Poly(propylene oxide): A very soft and extensible dielectric electroactive polymer

K Goswami[1], F Galantini[2], P Mazurek[1], A E Daugaard[1], G Gallone[2,3] and A L Skov[1*]

[1]DTU,　The Danish Polymer Centre, Department of Chemical and Biochemical Engineering, Kgs. Lyngby, Denmark

[2]"E. Piaggio" Research Centre, University of Pisa, Largo Lucio Lazzarino 2, 56122, Pisa, Italy

[3]Department of Civil and Industrial Engineering, University of Pisa, Largo Lucio Lazzarino 2, 56122, Pisa, Italy

E-mail- al@kt.dtu.dk *corresponding author

Abstract

Poly(propylene oxide) (PPO), a novel soft elastomeric material, and its composites were investigated as a new dielectric electroactive polymer (EAP). The PPO networks were obtained from thiol-ene chemistry by photochemical crosslinking of α,ω-diallyl PPO with a tetra-functional thiol. The elastomer was reinforced with hexamethylenedisilazane treated fumed silica to improve the mechanical properties of PPO. The mechanical properties of PPO and composites thereof were investigated by shear rheology and stress–strain measurements. It was found that incorporation of silica particles improved the stability of the otherwise mechanically weak pure PPO network. Dielectric spectroscopy revealed high relative dielectric permittivity of PPO at 10^3 Hz of 5.6. The relative permittivity was decreased slightly upon addition of fillers, but remained higher than the commonly used acrylic EAP material VHB4910. The electromechanical actuation performance of both PPO and its composites showed properties as good as VHB4910 and a lower viscous loss.

1. Introduction

The interest in using elastomers for electromechanical transducers has increased during the last decade due to their large strains, frequency responses of the order of milliseconds, work densities higher than human muscle, and a high degree of electromechanical coupling [1, 2]. A special class of elastomers known as dielectric electroactive polymers (DEAPs) has emerged as a strong candidate in this field due to their low density, fast response time, low cost of production, low

energy consumption and low heat generation. It has been found that these DEAPs possess mechanical properties very similar to human muscle and can mimic human muscular function, and thus they are commonly nicknamed 'artificial muscle' [3].

In a typical configuration for DEAP transducers, a thin film of dielectric elastomer is sandwiched between very thin layers of compliant electrodes, which are connected to the power supply for transduction. The equation governing the actuation of a DEAP actuator is given as [4]

$$p = \varepsilon_0 \varepsilon_r E^2 = \varepsilon_0 \varepsilon_r \left(\frac{V}{d} \right)^2 \tag{1}$$

where p is the electrostatic pressure acting on the dielectric elastomer due to an applied electric field E, V is the applied voltage, d is the thickness of the dielectric elastomer, ε_0 is the vacuum dielectric permittivity (8.85×10^{-12} F m^{-1}) and ε_r is the relative permittivity of the elastomer. At equilibrium, the electrostatic pressure equals the internal stress in the material so that the strain produced on the elastomer (S) can be written as

$$S = \frac{\varepsilon_0 \varepsilon_r}{Y} \left(\frac{V}{d} \right)^2 \tag{2}$$

where Y is the elastic modulus of the elastomer. Widely used DEAPs include poly(dimethyl siloxane) (PDMS), acrylics and polyurethane (PU), but each of them suffers from one or more drawbacks such as low dielectric permittivity, long response time or high elastic modulus etc. As a fact, none of the elastomers available on the market today are designed specifically for transduction, and this leaves room for further development of the materials. One downside of the currently used materials is the high voltage required for transduction, which adds cost to the transducer device due to expensive electronic components. From equation (2), it is seen that to lower the required voltage for a given strain of DEAP, we can decrease either the film thickness or the elastic modulus or alternatively increase the relative permittivity of the elastomer. The influence of material properties and processing parameters such as elastic modulus, dielectric constant and film thickness on the electromechanical properties for commercially available PDMS has already been discussed by Skov et al. [5]. For large scale processing a thickness of 40 µm is currently the threshold value for thin films with corrugations prepared from commercially available silicone so it is not regarded as a possible optimization parameter here [6].

A decrease of the elastic modulus is not easily achieved since filler particles are required in most systems to improve the mechanical properties, such as maximum elongation and tear strength.

