Thermal, Mechanical and Electrical Investigation of Elastomer-Carbon Black Nanocomposite Piezoresistivity

Giovanna Di Pasquale, Salvatore Graziani, Guido La Rosa, Fabio Lo Savio and Antonino Pollicino

Abstract Polymeric composites, where polymeric matrices are purposefully added with suitable fillers, have raised the interest of the scientific community, since materials with characteristics that depend on the nature of both the polymeric matrix and the filler can be obtained. The paper deals with the investigation of composites based on an insulating polymeric matrix, realized by using polydimethylsiloxane (PDMS) and carbon black (CB), as the filler, for realizing nanocomposites. The PDMS is an insulating matter, while the CB has conducting properties. If a suitable concentration of the CB is used, it is possible, therefore, changing the electrical properties of the composite from insulating to conducting. Such a possibility is, e.g. described in the framework of the percolation theory. Since a deformation of the composite causes a corresponding change in the concentration of the filler, it is possible using the described nanocomposites as piezoresistive elements. Based on the considerations reported above, composites were realized by using different concentrations of the filler, in order to obtain a reasonable value of the composite resistivity. The corresponding thermal, mechanical and electrical properties where, therefore, investigated in typical laboratory conditions.

Keywords Polydimethylsiloxane (PDMS) · Carbon black (CB) · Viscoelasticity
Piezoresistivity

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1 Introduction

In the past years, sensing systems, based on polymers, have raised a significant interest in the scientific community [1]. More specifically, composite materials, consisting of insulating polymeric matrix and a conductive filler have been used for realizing pressure, tactile sensors [2] and gas sensors [3]. In [4], a conductive mixture has been proposed for realizing a glove capable of posture and gesture monitoring. Further applications can be envisaged in the monitoring and preservation of cultural heritage. In [5], a device has been proposed by some of the authors to realize flexible tailored sensors for large deformation monitoring. Results obtained in the characterization of natural rubber, loaded with carbon black, as a piezoresistive material have been reported in [6].

Here, the possibility of using a silicone matrix, loaded by using carbon black nanoparticles, to realize piezoresistive sensing elements is investigated. More specifically nanocomposite based on polydimethylsiloxane (PDMS), loaded with acetylene carbon black (CB), have been considered and the characterization of such composites will be described in the following.

2 The Composite Synthesis and the Thermal Characterization

Samples analyzed in the following, were produced using PDMS, as the matrix, and various amount of CB as filler. The experimental conditions have been verified in order to obtain the most precise control of the degree of crosslinking, which has a high importance, since it influences the mechanical properties of the final polymer. The samples were fabricated using a linear poly(dimethylsiloxane)-hydroxy terminated (PDMS-OH, viscosity 18,000–22,000 cSt from Aldrich). The crosslinking reaction was carried out at room temperature from a mixture of PDMS-OH in presence of 4% (by mass) of TetraEthOxySilane (TEOS) and 1% (by mass) of Tin (II) 2-ethylhexanoate (SNB), as catalyst. A scheme of the crosslinking reactions is shown in Fig. 1.

CB (acetylene 100% compressed, bulk density 170–230 g/L from Alpha Aesar) has been utilized as filler (see Fig. 2). This type of CB is obtained by thermally decomposing acetylene gas. This method provides CB with higher structures and higher crystallinity, good for electric conductive agents.

The PDMS/CB composites have been obtained by solution blending. A small volume (about 2 ml) of dichloromethane was added to a weighted amount of PDMS-OH (4 g) in a Teflon mold, in order to decrease the viscosity of the starting matrix, and then to get better dispersion of the filler. Then, CB was added and the mixture was sonicated at 15 W for 10 min. Samples have been prepared with different percentage by weight of CB (6, 8, 10% of CB).

