

A study on a polyurethane-based blend with enhanced electromechanical properties

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Polyurethane elastomer is one of the electroactive polymers which show the ability to convert mechanical energy into electrical energy and inversely. Some approaches have been exploited to improve its properties, like random composites, interpenetration or blend system. The last approach, blend system can retain unexpected properties of existing polymers. In this work, a polyurethane-based polymer blend with a soft poly (ethylene-co-methyl acrylate-co-glycidyl methacrylate) (PEMG) by a simple solution method was studied to enhance the electromechanical properties. The resulting blend films exhibited both a little decrease of the dielectric constant and the elastic modulus. They present also an improvement of the strain under moderate electric fields with relatively low percentages of PEMG. For example at 10 kV/mm, a twofold increase of the strain is observed with only 9%wt of PEMG. Furthermore, DSC measurement was conducted to verify the compatibility between the two polymers.

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1. Introduction

Electroactive polymers (EAPs) have been attracted a great attention due to their various range of applications, like robotics, automotive control, micro electromechanical systems, adaptive structures, implanted medical devices, actuators and sensors [1].

Among all the categories of EAPs, the electronic-type EAPs including elastomer are particularly attractive for large strain, energy harvesting and high-power applications [2, 3]. When an external voltage is applied on the two opposite sides of a polymer sample, it contracts in thickness and expands in the planar area. Besides, in a first approximation and up to a certain electric field magnitude depending on the material, two important features of actuation performance of elastomers are: under moderate electric field magnitude E , i) the electrically induced strain is proportional to the square of the electric field and ii) the strain is proportional to the dielectric constant ϵ , that can be described as: $S = ME^2$, and M is proportional to the dielectric constant and inversely proportional to the Young's modulus Y of the material [4]. It also indicates that electrostriction effect (S_e) and/or electrostatic forces at the electrodes (Maxwell forces) (S_m) trigger the compression – negative strain - of the films [4, 5, 6], described respectively: (1) $S_e = Q \cdot \epsilon_0^2 \cdot (\epsilon_r - 1)^2 \cdot E^2$ and (2) $S_m = \epsilon_0 \cdot \epsilon_r \cdot E^2 / Y$, where Q is the coefficient of electrostriction, Y is the Young modulus, ϵ_0 is the permittivity of vacuum and ϵ_r is the relative permittivity of polymer. So, there is a relationship as $S = S_e + S_m$. Accordingly, an increase of the material permittivity and

decrease of Y provide a valuable mean to improve the performance of an elastomeric actuator [7].

The promising elastomeric polymers include silicone, acrylic and polyurethane (PU)[8]. The former two polymers can produce large strain, but they need a prestrain and high voltage to maintain it [9]. Compared with a silicone rubber or acrylic, PU has higher dielectric constant and high input electric energy density, which actually defines the upper limit of mechanical energy density stored in the elastomer and they exhibit a relative large strain under moderate electric field, suitable for mimic human motion and energy harvesting, actually, some papers are focused on the energy harvesting by using PU matrix [10, 11].

However, PU films present lower maximum strain levels than prestrained silicone and acrylic. Therefore, several previous studies focused on the production of PU random composites by incorporating inorganic or organic fillers, to obtain enhanced dielectric and thus improved electromechanical properties [12, 13]. Actually the efforts yield limited results that can get high dielectric constant but also induce dramatic dielectric loss and breakdown, especially the unexpected stiffness increase of the composite[14].

In order to overcome this shortcoming, Gallone et al [15] have firstly proposed a new approach that can lead to a new dielectric elastomer with improved electromechanical properties by simply blending poly(dimethylsiloxane)(PDMS)-based rubber and PU. The polymer blends have a higher dielectric constant with a gain factor of 3 for PDMS and 2 for PU below 200Hz.

This unexpected behaviour yielded remarkable actuation performance, better than neat PDMS but it was not compared with electromechanical response of neat PU in the work of Gallone and co-workers.

Some other researchers have reported the blending polymers system with different polymers. Chiou et al [16] adopted a way to polymerize the silicone and PU together to get a physically interpenetrating but chemically separated blending system. The author also introduced copper-coated phospholipid tubules as fillers, which preferred to stay in PU phase and the permittivity increased with the content of PMDS, like 75% PMDS in the blend, their permittivity increased about 40%-78% to the sample without PMDS. Carpi et al [17] proposed an approach to blend silicone with a conjugated poly(hexylthiophene) and found the blending polymer produce both an increase of the relative permittivity and an unexpected reduction of the tensile modulus by adding low percentage of poly(hexylthiophene) (1-6wt%). These two factors enhanced the electromechanical strain response.