Bejenariu et al. [7] showed that by use of an advanced mixing sequence, so-called heterogeneous bimodal networks could be prepared. The heterogeneous bimodal networks possessed very small elastic moduli and simultaneously improved tear strength and maximum elongation compared to unfilled silicone.

The first elastomeric material to be used successfully as a dielectric elastomer was the acrylic VHB tape from 3M. In an earlier article on dielectric elastomers, it was reported that this material showed extraordinarily high strain and high electrostatic pressure. It was also shown in the same article that the performance could be increased manifold by applying prestrain in the planar direction [8]. But the long response time and need for prestrain of VHB are the reasons for the decreasing trend of using VHB as DEAP material. On the other hand commercially available silicones do not require prestrain. However, prestrain of silicones is still favorable but not as necessary as for the acrylics, since the Young's modulus decreases after prestretch and the films become thinner [9]. Since the high operating voltage adds to the cost of the transducer, a great deal of research is focused on increasing the dielectric permittivity of the DEAP material in order to reduce the operating voltage. By blending two low dielectric constant elastomers, PDMS and PU, Gallone et al [10] obtained a new dielectric elastomer with improved transduction performance. Also, the use of a 0.5 wt% of properly functionalized carbon nanotubes as a filler for a polyurethane elastomer was demonstrated to be effective in increasing the ε_r/Y ratio, without worsening the dielectric losses, and doubled the transduction performance of the neat matrix [11]. Polyurethanes [12,13] possess higher dielectric permittivity than PDMS, but suffer from higher dielectric loss and lower breakdown voltage compared to PDMS due to moisture absorption, and therefore they must be maintained under strict environmental conditions with respect to temperature and humidity.

As an alternative to both PDMS and PU, in this study PPO has been investigated as a new DEAP material against commercially available acrylic (VHB4910). The aim was to develop a new DEAP material with enhanced electromechanical response, compared to VHB. In addition, a thorough electrical breakdown measurement of this system could also be made in the future in order to investigate the effect of filler addition on the electrical breakdown strength, as it is known that such a particulate filled system could suffer from low breakdown strength. Jensen et al [14, 15] investigated the networks from PPO as materials for very soft skin adhesives. They applied silicone hydride functional crosslinkers to crosslink the end-linked vinyl functional PPO, which was found to be inefficient. In the work presented here, novel, fast and efficient UV photo-crosslinking was employed to crosslink PPO and its composites with treated fumed silica. Mechanical, dielectric,

rheological and electromechanical characterization was performed on the new material and its composites in order to evaluate the potential of PPO as a new electroactive polymer.

2. Experimental

2.1 Materials

Allyl terminated PPO of approximate molecular weight 16500 g mol^{-1} (Kaneka Silyl ACS 003) was obtained from Kaneka Corp., Japan. 2,4,6-trimethylbenzoylphenylphosphinic acid ethyl ester (Lucirin TPO-L) was purchased from BASF. VHB 4910 was obtained as 1 and 0.5 mm thick films with polyethylene backing material from 3M. The filler used for the elastomeric composites was hexamethyldisilazane (HMDS) treated fumed silica AEROSIL R R812, from Evonik Industries. The reported Brunauer, Emmett and Teller (BET) surface area of AEROSIL R R812 was $260\pm30\text{m}^2\,\text{g}^{-1}$. All the other chemicals used in this work were purchased from Sigma-Aldrich.

2.2 Methods

Rheological tests were performed in a stress controlled rheometer (AR2000) from TA Instruments, with 25 mm parallel plate geometry. Measurement conditions were set to controlled strain mode at 1% strain, which was ensured to be within the linear viscoelastic region as determined from initial strain sweeps. Frequency sweep experiments were performed from 100 to 0.001 Hz at 25°C. Broadband dielectric spectroscopy was carried out on disk-shaped samples of both the pure matrix and the composites (diameter of 25 mm and thickness 1 mm) at 25°C in the frequency range 20 Hz–2 MHz by means of an ARES G2 rheometer equipped with DETA accessory including an inductance (L)—capacitance (C)—resistance (R) (LCR) meter (Agilent E4980A). The electromechanical response of the PPO films, shaped in rectangular material strips of dimension 20×25 mm^2 and thickness varying between 80 and 226 μm, was studied after they were provided with opposed compliant electrodes by smearing a carbon based conductive grease (Nyogel 755G, Tecnolube Seal, USA) on both their major surfaces. For each sample a vertical prestrain of 100% and a dc high voltage with stepwise increment of 250 V were applied across the elastomer by means of a power supply (HV-DC 205A-30P, Bertan, USA). At each voltage level isotonic transverse strains were measured by a displacement transducer, waiting until a constant deformation was obtained. One sample for each composition was measured. A twocolumn ultimate testing machine (5500R, Instron, UK) was used to perform uniaxial elongation tests for PPO and the composites at a constant deformation rate of 25 mm min^{-1} with a 10 N load cell. Molecular weights and