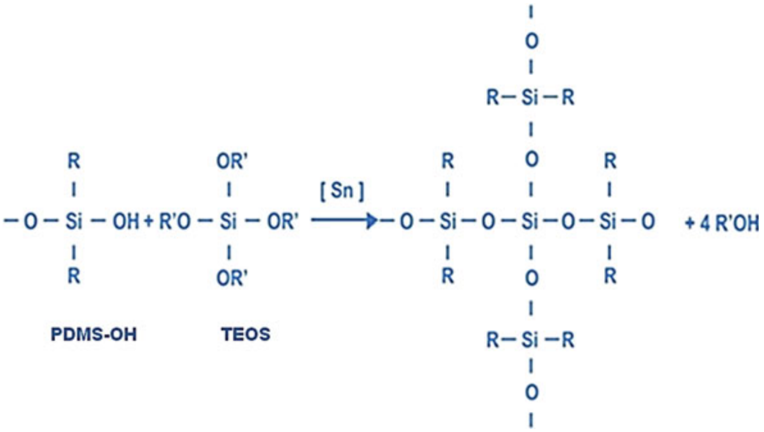


Fig. 1 A scheme of the crosslinking

Fig. 2 A view of CB, used as filler for the composite fabrication

Table 1 Weight percentage of CB used for composite realization

Samples	
Neat crosslinked PDMS-OH	PDMS-OH (%)
PDMS-OH + 6% by weight of CB	CB 6
PDMS-OH + 8% by weight of CB	CB 8
PDMS-OH + 10% by weight of CB	CB 10

Details about the composites investigated in the following of the paper are reported in Table 1.

Finally, 4% by weight of crosslinking agent (TEOS) and 1% by weight of SNB catalyst were added and the mixture was mixed for 10 min. The composites were then transferred into metal molds in order to obtain a better control of the thickness of the samples to be subjected to characterization. The crosslinking time was fixed in 4 h. A view of the molding system, along with a produced sample, is shown in Fig. 3.

Fig. 3 The molding system and a sample as obtained after the crosslinking phase

Table 2 Degradation temperatures (T_{d10}) of PDMS-OH/Carbon Black composites

Samples	T_{d10} (°C)	Gain in terms of Celsius degrees, compared to the neat matrix
PDMS-OH	389	–
CB 6% (A4106C CB)	405	+16 °C
CB 8% (A4108C CB)	405	+16 °C
CB 10% (A4110C CB)	421	+32 °C

2.1 Thermogravimetric Analysis (TGA) of the Obtained Composites

The Thermogravimetric analysis was performed in order to obtain information on the thermal stability of the nanocomposites. TGAs were carried out in static air in the range 25–700 °C, with a heating rate of 10 °C min^{-1}. The combined action of an oxidizing atmosphere and of high temperatures causes the initiation of degradative processes in the polymers which involve the breaking of the chains and/or variations of the structure and of the terminal groups. From these degradative processes, volatile gaseous products are obtained, which result in a decrease in the residual weight of the sample under test.

A measure of thermal stability can be obtained from the comparison of the degradation temperature determined on the basis of the weight loss. Considering as degradation temperature the one at which a weight loss of 10% (Td_{10}) is recorded, some information can be drawn on the effect of the filler presence.

T_{d10} of neat PDMS-OH is 389 °C (see Table 2), while TGA data for the filler containing samples testify to the good dispersion of the filler as evidenced by the increase of the thermal stability of the composites with respect to the virgin matrix. In fact, T_{d10} of CB 6% and CB 8% samples are 405, 16 °C higher than PDMS-OH, while the one of CB 10% sample is 421, 32 °C higher than neat matrix.

The comparison, between the thermogravimetric curves obtained for PDMS-OH and for the CB 10% samples, is shown in Fig. 4.

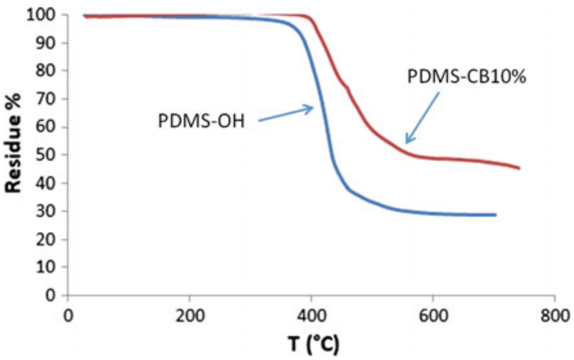


Fig. 4 Comparison between the thermogravimetric curves of PDMS-OH and composite with 10% by weight of CB, respectively

The higher thermal stability found in these samples is due to the fact that dispersed carbon black hinders the formation of radicals so that the temperatures at which there is 10% loss in weight are higher.

