



Electrostrictive thermoplastic polyurethane-based nanocomposites filled with carboxyl-functionalized multi-walled carbon nanotubes (MWCNT-COOH): Properties and improvement of electromechanical activity



K. Wongtimnoi^{a,*}, B. Guiffard^{b,2}, A. Bogner-Van de Moortèle^{a,3}, L. Seveyrat^b, J.-Y. Cavallé^a

^a MATerials Engineering and Science (MATEIS), INSA Lyon, CNRS-UMR 5510, Bâtiment Blaise Pascal, 7 Av. Jean Capelle, F-69621 Villeurbanne cedex, France

^b Laboratoire de Génie Electrique et Ferroélectricité (LGEF), INSA Lyon, Bâtiment Gustave Ferrière, 8 rue de la Physique, F-69621 Villeurbanne cedex, France

ARTICLE INFO

Article history:

Received 28 January 2013

Received in revised form 19 May 2013

Accepted 26 May 2013

Available online 3 June 2013

Keywords:

A. Polymers

A. Carbon nanotubes

B. Electrical properties

C. Deformation

E. Casting

ABSTRACT

The impact of small amounts of carboxyl-functionalized multi-walled carbon nanotubes (MWCNT-COOH) added into a polyether-based thermoplastic polyurethane elastomer (TPU) was studied considering mainly on the morphological, mechanical, electrical and electrostrictive properties. The electrostrictive properties were measured by the analysis of the deformation response occurring under external electric fields E applied on 50 μm -thick films. Dielectric measurements were carried out in order to determine the percolation threshold f_c , which was found near 1 v% loading. This volume fraction leads to a very high dielectric permittivity ϵ'_r up to ≈ 330 , i.e. about 50 times higher than that of the pure TPU, where $\epsilon'_r \approx 6-7$.

The thickness strain S_z and apparent electrostrictive coefficient M were measured at low electric fields, $E \leq 4 \text{ V}/\mu\text{m}$, by low frequency of 0.1 Hz. The maximum induced-compressive strain was obtained from an optimal volume fraction of 0.8 v% which yielded to a high $S_z = -11.5\%$ corresponding to almost a threefold increase of M compared to the neat TPU. Beyond f_c , the conductivity sharply raised up and thus the electrostrictive activity disappeared.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

High electromechanical activity was investigated in most of thermoplastic polyurethane elastomers (TPUs) [1–5]. They are consisted of block copolymers of hard segments (HS) with strong polar groups, and soft segments (SS) with low polar groups. With a high dielectric permittivity, the electric field-applied dipole interactions play a role yielding to a rather large compressive electrostriction. An explanation has been given based on their phase separation [6]. Nevertheless, improving electromechanical activities are still required to reach higher performance by lower electrical energy. Compared to several routes, the incorporation of conductive

particles is of a great interest, simple with no chemical reaction required and various available fillers [7].

Many studies have been conducted on the electromechanical activity of soft dielectric sheet submitted to an electric field E to describe the behavior of such materials. The total electromechanical strain S may be attributed as the sum of two main strains and is theoretically linked to the square of the electric field E and the apparent strain coefficient M [3,8]: $S = S_E + S_M = M \cdot E^2$.

- (i) S_M is the strain due to Maxwell stress, so-called electrostatic strain, of two charged electrodes attracting each other compressing soft dielectrics (Modulus $\sim 1 \text{ MPa}$) having low dielectric permittivity when the electrostriction is negligible [9–11]. S_M can be described as: $S_M = -\epsilon'_r \cdot \epsilon_0 \cdot E^2 / Y$, where Y is the Young's modulus, ϵ'_r is the real part of the relative permittivity and ϵ_0 is the vacuum permittivity, $8.854 \times 10^{-12} \text{ F/m}$.
- (ii) S_E is the strain due to the electrostriction, mainly occurs for strongly polar soft polymers where intrinsic dipole moment and dipole-dipole attraction lead to an intrinsic compression [12,13]. A high strain is obtained even under a moderate E . S_E can be written, as an empirical equation, as [8]:

* Corresponding author. Tel.: +33 4 72 43 83 82, +33 4 72 43 60 03; fax: +33 4 72 43 85 28.

E-mail address: komkrisd.wongtimnoi@insa-lyon.fr (K. Wongtimnoi).

¹ Current address: Ingénierie des Matériaux Polymères (IMP), INSA Lyon, UMR 5223 Site INSA, Bâtiment Jules Verne, 17 Av. Jean Capelle, F-69621 Villeurbanne cedex, France.

² Current address: Lunam Université, IETR UMR CNRS 6164, Université de Nantes, 2 rue de la Houssinière, BP 92208, F-44322 Nantes cedex 3, France.

³ Died on February 28, 2012.

$S_E = Q \cdot \epsilon_0^2 \cdot (\epsilon_r' - 1)^2 \cdot E^2$, where Q is the absolute electrostrictive coefficient due to the electrical field-induced polarization.

For strongly electrostrictive polymers, S_E may become largely predominant, compared to S_M [5]. Therefore, contrary to the dielectric soft elastomers, S_M can be considered negligible under moderate field and S is approximately close to S_E . However, for a dielectric material whose $\epsilon_r' \gg 1$, M is proportional to ϵ_r' and inversely to Y : $M \propto \epsilon_0 \cdot \epsilon_r' / Y$ [2]. Therefore, the ideal way to increase S is to increase ϵ_r' without reinforcement. Incorporating an amount close to the percolation threshold (f_c , a critical fraction) of conductive particles into the polymer matrix, ϵ_r' increases rapidly [14].

