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Abstract

Polyurethanes (PU) have demonstrated their ability to convert electrical energy into mechanical energy and vice versa. The incorporation into a PU matrix of nanofillers, such as carbon nanotubes (CNT), can even enhance the actuation and the harvested energy performances. However, it is well known that CNTs are hardly dispersed in a polymeric matrix, and that the interfacial adhesion strength is generally poor. Moreover, the improvement of electromechanical properties is limited by the low volume fraction of CNT that can be dispersed because of their low percolation threshold. In this study, we present how grafting polymer onto CNTs can improve the physical properties of PU nanocomposites and accordingly the electromechanical properties of the PU/ grafted CNT nanocomposites, compared to those of pristine PU. The dielectric permittivity is largely increased and the percolation threshold is found around 5 vol. %. Measurements of the thickness strain under an applied electrical field demonstrate a twofold increase of the electrostriction coefficient. The energy harvesting properties investigated by monitoring the evolution of the current under a DC electric field are also enhanced.

Keywords**:** A. Carbon nanotubes; A. Polymer-matrix composites (PMCs) ; A. Smart materials ; B. Electrical properties ; B. Mechanical properties

Introduction

In the field of smart materials, a tremendous amount of research has led to Electroactive Polymers (EAP), that can change in size or shape when stimulated by the right external electrical activation mechanism, meaning they can convert electrical energy into mechanical energy [1]. These materials are highly attractive for their large strain capability, and resilience. Among such materials, polyurethane (PU) elastomers are EAPs of great interest due to their significant electrical-field strains [2], and due to their attractive and useful properties such as flexibility, light weight, easy processing to large area films as well as their ability to be moulded into various shapes and biocompatibility with blood and tissues. In addition, it has recently been shown that the incorporation of nanofillers into a PU matrix, such as carbon nanotubes (CNTs) [3,4,5], can greatly enhance the expected strain, or the harvested energy [6]. This outstanding result seems to be related to the increase of the permittivity when nanofillers are incorporated within the polymers, hence requiring a lower bias electric field for the same effect. To develop high-efficiency polymer nanocomposites for energy harvesting and actuation applications, it is thus important to obtain large values of the dielectric permittivity while maintaining adequate mechanical properties [7].

However, it is well known that CNTs are hardly dispersed in a polymeric matrix and that the interfacial adhesion strength is generally poor [8]. An effective method to improve both dispersion and interfacial adhesion consists in functionalizing CNTs by grafting polymer chains onto their surfaces [9,10]. S. Li et al [11] reported that grafting chains with different molecular weights on the surface of MWCNTs increases the solubility of MWCNTs and as a consequence the conductivity of the nanocomposites decrease.

This study reports the effect of the incorporation of grafted CNTs on the physical properties of PU nanocomposites, namely microstructural, mechanical, electrical and electromechanical properties. A multi-scale characterization approach using TEM observations is performed to control the grafting process step-by-step. Optimization of nanocomposite film elaboration avoiding damage of the grafted layer is monitored with the help of TEM observations. Isochronal mechanical measurements are performed, as well as dielectric measurements over a wide range of frequencies and temperatures in order to study the influence of the grafted CNTs on the different relaxations processes of the polymer. Finally, the electromechanical performances of such nanocomposites films are evaluated.

Materials and methods

Multi-walled CNTs were provided by Cheap Tubes and had average diameters of 30 nm and lengths of 10 to 20 µm. The grafting reactions were performed using a "grafting onto" technique [10] to form a PU thin layer on the surface of the CNTs. First, functional groups such as –COOH –OH were created on the sidewalls of CNTs, by oxidation of the CNTs. Then as a second step, polyTDI-tolylene-2,4-diisocyanate terminated poly(propylene glycol)- was grafted on the functionalized CNTs. Finally, polyol was also grafted on CNT-PolyTDI [12], see Fig. 1(a).

The matrix was a polyether-based thermoplastic polyurethane (Estane 58888 NAT021 – Lubrizol. It is a co-block polymer with two major blocks, made of hard and of soft segments. Hard segment (HS) are composed of 4.4' methylene bis (phenyl isocyanate) (MDI) and 1,4-butanediol (BDO). Poly(tetramethylene oxide) (PTMO) is used as soft segments (SSs).