2.2 Mechanical Dynamic Analysis (DMA) of the Obtained Composites

Further insight on the chemical structure of the nanocomposites was investigated by performing the Mechanical Dynamic Analysis (DMA) of the samples. Tests were carried out in compression mode at a frequency of 1 Hz in the temperature range $-135 \div 30$ °C (scan rate 10 °C min^{-1}). Tritech2000, from Triton Technology Ltd, was used for the experiments. The presence of the CB determines a shift at higher temperatures of the melting of the crystalline domains of the PDMS (fall of the module ~ − 40 °C in the PDMS-OH, and ~ − 38, 36 and 29 °C in the CB 6%, CB 8% and CB 10% composites, respectively) and an increase in the storage modulus of the composite at room temperature. A comparison between the storage modulus as a function of temperature in PDMS and CB 10% nanocomposite is shown in Fig. 5.

3 Investigation of the Composite Piezoresistivity

The electric properties of samples based on PDMS and different concentrations of CB, as the filler, were investigated in order study their piezoresistive properties. More specifically, while in a first production phase, the CB varied in the interval 0.1–10% in weight, it was found that relevant changes in the composite resistivity occurred in a smaller range of concentration values. For such a reason, the investigations were further focused for CB concentrations in the range 6–10%, as reported in Table 1.

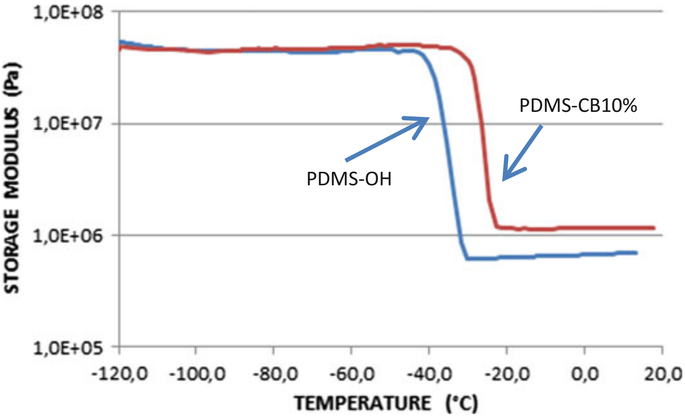
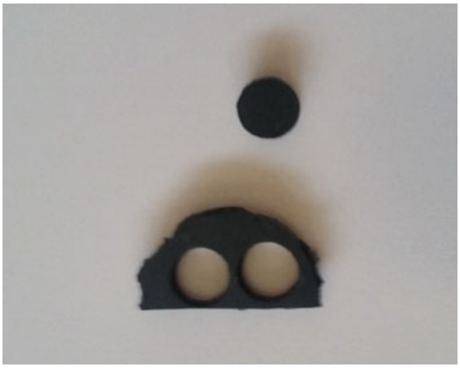


Fig. 5 Comparison between the storage modulus, as a function of temperature, in PDMS and CB 10% composite, respectively

Fig. 6 A CB based sample, extracted from the molded composite



3.1 *The Measuring System for Piezoresistivity Investigation*

A measurement campaign has been executed in order to investigate the piezoresistive behaviors of the samples. More specifically, all samples have been cut from the molded composites by using a punch and samples thickness has been determined by using a gauge. A view of a sample extracted from a produced composite, as obtained by the molding phase, is reported in Fig. 6.

A system was realized for imposing the deformation to the devices under test. Both a CAD representation and a picture of the set up are reported in Fig. 7. A micrometer (Mitutoyo, model n. 148–316) was used for applying the deformation to the device. The system was, also, equipped with two copper electrodes for measuring the corresponding values of the device resistance.