Aradoaei [18] once adopted poly(ethylene-co-glycidyl methacrylate) (PE-co-GMA) to evaluate the properties dielectric constant and the presence of the glycidyl methacrylate groups seemingly influenced all dielectric properties. According to the blend approach, the present study shows that if it is possible to enhance the electromechanical properties of PU matrix by simply blending it with a soft functional polymer poly (ethylene-co-methyl acrylate-co-glycidyl methacrylate) (PEMG), which has as low Young modulus (6MPa) of PEMG and the same glycidyl methacrylate group. We tried different PEMG content in the blend and studied the change of electrical induced strain and dielectric properties.

2. Experiment and characterization

The chosen PU is the polyester-based thermoplastic polyurethane (Estane® 58888 NAT 021) and PEMG is purchased from Sigma-Aldrich Company (product n° 433640). Interestingly, these two polymers can be dissolved in the same solvent, which is cyclohexanone, so the polymer films can easily be prepared by solution cast method.

The PU pellets with various amount of PEMG were placed into a beaker, which contained already cyclohexanone. The concentration of the polymer blends

was between 5% and 7% initially. Then the solution was heated to 80°C with magnetic stirring for about 4h to gain a proper viscosity. After that, the solution was left rested for 12h to remove the bubbles and subsequently deposited with an adjustable applicator (elcometer® 3700 doctor blade) to prepare the films of thickness around 50µm (+/- 5µm). These films were dried at 60°C in an oven for one night and afterwards at 85°C in a vacuum oven to eliminate any residual solvent. It was the same procedure for both PU and PEMG neat films.

The films were cut into round disc-shaped samples with 25mm in diameter for measurements. The low frequency (100 mHz) electric field-induced thickness strain S_3 was measured by using a double beam laser interferometer (Agilent 10889B), with a precision of the order of 10 nm. Experimental details for room temperature measurement are given in reference [12].

The dielectric properties were tested by a permittivity measurement system (including 1255A Frequency Response Analyzer and a 1296 Dielectric Interface, Solartron, United Kingdom), from 0.1Hz to 1000Hz. For this measurement, gold electrodes (20 mm in diameter) were sputtered on the two sides of the disc-shaped samples.

Supplementary, samples were cut into rectangle of $26 \times 10 \text{ mm}^2$ for Young's modulus using a house made tensile test. On one end, the sample was clamped onto a Newport platin and the other end onto a force sensor. The Young's modulus was determined at the beginning of the curve strain / stress for elongations of 2.5% [11].

The morphology and miscibility of the polymer blends was studied by differential scanning calorimetry (DSC) (Setaram DSC131 evo device) under a nitrogen atmosphere. The sample (~20 mg) was cut into small strips and placed in a closed aluminum crucible which was precisely weighed previously. The sample was cooled from ambient temperature down to $-80 \text{ }^\circ\text{C}$ ($10^\circ\text{C min}^{-1}$) and then heated to 200°C at the same heating rate. All the tested neat polymers and blends were subjected successively to two thermal runs, in order to eliminate the influence of the residual solvent.

3. Result and discussion

The dielectric properties of the neat polymers and polymer blends are represented in Fig. 1.

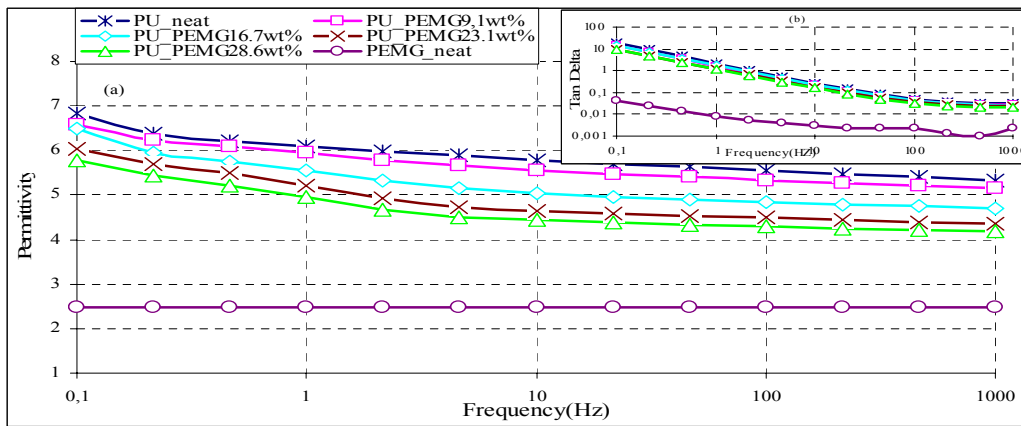


Fig. 1. Frequency spectra of the dielectric properties of both the neat two polymers and polymer blends with different content of PEMG: (a) relative permittivity; (b) dielectric loss (solid lines are guide for eyes).

