within a blowing agent [2]. This class of polymers can lead to flexible foams, rigid or semi-rigid depending on the composition and chemical structure of the used reagents [3]. The expected filled polyurethane foam within open cells will be physiochemically characterized and evaluated under using and dynamic tests.

2.1 Elaboration of polyurethane foams (PUR)

The elaboration of flexible polymeric foam materials, shockproof nature, selects the type of polyol, isocyanate, and the most consistent catalyst to arrive at a reliable recipe that allows us to achieve flexible foam with the desired characteristics.

Obtaining the optimum formulation of PUR by free expansion is first carried out in small cups at low stirring speeds (1000 RPM). All formulations are summarized in the 6 main formulations after each step; the formulation is rectified based on the appearance of the obtained foam. Various formulations are reported in Table 1. Additives are materials that, added to a polymer, alter its properties or characteristics. Some additives included in the polyurethane foam (PUR) are given in Table 1.

Table 1. Basic compounds in the preparation of polyurethane foam.

	Polyol (g)	PMDII (g)	Catalyst (g)	Glycerin (g)	Silicon (g)	Bentonite (g)	Dichloro-methane (g)	PEG (g)	Alumina (g)
Formulation Ep_1	100	40.88	23.22	3.77	2.11	0	2.11	0	39
Formulation Ep_2	100	42.09	2.11	3.71	3.51	17.81	0	0	0
Formulation Ep_3	100	47.44	1.57	3.69	2.48	5.66	0	0	0
Formulation Ep_4	100	51.61	1.48	2.21	1.32	0	1.19	2	0

The development of PUR in free expansion mode, that is to say at atmospheric pressure in use, is done using a 300 ml volume reactor and mixing using a mechanic stirrer reaching the speed of 2500 RPM and after thickening of the PUR and its cooling, it is demolding. Foam propagation is produced in a preparation vessel.
The characteristic times of the production cycle are measured using a digital stopwatch. The demolding product is left in the open air (for curing) for 24 hours before being stored away from light and moisture and then characterized.
The final properties of the polyurethane foam depend on the nature of chemical components, the blowing agent, the process conditions, and the nature of the mold facings. Thanks to constant developments of new formulations, polyurethane foams are today made with a wide variety of samples. Several test pieces were made based on different formulations.
Four test pieces were used for tests of the pneumatic launcher and a rigid wall. Where the samples of polyurethane foam (PUR) made in the laboratory are cylindrical with a convex spherical head glued with a holder made of HDPE high-density polyethylene realized by a 3D printer. This is done for master highlighting the effect of the variation of the machining direction on the mechanical behavior dynamic tests. Specimen referenced XM1006 non-lethal projectile (Ep_R) and manufactured non-lethal projectile of different optimal formulations are shown in figure 1. Different non-lethal projectiles are designed based on existing models in the market (Figure 1).

Fig 1. a- Range of specimens elaborated respectively on the non-lethal projectile polyurethane foam
b- Specimen referenced XM1006 non-lethal projectile

2.2 Physical-chemical properties

2.2.1 Raman spectroscopy

Raman spectroscopy is a complementary technique to infrared spectroscopy and is used for the organic and inorganic characterization of polymers and pigments [4, 5]. The Raman spectrum generally shows peaks whose Raman offsets by the wavelength differences with the laser excitation light; characterize the vibration frequencies of the atoms in the molecules present.
Raman spectroscopy is based on the absorption of photons at a specific frequency followed by a diffusion phenomenon at a higher or lower frequency. The modification of scattered photon scattering either by gaining or losing energy results from the vibratory and rotational movement of the molecules in the sample [6, 7].
For the Raman characterization, we have used a Forman 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 is 10 sec, 3 accumulations for each spectrum (Figure 3).

2.2.2 X-Ray Diffraction Analysis (XRD)

X-ray diffraction is used to determine the nature of the phases present in porous materials and structural characterization is mainly carried out by X-ray diffraction technique (XRD).
In polymers, there is no perfect crystal and the partial crystallinity must be considered as the juxtaposition of amorphous zones (where the molecules are disordered) and crystalline zone in which

the polymer chains are parallel to each other to others. In the amorphous matrix, there are no long-range molecular arrangements but arrangements of chain segments that are not sufficient to create a crystalline order. As for the crystalline phase, its morphology depends on the crystallization mode of the polymer: mass solidification from the molten state, slow crystallization from dilute solutions. From the spectra of X-ray diffraction, it is possible to determine the degree of crystallinity [8]. It makes it possible to determine the nature of the studied body and its structure by using the single-crystal methods with a Bragg Brentano montage which allows us to determine the inter-reticular distances. This is the most common and easiest method to implement.