Loading cycles have been, therefore, applied to the samples with a constant compressive step equal to 2.5%, up to a maximum compressive value equal to 25%.

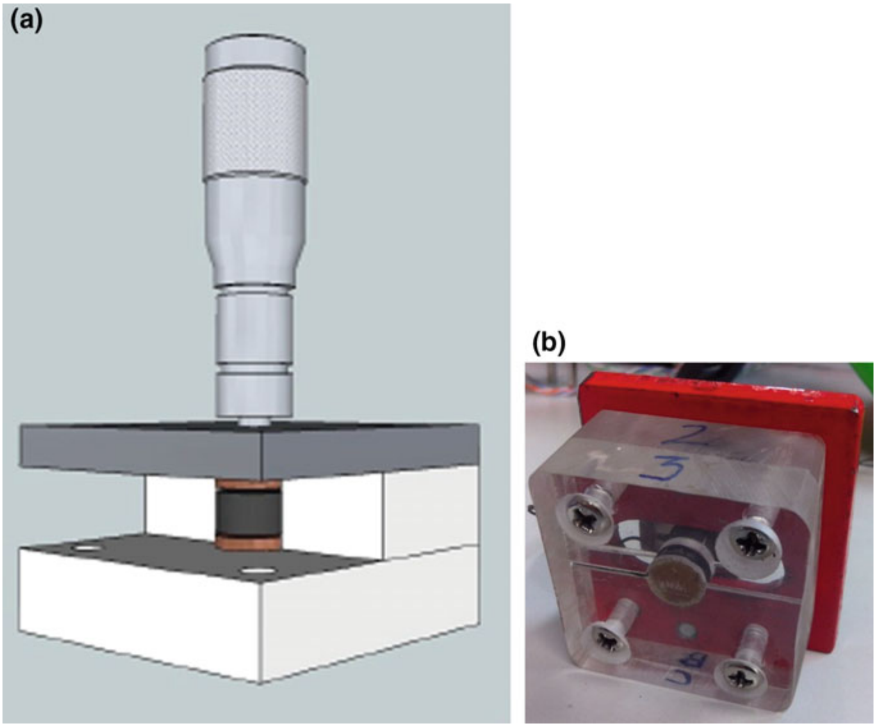


Fig. 7 A scheme of the set up (**a**) and a picture of the realized set up (**b**)

Experiments were performed in hydrostatic conditions. The corresponding values of the sample resistance were measured both by using a linearized Wheatstone bridge and with Agilent 33301A digital multimeters.

3.2 *The Experimental Results*

It has been reported in the literature that resistive devices, based on polymeric composites, even in the presence of a constant load, show a change in the value of the resistance with time, which is known as resistance creep [2, 6]. For such a reason, a preliminary investigation was performed in order to determine the time scale of such a phenomenon. In Fig. 8, the time plot of the changes in the resistivity values for a sample with 10% of CB, following the application of a 5% compressive load are reported.

More specifically, the results of three experiments are reported in the figure. From the results reported in Fig. 8, it can be concluded that the changes in the resistivity value can be considered occurring in a time interval smaller than about 10 min.

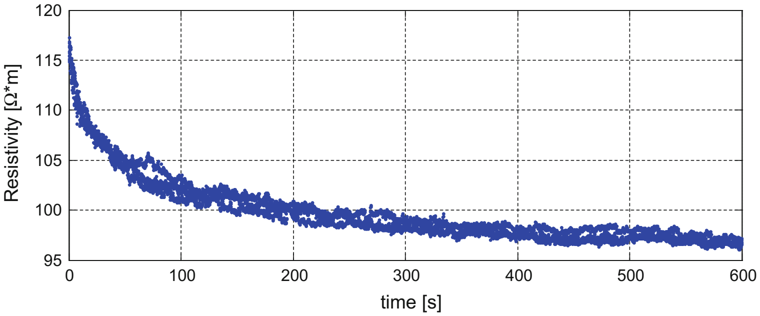


Fig. 8 Time evolution of the resistivity of the CB 10% sample, after applying 5% compressive load

According to the considerations reported above, data used in the following have been acquired 10 min after the application of the mechanical deformation.