It is clearly seen that the value of relative permittivity and dielectric loss of the polymer blends are between that of the neat PU and neat PEMG, according to rules of normal polymer blends. And they decreased as the content of PEMG increased. The dielectric loss of blending is smaller than that of neat PU (normally less than 10%), maybe interesting for energy harvesting under given

conditions. It is worth noting that the relative permittivity of PEMG remains constant in the considered frequency domain, which means that the glycidyl methacrylate polar group has no time to align or the molecules are symmetrical, and the polar group has no evident effect on the dielectric property of blends.

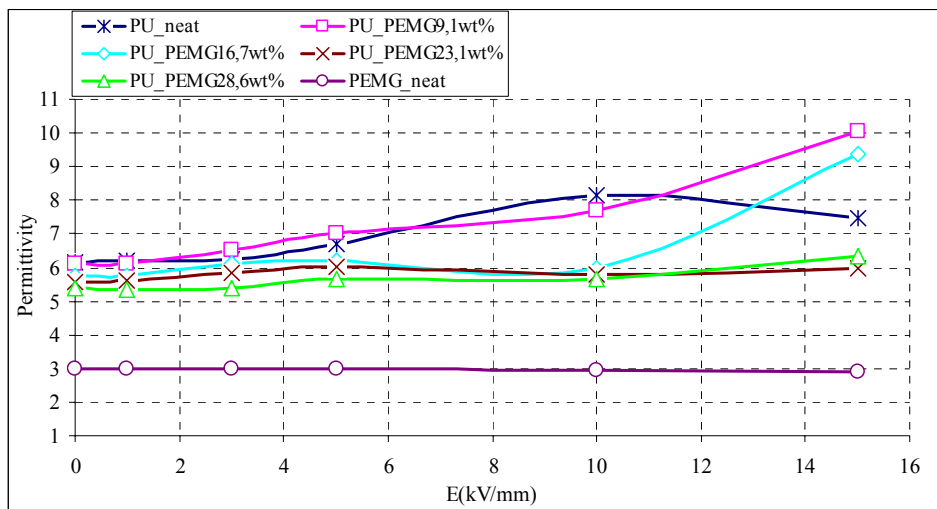


Fig. 2. The relative permittivity of the neat polymer and its blends at different electric fields (at 0.1 Hz).

Fig. 2 depicts the dielectric properties as a function of the electric field amplitude at room temperature (DC field); there are some differences in neat polymer and polymer blends, the curve of PU first is upward as electric field increase, and reach its maximum at 10kV/mm and then slightly decrease; while the permittivity of polymer blends almost increase as the electric field increase till 15kV/mm. Their peaks locate at 15kV/mm. The dielectric constant and the loss of PEMG also do not change much during the electric field range. It was found that at 15kV/mm, the summit of blends with 9.1wt% and 16.7wt% PEMG are bigger than neat PU, but the neat PU and PEMG both do not increase the permittivity. Maybe the interfacial polarization by external field of blends plays

an important role but when there is more PEMG in blends, the permittivity stop increasing.

The induced thickness strains amplitude of the neat polymers and blends vs. electrical field are shown in the Fig. 3. The polarity of dependence with electrical field is consistent to the maximum strain. In the figure, the strain can be divided into two parts: strain at the low field and the saturation strain. The neat PU exhibits large strain under low electrical field strength ($E \leq 4$ kV/mm), and quickly reaches a plateau (saturation strain) as it is commonly observed for electrostrictive elastomers [4]. It's in agreement with the explanation of the saturation strain in electroactive polymers developed by Guyomar et al [19].