The aim of this study was to determine the influence of carboxylic functionalized multiwall carbon nanotubes (MWCNT-COOH) on the mechanical, electrical and, particularly electromechanical properties of a TPU host matrix.

2. Experimental section

The TPU was Estane 58888 NAT 021, having a density of 1.13 g/cm³ purchased from Lubrizol. MWCNT-COOH, called as CNTC, were purchased from Nanostructured & Amorphous Materials, Inc. They have a diameter below 8 nm, a length ranging of 0.5–2 μ m, a bulk density of 1.7–1.9 g/cm³, and a specific gravity of 2.1. Their surface is functionalized with ≈ 4 w% -COOH, promising a good dispersion into polar solvents [15] and so our polymer solution. “xCNTC” represents a composite filled with x v%.

Film samples were made by solution-casting. The first step was to dissolve TPU in N,N-dimethylformamide (DMF) at 80 °C. In parallel, CNTC were dispersed in DMF using an ultrasonic probe (UP400S, Hielscher) for 15 min. Subsequently, the two solutions were mixed together, heated and stirred to obtain a viscous solution. The solution was spread onto a glass plate by the Doctor Blade applicator (Elcometer®), dried at 60 °C for 1 day and 130 °C for 3 h. The thickness of dried films was 50 ± 1 μ m.

The dispersion was checked by an environmental scanning electron microscopy (ESEM) in classical mode, namely FEI XL30 FEG ESEM, within the frame of the Centre Lyonnais de Microscopie (CLYM). Prior to observations, samples were fractured in liquid nitrogen and both fractured cross-sections and gold-coated by plasma sputtering for preventing electron charging on sample surface.

Mechanical property was measured with a multifunctional dynamic mechanical analyzer, Eplexor® of Gabo, in tensile mode with a load cell of 500 N. Films were cut into 10 \times 40 mm² rectangular samples with 20 mm long for testing. The tests were carried out with an elongation speed of 24 mm/min (corresponding to 0.02 s⁻¹ strain rate) at room temperature. Young modulus was obtained from the 3% first elongation.

Prior to the electrical measurements, the films were coated with gold on their two faces by sputtering. The conductivity was measured with a Solartron 1296 impedance-meter from Ametek. At an average AC at 1 Vrms, a frequency scan was performed in a range of 0.1–10⁶ Hz at room temperature.

The induced strain S_z was determined at room temperature using a laser interferometer (Agilent 10889B) with a 10 nm precision, as described elsewhere [16]. A film was placed between two circular electrodes with 20 mm diameters which an alternative electrical potential (triangular function) was applied at 0.1 Hz. A mirror was placed on the upper electrode to reflect the laser beam to determine the displacement. The electrical potential was generated by a generator (Agilent 33220A) and amplified 1000 times by a lock-in high tension amplifier (Trek 10/10B).

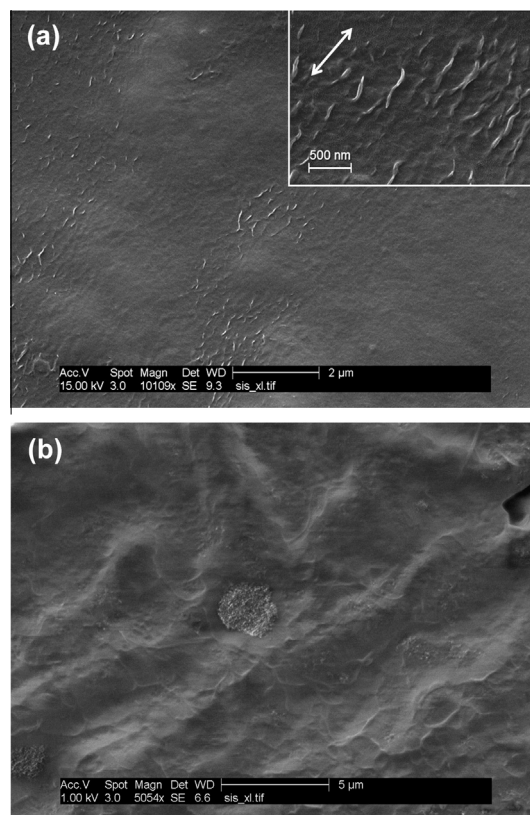


Fig. 1. ESEM images of 1CNTC film (a) gold-coated upper surface observed with high voltage and (b) cryo-fractured section observed with low voltage.