Devices have been realized by using the CB concentrations reported in Table 1. The changes in the resistance value as a function of the applied deformation *d* have been recorded. The corresponding changes in the resistivity value have been, finally, estimated. As an example, in Fig. 9, the results obtained for a device with CB equal to 8% are reported. More specifically, Fig. 9a reports the values of the resistance, while in Fig. 9b, the corresponding resistivity values are shown. In Figs. 9a and 9b, the results obtained by using a polynomial interpolation are also reported. The corresponding modelling RMSEs are equal to 61,7 kΩ and $1.23 * 10^3$, respectively. Similar results have been obtained, also, for samples CB 6% and CB 10%.

From the analysis of the results shown in Fig. 9, it can be observed that for small values of the applied compressive deformation, a piezoresistive effect has been observed, with a reduction of both resistance and resistivity. Nevertheless, for larger values of the deformation, both parameters increase their values.

A further elaboration has been performed for investigating the piezoresistivity the devices, as a function of the CB volume concentration. More specifically, using the density values of the main components (0.97 g/cm^3 and 0.56 g/cm^3, for PDMS and CB, respectively), the values of the volume concentrations for samples CB 6%, CB 8% and CB 10% in absence of any deformation, become 10%, 13%, and 16%, respectively.

Finally, the applied deformations have been transformed into corresponding values of the CB volume concentration [7]. Obtained results are reported in Fig. 10.

The analysis of results reported in Fig. 10 show that though the devices show a piezoresistive behavior, the phenomenon cannot be described as a function of the applied volume filler concentration and further investigations are required for better understanding the involved phenomena.

4 The Viscoelastic Characterization of the Composites

The analysis was carried out in order to characterize the composites from a mechanical point of view, with particular attention to the viscoelastic aspect. The work performed, therefore, should be inserted into a broader context that concerns the study and complete characterization of new types of CB filled polymers.

As previously stated, nanocomposite devices with CB content ranging from 6% to 10% have been investigated and have shown a change in the resistance with the applied deformations. Among the mentioned composites, the results obtained in the viscoelastic characterization of the CB 10% will be reported. More specifically, the investigation is intended to evaluate the influence of the kinematic viscosity of the filled PDMS on the relaxation of the system.

4.1 Description of the Testing Machine

The testing machine used to carry out stress relaxation tests on polymeric materials consists of:

- Aluminum frame on which the various components are fixed;
- Electrostatic actuator Physik Instrumente M-230.25, with relative software, to impose the desired deformations on the specimens;
- Controller Mercury II C-862, to maneuver and control the actuator via PC;
- Load cell Tekkal L2320/50LBS, to measure the force applied to the specimen;
- Board Transducer Techniques TM0-1, to amplify the load cell signal;
- Laser Baumer OADM 12U6460/S35A, to measure the displacement imposed by the actuator;
- Acquisition board NI-DAQ USB-6009 for detecting, processing and transmitting signals from the load cell and the laser to a PC;
- Steel plate, fixed to the base of the machine, to host the specimens to be compressed;
- Calibrated screw, fixed to the load cell and having the task of transmitting the compression force to the specimens, prepared ad hoc in order to have the same diameter of the screw itself;
- A dedicated NI-LabVIEW 2017 software to capture, filter, save and instantly display the output signals (from the load cell and the laser) has been implemented.

