

Preparation and dielectric properties of silver@poly(vinyl pyrrolidone)/poly(vinylidene fluoride) composites

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Silver@poly(vinyl pyrrolidone) (Ag@PVP) core-shell nanoparticles are synthesised via a one-step method. Ag@PVP/poly(vinylidene fluoride) (PVDF) composites with desirable dielectric properties were reported. It was found that the dielectric losses for Ag@PVP/PVDF composites were rather low similar to that of pure PVDF because of the insulating PVP coating. The Ag@PVP/PVDF with PVP of lower molecular weights exhibited more desirable dielectric properties than those with PVP of higher molecular weights. PVP can offer interesting permittivity enhancements without significantly adversely affecting the dielectric losses of the PVDF matrix. The results of this work make it possible to obtain the percolative composites with low dielectric loss and high permittivity by using Ag@PVP through simple methods.

1. Introduction: Metal/polymer composites, which are composed of metal fillers and polymer matrix, have attracted considerable interest because of their potential applications in electronic devices as promising dielectric materials [1–3]. Silver (Ag) has been one of the main metal fillers investigated in dielectric composites due to its good electrical and thermal conductivities and chemical stability. Recently, particular attention has been paid to Ag/poly(vinylidene fluoride) (PVDF) nanocomposites because of their preferred electrical and mechanical properties [4–6]. It has been demonstrated recently that the presence of a large amount of interfaces in the composite between the polymer and nanoparticle (NP) would promote the exchange coupling effect through a dipolar interface layer, affording higher polarisation levels and benefiting dielectric properties of the polymers [6–10]. Polyvinyl pyrrolidone (PVP) is almost exclusively used as a protective agent or dispersant in the synthesis of silver NPs (AgNPs) [11]. After synthesis, much of PVP needs to be removed from the particle surface by multiple washing, which leads to increase in processing time and costs. For percolative composites, the large dielectric loss caused by the direct contact between the conductive fillers has recently gained considerable attention. During the past few years, many efforts [12–14] have been made to reduce loss by coating conductive fillers. In this Letter, we have applied PVP not only as a stabiliser but also as the surface coating of AgNPs for reducing loss. PVP with polar pyrrolidinone substituents is also expected to interact with the polar polymer matrix and thus improve the dielectric properties of Ag/PVDF nanocomposites.

2. Experimental: Two PVP polymers with different average molecular weights, PVP K30 ($M_w = 40,000$) and PVP K90 ($M_w = 1,300,000$), were used. Ag@PVP NPs were prepared by reducing $[\text{Ag}(\text{NH}_3)_2]^+$ complex with ascorbic acid aqueous solution. The Ag particles coated by PVP K30 and PVP K90 are denoted as Ag@PVP30 and Ag@PVP90, respectively. The mixtures of Ag@PVP and PVDF were moulded by hot-pressing at 180°C under 10 MPa. The final Ag@PVP/PVDF samples were disks of 12 mm in diameter and about 1.5 mm in thickness. The samples were polished mechanically and coated with an Ag film on the top and bottom surfaces of the disks for dielectric measurement. Transmission electron microscopy (TEM, Joel JEM-2001F, Japan) images were obtained by placing a few drops of the dispersion on

a copper grid, and evaporating them prior to observation. Scanning electron microscopy (SEM) measurements were performed with a Hitachi S-4800 field emission electron microscope (Japan). The dielectric properties of the composites at various Ag volume fractions were determined using a Hioki 3532-50 LCR meter (Japan). The Ag@PVP volume ratio data in the Ag@PVP/PVDF composites shown in this Letter exclude the volume of PVP.

3. Results and discussion: Fig. 1 illustrates the TEM images of typical Ag@PVP NPs. Fig. 1a reveals the well-dispersed Ag@PVP30 NPs 30–80 nm in diameter. Fig. 1b indicates the presence of polymeric layer on the surface of AgNPs. The structure of the Ag@PVP30 particles is of a well-defined core-shell type with a shell thickness of 5–10 nm. This ensures the stabilisation of particle dispersion in PVDF matrix owing to the inter-particle repulsion resulted from the polymeric spacer in the Ag@PVP NPs. As illustrated in Fig. 1c, large spherical particles coated with PVP on the surface can be seen in the Ag@PVP90 particles. PVP can promote the nucleation of metallic Ag because Ag ions are easily reduced by the lone-pair electrons of PVP [15]. Thus the significantly higher molecular weight of PVP K90 has given it more chances to form a complex with Ag ions than PVP K30. Thus the sizes of Ag@PVP90 particles are fairly higher than those of Ag@PVP30.