The polymer films were prepared by a solution casting method. Before use, PU granules were heated at 350 K for 3 hours. The grafted CNTs were first dispersed in N,N-dimethylformamide (DMF, Sigma-Aldrich D158550, 99%) using sonication in an ultrasonic bath (UB) (Bioblock Scientific TS540 (power 10 %)) and /or using an ultrasonic processor (UP) with a 7 mm sonotrode (Hielscher UP400S 400W, 24 kHz, (power 30%)). PU granules were added to this solution with a ratio of 15 wt.% of PU into DMF. The solution was heated at 350 K for 4 hours under mechanical agitation, until a homogeneous solution was obtained. This operation was carried out in a closed device, to avoid evaporation of DMF and to ensure good reproducibility of films. Then, the solution was kept overnight to remove air bubbles. Afterwards, this solution was cast on glass plates with an Elcometer 3700 Doctor Blade ® film applicator, put in an oven at 335 K for one day, and then removed from the glass. A second heating treatment at a temperature below the HS melting temperature was performed at 400 K for 3 h in order to eliminate any residual solvent. The thickness of the films was about 100 µm after drying.

The control of the grafting process as well as the control of the CNT dispersion state in DMF was performed using Transmission Electron Microscopy (TEM). Observations were carried out in the bright field mode with a JEOL 2010F operating at 200 kV.

The microstructural observations on the cryofractured surfaces - in order to control the CNT dispersion state and interfacial adhesion strength - were performed using a Zeiss Supra 55VP Scanning Electron Microscope operating under high vacuum, at low accelerating voltage (typically 1000 V) and without any gold coating. Images were acquired with the Everhart-Thornley secondary electron detector.

The dielectric properties of these films were measured with a Modulab MTS at an AC voltage of 1 V RMS, over a frequency range of 10^{-1} to 10^{6} Hz. Both surfaces of the film were coated with a gold electrode of 20 mm in diameter, deposited by sputtering (Cressington 208 HR). Isothermal measurements were performed under liquid nitrogen using a cryostat (JANIS-STVP-200XG), in the temperature range 100-400 K, and the activation energy and characteristic relaxation time (τ) were determined for all the relaxation processes. Dielectric data were fitted with the Havriliak Negami (HN) function with of the help of WINFIT software (Novocontrol):

$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{[1+(i\omega\tau_0)^a]^b} \qquad (1)$$

With Δε the dielectric strength, τ the relaxation time and a, b the parameters giving respectively the width and the skewness of the distribution of the relaxation function. As the contribution due to the Ohmic conduction was not visible in ε ', the following relation was beforehand used to estimate the conduction free loss ε_D'' [13]:

$$\varepsilon_D'' = -\frac{\pi}{2}\frac{\partial \varepsilon'(\omega)}{\partial \ln(\omega)} \qquad (2)$$

The dynamic shear measurements were measured by Dynamic Mechanical Analysis (DMA) on samples of 12 mm in length and 3 mm in width. A sinusoidal shear stress was applied, the complex shear modulus ($G^* = G' + iG''$) was measured and then storage (G') and loss (G'') dynamic shear moduli were calculated. The loss factor $tan\ \delta_m = G''/G'$ was also determined. Experiments were performed in the isochronal mode (0.1 Hz, temperatures 100-400 K, with a heating rate of 1 K/min) under helium, to insure a better thermal conductivity. The mechanical behaviours of the PU and PU/grafted CNT films were measured with a multifunctional dynamic mechanical analyzer, Eplexor from Gabo, in the simple tensile mode. The tests were carried out on 10 x 40 mm^2 rectangular specimens fixed at both ends thus leaving 20 mm long for the measurements, with an elongation speed of 24 mm/min.

The field-induced thickness strain was measured on circular samples (25mm of diameter) with a homemade setup based on a double-beam laser interferometer measurement (Agilent 10889B) [2]. Samples were placed between two cylindrical brass masses acting as conductive electrodes. A mirror was placed on the upper electrode to reflect the laser beam. A bipolar electric field was supplied by a high voltage amplifier (Trek10/10B) driven with a function generator (Agilent 33250A).

Results and discussion

Synthesis and microstructure

Fig. 1presents the different steps of the grafting process, and the corresponding TEM observations. As shown in Fig. 1 (b), the raw nanotubes are well crystallized and their outer surfaces rarely exhibit amorphous layers. During the grafting process, an amorphous layer appears and its thickness changes. At the end of the grafting process, this layer obviously covers the entire CNT surface. It is rather homogenous and uniform with an average thickness of 5 nm. Thermogravimetric Analysis (TGA) on grafted CNT shows a degradation of the grafted layer at a temperature similar to that of the pure PU degradation (not shown). Differential Scanning Calorimetry (DSC) confirms that the grafted CNTs contain PU, which indicates a successful grafting. Furthermore, the grafting leads to an impressive improvement of the CNT suspension stability in DMF (not shown).