3. Results and discussion

3.1. SEM observation of CNTC/TPU films

In Fig. 1a, the upper surface of a 1CNTC film shows well-dispersed nanotubes. Due to the solution-casting technique, most of them are oriented as shown by the white arrow. They exhibit diameters around 20 nm, i.e. larger than their real diameter. This may be due to the fact that the nanotubes are embedded by polymer matrix which makes their diameter thicker than their real size. Furthermore, checking out of the nanotubes dispersion within the film through the thickness is still required. The same film was cryo-fractured in liquid nitrogen at a temperature lower than T_g of the soft segment domain (SSD) of TPU (-45 °C⁴) in order to observe the intrinsic morphology of elastomers. Fig. 1b reveals some micro-aggregates inside the film. This re-agglomeration of CNTC might be the result of DMF evaporation which decreases the total solubility of solution and increases the difference of the solubility of the solution and the nanotubes. This might be a key factor. Two mobile elements with adjacent solubility are probably easier to homogeneously mix together. The total solubility parameter δ_t of an element is widely known, also called “Hansen solubility parameters” [17], based on the fact that all types of physical bonds are broken when the evaporation takes place, including those commonly called ‘nonpolar’, ‘polar’, and ‘hydrogen bonding’. Solubility parameters of the elements constituting our composite system are gathered in Table 1.

Assumedly the TPU based of P(MDI-BDO) and PTMG is an homogeneous mixture. Its δ_t could be approximated by the classic

⁴ Also from the Lubrizol’s technical information.

Table 1
Solubility parameters of some concerned elements.

Elements	δ (J/cm ³) ^{1/2}	References
Poly(tetramethylene glycol), PTMG	16.6	[18]
4,4'-Methylene diphenyl diisocyanate, MDI	41.0	[19]
1,4-Butane diol, BDO	50.6	[19]
P(MDI-BDO), 100% rigid segments	23.2/25.3	[18]/[20]
N,N-dimethylformamide, DMF	24.8	[21]
Carbon nanotube, CNT	15–30	[22,23]
Carbon black, CB	20–25	[24]

mixture rule: $\delta_t = f_1\delta_1 + f_2\delta_2$, where f is the volume fraction and $f_1 + f_2 = 1$. As the TPU consists of 45 w% of P(MDI-BDO) (1.30 g/cm³ [25]), and of 55 w% of PTMG (0.974 g/cm³ [26]), the δ_t of this TPU should approximately be 19.4 (J/cm³)^{1/2}. Compared to the pristine nanotubes, CNTC surly has higher δ_t . This might lead an easy dispersion and a stable suspension in DMF rather than in TPU. This points out why the dissolved CNTCs (as observed, Fig. 1a) tend to re-agglomerate in concentrated TPU/DMF solutions, so the cast film while drying.

3.2. Uniaxial tensile testing, Young's modulus (Y)

For initial elongations, the stretched film exhibits a linear elastic behavior from which Y can be determined. In Fig. 2, the increase of Y with the incorporation of nanotubes into the polymer matrix exhibits a linear relation to the CNTC loadings. By the aspect ratio and the volume fraction of filler, Y may be predicted by classical models such as the Guth model [27] and the Halpin-Tsai model [28,29]. But it is worth to notice that the reinforcing capability of nanotubes is overestimated, probably because they are far to be stiff rods but as coils which decrease their effective aspect ratio. As an increase of Y impart a negative effect on the electromechanical activities, including M and S_z . Besides, the increase of Y may lead to higher actuating energy ($0.5Y \cdot S_z^2$) and force, than the softer pure matrix, under the same applied electric field. Thus, a compromise between Y and S_z has to be done, depending on the actuation application.

3.3. Electrical conductivity, percolation threshold and dielectric permittivity

The f_c of carbon nanotubes-filled composites is practically reached with a quite low fraction at 1 w% (0.5 v%) [30] or very

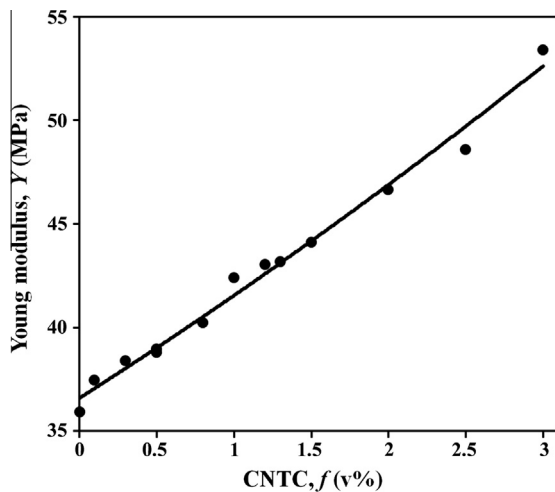


Fig. 2. Evolution of Y versus CNTC contents.

low at 0.0025 w% (0.001 v%) for long nanotubes [31]. The short type was then chosen. They have high electrical conductivity promising significantly to raise the dielectric permittivity of the incorporating polymer.

In Fig. 3a, the real part of electrical conductivity (σ') of TPU and composites is plotted as a function of frequency. The conductivity jump between 1 and 1.3 v% is related to the insulating-conductive transition behavior. f_c can be determined by the classical power law of electrical conductivity [32–35] when $f > f_c$ as: $\sigma' \propto [(f - f_c)/(1 - f_c)]^t$, where t is the critical exponent, typical for each system. At 0.1 Hz, σ' increases with the CNTC loading and the plot of $\log(|\sigma'|)$ versus $\log[(f - f_c)/(1 - f_c)]$ is presented in Fig. 3b. Above f_c , the best fit of σ by fraction is $f_c = 0.98$ v% with $t = 2.0$. It is often found in many pristine MWCNT-filled composites that the insulating-conductive transition occurs around 0.05 v%. This could be simply interpreted that the nanotubes are in general long, entangled into large bundles, and non-functionalized whilst the ours provided are typically short and functionalized with -COOH groups all over the outer surface rendering less entangling and easier dispersible into the polar solvent used and thus in composite films. Beside, t has been concluded to be inversely proportional to the aspect ratio of nanotubes [34]. This may explain why the short CNTC (our case) could attain a high f_c close to 1%. Moreover, t usually places between of 1.3 and 4 and frequently near 2.