Structural XRD analysis of alveolar PUR is carried out on an ITALSTRUCTURES brand diffractometer, model APD 2000, designed for powders and polycrystalline materials. The device is equipped with a GD 2000 goniometer and managed by WinDust32 data management and operating software.

For the deconvolution of the diffractogram, the origin 5.0 software using the Gaussian function is used and for the determination of the ratios of the amorphous and crystalline parts, the peak areas given by the WinAcq32 software is well used. The APD 2000 system uses the principle of X-ray reflection by crystalline materials. This phenomenon obeys Bragg's law:

$$\lambda = 2d.\sin\theta \qquad (2)$$

Where: λ: the wavelength of the X radiation used (1.5418A °), d: the distance between the planes, θ: the angle of incidence of the X-rays on the planes. The radiation used is of CuKα type with a voltage of 40 kV and 30 mA and an angle speed of 0.01 ° / s.

2.3 Mechanical characterization

2.3.1 Dynamic characterization of the non-lethal projectile by the pneumatic launcher

Four series of samples were tested, each containing three samples of the same composition cylindrical test pieces prepared from known formulations. The sample is placed inside the pneumatic launcher, where a constant pneumatic pressure is applied. All data related to this test are shown in table 2.

Table 2. Characteristics of the used non-lethal projectile.

	Length(mm)	Diameter(mm)	Mass(g)
Projectile polyurethane foam Ep_1	80	35.4	28
Projectile polyurethane foam Ep_2	60	35.6	19.7
Projectile polyurethane foam Ep_3	60	35.2	28.1
Projectile polyurethane foam Ep_4	80	35.6	26.9
Projectile polyurethane foam Ep_R	60	35	26.9

Several tests have been carried out on samples made of filled polyurethane foams. Non-lethal laboratory projectiles are designed and made according to the XM1006 commercial projectile labeled as Reference Projectile (Ep_R). Which is named Ep_R directly from the global response of the projectile on a Rigid Wall equipped with a piezoelectric force sensor. The projectile displacement signal son the Rigid Wall is created to track the velocity and force of the shell. This is done using the internal tracking by the oscilloscope software. When the power and displacement signals are generated from two different devices, it must be confirmed that the signals are synchronized with each other. The relationship is considered the maximum impact force. Therefore, more than one experiment for each sample is achieved where the effects have different affect velocities. In all tests, a pressure of 5 bars is applied. Various parts of the pneumatic launcher are shown in figure2.

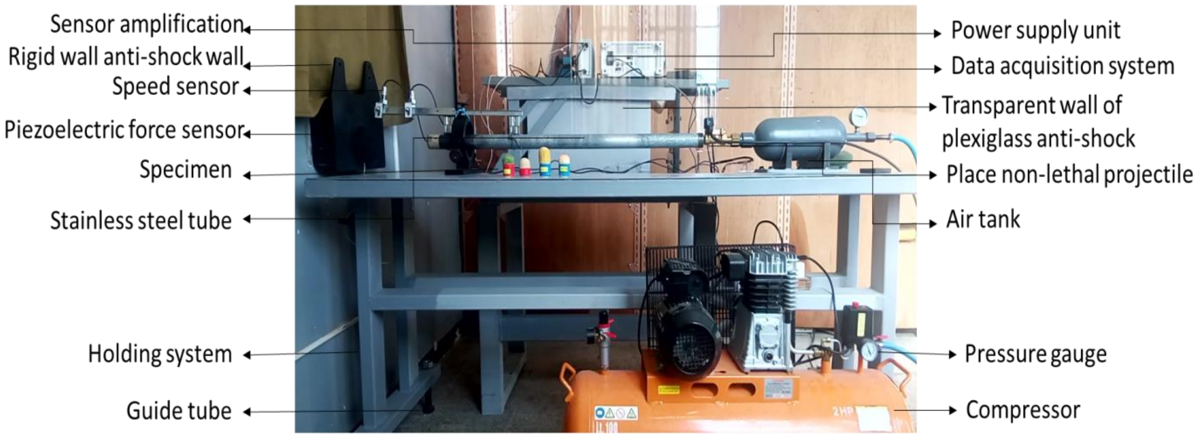

Fig 2. The overall sight of the pneumatic launcher

3. RESULTS & DISCUSSIONS

3.1 Physical-chemical properties

3.1.1 Raman spectroscopy

The purpose of Raman spectroscopy analysis is to confirm that the addition of additives always gives rise to a PUR and to affirm, at the same time, the non-existence of side reactions leading to other undesired products as shown in the spectra bellow of figure 3.

