Enhanced interfacial dielectric polarization in PVDF-HFP copolymer with treating PPy by using silane coupling agent

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Abstract. Dielectric materials are polar materials for energy storage applications such as capacitors, transformer, and other electrical devices. The great dielectric properties generally depend on easily switchable polarization and higher-order structure in a material. Filler composite in the flexible dielectric polymer is then considered to rearrange polymer chain. However, the filler becomes agglomeration easily at high loading content in polymer, resulting in high energy loss and low electrical breakdown. This work presents the treated Polypyrrole (PPy) filler by 3-Aminopropyltriethoxysilane for avoiding agglomeration in PVDF-HFP thin film. These 30 μm PVDF-HFP film thickness is fabricated by tape casting method with N,N-dimethylformamide (DMF) solvent. The distributions of PPy filler on PVDF-HFP are observed by SEM image. Dielectric constant, dielectric loss, and conductivity are analyzed. As a result, the maximum silane content was found on 1 wt% for 1 wt% PPy/PVDF-HFP to maximized dielectric constant and reduce dielectric loss and conductivity. The conductive of PPy filler was lowered by covering with electrical insulating silane, resulting in decreased dielectric loss and conductivity. Then, polymer chain with silane bonding easily polarized under the electric field, resulting in an intensification of dielectric constant around 2.5 times compared with non-silane. Afterward, this dielectric constant clearly decreased when it reached to exceeded silane content as 5-20 wt%. Treated PPy with the suitable silane content in PVDF-HFP performs good dielectric properties for advanced energy storage in this work.

1. Introduction
A dielectric polymer is a flexible polar material that produces a large net dipole moment under an electric field. High dielectric properties, high chemical resistance, and low cost are key features to consider for dielectric polymer matrix in this field such as Polyvinylidene fluoride-hexafluoropropylene (P(VDF-HFP)). Conductive filler in dielectric polymer has been one of the other techniques to improve these properties. However, the large amount of this filler easily agglomerates, resulting in failure from energy loss heat. For example, Putson and colleagues found that dielectric loss of PVDF-HFP was increased with conductive filler [1]. This problem can be solved by using a Silane coupling agent to connect between filler and polymer on PVDF composite [2, 3]. An electrical insulator of Silane covered conductive fillers, bonding with polymer chain. The specific polymer has a specific silane along with filler content [4]. One of the high conductive fillers as Polypyrrole (PPy) is interesting to improve the dielectric properties of PVDF-HFP. There are no prior works to develop dielectric properties on PVDF-
HFP by using a silane coupling agent on PPy filler. In this work, the 3-Aminopropyltriethoxysilane coupling agent is considered for preventing agglomeration and aiming to achieve better dielectric performance.

2. Experimental
Composite film preparation, the polypyrrole (PPy) as 0.25, 0.50, 0.75, and 1.00 wt% is blended and stirred with Polyvinylidene fluoride-hexafluoropropylene (P(VDF-HFP)) (purchased from Solvay Solexis, Belgium) in 99% purity N,N-dimethylformamide (DMF) (purchased from RCI Labscan Limited, Thailand) before cast on the smooth glass by tape casting method. The suitable PPy content in PVDF-HFP is observed.

For the silane coupling agent process, the PPy is treated by Hydrogen peroxide 30% (H₂O₂) to get OH group on the surface by sonicating 30 min (250W) and drying 12 h (100°C). Afterward, the 3-Aminopropyltriethoxysilane (silane) is hydrolyzed by DI water and Ethanol (50 ml: 50 ml) for 20 min to open the functional group. The silane contents are considered as 1, 5, 10, and 20 % of PPy filler. These solutions are completely stirred with the suitable PPy content for 24 h. Resulting, treated PPy is obtained by removing the exceeding silane by DI water (5 times centrifuges). The treated PPy is completely dried 100°C (12 h). The treated PPy powder with several silane content is finally prepared to fabricate composite films as mentioned in the previous step.

For characterization, morphological PPy/PVDF-HFP image is observed by using the SEM (FEI Quanta 400, USA). Dielectric loss (ε''r) and capacitance (C, in F) are recorded by applying 1 V ac voltage to the sample by two electrodes of LCR meter (IM 3533, HIOKI, Japan) in frequency from 1 to 10⁶ Hz. Moreover, dielectric constant (εr) and conductivity (σac, S/m) are calculated by using the equation (1) and (2), respectively. Here d is sample thickness (m), A is the area of the electrode (m²), and ε₀ is free space permittivity (8.853 x 10⁻¹² F m⁻¹), f is frequency (Hz).