In order to have a good dispersion of grafted CNTs in DMF without damaging the grafted layer, four tests were performed using the two ways of sonication described above, ultrasonic processing (UP) or ultrasonic bath (UB). A control of the CNT surface and entanglement was carried out for the 4 tests using TEM observations (not shown). Two dispersion conditions lead to the best compromise, with good dispersion and negligible damage in the grafted layer; (i) UB during 1h30 (used for films with 1 and 2 vol. % CNT), (ii) UB during 1h30 followed by UP during 5 min (used for films with higher 3, 4 and 5 Vol.).

Fig. 2 displays SEM photomicrographs of the PU nanocomposites filled with either grafted or ungrafted CNTs. Observations were performed on cryofractured samples. Although it is quite difficult to extract quantitative data, grafting seems to lead to a better dispersion of the nanotubes within the PU matrix as the proportion of CNT aggregates seems to decrease upon grafting. This good dispersion may be associated to the initial good dispersion of nanotubes in the organic solvent after sonication.

It is noteworthy that grafted CNTs were cut (see white circles in Fig. 2 (a)), meaning that the adhesion at the grafted CNT/ PU interface is strong enough to propagate the fracture through the nanotube and not along the interface. A better interfacial adhesion was expected since the same chemical component is present in both sides of the interface (PU in the grafted layer and in the matrix). On the contrary, with ungrafted CNTs, the presence of pulled-out tubes (red circles) and holes (green circles) indicate a poor adhesion between ungrafted CNTs and PU.

Viscoelastic and mechanical properties of PU / grafted CNT nanocomposites

Loss factors of pure PU and PU / grafted CNT nanocomposites were obtained at constant frequency as a function of the temperature (see Fig. 3 (a)). There are typically three relaxations, characterized by maxima of the mechanical losses. The process known as "γ-process" is related to the local intermolecular relaxation at a temperature below $T_{g(SD)}$ [14]. The second one, β-relaxation, seems to be related to the motions of side group chains or branches occurring in the amorphous phase [15]. The third one is the "α-relaxation" or main relaxation, and is related to the intermolecular cooperative motions of chain segments and is observed around the glass-rubber transition temperature. Moreover, a peak appears around 330 K for some films 1 and 3 Vol.%. This peak might be related to measurement conditions- we reach border measurement conditions in DMA, with a soft sample of thickness of 100 µm . Nevertheless, these different viscoelastic relaxations are almost similar for all compositions. This behaviour reveals that the viscoelastic relaxations and so the macromolecular mobility is almost not affected by the presence of CNTs.

The incorporation of grafted CNTs into PU increases the tensile strength and modulus, as shown in Fig. 3 (b) and (c). The Young modulus increases from 29 MPa in pure PU to 75 MPa when the grafted CNT content reaches 5 vol.%. Strengthening the overall mechanical performance of the composites, it may be a result of strong interactions between the functionalized CNT and the PU matrix due to a great enhancement of the dispersion state and the interfacial adhesion.

Dielectric permittivity, electrical conductivity, percolation threshold

The real parts of the electrical conductivities (σ') of pure PU and PU / grafted CNT nanocomposites are displayed in Fig. 4 (a). Two regions can be observed: (i) one at low frequencies, where the conductivity is almost independent of the frequency and (ii) the other at higher frequencies, where the conductivity increases linearly with the frequency. For dielectric materials, the frequency-independent conductivity (thus mainly resistive) is generally attributed to electric charge displacements whereas the frequency-dependent part corresponds to a capacitive behaviour [16].

In Fig.4 (b), σ' first increases gradually up to 4 vol.% of grafted CNTs. But for higher contents, it jumps rapidly. This behaviour corresponds to the insulating-conductive transition behaviour (or percolation). The percolation threshold (f_c) is the volume fraction of CNTs necessary to form a continuous conductive network through the matrix. Composites with PU-grafted CNTs present a higher f_c compared to those with ungrafted CNTs [17]. This is mainly due to the fact that grafted CNTs are electrically isolated from each other by the PU layer. Nevertheless, the appearance of a percolation threshold suggests that the layer was damaged during the film fabrication process, for contents around 5 vol.%. At this content, the viscosity becomes high and during heating at 350 K – with mechanical agitation - and film casting, friction between neighbouring CNTs may alter the grafted layer, inducing conductivity between the nanotubes.