Figs. 2a and b show typical SEM micrographs of cryogenic fractured surfaces of the Ag@PVP30/PVDF composites. There are large particles in the 200-nm range and small particles in the 50-nm range. Those large particles are actually the polymer matrix. The small Ag@PVP30 particles were homogeneously dispersed in the PVDF matrix. This implies that PVP not only served as the stabiliser during synthesis, but also as a coating layer to improve the particle dispersion. Increased interfacial interactions between the particles and PVDF increased the effective interfacial area and, in turn, increased interfacial polarisation, which could contribute to the better dielectric properties of the Ag@PVP30/PVDF composites.

Fig. 3a shows the variations of dielectric permittivity of Ag@PVP30/PVDF composites with frequency at room temperature. It can be seen that the frequency dependence of the permittivity for the composites was relatively weak. No abrupt increases in dielectric permittivity were observed below 17 vol.% of Ag content. This means that conductive pathways were not formed

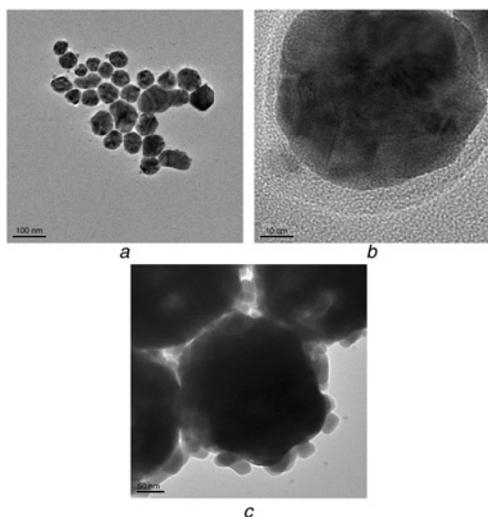


Fig. 1 TEM images of (a, b) Ag@PVP30 and (c) Ag@PVP90 particles at different magnifications. Scale bar
a 100 nm
b 10 nm
c 50 nm

yet in the specimens. The composites exhibited a pronounced increase in dielectric permittivity when Ag@PVP30 content reached 0.17, showing the occurrence of percolation phenomenon. At filler volume fraction of 0.17, the highest dielectric permittivity of 126 at 100 Hz can be obtained, which is about ten times higher than that of pure PVDF. The significant permittivity enhancement is mainly attributed to the enhanced interfacial interactions and increased interfacial area created by good particle dispersion.

Regarding the dielectric loss (Fig. 3b), the loss tangent of the Ag@PVP30/PVDF composites is slightly higher in the low frequency region (10^2 – 10^5 Hz), whereas even lower than that of pristine PVDF in the high frequency region (10^5 – 5×10^6 Hz). The dielectric loss is weakly dependent on the frequency in the low frequency region. The Ag@PVP30 NPs loading did not have an appreciable influence on the dielectric loss in the measured frequency range. Surface coating by PVP improves the compatibility between AgNPs and PVDF as well as passivating the surfaces of AgNPs.

The improved insulation property of the Ag@PVP30 compared with bare Ag particles could reduce the filler volume fraction dependence of dielectric loss of the composites. The loss tangent of Ag/PVDF composite exceeds 3 near the percolation threshold at 100 Hz [6], while that of the Ag@PVP30/PVDF composite (~ 0.06) is two orders of magnitude lower than it. The nanoscale structure comprised of AgNPs isolated by PVP and PVDF space layers hindered the formation of filler networks, resulting in the decreased dielectric loss in the composites, even at a high filler loading. The conductivity of the Ag@PVP30/PVDF

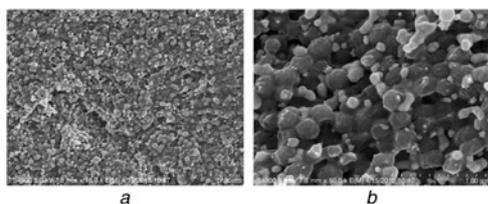


Fig. 2 SEM images of freeze-fracture surfaces of 17 vol.% Ag@PVP30/PVDF composites at different magnifications. Scale bar
a 5 μm
b 1 μm