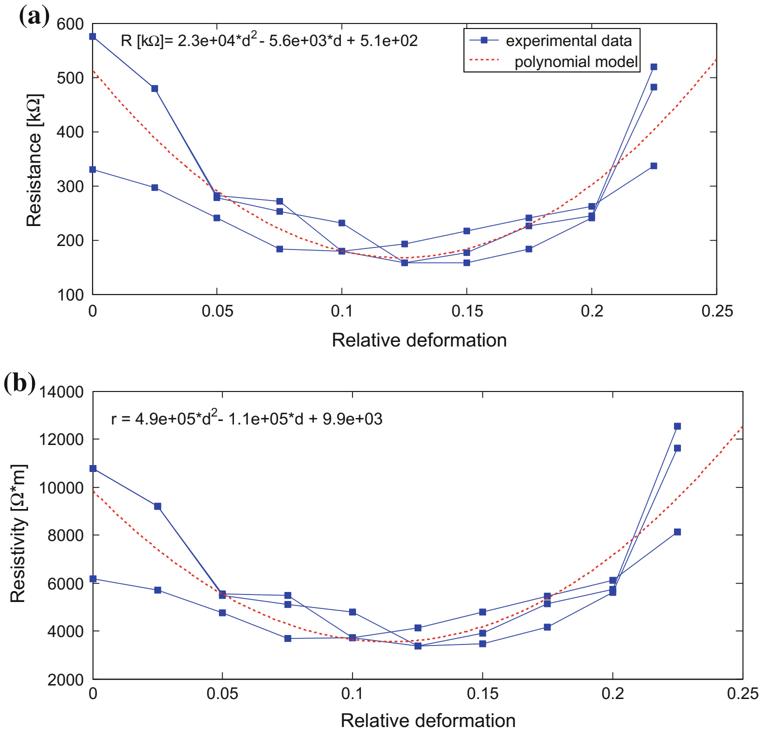


Fig. 9 Dependence of the electrical properties of a CB 8% nanocomposite based device as a function of the applied deformation *d*. Resistance values (**a**), and resistivity values (**b**)

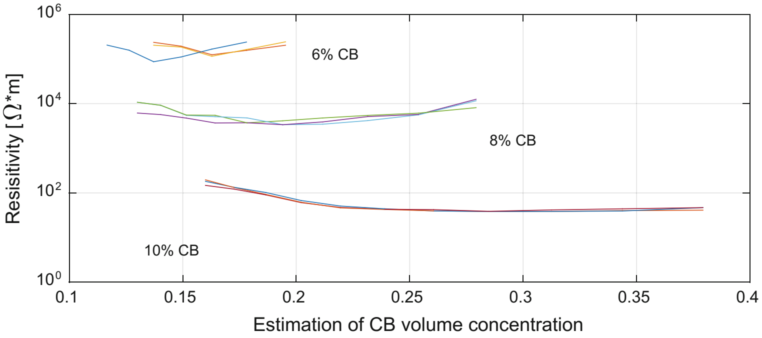


Fig. 10 Dependence of the electrical resistivity on the CB volume concentration

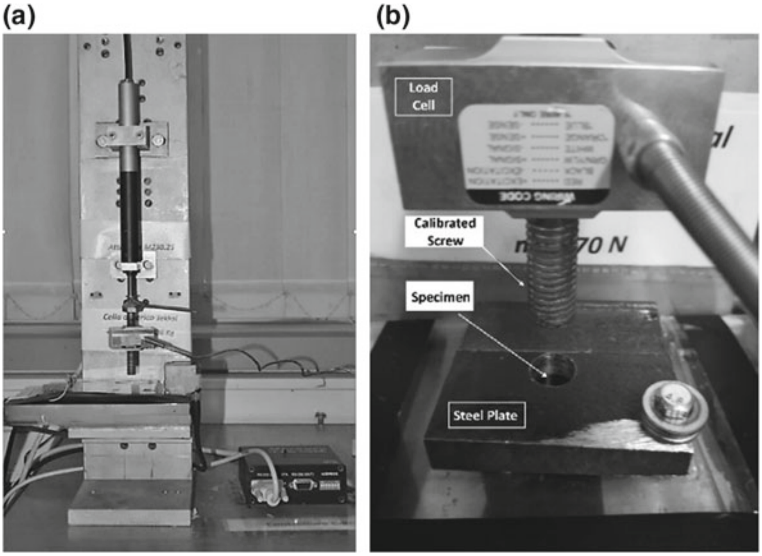


Fig. 11 The set up for the mechanical investigation of the nanocomposite. The compressing system (**a**), and the sample casing (**b**)

The tests were performed under compressive load in confined way inside a steel constraint; in this way, the specimen was compressed under conditions of hydrostatic pressure. Figure 11a, b show the mechanical set up and the casing system used for performing the mechanical investigation.