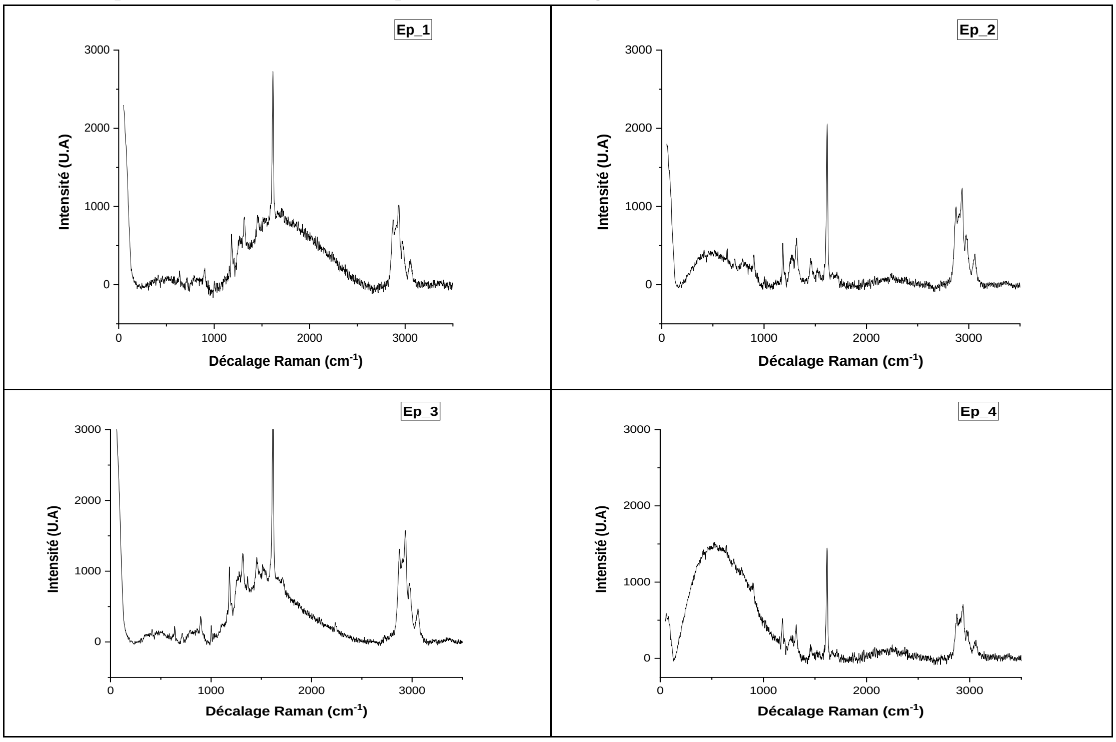

Fig 3. Raman spectra of different PUR with various additives

From figure 3, it becomes clear that the addition of the additives does not in any way change for the basic formulation (PUR) and does not give secondary reactions detected by this combined spectral technique. The peak at 1530 is attributed by some [9] 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) [10].