polydispersity index (PDI) were estimated by size exclusion chromatography (SEC) using Viscotek GPCmax VE-2001. The machine was equipped with Viscotek TriSEC Model 302 triple detector array (refractive index detector, viscometer detector, and laser light scattering detector with the light wavelength of 670 nm, and measuring angles of 90° and 7°) and a Knauer K-2501 UV detector using two PLgel mixed-D columns from Polymer Laboratories (PL). The samples were run in tetrahydrofuran (THF) at 30°C (1 ml min^{-1}). Molecular weights were calculated using polystyrene (PS) standards from PL. Nuclear magnetic resonance (NMR) spectroscopy was performed on a 300 MHz cryomagnet from Spectrospin and Bruker, in $CDCl_3$ at room temperature. Fourier transform infrared spectroscopy (ATR-FTIR) was performed on a Nicolet iS50 from Thermo Fischer Scientific with a universal attenuated total reflection sampling accessory on a diamond crystal.

2.2.1 Standard procedure for preparation of PPO networks. Pentaerythritol tetrakis (3-mercaptopropionate) (4 functional crosslinker, 0.244 g, 0.5 mmol) and 2,4,6-trimethylbenzoylphenylphosphinic acid ethyl ester (Lucirin TPO-L) (photoinitiator, 0.192g, 0.6 mmol) were added to α,ω-diallyl PPO (10 g (0.6mmol of allyl groups) M_n= 16500 g mol^{-1}) and mixed in a SpeedMixer™ at 3500 rpm for 5 min. The mixture was poured into an 8 cm × 10 cm steel mold placed over a glass plate lined with Parafilm® M. This setup was kept in a well-ventilated place for 45-60 min and subsequently transferred to the UV chamber (λ= 365 nm, 4.5 mW cm^{-2}) and irradiated for 45 min in ambient atmosphere.

2.2.2 Standard procedure for filled PPO systems. The system was prepared as above for PPO networks. The filler was added with 40–60 wt% toluene directly into the PPO–crosslinker mixture prior to speed mixing; otherwise, the procedure was unchanged. The resulting films were studied by scanning electron microscopy (SEM) to ensure proper mixing of the fillers into the elastomer.

3. Results and discussions

3.1. Sample preparation and characterization

In this study a novel network material for DEAP applications based on PPO was prepared. The network was prepared through highly efficient crosslinking of a commercially available α,ω-diallyl poly(propylene oxide) with pentaerythritol tetrakis(3-mercaptopropionate), a tetra-functional thiol. Thiol-ene reactions are a type of 'click' reactions that are characterized by being highly efficient

and easy to perform in bulk processes [16, 17]. The reaction is tolerant to a large number of functional groups and can be initiated through both thermal and photochemical initiators, as shown in scheme 1 for the photochemical initiator (Lucirin) applied here.