4.2 The Testing Procedure Acquisition

Relaxation tests were performed with duration of just over an hour each. The tests were carried out under displacement control. Each test requires the actuator to perform a series of movements (loading and unloading cycles, 0.1 mm pre-loading step, compression and unloading steps), as shown in Fig. 12. These phases are commonly used for the initial conditioning of the viscoelastic material, mainly for biological tissues and elastomers. In particular, the following phases were observed: five cycles of loading and unloading at 30% of the specimen thickness, 0.1 mm preloading, compressive loading (start of relaxation test). Between the end of the last loading-unloading cycle and the beginning of the pre-compression, as well as between the end of the latter and the beginning of the final relaxation compression, a waiting time of 10 s has been set, to allow the redistribution of internal stresses created in the polymer by the imposed deformations.

Since deformations of different entities (20, 40 and 50% of the thickness) were imposed on each specimen, it would not have been possible to carry out the unloading

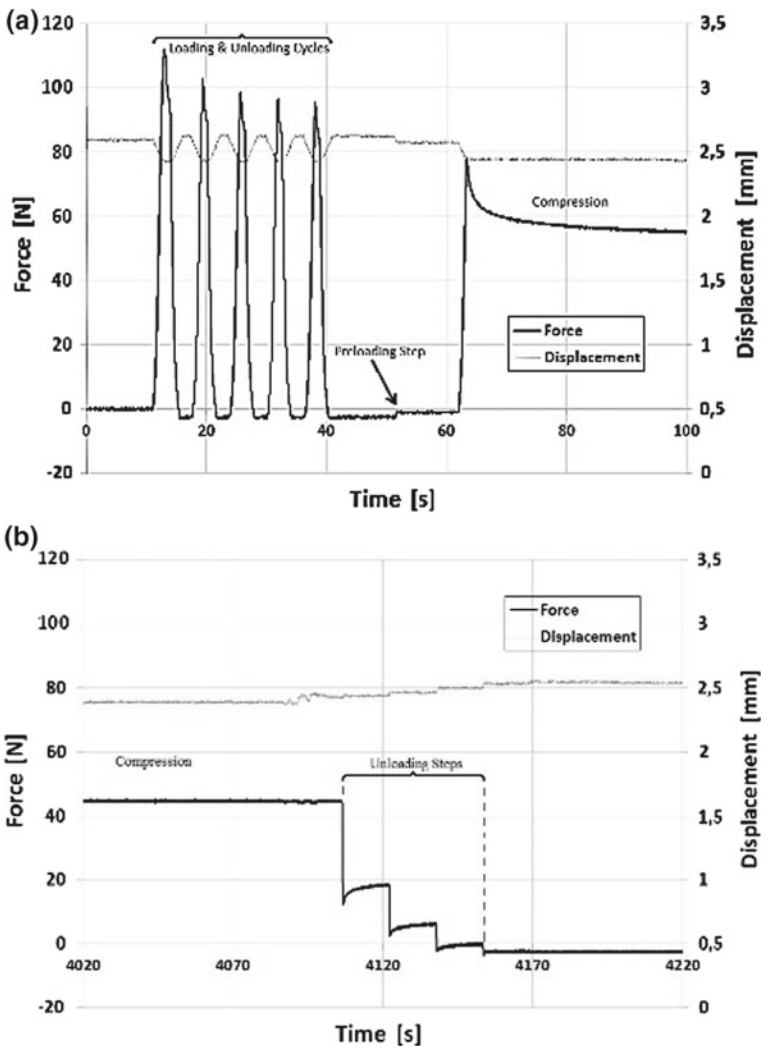


Fig. 12 Initial (**a**) and final (**b**) phases of the relaxation test on CB 10%

phase in the same way for the different types of tests. In all cases, the last step has the same amount (0.1 mm), so as to cancel the effect of the initial preload and return the actuator to the total rest position. Among all the steps, a waiting time of 15 s has been set, to check the elastic response of the material.