Below f_c , our composites are almost perfect insulators and their ϵ can be measured. ϵ increased of composites is due to the space-charge polarization induced on conductive filler surface. Fig. 4a shows the real part ϵ' increasing with the CNTC content. The high-

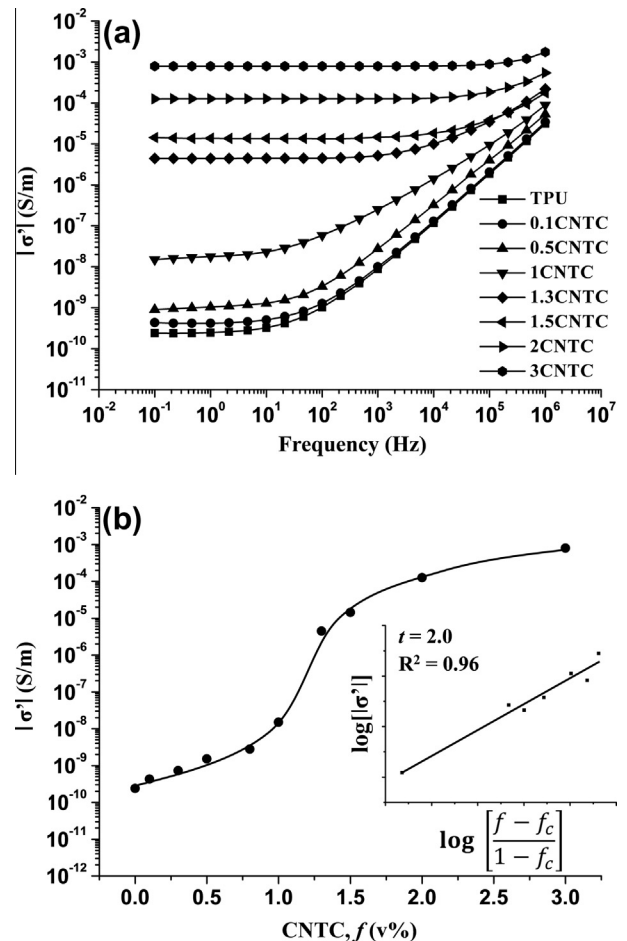


Fig. 3. Electric conductivity as a function of (a) frequency and (b) CNTC content at 0.1 Hz associated with the percolating power law over f_c .

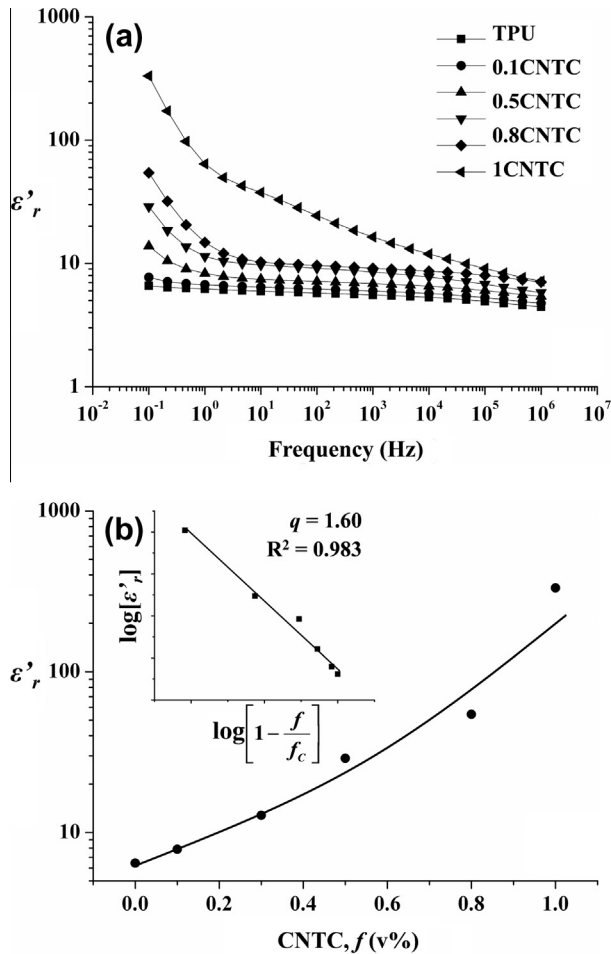


Fig. 4. ϵ'_r of TPU and composites as a function of (a) frequency and (b) CNTC loading at 0.1 Hz associated with the percolating power law below f_c .

est value is obtained near f_c , before the composites become conductive. In addition, ϵ'_r increases when the frequency decreases.