PPO   **4-f crosslinker**   **Crosslinked network**
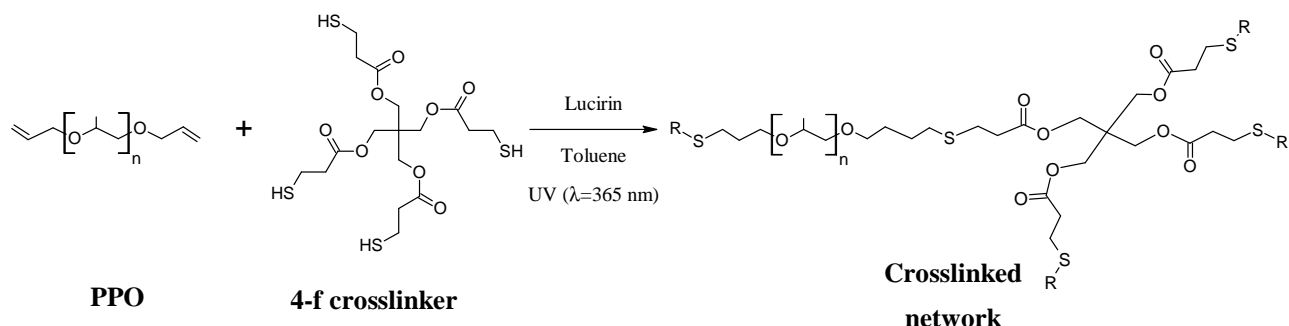
Scheme 1: Photoinitiated crosslinking of α,ω–diallyl poly PPO by thiol-ene chemistry, where R signifies the network.

The thiol-ene crosslinking reaction shown in scheme 1 relies on a high degree of end-group functionality in order to be efficient and produce a crosslinked network with a minimum of dangling chains. The presence of the end groups on the commercial α,ω-diallyl PPO base material has been confirmed by ^{1}H-NMR spectroscopy, where the presence of the allyl end group was confirmed with a characteristic set of doublets at 5.2 ppm and a multiplet at 5.9 ppm. The presence of the allyl end groups was also confirmed by FT-IR, where the double bond stretching was found at 1650 cm^{-1}.

The crosslinked PPO networks were prepared with a controlled stoichiometric imbalance (r) [18], which is defined as $r = \dfrac{f\,[thiol]_0}{2\,[vinyl]_0}$,where f is the average functionality of the crosslinker used and $[...]_0$ is the initial molar concentration of the reactive groups present in the crosslinker (*thiol*) and in the polymer (*vinyl*).

In order to obtain the mechanically strongest network, rheological tests were performed on PPO networks by monitoring the storage modulus (G') in the linear viscoelastic region for different compositions. The storage moduli at 10^{-3} Hz are summarized in **Table 1**.

Table 1: Storage modulus (G') of networks at different crosslinker contents at 10^{-3} Hz (The complete data series has been included in SI-Figure 1 (available at stacks.iop.org/SMS/22/115011/mmedia).)

Stoichiometry (*r*)	0.8	1.0	1.2	1.32	1.65	1.85
G′(kPa)	0.49	0.30	0.43	25.2	34.7	27.9

From **Table 1**, it can be seen that the mechanically strongest network was obtained at approximately $r = 1.65$ corresponding to the highest G' among other pure PPO networks and this stoichiometry was thereafter kept constant throughout the study for the pure PPO network and PPO composites. The pure PPO network was prepared as shown in scheme 1. Particle composites were prepared as for the pure PPO network, with the addition of different amounts of filler before mixing and UV crosslinking. In the compositions, the non-rubber ingredients (such as fillers in this case) are expressed as parts per hundred rubber (phr). In this convention, the filler amount is taken as the ratio against 100 parts (by weight) of rubber. In a typical composition, PPO_10 indicates 10 phr (1 g) treated fumed silica was mixed with 10 g pure PPO.

3.2. Rheological measurements

The linear viscoelastic (LVE) properties of pure and composite PPO networks were measured in order to characterize the material response in the low strain limit. Figure 1(a) shows the storage modulus (G') and figure 1(b) shows the loss tangent (tan delta) of the materials. Tan delta is also known as the damping of the material. It is obvious that, with respect to the viscous loss in the investigated frequency regime, all PPO networks are superior to VHB (see inset in figure 1(b) for comparison).

From figure 1(a) it can be seen that the storage modulus (G') at the plateau (terminal) region (10^{-3} Hz) is approximately 35 kPa for pure PPO which is very low compared to VHB as well as non-filled silicone elastomers [18]. On the addition of treated fumed silica into the soft PPO network, the storage modulus (G') at low frequencies gradually increases from 35 to 106 kPa due to the hindrance in chain movement imposed by the filler.