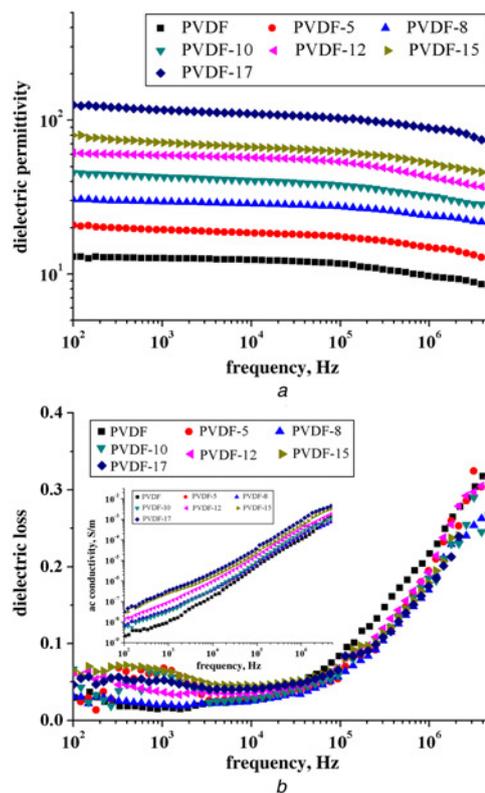


Fig. 3 Dielectric permittivity and dielectric loss of Ag@PVP30/PVDF composites

a Dielectric permittivity

b Dielectric loss of Ag@PVP30/PVDF composites with different Ag@PVP30 contents as a function of frequency. The inset shows the dependence of conductivity on the frequency and Ag@PVP30 content

nanocomposites roughly shows linearly increase with increasing frequency. No sudden rise in the conductivity is observed with increasing loading of Ag@PVP30 due to insulating PVP coating layer. The insulating character of Ag@PVP30 NPs thus also contributes to the low loss of the composites. Near the percolation threshold, Ag@PVP30 NPs are almost touching each other, but still remaining insulative due to the existence of PVP layer. Accordingly, PVP layer can offer interesting permittivity enhancements without significantly adversely affecting the dielectric losses of the PVDF matrix.

The dielectric properties of Ag@PVP90/PVDF composites were compared with those of Ag@PVP30/PVDF to reveal the effect of the molecular weight of PVP on them. As illustrated in Fig. 4, it

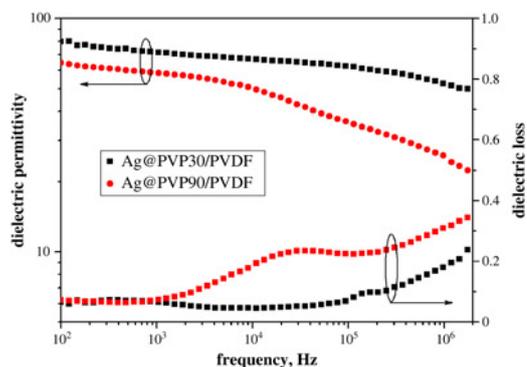


Fig. 4 Dielectric properties of 15 vol.% Ag@PVP/PVDF composites as a function of frequency

has been found that for the same Ag@PVP loading dielectric characteristics of the composites strongly depend of the type of PVP. The dielectric permittivity of Ag@PVP30/PVDF is higher than those of Ag@PVP90/PVDF over the whole frequency range. Moreover, lower dielectric losses were observed in Ag@PVP30/PVDF, compared with those of Ag@PVP90/PVDF. It is obvious from Fig. 4 that the dielectric properties of the two types of composites show dissimilar frequency dependence, which should be attributed to the different relaxation behaviours of PVDF affected by the difference between the two particles [16]. With increasing particle size, the interfacial bonding strength between Ag particles and PVP was weakened as a result of the steric effect [17]. The deteriorated dielectric properties in Ag@PVP90/PVDF are thus attributed to the weakened interfacial adhesion between Ag particles and PVP layers. Moreover, the increased particle size resulted in the large average inter-particle distance and lowered interfacial area [6], the composite containing Ag@PVP90 particles therefore showed a decrease in dielectric permittivity.

4. Conclusion: Ag@PVP core-shell NPs are synthesised via a one-step simplistic method. PVP serves not only as a stabiliser but also as the surface coating of AgNPs. A new kind of Ag@PVP/PVDF composite was prepared by melt blending. PVP can form strong interface between PVDF and AgNPs, which thus stabilised the dispersion of AgNPs in PVDF host. The molecular weights of PVP were found to considerably affect the average size of the resulting AgNPs and the dielectric properties of the composites. The Ag@PVP30/PVDF composite achieved the highest dielectric permittivity at about 126 at 100 Hz. The dissipation factors for Ag@PVP30/PVDF composites were rather low similar to that of pure PVDF because of the insulating PVP coating. The Ag@PVP30/PVDF exhibited more desirable dielectric properties than Ag@PVP90/PVDF. These differences were explained in terms of the effects of PVP molecular weight on the size and dispersion of Ag particles and the interfacial adhesion in composites. Accordingly, PVP can offer interesting permittivity enhancements without significantly adversely affecting the dielectric losses of the PVDF matrix. The results of this work reveal that Ag@PVP can be effectively used to develop new materials for electric storage applications.

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6 References

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