Preparation and electrostrictive properties of polyurethane filled with polypyrrole-carbon black for the energy harvesting application

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Abstract. The polymer composites based on electrostrictive materials with high polarization are attracting scientists because of the prospect of application in energy conversion and electromechanical performance. Polyurethane is one of a good flexible dielectric polymers which is more interesting in electromechanical applications due to its easy fabrication, high dielectric constant, and high electrostrictive coefficient. This work focuses on the dielectric properties and electrostrictive properties of Polyurethane (PU) filled with Polypyrrole-Carbon Black (PPy-CB) various the different concentrations. All polymer composites were prepared by using a film-casting process in solution with DMF solvent. The dielectric properties and conductivity of thin films were investigated by using LCR meter at $1\text{-}10^5$ Hz. The results showed that the dielectric constant of composites significantly increases when the concentration of PPy-CB was increased. Moreover, the electrostrictive coefficient of composites also increases when the concentration of PPy-CB was increased. Furthermore, the electrical breakdown stretches were analyzed by using the Weibull model, this result will discuss the relationship when the PPy-CB fillers were used.

1. Introduction

Nowadays, smart material technology advancement has widely evolved in sensors and actuators, which can be applied to the fields of medicine, the electronic industry, and robots. Electrostrictive polymer is one of the smart materials that can change shape or size under an electric field. It has lightweight, high flexibility, quick response, and high specific energy. Electrostrictive materials can cover the mechanical properties to electrical properties. In fact, an increase of permittivity is needed to enhance energy harvesting. Polyurethane is one of the electrostrictive polymers which provide the large electrostrictive coefficient [1]. Moreover, Polyurethane can be considered as an heterogeneous material with soft and hard segments. The electric properties are controlled with hard segments, while mechanical properties relate to the soft segment. The hard/soft ratio of Polyuethane can be adjusted with the conductive fillers [2]. Polypyrrole is one of a conductive polymer that is widely used due to its good electrical conductivity and thermally stability. Moreover, dropping carbon black in the polymers has improved electrical conductivity. Among the various ways to enhance the dielectric constant, the development of polymer nanocomposites introduced with conductive fillers is of great interest. Owing to it is more flexible to tune their electrical and mechanical properties by choosing a suitable condition. The electrostrictive properties are significantly related to the dielectric constant and modulus, which strongly depend on the

dispersion of the fillers in the polymer matrix, and the microstructure state of the composite. This work proposed the dielectric and electrostrictive properties of polyurethane/polypyrrole-carbon black thin films. Furthermore, the electrostrictive performance with the electrical breakdown stretches will be discussed.

2. Experimental

2.1. Preparation of thin films filled with polypyrrole-carbon black

Polyurethane (PU) pellets, DP 9370A, supplied from Covestro AG (Germany), N, N-dimethylformamide (DMF, 99% purity) purchased from RCI Labscan Limited, Thailand. All polymer composites were dissolved in DMF by magnetic stirring at 80°C for 3 hours. Polypyrrole-carbon black (PPy-CB) particles were then added to DMF and dissolved with sonication for 20 minutes. The PPy-CB solution was dropped in the PU solution. Then, the PU and PPy-CB solution was stirred at 80°C for 1 hour to ensure homogeneity. PU composite films were obtained by using a film-casting process of polyurethane/polypyrrole-carbon black (PU/PPy-CB) composited with 0.25, 0.50, 0.75, or 1.00 %wt. The solution was dried in the oven for 16 hours to remove the solvent. Finally, the PU/PPy-CB films were taken off from the glass surface.

2.2. Characterization methods

2.2.1. *Measuring the dielectric properties by using LCR Meter.* Samples thickness is 100 ± 5 µm in all cases. The dielectric constant, loss tangent, and AC conductivity of all polymers composites were investigated by LCR meter (IM 3533 HIOKI) at room temperature with a frequency range of $1\text{-}10^5$ Hz.

2.2.2. *Measuring the electrostrictive properties by using an electrostrictive setup.* The electrostriction is generally defined as a quadratic coupling between strain (S), and electric field (E). The electrostrictive coefficient (M) depends on the dielectric properties (ε_r) and Young's modulus (Y) [3], as shown in equation (1).

$$M = \frac{\varepsilon_0 \left(\varepsilon_r - 1\right)^2}{Y}$$

(1)

where ε_0 is the permittivity of free space. The electrostrictive coefficient (M) relates strain (S) to the square of the applied electric field [4].

$$S = ME^2$$

(2)

The electric field-induced strain was investigated with the electrostrictive setup with help of a photonic sensor (MTI-2100) and high voltage supply (Trek Model 610E).

2.2.3. *Measuring the dielectric breakdown properties by using polarization loop & dielectric breakdown test system.* The dielectric breakdown (E_b) of obtained polymer composites were measure with the electric field between 0 and 10kV by Dielectric Breakdown Test System (PolyK Technologies State College). In this case, 12 breakdown tests were used to evaluate the E_b which was analysed by using the Weibull model, as shown in equation (3).

$$P(E) = 1 - \exp\left[-\left(\frac{E}{\lambda}\right)^k\right]$$

(3)

where P is the breakdown probability of the material when the electric field E was increased, λ is the breakdown probability of dielectric breakdown at 63.2%, and k is the parameter related to the reliability of the sample and the shape parameter k shows the distribution of E_b.