The tan delta plots (figure 1(b)) also give some insight into the molecular motion and damping behavior of the polymers. At 5 phr treated fumed silica loading, the viscous loss of pure PPO is reduced significantly in the entire frequency range, and it continues to decrease as the filler content is raised up to 10 phr. However, upon addition of 15 and 30 phr treated fumed silica the composites show increased tan delta, indicating prominent damping behaviour of the composites and hence a possible destruction of the network properties [18]. Moreover, at low frequencies the samples containing treated fumed silica exhibit an almost stable tan delta, as is typical for a loaded crosslinked rubber in which chain movements are further restricted due to the presence of filler particles. Compared to PPO, VHB remains a material with a significant loss, a higher tan delta and showing a much more dispersive behavior than PPO and any of the composites (figure 1(b)).
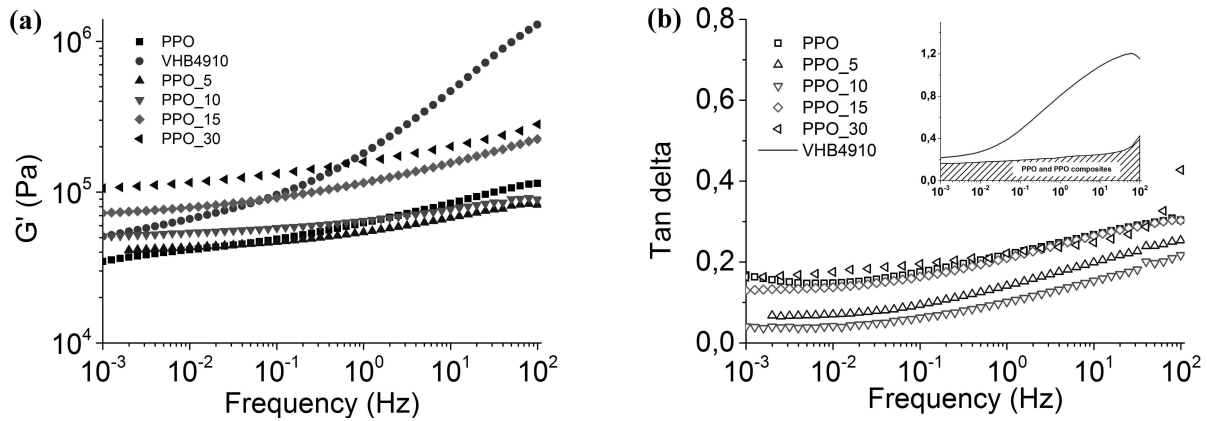
Figure 1: (a) Storage modulus and (b) tan delta versus frequency for pure PPO and filled PPO networks at 25°C. Inset shows the difference in tan delta between the PPO formulations (shaded region) and VHB.

3.3. Dielectric spectroscopy

One interesting aspect of this study is the measurement of the effect of incorporating treated fumed silica as a reinforcing agent on dielectric permittivity of PPO. Figures 2(a) and (b) show dielectric spectra for PPO and its composites.