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\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \tag{1}
\]

\[
\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon_r \varepsilon''_r \tag{2}
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3. Results and discussion

3.1. The PPy filler contents on PVDF-HFP transformation
Figure 1 shows the relationship between dielectric properties and frequency. The 0, 0.25, 0.5, 0.75, and 1 %PPy in PVDF-HFP is measured (Figure 1 (a)). The low frequency (10-10⁶ Hz) provides the largest dielectric constant (εr) because interfacial polarization is mainly active and easily switchable explaining by the Maxwell-Wagner-Sillars (MWS) theory [5]. In PPy content, εr is increased with PPy content. For example, 0.75%PPy immediately increase εr from 5 (pure PVDF-HFP) to 76 at 10-10⁶ Hz. The εr of 1 wt% PPy at low frequency is clearly disturbed by conductive filler loading to be unstable value, resulting in larger conductivity (σac) and dielectric loss (ε''r) as in Figure 1 (b) and (c), respectively. For an example of increase σac includes pure PVDF-HFP (10⁻¹⁰ S/m) to 1 wt% PPy (10⁻⁴ S/m) around 10⁶ times. In addition, ε''r are clearly increased with PPy content. The fixed dipole with conductive filler is easily polarized under electric field, resulting in larger εr and σac when adding conductive filler, as prior theory [5].
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3.2. Silane effect on 1%PPy/PVDF-HFP dielectric properties
To enhance interfacial polarization, silane contents are considered. The 1, 5, 10, and 20% Silane on 1%PPy/PVDF-HFP are continuously prepared. As Figure 1 (d), dielectric constant at 10-10 Hz sharply increases from 111 (0%Silane/1PPy) to around 222 (1%Silane/1PPy), which seem 2 times differently. Dielectric constant, then, suddenly drops to 75 (5%Silane/1PPy), which is lower than the 0%Silane/1PPy. Afterward, there is a gradual decrease to 8.8 (20%Silane/1PPy) that is the lowest value. Surprisingly, this 1%Silane/1PPy can decrease their conductivity from 2.06x10 S/m of 0%Silane/1PPy to be 3.30x10 S/m. Afterward, the conductivity slightly increases at 5%Silane/1PPy before sharply decreased to 7.32x10 S/m at 20%Silane/1PPy. The trend of this conductivity is similar behavior with dielectric loss, matching with a prior study [2].

The larger insulating silane that covers on PPy has the ability to reduce PVDF-HFP conductivity as well as dielectric loss. The silane head (Si-Si with OH group) is bonded with the OH group on PPy filler surface, and the silane tail (Amino group) is completely connected with the PVDF-HFP polymer chain. It seems that the 1%silane on PPy filler is the suitable silane content that performs a good connector between polymer chain and PPy filler, resulting in the easiest switchable polarization and the largest dielectric properties. Surprisingly, this silane has ability to reduce conductivity as well as dielectric loss. Compared with thicker silane content, the stronger chemical bonding in thinner silane content is likely easier in switchable polarization, resulting in great dielectric properties [2].

3.3. Morphological PPy distribution and dispersion on treated PPy
Scanning Electron Microscopy (SEM), Hitachi TM 3030plus, is observed in the morphology on the sample surface. The PPy filler distribution is distinguishable between treated and untreated silane on 1%PPy in PVDF-HFP as showed in Figure 2. There are several big porosities on this sample by the DMF evaporation after drying. The PPy is noticeable as the small black dot. These dots have more noticeable and completely separated two phases on untreated PPy by silane (Figure 2 (a)). As a result, it seems a lot of PPy particles dispersing on PVDF-HFP. In contrast, when the treated PPy is connected to PVDF-HFP by silane, the separation between two phases is blurred. As a result, it seems less of PPy particles dispersing on PVDF-HFP.
Figure 2 SEM images of untreated (a) and treated (b) PPy by a silane coupling agent.

4. Conclusion
The 0.25, 0.50, 0.75, and 1.00%PPy in PVDF-HFP polymer composites were fabricated by tape casting method. The dielectric constant, conductivity, and dielectric loss were increased with PPy content. Among them, the best dielectric constant was shown by 1.00%PPy in PVDF-HFP. Nevertheless, that condition also possessed the highest conductivity and dielectric loss. To reduce those two conductivity and dielectric loss, the 3-Aminopropyltriethoxysilane coupling agent was added into these composites. The silane content was varied of 1, 5, 10, and 20%. As a result, 1%silane improved dielectric constant, and reduced both conductivity and dielectric loss. On the other hand, adding silane more than 1% could cover the filler to be thicker. As a consequence, the dipole moment is hard to polarize following the external electric field, resulting in decrease dielectric constant, conductivity along with dielectric loss. This silane content in this work has a potential role to increase dielectric properties for the advanced capacitor in the future.

5. References
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