Again, the percolation theory for the insulating behavior under f_c , gives a linear logarithmic relation between ϵ'_r and the fraction as [33,36]: $\epsilon'_r \propto [1 - (f/f_c)]^{-q}$, $f < f_c$, where ϵ'_r is the dielectric permittivity, and q is the critical exponent for the composite. Fig. 4b shows that, below f_c , ϵ'_r increases with the CNTC content and follows a linear relation between $\log[\epsilon'_r]$ and $\log[1 - (f/f_c)]$ is also put in. The best fit leads to $f_c = 1.1$ v% with $q = 1.6$. The highest observed ϵ'_r is 330 at 0.1 Hz, about 50 times higher than the neat TPU, $\epsilon'_r = 6$ –7. The found f_c is close to that from the electrical conductivity. On the other hand, q for our composites is higher than the universal critical exponent $q = 1$. In fact, different elaboration techniques may lead to different final materials, and this means that the ideal conditions for the application of the percolation theory are not met: the main point is that particles should have been randomly dispersed.

Below f_c , the dielectric loss (ϵ''_r) remains low as same value as the matrix. Above f_c , ϵ'_r and ϵ''_r both increase but the latter increases more rapidly than the real part. Thus $\tan \delta$, the ratio of ϵ''_r/ϵ'_r , drastically increases as shown in Fig. 5. It depends on the conductive network in the composite film, which transforms a part of the electrical energy into heat (Joules effect).

3.4. Electromechanical activity improvement

Non-piezoelectric electronic EAPs always perform a thickness compression when subjected to an electric field (E) applied in the

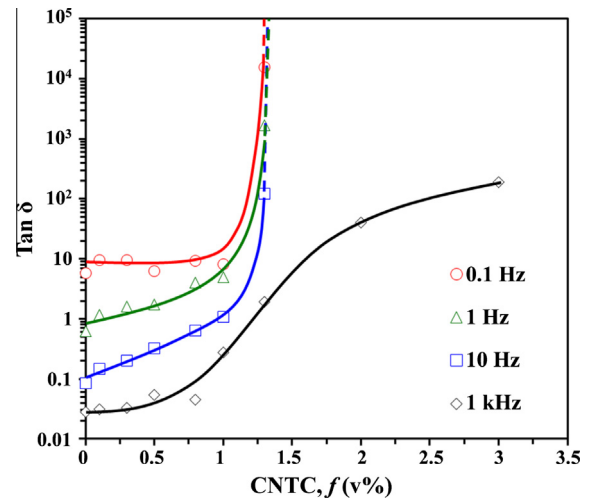


Fig. 5. Loss tangent at different frequencies as a function of CNTC contents.

thickness direction. Consequently, the strain and the related electrostrictive coefficients (M_{33} or Q_{33}) are also negative [2,37,38]. By using an interferometer [16], the E -induced strain (S_Z) of TPU typically presents two parts; the first part at low E with a quadratic relationship between S_Z and E and the second part at high E , a saturation plateau until the dielectric breakdown, cited in our previous work [5] when we concluded that the major electromechanical activity of the TPU was totally electrostrictive giving a strain contribution about 1000 times larger than the electrostatic Maxwell strain. The same behavior is here expected.

As shown in Fig. 6a, TPU and some composite films, filled with CNTC below f_c , with 50 μm in thickness exhibit a “butterfly” strain response to E . This behavior strongly suggests electromechanical losses whatever the film sample. Below f_c , the strain amplitude increases effectively with CNTC contents up to 0.8 v%, as shown in Fig. 6b. For some composites with CNTC contents close to or just above f_c (1, 1.2, and 1.3 v% CNTC), the dielectric breakdown occurs even by a moderate E . High current passes through the film sample, heats it up, and breaks it down finally. For these early broken samples, dashed lines are used to estimate the expected S_Z if the samples did not break down yet.

The origin of the strain saturation S_{sat} is a complex phenomenon, up to now only a few research groups have tried to interpret this behavior [39–41]. Fig. 7 reveals that S_{sat} slowly decreases from around -20% for the neat TPU and brutally drops after f_c . This is related to the conductive CNTCs networks and also to the mechanical reinforcement. The complete understanding of this phenomenon requires further studies.

By plotting S_Z (in the quadratic range) versus E^2 in Fig. 8, a linear response appears with a slope relating to the strain coefficient, so called the apparent electrostrictive coefficient M or M_{33} . Contrarily to S_{sat} , M increases up to f_c . S_Z and M under $E = 4 \text{ V}/\mu\text{m}$ at 0.1 Hz plotted against the CNTC fraction exhibit a maximum near f_c (0.8 v%), as shown in Fig. 9. Thus S_Z (-11.5%) appears to almost 3 times higher than TPU ($S_Z = -4.3\%$), and also M increases. The 0.8CNTC exhibits $M = -7.4 \times 10^{-15} \text{ m}^2/\text{V}^2$, compared to $M = -2.7 \times 10^{-15} \text{ m}^2/\text{V}^2$ for TPU. Above f_c , the response falls down.