At low frequencies, an increase in the dielectric constant of both PPO and its composites is observed as frequency is progressively lowered from about 10^2 down to 20 Hz (figure 2(a)), which is accompanied by a parallel increase of tan delta (figure 2(b)). Such an increase, which shows up as a low frequency dispersion in all dielectric spectra, can be ascribed to Maxwell–Wagner polarization, which is caused by a limited displacement of charges induced by the electric field in corresponding interfaces between different phases. While in the case of pure PPO such dispersion could arise only from a polarization contribution at the level of the sample/electrode interface, in the composites it could be indicative of the presence of further interfaces. Indeed, the fact that in the composites such polarization effects are more significant than in pure PPO is likely due to the presence of interfaces between the PPO matrix and the filler. Coherently, it is also found that as the filler amount is increased, the interface polarization effect increases. In the region of medium–high frequencies (10^2–10^6 Hz), where the dielectric response mainly depends on the bulk polarization processes [19], there are no significant changes in the ε' (figure 2(a)) for all the materials. However, the dielectric constant varies with the composites compared to that of the pure matrix. From figure 2(a) the relative dielectric constant for pure PPO at 1 kHz can be determined to be 5.6, which is higher than the value reported for VHB4910 (3.21 at 1 kHz) [20, 21].
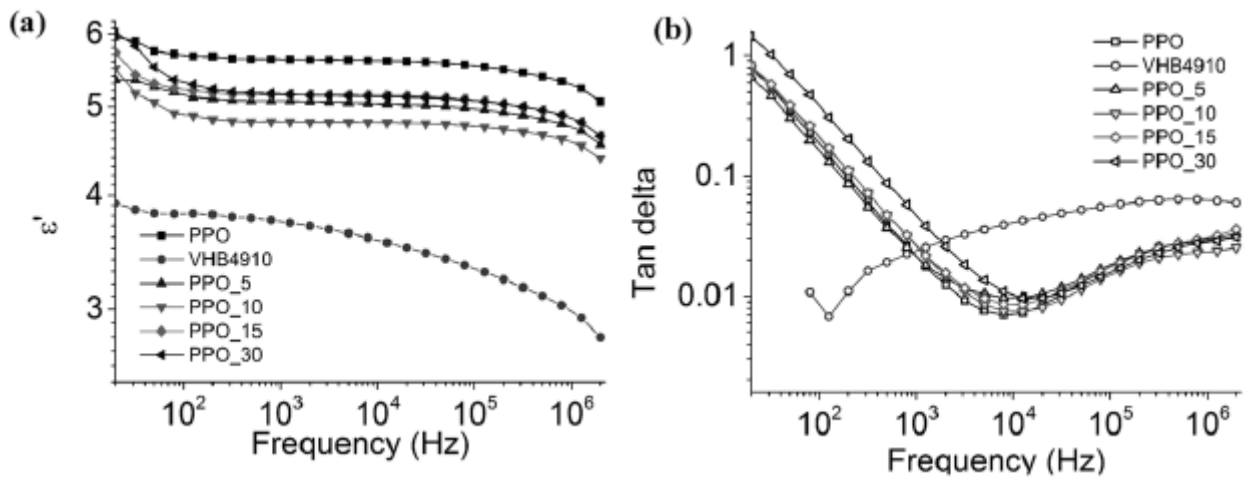
Figure 2: Dielectric spectroscopy plot (a) real part of permittivity versus frequency and (b) imaginary part of permittivity versus frequency for PPO and the composites.

Treated fumed silica was used as a filler for reinforcement, and since it is a low dielectric constant filler (ε_r = 3.9) it gives a minor decrease in the dielectric permittivity, as predicted by common mixing rules [22]. Although, at higher treated fumed silica content the bulk permittivity of PPO_15 and PPO_30 becomes higher than PPO_5 and PPO_10, it remains lower than the pure matrix. This change in the behavior of the dielectric properties at higher filler loading factors could be the result of a larger contribution from interfaces at filler/matrix boundaries as the filler volume fraction is increased. Some studies have already revealed that the presence of such boundary layers inside a material increases the dielectric permittivity. For instance, at the interface between matrix and filler in a particulate composite or between two immiscible phases in a polymer blend, intermediate interaction regions can provide additional polarization properties, which can play a major role in determining the final permittivity of such material [10, 23–25].

3.4. Mechanical analysis

The mechanical properties of PPO and reinforced composites were investigated by tensile testing as shown in figure 3.

Each test was stopped either at sample break, which occurred for all samples except PPO_30, or when the load cell reached maximum limit (10 N). Observed elongation at break of pure PPO is 170% while all the composites show maximum elongation exceeding 500%. Thus, filler incorporation in PPO network increases the extensibility of the networks, clearly showing the desired improvement in mechanical stability of the prepared composites.
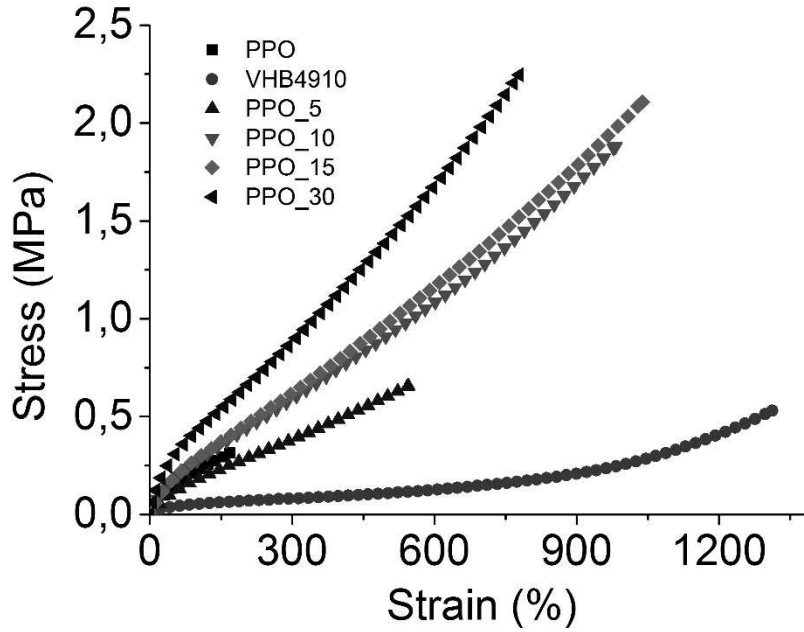
Figure 3: Tensile testing of PPO and the reinforced composites