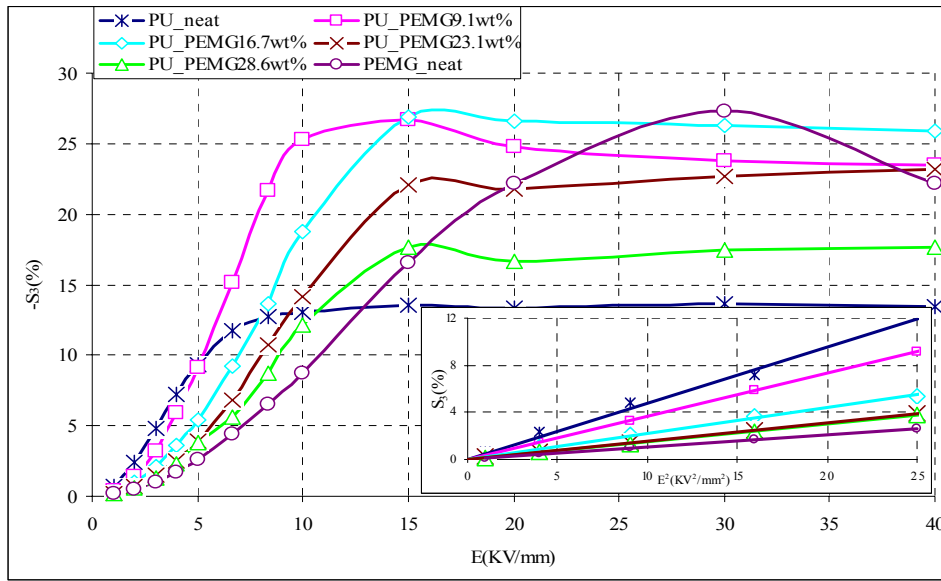


Fig. 3. The field-induced thickness strain versus the electrical field (both neat polymers and blends).

The neat PEMG film displays a different behavior since its strain amplitude increases less sharply with a much less pronounced saturation effect at high electric field than neat PU. This behavior is quite common for low permittivity dielectric elastomers, such as silicone rubber (poly(dimethylsiloxane) [20]. Thus, compared with electrostrictive PU, PEMG exhibits the smallest strain in the low electrical field region ($E \leq 10$ kV/mm) and after it reaches the highest deformation at approximately 30 kV/mm, and then it slightly decreases. Concerning polymer blends, Fig. 3 clearly demonstrates they exhibit a combination –or mixing – of actuation behaviour of neat PU and PEMG. Besides, the electric field dependence of thickness strain of the polymer blends presents the interesting actuation characteristics of both neat elastomers. That is to say, in the low electrical field regime, even if it decreases with the contents of PEMG increase, the strain of blends is systematically higher than that of neat PEMG (and lowers than that of neat PU). While in the high electrical field regime, the strains are much larger than neat PU, similarly to the strain level of neat PEMG. For instance it is well seen under 15 kV/mm, and the largest beneficial effect of PEMG on the

electromechanical activity of PU is obtained for 9.1wt% PEMG. For this concentration, a twofold increase of the strain is observed for a moderate electric field strength $E = 10$ kV/mm. In general, the blends with 9.1wt% and 16.7wt% of PEMG show the best performance from 6.5 kV/mm to 15 kV/mm.

As experimentally observed and already mentioned in introduction, a typical quadratic relationship between S and E is found for every film compositions at low electric field level. As Fig. 1 inlet picture illustrates, the thickness strain at low electrical field magnitude ($E \leq 5$ kV/mm) is quite proportional to the square of electrical field.

Maxwell stress effect has been recently found to be negligible compared with electrostriction phenomenon and the strain is mainly induced by electrostriction effect, according to reference [4], the determined Young modulus and value of M and Q are displayed in Table 1. It was found, the value of Young modulus decreases with the PEMG augment and basically at low E , the coefficient M and Q both decrease with the percentage of PEMG increased, except the Q of neat PEMG. That is why the blending system has small strain in the low electrical field.

Table 1. Young modulus, dielectric permittivity and electrostrictive coefficients versus the amount of PEMG blended with PU.

PEMG (wt%)	Y(MPa)	ϵ_r (1V, 0.1Hz)	M (m ² /V ²)		ϵ_r (15kV/mm,DC)
			($E \leq 5$ kV/mm, 0.1Hz)	Q (m ⁴ /C ²)	
0	32,8	6,8	4,77E-15	1,79E+06	7.5
9,1	25,4	6,5	3,65E-15	1,49E+06	10.1
16,7	23,3	6,4	2,20E-15	9,37E+05	9.4
23,1	22	6,0	1,57E-15	7,90E+05	6.0
28,6	18,5	5,7	1,50E-15	8,39E+05	6.3
100	6,02	2,5	1,06E-15	6,18E+06	2.9

It also indicates that the unexpected large strain at 10-15 kV/mm is mainly induced by the permittivity increased and the decrease of Young modulus.

The Fig. 4 presents the DSC thermograms of the different blend polymers films and Table 2 lists some enthalpies. Because the Cyclohexanone boiling point is about 155°C, the samples are processed for two cycles in order to eliminate the influence of solvent.