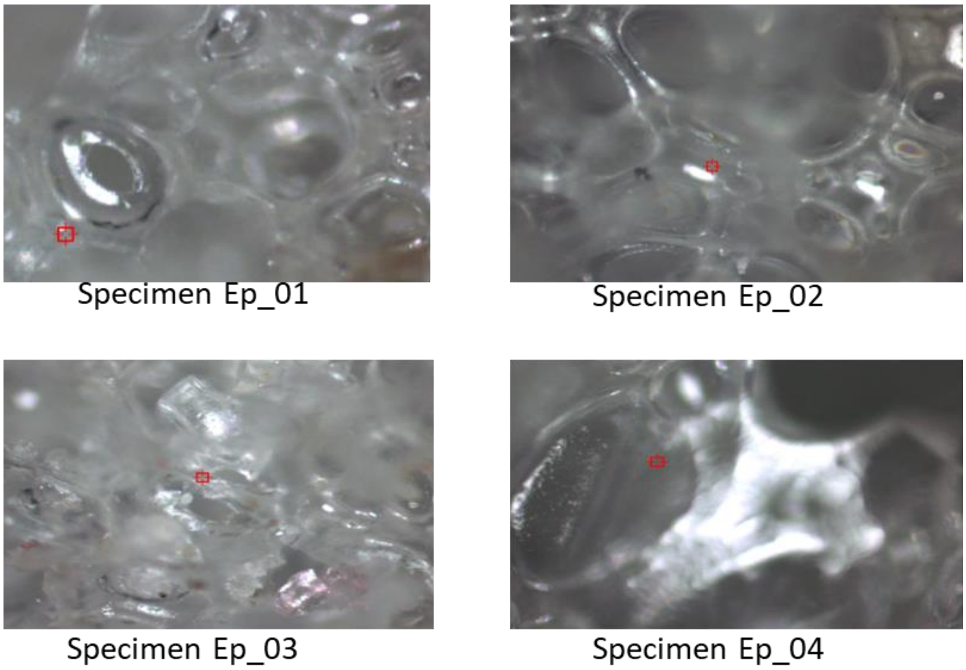

Fig 4. Images obtained by Raman microscope for polyurethane foams

The Microstructural properties of these materials were analyzed by Raman Spectroscopy to discover their structure in good agreement with the standard American Standards Testing Methods (ASTM) sheets. These polymers led to single-phase and heterophase materials analyzed from a morphological point of view microstructural analysis revealed the open cell nature of the elaborate foam. The image obtained by the Raman microscope shows partially open-cell foam. Given the results obtained; it appears that the elaborate pieces have stubborn regular cellular structures with remarkable overlap reversibility (figure 4).

The results of microstructural characterization of the polyurethane foam used as reference material are presented. The image obtained by Raman microscope shows 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 soft or semi-flexible foam. In our case, the partially open cell structure is consistent with the soft nature of the foam.

3.1.2 X-Ray Diffraction (XRD)

The result of the analysis of virgin PUR by XRD gave the diffractogram below in figure 5.

Given the crystalline nature of BNT and Alumina bentonite fillers, we characterized them by XRD to determine their exact crystalline natures. The search through the software WinDust 32 and WinSearch, confirms that it is indeed loads with respectively a tetragonal crystalline system (with parameters of mesh a = b = 3,780A ° and c = 9,510A °) and a hexagonal system (with parameters of mesh a = b = 4.98032A ° and c = 17.01869A °).

Taking the BNT samples, we can better observe the effect of purification on PEG in the first place by comparing which has been purified locally, and thus a slight increase in the interlamellar distance following the evacuation of impurities such as quartz, Illite, pyrite, and plagioclase field paths (calcium albite) in low concentration.

In the virgin PUR diffractogram, we find that there are two main peaks of angle 2θ of 19.25 ° and 25 °. These indicate a certain degree of crystallinity of our PUR and they are assigned to a dispersion of PUR chains with a constant inter-reticular distance (d). The structural morphology of our PUR is semi-crystalline type. This semi crystallinity is a kind of partial arrangement of macromolecular chains of PUR.