Table 2: Local elastic modulus of PPO and its composites at different strains.

Sample	Modulus at 25% strain (kPa)	Modulus at 50% strain (kPa)	Modulus at 100% strain (kPa)
PPO	264	205	143
VHB4910	78	31	19
PPO_5	200	160	119
PPO_10	327	241	176
PPO_15	338	240	178
PPO_30	474	344	239

Table 2 summarizes the local elastic moduli (tangent slope) at different strains of PPO and the composites.

From the table, it is clear that for PPO composites the local elastic modulus steadily decreases as the strain is increased up to about 100%, which is a common feature of elastomeric behavior.

At higher elongations the situation changes and a steeper monotonic increase in the stress curves is observed (except for pure PPO as the sample failed at about 170% strain), recognizable as an up-swing after a flex point above 100% strain, which is due to the preferred orientation of the polymer chains in the direction of extension. When the filler amount is increased, the respective curves shift to higher stresses at corresponding strains (figure 3) with the exception of PPO_5, for which the response remains below that of the pure matrix. One plausible reason might be that in the case of

PPO_5 the reduction of crosslink density dominates induced mechanical improvement due to filler addition thereby making the sample softer than PPO. A markedly different stress–strain behavior is observed for VHB, where a very low modulus at strains below 600% is observed (which is advantageous for electromechanical actuation) followed by a moderate increase at strains beyond 900%.

3.5. Actuation study

Electromechanical tests were performed on 100% prestretched samples of both PPO and its composites, and the results are presented in figure 4. The electromechanical response of prestretched VHB4910 is included in figure 4 for easy comparison. Due to the detection of partial electrical conduction at fields over 20 V μm^{-1} in samples containing treated fumed silica, the effective electric field acting on these samples was not considered reliable beyond this threshold value. Therefore, data have been reported only for reliable values below 20 V μm^{-1} (with the exception of PPO_30, which showed reliable actuation at an electric field as high as 27 V μm^{-1}). For pure PPO the sample failed at fields around 17 V μm^{-1}, while VHB4910 did not show any such failure.
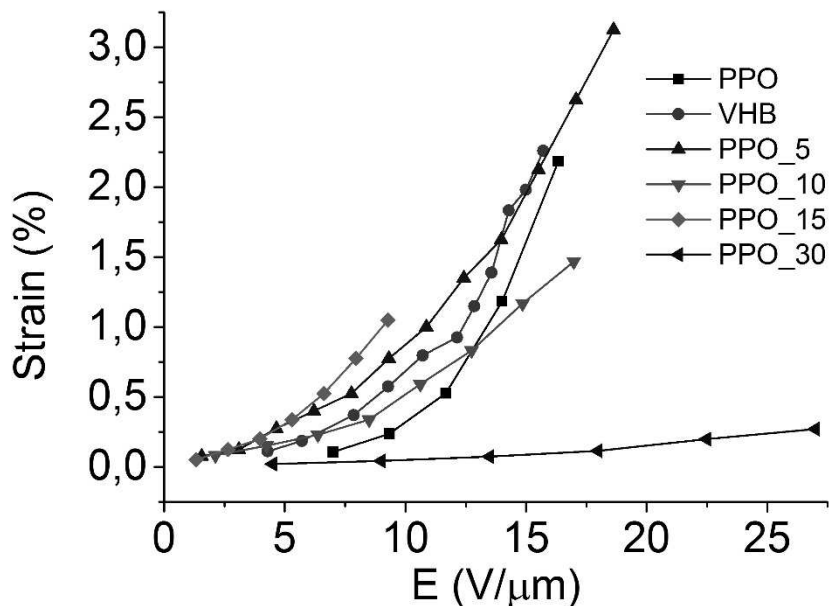

Figure 4: Electromechanical response of PPO and the composites.

