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All-organic dielectric nanocomposites using conducting polypyrrole nanoclips as filler

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ABSTRACT

All-organic nanocomposites using conducting polypyrrole (PPy) nano-clips as fillers and poly(vinylidene fluoride-chlorotrifluoroethylene) (PVDF-CTFE) as the matrix are studied. The nanocomposites with a uniform microstructure were fabricated via a combination of a solution casting and a hot pressing process. Due to the uniform microstructure, the composites exhibit a single glass transition process, whose temperature decreases with increasing PPy content. The dielectric properties of the nanocomposites are systemically studied and analyzed over a wide temperature range from −60 °C to 140 °C and a broad frequency range from 100 Hz to 1 MHz. The nanocomposites have a low percolation threshold (~7.4 wt%) and exhibit a high dielectric constant and a low dielectric loss. For the composites with 7 wt% of PPy at room temperature, the dielectric constant at 1 kHz is 23 times higher than that of the polymer matrix and the dielectric loss over a broad frequency range is less than 0.4 which is lower than the loss reported in other composites with the composition close to the percolation threshold. It is concluded that mixing PPy with P(VDF-CTFE) results in a new relaxation process that dominates the observed dielectric loss at low temperatures including room temperature. It is demonstrated that it is the DC conductivity rather than the dielectric constant that should be used to determine the percolation threshold.

1. Introduction

To satisfy the high integration of modern microelectronics, i.e. embedded capacitors, energy storage devices, pulsed-power devices, polymer-based dielectric nanocomposites, in which a dielectric polymer is used as matrix, have drawn considerable attention due to their excellent mechanical flexibility and dielectric properties as well as easy processing [1–3]. Different types of fillers have been used to enhance the dielectric performance, such as dielectric constant (ε_r) of the dielectric polymers. According to the electric properties of fillers used, the polymer-based dielectric composites can be classified into two types [1]. One is dielectric-dielectric composite (DDC) in which the fillers are dielectric materials (i.e. ferroelectric ceramics) with a high dielectric constant. The advantages of DDCs are they usually possess a relatively low loss and high breakdown electric field [1,4]. However, the dielectric constant is usually low (less than 100) [1]. In some cases, the dielectric constant of these composites can be high [5–7]. For example, the composites using $CaCu_3Ti_4O_{12}$ as the filler can exhibit a dielectric constant of 700 at room temperature and about 1000 at certain temperatures [5,6]. However, the high dielectric constant is only achieved in these composites with a high ceramic content (> 50 vol%), which is detrimental to the flexibility of the composites. The other is conductor-dielectric composite (CDC) where the fillers are conducting materials [1]. According to the percolation theory, the dielectric constant of CDCs increases drastically as the content of conductive fillers approaches a critical concentration (i.e. the percolation threshold, φ_c) from the lower concentration side [1,8]. Therefore, a high dielectric constant can be obtained in the composites when the filler content is close to the φ_c. That is, even a high dielectric constant can be achieved in the composites with a low filler content when the φ_c is small, which would result in the composites with a good flexibility.

CDCs represent dielectric materials with an ultra-high dielectric constant and balanced mechanical properties and have been widely studied recently [1]. Numerous conductive fillers, including metal

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nanoparticles [9,10], carbon fibers and nanotubes [11–15], and graphene [16,17], have been used for the development of CDCs with outstanding dielectric properties. The critical challenge for CDCs is how to achieve a low φ_c in the composites with a uniform microstructure when considering the requirements of mechanical and electrical applications. Due to their high conductivity, homogeneous size distribution, low cost, and easy to obtain, spherical nanoparticles of different metals including Ag, Ni, Cu, and Fe were initially used as fillers [9,10,18–22]. However, for a composite using spherical fillers with a uniform microstructure, the φ_c is always high, as high as 50 vol% [9]. The composites with a uniform microstructure are certainly desirable since it means a better repeatability [9,23]. Therefore, it is interesting to use the filler with different shapes. Theoretically, the φ_c can be lowered by using one-dimensional (1D) and two-dimensional (2D) particles as fillers. For example, when fiber-like 1D particles are used as filler, it is known that the φ_c decreases with increasing the length-to-diameter ratio (i.e. aspect ratio) of the filler particle [8].

The CDCs that use of different 1D and 2D fillers have been studied. Experimentally, a lower φ_c ($<$ 10 vol%) has been achieved by using 1D filler, such as carbon fibers (CFs) and carbon nanotubes (CNTs) [14,24]. However, there are two issues associated with the composites using CFs and CNTs as the filler: their poor wettability with polymer matrix and straight shape. Due to the poor wettability between the CFs and CNTs, it is difficult to evenly disperse CNTs in a polymer matrix and obtain homogenous nanocomposites [25,26]. Therefore, the dielectric constant obtained in these composites shows a limited enhancement. For example, the ratio ($\varepsilon_r/\varepsilon_m$) of the composite's dielectric constant (ε_r) to the matrix's dielectric constant (ε_m) is usually less than 10 [11]. To overcome this, modifying the surface of CNTs using specific agents has been investigated to achieve a uniform dispersion of CNTs in the polymer matrix [27–29]. The CNT with a better distribution in polymer matrix results in a lower conductivity for the composites close to the percolation threshold. Due to the straight-like shape of CFs and CNTs, it is easy to form the long conductive channels in the composite. The long conductive channels in a composite would result in the dielectric constant: 1) becoming very sensitive to concentrations close to φ_c and 2) associated with a high loss ($>$ 10). The former means that the composites have a low composition tolerance [9,30]. The latter is not desirable for the dielectric applications. 2D carbon-based materials (i.e. graphene, graphene oxide, graphite) have been used as conductive fillers in the development of CDCs in recent years [31–34].