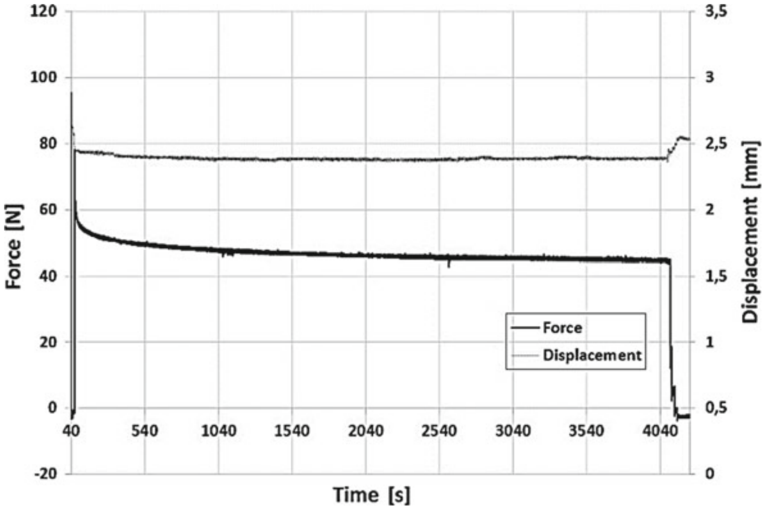


Fig. 13 Relaxation curve of the CB 10% sample

4.3 *Results of the Relaxation Phase*

The results shown in Fig. 13, obtained by the direct measures (displacement imposed on the specimen, force by the load cell) allow to define the stress-strain behavior.

From the experimental data obtained, assuming an isotropic sample subjected to hydrostatic pressure, it was possible to derive the value of the Young Modulus (E) and Bulk Modulus (K) of the CB 10% sample [8]:

$$E = 5.1 \pm 0.2\,\text{MPa}$$
$$K = 2,820 \pm 5\,\text{MPa}$$

From the equation $= 3\ (1–2\nu)$ the value of the Poisson coefficient for the material has been obtained (ν):

$$\nu = 0.499699 \pm 1 \cdot 10^{-6}$$

Once the experimental data were acquired, some types of parametric models were studied, in order to choose the model that best suited the real behavior of the material. The experimental data was first filtered using MATLAB. Then, the fitting has been completed using both polynomial and exponential fitting, by spring and damper models in series (Maxwell), in parallel (Kelvin-Voigt, Zener) or more complex. The model with the highest value of R^2, as well as the lowest Root Mean Square Error (RMSE) was the generalized model of Maxwell with three elements in parallel (Fig. 14). The results obtained find excellent concordance in the literature [9].

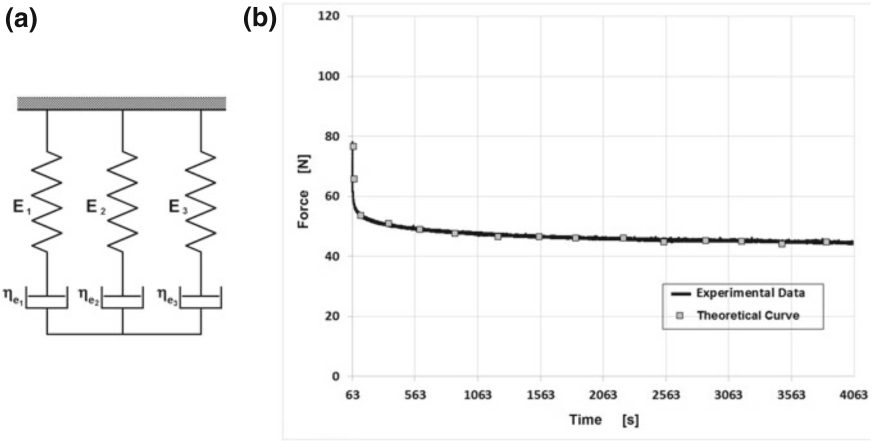


Fig. 14 Scheme of a three-elements of Maxwell generalized model (**a**) and comparison between experimental data and this model (**b**)

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