As seen in figure 4, the electromechanical response of pure PPO is very close to that of VHB4910. Addition of filler significantly reduces the stickiness of PPO and improves its mechanical performance manifold (figures 1 and 3). The decrease in Young's modulus at low filler loading, followed by an increase as filler amount is increased, directly reflects on the electromechanical response of PPO composites. From figure 4, it can be seen that PPO_5 shows the maximum actuation strain among the studied PPO composites, followed by PPO_10 and PPO_15. The relatively low actuation strain of PPO_10 and PPO_15 is due to the higher modulus and lower dielectric permittivity compared to pure PPO and PPO_5. At higher content of treated fumed silica the strain induced by the electrostatic pressure becomes very small as can be seen for PPO_30. These observations are in good agreement with equation (2) and all measurements agree well at low voltages whereas the different losses start to play an important role at higher voltages for all types of materials investigated here. Considering the results obtained from electromechanical tests, PPO filled with small amounts of filler has very good actuation behavior and good mechanical properties. Higher filler content gave better mechanical property, but severely hindered the electromechanical performance of the material. Therefore a convenient tradeoff between the required mechanical reinforcement of PPO composites and the electromechanical response opens a pathway into the development of stacked actuators [26, 27]. The PPO samples possess natural adhesiveness, which would be beneficial for sandwiching several actuators on top of each other. Future development of this material would be to strike a balance between improving mechanical properties and electromechanical response by either employing chemical modification of the base polymer or using novel filler materials. However, the filler selection is limited to fillers with little UV absorption.

Table 3 summarizes and compares all the material data for PPO, PPO_5 and VHB4910 obtained in this study.

From table 3 it is seen that pure PPO is a relatively soft material; however, it shows high viscous loss owing to high tan delta. When treated fumed silica is added, the shear modulus increases, indicating reinforcement effect of the PPO matrix with a parallel decrease in viscous loss. The storage permittivity of pure PPO is about 1.5 times higher than VHB4910 although a slight decrease in permittivity can be seen in the case of PPO_5 as predicted by the mixing rule mentioned earlier. PPO_5 and VHB4910 show similar electromechanical behavior which is an improvement over pure PPO.

Table 3: Material data comparison between PPO, PPO_5 and VHB4910.

Sample	Shear modulus (kPa) at 10^{-3} Hz	Tan delta from rheology at 10^{-3} Hz	Storage permittivity at 1 kHz	Tensile modulus (kPa) at 100% strain	Electrically induced strain (%) at ~14 V μm^{-1})
PPO	34.7	0.16	5.6	143	1.2
PPO_5	41.2	0.07	5.1	119	1.6
VHB4910	50.7	0.2	3.7	19	1.8

4. Conclusion

This study reveals the potential of PPO reinforced with treated fumed silica filler as a new dielectric electroactive polymer actuator. A novel PPO elastomer and its composites were developed by a simple and easily manageable processing scheme. Shear rheology showed enhancement in the mechanical stability of PPO composites over the mechanically weak pure PPO network, and additionally, both PPO and its composites showed significantly less viscous loss as compared to the widely used VHB elastomer. The reinforcement effect was also reflected in mechanical tests, where the composites showed elongations of more than 500% compared to the 150% for the pure network. The relative permittivity of pure PPO at 10^3 Hz was found to be 5.6, and all the PPO composites showed permittivities above 4.8, which is significantly higher than VHB4910. The electromechanical test showed that PPO composites with small amounts of filler (5–10 phr) have the best electromechanical behavior.

The observed performance, combined with their intrinsic stickiness, suggests that these materials have a great potential in the application area of stacked actuators. PPO composites were also found to be similar to VHB4910 in their electromechanical response with the added advantage of possessing very low viscous dissipation. Furthermore, PPO presents another advantage over VHB4910 since further optimization of PPO networks is allowed due to the reactive handles resulting from an excess of thiol groups. This will be studied in the future.

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