Regarding the conductive fillers used in CDCs, besides metals and carbon, conducting polymers (CPs) provide a new avenue for the development of high performance dielectric composites [1,35]. The CPs as the filler for the development of dielectric composites have some unique advantages over other conductive fillers: 1) the excellent wettability between the CPs and polymer matrix can be achieved, which significantly benefits the homogeneity of the nanocomposites and reduce the gradient in the properties cross of the interface between the matrix and filler; 2) the conductivity of CPs can be easily adjusted over a large range by simply doping CPs with different concentrations; and 3) as polymer, the CPs can be very flexible, which is important to develop the flexible composites. Due to these, the CPs have been used in the development of dielectric composites, which result in all-polymer or all-organic composites. Polyaniline (PANI) is one of the most studied CPs for fabricating all-organic composites [36–40]. In these studies, CPs in fiber-like shape have been used to reduce the φ_c. Similarly with the 1D carbon fillers, the fiber-like CPs result in the long conductive channels which cause a high conductivity in the composites. Therefore, it is highly desirable to use the CPs in different shapes that can reduce the φ_c and the electrical conductivity. Recently, a novel process was developed to prepare conductive polymer - polypyrrole (PPy) - with a unique microstructure that is somewhere between the 1D and 2D structure [41]. Specifically, nanostructured PPy in clip-shape was formed. These nanoclips can be treated as 1D fiber with a high aspect-ratio but in a much smaller size so that the formation of long conductive channels can be limited. These nanoclips can also be treated as 2D materials of a very low density. The nanoclips open a new avenue to develop high performance nanocomposites [42]. For example, the nanocomposites using PPy nanoclips as filler and poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] as matrix exhibit a very low φ_c ($\sim$8 wt%). A relative low loss is also observed in these composites. For example, for the composites with 7.0 wt% of PPy nanoclips, the composites exhibit a high dielectric constant associated with a dielectric loss of about 1.0 [42].

In this work the nanocomposites using PPy nanoclips as filler and poly(vinylidene fluoride-chlorotrifluoroethylene) [P(VDF-CTFE)] as the polymer matrix are studied. It is well known that P(VDF-TrFE) exhibits a ferroelectric-to-paraelectric phase transition and a strong piezoelectric effect [43–45], which are not desirable for the dielectric applications. P(VDF-CTFE) used here does not show a clear phase transition and exhibits a very weak piezoelectric effect [46,47], which makes the P(VDF-CTFE) based composites more suitable for dielectric applications. Additionally, P(VDF-CTFE) has a much lower crystallinity than P(VDF-TrFE), which makes P(VDF-CTFE) more flexible than P(VDF-TrFE). The PPy-P(VDF-CTFE) nanocomposites reported here exhibit a high dielectric constant with a low percolation threshold (7.4 wt%). More importantly, these composites exhibit a much lower dielectric loss. For example, the composites with 7.0 wt% PPy nanoclips exhibit a dielectric constant at 1 kHz that is 23 times the polymer matrix and a dielectric loss that is less than 0.4 over a broad frequency range. More importantly, it is concluded that the loss observed in the PPy-P(VDF-CTFE) nanocomposites is dominated by a new relaxation process rather than the conductivity. The new relaxation process is induced by mixing two polymers. Additionally, due to the lack of a clear phase transition in polymer matrix, a better way to determine the percolation threshold is introduced by using the DC conductivity.

2. Experimental

2.1. Nanocomposites preparation

P(VDF-CTFE) 88/12 mol.% copolymer obtained from Solvey was used as received. PPy with the unusual nanoclip-like morphology was chosen as the filler. The PPy nanoclips were synthesized by an "oxidative template assembly" approach as described in Refs. [41,48]. The conductivity of PPy clips used in this nanocomposite is around 3 S/cm. As shown in Fig. 1 (a), the dimension of each nanoclip is about 1.0 μm × 0.5 μm and the diameter of PPy fiber is 100–200 nm. The length of PPy fiber for a single nanoclip will be more than 3 μm if it is unfolded. That is, the aspect ratio of 1D PPy is more than 10.

The PPy-P(VDF-CTFE) nanocomposites with different PPy contents (0, 3, 4, 5, 6, 7, and 8 wt%) were prepared using a two-step method that combines the solution cast with a hot press process. Usually, the microstructure uniformity of the composites can be examined using SEM. However, due to the fact that both matrix and filler are polymers, it is difficult to determine the microstructure uniformity of the all-polymer composites using SEM. In the study of composites, especially the composites with ceramic and metal fillers, it was found that the wettability between the polymer matrix and ceramic/metal filler is usually not good, which results in a nonuniform microstructure. To improve the microstructure uniformity of the composites, different approaches, such as using coupling agent, have been introduced [49]. One of these approaches is the combination of solution-casting with hot-pressing process. To make sure the composites prepared in this work have a uniform microstructure, the combination of solution-casting and hot-pressing process was used to prepare the PPy-P(VDF-CTFE) composites. It was experimentally demonstrated by different composite systems that this process results in a uniform microstructure [6,23,24,47,50]. That is, P(VDF-CTFE) was first dissolved in N,N-dimethylformamide (DMF) at room temperature for 12 h. PPy nanoclips were then dispersed in the solution by sonication for 1 h and magnetic stirring for 8 h at room