Fig. 4 (c) shows the variations of the relative permittivity with the grafted CNT fraction. For a volume content of grafted CNTs lower than the percolation threshold (≈5%), the increase in dielectric permittivity versus the filler content can be explained by space charges induced by the conductive fillers, according to the Maxwell Wagner mechanism [18]. Near the percolation threshold, the fillers behave like microcapacitor networks [19]. Each of these capacitors is formed by the neighbouring conductive grafted CNTs with a very thin layer of insulating PU in between and on the surface of each CNT. Close to the percolation threshold, the composite presents a high dielectric constant ε_r'=460 at 0.1 Hz, i.e. about 60 times higher than that of pure PU (for which ε_r'=7), see Fig. 4 (d). The variation of the relative permittivity for $f < f_c$ can be described by the following relation [20], when the embedded particles are dispersed:

$$\varepsilon_r' = \varepsilon_{rm}' \left(1 - \frac{f}{f_c}\right)^{-q} \qquad (3)$$

where ε_{rm}' is the relative permittivity of pure PU, f the volume fraction of grafted CNTs, f_c the percolation threshold and q the critical exponent.

The percolation theory for the insulating behaviour under f_c gives a linear logarithmic relation between log (ε_r') and log $(1 - (f/f_c))$, as shown in Fig. 4 (d). The best fit is obtained with f_c = 5 vol.% and q = 2. The value q is higher than the so-called universal value, q=1, as shown by Stauffer [21]. This may reflect a non-random CNT dispersion. Indeed, the classical percolation equations, with so-called universal exponents, are valid only for pure randomly dispersed particles in a continuous matrix. If this random feature is not reached, because of local orientation, aggregation, flocculation, etc., there is no more reason for the various quantities (here the dielectric permittivity) to follow these equations (here equation 3) with the appropriate exponent.

Dielectric relaxation of PU nanocomposites

Fig. 5 (a) presents the imaginary part of the dielectric modulus M^* at 0.1 Hz versus temperature, calculated from ε' and ε'' with the following relation:

$$M'' = \frac{\varepsilon''}{\left(\varepsilon'^2 + \varepsilon''^2\right)} \qquad (4)$$

The main advantage of this expression is that the space charge effects often do not mask the features of the spectra, owing to suppression of high capacitance phenomena in the plot *M''(f)* [22].

Four relaxation processes can be observed for the three investigated samples (pure PU, composites containing 1 and 2 vol.% of grafted CNTs). At low temperature, around 125 K, the γ-relaxation corresponds fairly well with the mechanical γ-relaxation which was previously attributed to local motion of $(CH_2)_n$ segments [23]. Around 175 K, the *β*-relaxation appears with a smaller amplitude compared to that of the γ-relaxation. It has been attributed in the literature to the motion of the polymer chain segments with attached water molecules [24]. The *α*-relaxation appears around 230 K, and has a larger amplitude than the two secondary γ- and *β*-relaxations. This relaxation corresponds to a longer scale segmental motions, and is associated with the glass transition [25]. A fourth process starts at 280 K at low frequency. This phenomenon is very sensitive to frequency and shifts to higher frequencies at increasing temperatures (not shown). It corresponds to high values of the DC conductivity. This phenomenon can be attributed to the existence of ionic polarization in the polyurethane network due to "free" charge motion within the material. Upon incorporation of CNTs, an additional relaxation appears, which can also be attributed to conductivity. A study performed by Gorgeoussis et al [26] on PU with metal chelates in the main chain reported that two mechanisms associated to conductivity can be observed, identified as conductivity (i) in the bulk material, and (ii) more localized at the interface.

The three dielectric γ-, -β- and α- relaxations are similar to the viscoelastic relaxations reported above. This confirms that incorporating CNTs does not affect the relaxation processes of these PU nanocomposites. For the different relaxation processes, using $M''(T,f)$ data, and more precisely the frequencies f_M at which M'' passes through a maximum, it is easy to determine the relaxation time $\tau = 1/2\pi f_M$ and to get a set of $\tau(T)$. For the cooperative α-relaxation, the temperature dependence of τ is often described by the Vogel-Tammann-Fulcher (VTF) equation.

$$\tau = \tau_0 . exp \frac{B}{(T - T_0)} \tag{5}$$

where τ_0 is the pre-exponential time, B is an activation parameter and T_0 is so-called the ideal glass transition temperature (or the Vogel temperature) [27]. For the other relaxations it is usual to plot $\log(\tau)$ versus $1/T$ (in Arrhenius plot). If the curve is a straight line, then the relaxation time follows the Arrhenius equation:

$$\tau = \tau_0 . exp \frac{E}{k_B T} \tag{6}$$

Where $\tau_0$is the pre-exponential time, k_B the Boltzmann constant and E the activation energy.