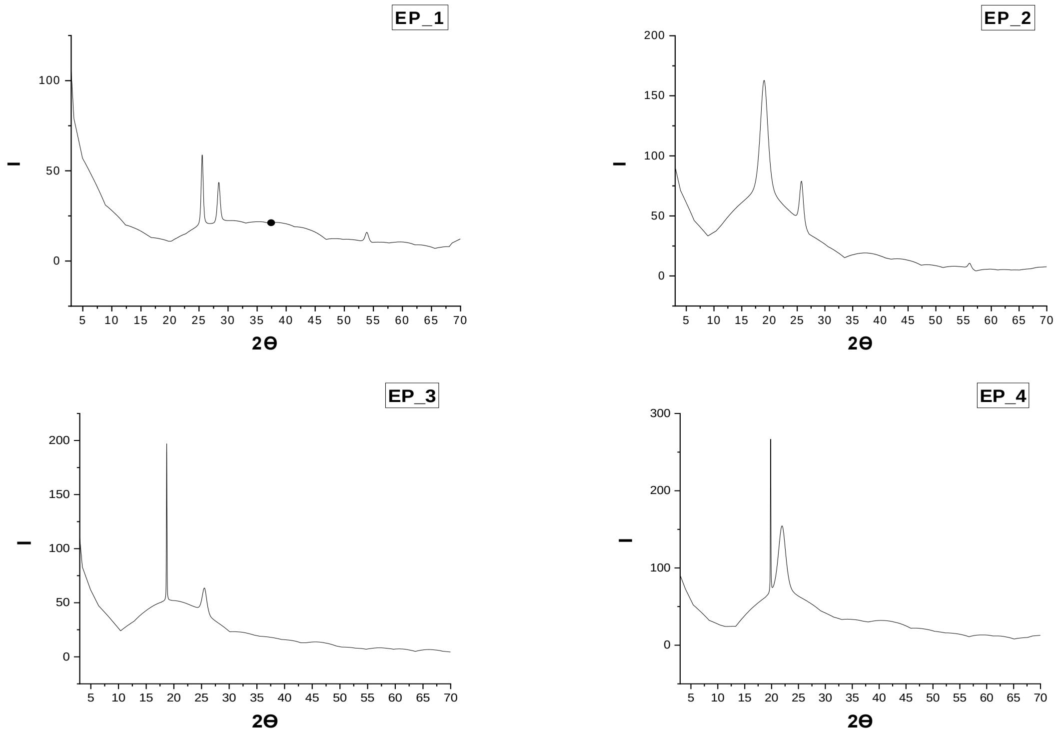

Fig 5. X-ray diffractogram for samples of polyurethane foam

The XRD analysis of the other PUR with additives and charges gave us the diffractograms of figure 5, we deduce that the PUR elaborated are of a semi-crystalline type and the addition of additives and charges always leads to a semi-crystalline structure. The highest crystallinity is that of the polyurethane foam formulation Ep_1 and decreases after the addition of alumina.

3.2 Mechanical characterization

3.2.1 Dynamic characterization of the non-lethal projectile by the pneumatic launcher

It is planned to carry out dynamic tests to evaluate the behavior of the filled foam during the impact.
The results obtained are summarized in the following from the curves of figure 6, we drill it whenever the sample is solid and very dense increased strength and pulse duration. That is, there is a correlation between the microscopic structures of the shell and the actual effect. The results show a good agreement between the shell and shell curves of the XM1006 reference projectile in terms of the prediction of the maximum head impact force for the lateral impacts. The results of XM1006 are very important to the development of evaluation approaches. There is complete consensus on non-lethal effects. The maximum impact head force can be then proposed as injury criteria.

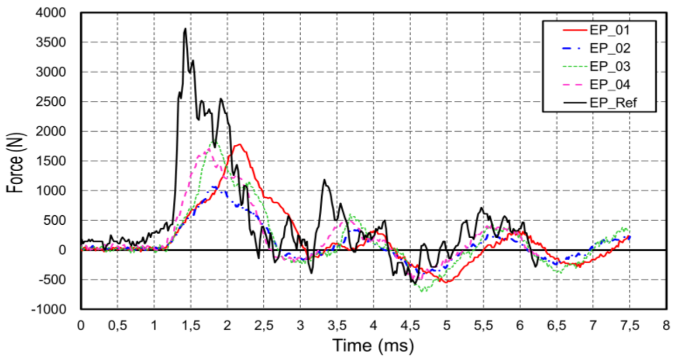

Fig 6. Characteristic force-time of the non-lethal projectile by the pneumatic launcher

There is a similarity between experimental test curves between manufactured and commercial projectiles carried out in this work. However, the shock sensor used in the experiments gives good results whenever the impact is significant and this is achieved by the pressure of the air used. The results of the pneumatic launcher tests showed typical behavior of the viscoelastic materials in three phases: linear elastic deformation, plate, and densification. Noting that all samples were applied to their physical properties before and after the test and stimulate its properties and the same dimensions. Results are summarized in table 3 by each sample.

Table 3. Test results of the pneumatic launcher experience are used for the dynamic characterization.

Tests	Speed (m/s)	Force max(N)
Projectile Ep_1	130	1779
Projectile Ep_2	130.6	1067
Projectile Ep_3	68.6	2135
Projectile Ep_4	25.1	1601
Projectile Ep_R	45.5	4270

Tests are carried out on foam samples of standard density and density required. The stress curve provided by the results may not be sufficient because the laboratory shock meter is under test for this cannot capture the condensation part of the foam pressure. Therefore, if necessary, the curve can be partially extrapolated. Therefore, before any foam material is used with confidence in non-lethal missile impact operations, it must be distinguished by correlating with physical tests at the component level. Then, good confidence can be developed in predicting the injury parameters predicted.