For many TPUs, the apparent M lies often between -10^{-18} and $-10^{-17} \text{ m}^2/\text{V}^2$ [1,2,9,42,43]. However, higher values were reported. TPU based of isofuran DI-BDO and PEGA with $Y = 15 \text{ MPa}$ and $\epsilon'_r = 7$ exhibits a strong activity with $M_{33} = -1.7 \times 10^{-15} \text{ m}^2/\text{V}^2$ at 0.05 Hz [3]. Certainly, the electrostriction depends on the mechanical and dielectric properties, and probably on the morphology of its microstructure (phase separation, etc.) [6]. However, the performance of any EAPs extremely depends on the frequency of applied

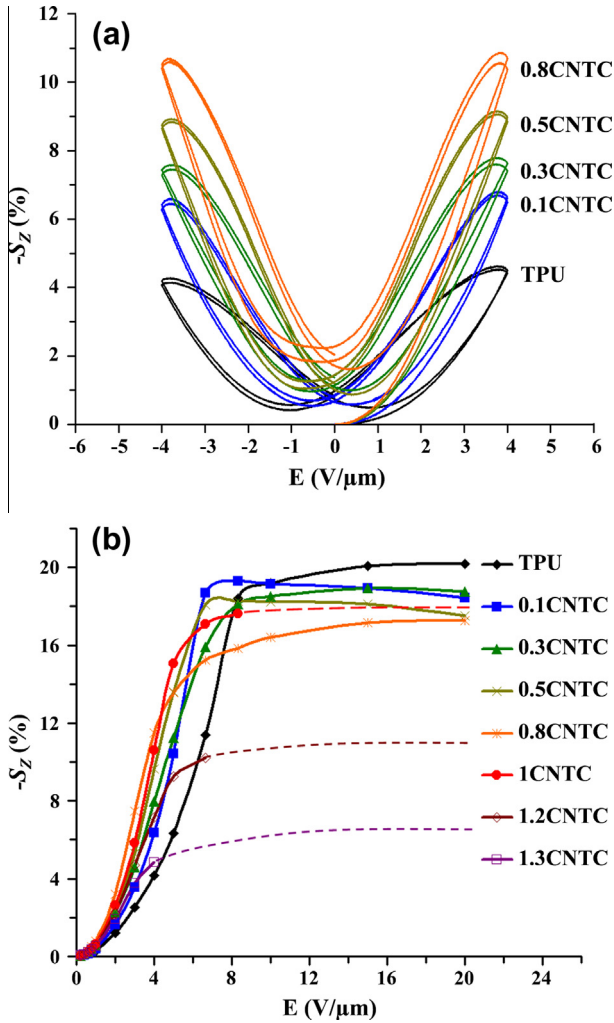


Fig. 6. (a) Real-time S_z induced by 2 cycles of $E = 4 \text{ V}/\mu\text{m}$ maximum at 0.1 Hz and (b) the strain amplitude as a function of E up to $20 \text{ V}/\mu\text{m}$.

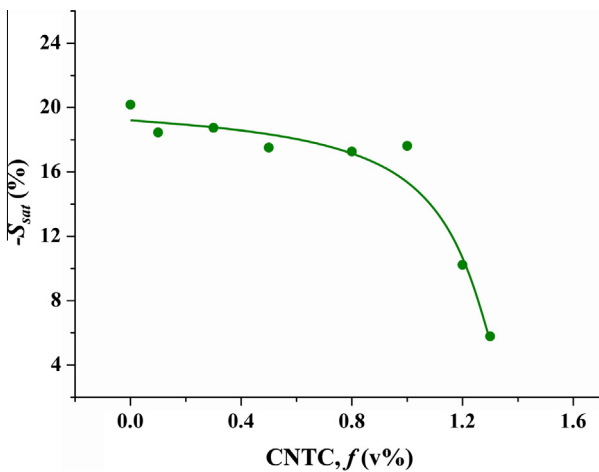


Fig. 7. Saturation strain amplitude as a function of CNTC content.

excitation. M decreases systematically with the frequency. It is mainly related to (i) the decrease of the dielectric permittivity with frequency, and (ii) to the mechanical loss (damping) expected to increase for an elastomer just above its glass transition temperature. Therefore, the results need to be carefully compared only

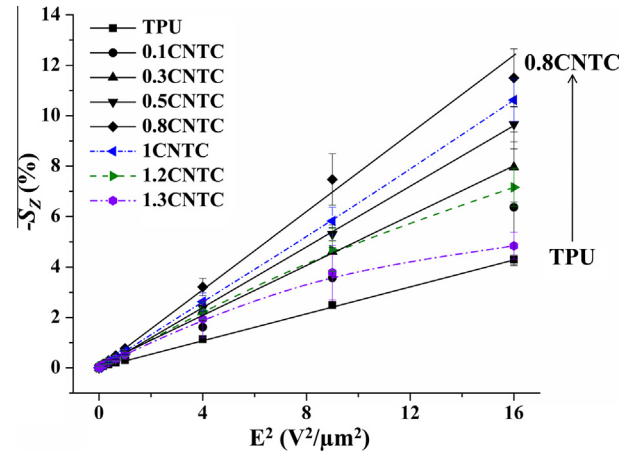


Fig. 8. Quadratic strain S_z versus E^2 at low field depending on CNTC loadings.