Fig. 5 (b) shows a semi-logarithmic plot of τ in a function of the reciprocal temperature, 1/T, for pure PU and the nanocomposites and Table 1 summarizes the parameters of the fits. The γ- and β-relaxations are described by almost the same parameters E and τ_0 for the three materials. The relaxation times of the β-processes are not significantly affected by the grafted CNTs and the values of the activation energies are similar to those of pure PU as it is the case for other reported values [25]. For the α-relaxation, it is striking that the VTF parameters are quite similar for pure PU and for the nanocomposites. It is worthy to notice that the two conductivity processes are different: the first conductivity process-I seems to be related to a conductivity of ionic type only, with almost the same activation energy and only a slight dependence to the volume fraction of grafted CNTs, while the second one is more related to the volume fraction of grafted CNTs.

The $\Delta\varepsilon$ dielectric strength and the ε_∞ value increase with the CNT amount for the 3 relaxations, as already reported on other conductive nanofillers based composites [28]. This increase may reflect a reduction in crystallinity, in agreement with DSC analysis (not shown). For secondary relaxations, the high values of $\Delta\varepsilon$ for composites cannot be explained by the molecular origin but rather by the increase of the internal field due to the conductive nanotubes.

Electrostriction properties

Fig. 6 depicts the variations of the apparent electrostrictive coefficient M_{33} as a function of the grafted CNT volume content at 0.1 Hz. Below the percolation threshold, M_{33} increases effectively with grafting CNT contents up to 3 vol.%. M_{33} exhibits a maximum value for a filler content around 3%, not far from the percolation threshold (around 5 vol.%.). At the maximum, the value of M_{33} is twice larger than that for pure PU. These data show the advantage of the addition of nano-fillers for increasing the coupling within the polymers with a significant decrease in driving voltage of the films, which is currently the major technological barrier to electroactive polymer films for application development. Indeed, the same level of deformation is obtained in the case of composites for an electric field 1.5 times lower. Furthermore, for a grafted CNT content above 3 vol.% and near f_c, M_{33} starts to decrease. This is consistent with the appearance of electric losses due to the Joule effect through the conducting filler network (resistive behaviour exhibited in Fig.4.)

Increasing the electromechanical response of the composite seems to indicate an effect of the space charges at its origin resulting in an increase in the permittivity. As the M_{33} coefficient depends on the ratio of the permittivity on the Young modulus [29], one should expect a 4-fold increase of the electrostrictive coefficient at a filler content of 3%. The moderate 2-fold increase could be partially explained by a decrease of permittivity under electrical field, some measurement showed indeed a decrease of 25% of the ε value. Another explanation could be the local field or field gradient which decreases due to the increased incorporation of conductive nanotubes.

Despite strong permittivity values and the grafting of the nanotubes with the PU, it was not possible to obtain a strong improvement electromechanical performance. The results are similar to those obtained with CNT grafted COOH groups [5]. Recently, a theoretical model was developed to quantitatively understand the high electrostriction coefficient of polymers like such PU used in this study [30]. Such a model should be adapted to account for the contribution of electrically conducting fillers.

Conclusion

Grafting a thin layer of PU - 5 nm in thickness- on the surface of CNTs was performed using a “grafting onto” technique. The interfacial adhesion between grafted CNTs and the PU matrix was improved thanks to the compatibility between grafted layer (PU) and polymer matrix (PU). Dielectric and viscoelastic measurements over a wide range of frequencies and temperatures showed similar relaxation times. Only the dielectric strength was increased for composites. An important change was found to lay in the coexistence of two conduction relaxations for composites instead one for pure PU. Grafting PU macromolecules on the CNT surface lowered the conductive properties by insulating the nanotubes. This led to the increase of the percolation threshold to around 5%. Thanks to the increase of the permittivity and by maintaining adequate mechanical properties, the electromechanical performances have been increased by a factor of 2.

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