The first slope phenomenon is related to the glass transition (T_g) of the soft segments, both in PU or PEMG.

This gives an indication of the degree of hard-soft segments mixing. In Fig. 4, -38°C illustrates (T_g) of PU and -32.9°C is the T_g of PEMG. The blending polymer is homogeneous as it seems there is only one T_g in the system. No substantial influence of the blend composition on the glass transition dynamics was found.

The first endotherm peak around 37°C is correspondence to the melting point of PEMG and it is also clear to see that an increase in melting enthalpy (ΔH_{m1}) in this temperature with more PEMG in the blend.

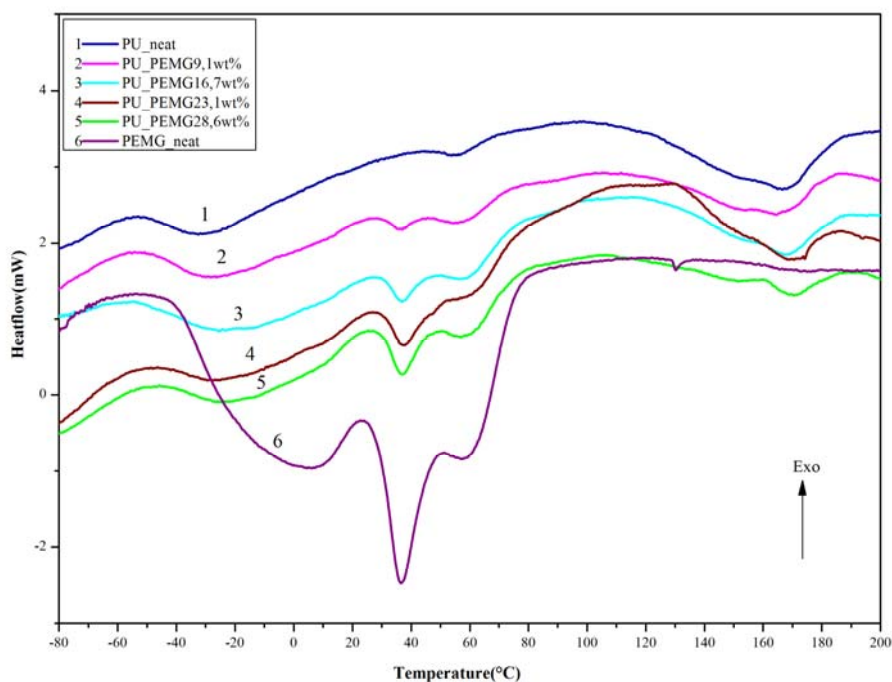


Fig. 4. The DSC curves of neat polymers as well as polymer blends (the second cycle).

At temperatures near 160-180 °C, it was observed an endotherm that can be related to the micro-mixing of non-crystalline or semi-crystalline hard and soft phases followed by the melting of crystalline hard segments [21]. The increase of the crystallinity would be

accompanied by an increase of these temperatures and/or an increase of the total enthalpy of the phenomena. No evident change in this point indicates that the blend system is physical interpenetrated [12].

Table 2. The mainly thermal points and enthalpy versus the amount of PEMG blended with PU.

PEMG (wt%)	T_g (°C)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)
0	-38,04	-	-	166,51	5,003
9,1	-37,43	36,9	0,307	164,48	5,503
16,7	-39,83	36,89	0,797	167,29	5,553
23,1	-32,48	37,8	1,087	168,28	4,951
28,6	-37,05	36,91	1,328	170,4	3,318
100	-32,91	36,53	5,895	-	-

In addition, the granules are visible in the film when the content of PEMG is above 28.6wt% and the solution was separated obviously into two parts after several days,

which indicated a separated phase existed when a high PEMG percentage in the blend.

4. Conclusions

After blending PU with PEMG, the electromechanical properties of PU have been obviously enhanced. Although the blend approach decreases both the permittivity and Young modulus of the system, the maximum strain can be reached at not too much augment of the saturation electrical field than PU. And the decrease of losses and Y modulus may be interesting used for energy harvesting or human motion. The result also demonstrates that the thickness strain is mainly contributed by the electrostrictive effect. Additionally, a relative large strain at moderate electric fields can be obtained in low percentage of PEMG, for example, the strain of blend with 9.1wt% PEMG is higher than 16.7wt% and 23.1wt% at 10kV/mm, enhanced up to 100% than neat PU. The DSC test indicates the blend system is physically compatible. Thus, the method of simply blending two polymers is an easy way to find new polymer systems for electroactive application.

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