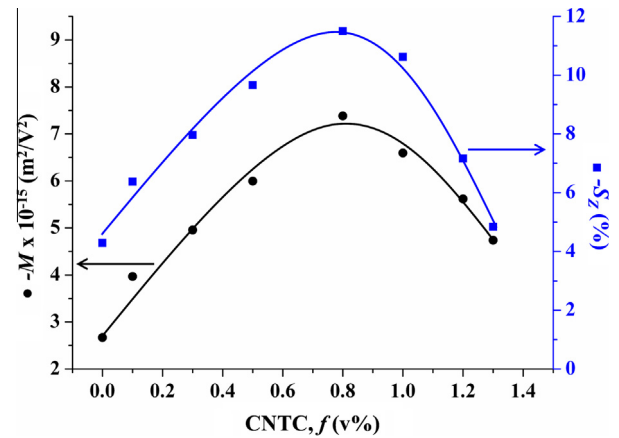


Fig. 9. M and S_z versus CNTC fraction at $E = 4 \text{ V}/\mu\text{m}$ and 0.1 Hz.

with the values obtained in the same ranges of frequency and temperature.

4. Conclusions

In this work, electrostrictive TPU composites were elaborated by filling the polymer with soluble carboxyl-functionalized multi-walled carbon nanotubes. The Young's modulus of TPU was monotonically increased with nanotube loadings.

According to the percolation theoretical power law of electrical conductivity and dielectric permittivity, the f_c of this composite system was found around 1 v%. Close to f_c , the dielectric permittivity of composites sharply increases and a high dielectric permittivity of 330 was found with 1CNTC. Consequently, the electromechanical activity of the composites also increased. For a moderate applied field $E = 4 \text{ V}/\mu\text{m}$ at 0.1 Hz, the highest strain S_z (−11.5%) with the apparent electrostrictive coefficient $M = -7.4 \times 10^{-15} \text{ m}^2/\text{V}^2$ was obtained with 0.8CNTC, just below f_c . This M is almost three times higher than that of the neat TPU. As the CNTC content more than 1 v%, the conduction of the nanotube network leads to an increase of dielectric loss and the drop of the electromechanical activity.

In order to further, a modeling of the electrostriction effect should be developed. The purpose should be to optimize the choice of the matrix and of the filler, of their characteristics (size, volume fraction, etc.). Such a work is now going on.

Acknowledgements

This work was financed by the MACODEV research foundation of the Rhône-Alpes region and carried out by the collaboration of MATEIS and LGEF laboratories, INSA de Lyon. The CLYM is acknowledged for the access of the FEI XL30 FEG ESEM microscope and the FIB. Agnès Bogner-Van de Moortèle and her PhD. student, Yang Liu, deserve to be also acknowledged for their expertise. At last, by all impressive pleasures, the author would like to thank honestly back to all advisers whose many brilliant ideas helped completely realize the works.