3. Results and discussion

3.1. Dielectric properties

The dielectric constant, loss tangent and conductivity from 1 Hz to 10^5 Hz of PU/PPy-CB composites is shown in figure 1 (a), (b) and (c), respectively. It is found that the dielectric constant of PU and composites decreases when the progressive increase of frequency. This behavior occurs due to the loss of one of the polarization contributions (interfacial polarisation, orientation polarisation, etc.). Thus, this decrease can be unambiguously attributed to the loss of the space charges induced interfacial polarization contribution. Furthermore, it is shown that the dielectric constant, loss tangent, and conductivity of PU/PPy-CB film composites increase when the concentration of PPy-CB was increased, which is related to the increasing of the charge density on the surface of the dopant, induced the interfacial polarization. It may be attributed that an addition contribution to the quantity of accumulated charge when the PPy-CB was used. The loss tangent of PU/PPy-CB 0.75%wt is higher than PU/PPy-CB 1.00%wt because of the degree of filler dispersion in PU matrix. It may be attributed to some agglomerates of PPy-CB when increasing fillers. Thus, the conductivity of PU/PPy-CB 0.75%wt and PU/PPy-CB 1.00%wt at very low frequency is not different.

3.2. Electrostrictive properties

The electrostrictive property of PU and PU/PPy-CB film composites was observed in figure *2*, the electrostrictive coefficient can be evaluated from the slope of the curve, following equation (2). Figure *3* shows the electrostrictive coefficient of PU and PU/PPy-CB film composites. The results show that the electrostrictive coefficient slightly increases when the concentration of PPy-CB was increased. In fact, the electrostrictive properties are directly related to the dielectric constant and modulus. Consequently, the increment of the dielectric constant can be explained by the dipole moment, the interfacial polarization, and conductive charge distribution. However, the modulus of composite increases with increasing filler content. It may be attributed that the elastic properties of PU composites decrease due to the polymer chains was stocked when fillers were used. Therefore, the slight enhancement of the electrostrictive coefficient versus PPy-CB content can be explained by the additive of conductive charges in PU matrix compare with the increasing the dielectric constant as compared to the increasing modulus.

3.3. Dielectric breakdown properties

Figures 4 and 5 present the electrical breakdown probability and the electrical breakdown strength of PU and PU/PPy-CB film composites, respectively. It showed that a decrease of the electrical breakdown strength was observed when PPy-CB loading was increased. It can explain that the decreased electrical breakdown strength of PU with PPy-CB loading is related to (i) enhanced mobility of charge carriers (ii) the high conductivity of fillers and (iii) increment of heterogeneousness of polymer matrix when the filler was used [5].
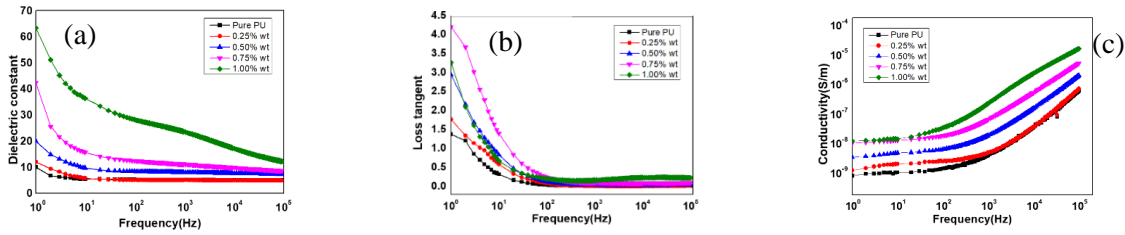
Figure 1. Frequency dependences of (a) the dielectric constant (b) the loss tangent and (c) the conductivity for composites with various PU/PPy-CB contents**.**
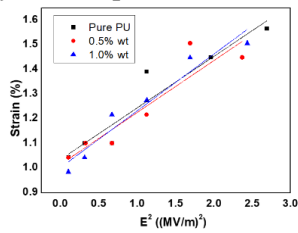

Figure 2. Strain response of PU/PPy-CB composite as a function of squared electric field.
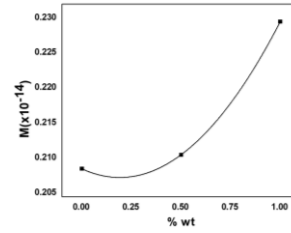

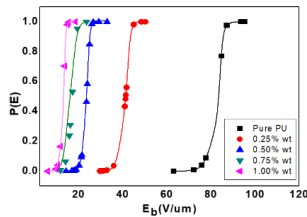**Figure 3.** The electrostrictive coefficient versus the PPy-CB loading**.**

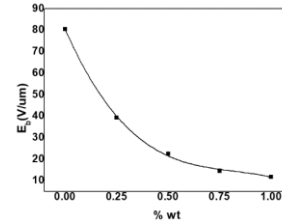**Figure 4.** Breakdown probability versus electrical breakdown strength.

Figure 5. Electrical breakdown strength versus the PPy-CB loading.

4. Conclusion

This work studied the dielectric and electrostrictive properties of PU/PPy-CB film composites. All samples were prepared by using a film-casting process. The results showed that the dielectric constant and the electrostrictive efficiency of PU/PPy-CB film composites increase when the PPy-CB loading was used. While a decrease of the electrical breakdown strength was observed with the PPy-CB loading. They can be candidate materials for electromechanical application which is related to the high conductivity of fillers, charge mobility, and polarization distribution based on the heterostructure materials.

References

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