4. CONCLUSIONS

The goal for this work is the mechanical characterization of filled polyurethane foams having a certain density. These last warheads based on these alveolar materials must be able to put out of harm's away a target without causing a permanent injury or a fatal outcome. The experimental results of the mechanical tests are presented. Dynamic tests are carried out on polyurethane foam drop weight tests on a machine designed and built locally. Then, a spectral and microscopic analysis using a Raman spectroscopy analysis to visualize the semi-open cells of the alveolar polymer is fulfilled. According to the obtained results; it appears that the pieces made of the cellular polymer have stubborn regular cellular structures with noticeable overlap reversibility.

This work aims to develop and characterize various polyurethane foams for their use as a base material for non-lethal projectiles. The final properties of the polyurethane foam depend on the chemical components, the blowing agent, the process conditions, and the nature of the mold facings. Thanks to the constant developments of new formulations, polyurethane foams are today manufactured with a great variety.

The results achieved for comparing ballistics in terms of impact strength and pressure by measuring instruments confirm that the ballistics that has been manufactured is more effective than commercial and this encourages the exploitation of this research in terms of efficiency and quality as chemical compounds are available, low cost and non-toxic. Therefore, this work can be a good method used to assess the risk of injury to these types of effects. The various findings thresholds provided in the current work can be applied to ensure safer use of Kinetic Energy Non-Lethal weapons.

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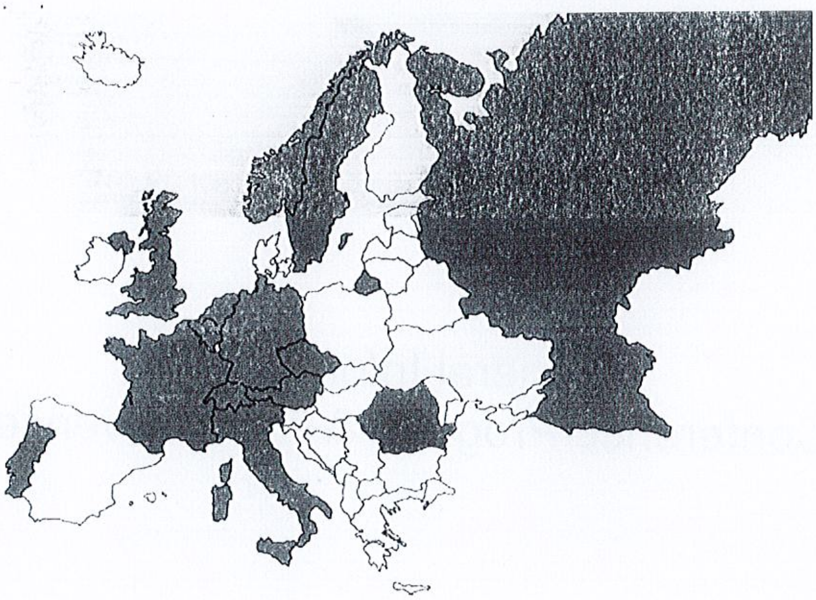

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On the mechanical and chemical characterizations of foams used for non-lethal projectiles

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The Kinetic Energy Non-Lethal Weapons are used to repel or neutralize a dangerous person with a low probability of permanent or fatal injuries. Nevertheless, the use of such weapons is not without risk. Many real cases show that the non-lethal projectiles can lead to severe lesions and sometimes to the death. Consequently, there is a necessity to develop and control the manufacturing of the projectile materials in order to ensure a good effectiveness with a lower injury level. In the present article, a methodology of elaboration and characterization of polyurethane foams is proposed. The proposed methodology tends to control the development of the microstructure leading to a final product with desired properties for non-lethal application. The mechanical characterization was carried out using both quasi-static and dynamic tests. A homemade pneumatic launcher and a rigid wall are used for the dynamic characterization. Moreover, a physicochemical characterization of the developed foams was carried out: spectroscopy and DRX analysis, in order to highlight the opened-cell morphology and chemical irregularities, respectively.

BOUMDOUHA Noureddine was born the 29th of December 1990 in Algeria (M'sila). He obtained a Master degree in Materials and component at the University of Science and Technology Houari Boumediane -- USTHB- (Bab ezzouar, Algiers). He is now a second year PhD student at Ecole Militaire Polytechnique –EMP- . His thesis is entitled: "Development and Dynamic Characterization of Polymeric Foams: Application to Non-Lethal Projectiles". The main objective of this work is to improve the physicochemical and mechanical properties of polymeric foams with the intent to use them as materials for non-lethal projectiles.

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