References

- [1] Ma Z, Scheinbeim J, Lee J-W, Newman B. High field electrostrictive response of polymers. *J Polym Sci Part B: Polym Phys* 1994;32:2721–31.
- [2] Guillot F, Balizer E. Electrostrictive effect in polyurethane. *J Appl Polym Sci* 2003;89(2):399–404.
- [3] Diaconu I, David A, Dorohoi D-O. An experimental investigation of electroactive polyurethane. *J Optoelectron Adv Mater* 2005;7(6):2797–801.
- [4] Guiffard B, Seveyrat L, Sebald G, Guyomar D. Enhanced electric field-induced strain in non-percolative carbon nanopowder/polyurethane composites. *J Phys D: Appl Phys* 2006;39:3053–7.
- [5] Wongtimnoi K, Guiffard B, Bogner-Van de Moortèle A, Seveyrat L, Gauthier C, Cavaillé J-Y. Improvement of electrostrictive properties of a polyether-based polyurethane elastomer filled with conductive carbon black. *Compos Sci Technol* 2011;71:885–92.
- [6] Cavaillé J-Y. Physical Modeling of the Electromechanical Behavior of unfilled Polymers. In: 8th ICFD, Tohoku; 2011.
- [7] Huang C, Zhang Q. Enhanced dielectric and electromechanical responses in high dielectric constant all-polymer percolative composites. *Adv Funct Mater* 2004;14(5):501–6.
- [8] Su J, Harrison J, Clair T, Bar-Cohen Y, Leary S. Electrostrictive graft elastomers and applications. in MRS Symposium: FF: Electroactive Polymers, Boston, MS; 1999.
- [9] Pelrine R, Kornbluh R, Joseph J, Heydt R, Pei Q, Chiba S. High-field deformation of elastomeric dielectrics for actuators. *Mater Sci Eng C* 2000;11:89–100.
- [10] Goulbourne N, Mockensturm E, Frecker M. Electro-elastomers: large deformation analysis of silicone membranes. *Int J Solid Struct* 2007;44:2609–26.
- [11] Ma W, Cross L. An experimental investigation of electromechanical response in a dielectric acrylic elastomer. *Appl Phys A* 2004;78:1201–4.
- [12] Wang Y, Sun C, Zhou E, Su J. Deformation mechanisms of electrostrictive graft elastomer. *Smart Mater Struct* 2004;13:1407–13.
- [13] Lee H, Peng Y, Shkel Y. Strain-dielectric response of dielectrics as foundation for electrostriction stresses. *J Appl Phys* 2005;98:074104–9.
- [14] Foulger S. Electrical properties of composites in the vicinity of the percolation threshold. *J Appl Polym Sci* 1999;72:1573–82.
- [15] Lee J, Kim M, Hong C, Shim S. Measurement of the dispersion stability of pristine and surface-modified multiwalled carbon nanotubes in various nonpolar and polar solvents. *Meas Sci Technol* 2007;18:3707–12.
- [16] Guiffard B, Guyomar D, Seveyrat L, Chowanek Y, Bechelany M, Cornu D, et al. Enhanced electroactive properties of polyurethane films loaded with carbon-coated SiC nanowires. *J Phys D: Appl Phys* 2009;42:055503 (6pp).
- [17] Hansen C. Polymer additives and solubility parameters. *Prog Org Coat* 2004;51:109–12.
- [18] Van Krevelen D, Hoftyzer P. Properties of polymers: correlations with chemical structure. Elsevier; 1972. p. 135–43.
- [19] Nishimura H, Kojima H, Yarita T, Noshiro M. Phase structure of polyetherpolyol-4,4'-diphenylmethane diisocyanate-based reaction injection molded (RIM) polyurethanes. *Polym Eng Sci* 1986;26(9):585–92.
- [20] d'Arlas B, Rueda L, de la Caba K, Mondragon I, Eceiza A. Microdomain composition and properties differences of biodegradable polyurethanes based on MDI and HDI. *Polym Eng Sci* 2008;48:519–29.
- [21] Burke J. Solubility parameters: theory and application. The Book and Paper Group: Annual, vol. 3, 1984.
- [22] Bergin S, Sun Z, Rickard D, Streich P, Hamilton J, Coleman J. Multicomponent solubility parameters for single-walled carbon nanotubes-solvent mixtures. *ACS Nano* 2009;3(8):2340–50.
- [23] Launay H, Hansen C, Almdal K. Hansen solubility parameters for a carbon fiber/epoxy composite. *Carbon* 2007;45:2859–5865.
- [24] Abbott S, Hansen C. Hansen solubility parameters in practice. Hansen-solubility.com, Steven Abbott and Charles Hansen; 2008.
- [25] Blackwell J, Nagarajan M, Hoitink T. Structure of polyurethane elastomers: effect of chain extender length on the structure of MDI/Diol hard segments. *Polymer* 1982;23:950–6.
- [26] INVISTA, Properties, Uses, storage and handling of INVISTA TERATHANE PTMEG, Technical Information, INVISTA Inc.
- [27] Guth E. Theory of filler reinforcement. *J Appl Phys* 1945;16(1):20–5.
- [28] Halpin J. Stiffness and expansion estimates for oriented short fiber composites. *J Compos Mater* 1969;3(4):732–4.
- [29] Bokobza L. Multiwall carbon nanotube elastomeric composites: a review. *Polymer* 2007;48:4907–20.
- [30] Sandler J, Kirk J, Kinloch I, Shaffer M, Windle A. Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites. *Polymer* 2003;44:5893–9.
- [31] Sahimi M. Applications of percolation theory. London: Taylor & Francis; 1994.
- [32] Flandin L, Prasse T, Schueler R, Schulte K, Bauhofer W, Cavaillé J-Y. Anomalous percolation transition in carbon-black-epoxy composite materials. *Phys Rev B* 1999;59(22):14349–55.
- [33] Dang Z-M, Fan L-Z, Shen Y, Nan C-W. Dielectric behavior of novel three-phase MWNTs/BaTiO₃/PVDF composites. *Mater Sci Eng B* 2003;103(2):140–4.
- [34] Bauhofer W, Kovacs J. A review and analysis of electrical percolation in carbon nanotube polymer composites. *Compos Sci Technol* 2009;69:1486–98.
- [35] Zois H, Apekis L, Omastova M. Electrical properties of carbon black-filled polymer composites. *Macromol Symp* 2001;170:249–56.
- [36] Pelrine R, Kornbluh R, Joseph J. Electrostriction of polymer dielectrics with compliant electrodes as a means of actuation. *Sens Actuators A: Phys* 1998;64(1):77–85.
- [37] Eury S, Yimnirun R, Sundar V, Moses P, Jang S-J, Newnham R. Converse electrostriction in polymers and composites. *Mater Chem Phys* 1999;61:18–23.
- [38] Diaconu I, Dorohoi D-O, Ciobanu C. Electromechanical response of polyurethane films with different thickness. *Rom J Phys* 2008;53(1–2):91–7.
- [39] Guyomar D, Cottinet P-J, Lebrun L, Putson C, Yuse K, Kunda M, et al. The compressive electrical field electrostrictive coefficient M33 of electroactive polymer composites and its saturation versus electrical field, polymer thickness, frequency and fillers. *Polym Adv Technol* 2011:5.
- [40] Guyomar D, Yuse K, Kunda M. Thickness effect on electrostrictive polyurethane strain performance. A three-layer model. *Sens Actuators A* 2011;168:307–12.
- [41] Lam K, Wong Y, Tai L, Poon Y, Shin F. Dielectric and pyroelectric properties of lead zirconate titanate/polyurethane composites. *J Appl Phys* 2004;96(7):3896–9.
- [42] Lam K, Wong Y, Tai L, Poon Y, Shin F. Electrostriction of lead zirconate titanate/polyurethane composites. *J Appl Phys* 2005. 104112:1–6.
- [43] Zhang Q, Su J, Kim C. An experimental investigation of electromechanical responses in a polyurethane elastomer. *J Appl Phys* 1997;81(6):2770–6.