MICROWAVE-ASSISTED SYNTHESIS OF SILVER NANOWIRES AND ITS APPLICATION IN EPOXY COMPOSITES

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Abstract

A rapid, microwave-assisted synthesis of silver nanowires by polyol method is described. Dissolution of Na_2S and AgNO3 (ratio 1:8 to 1:2) in ethylene glycol and subsequent heating using microwave irradiation in the presence of polyvinylpyrrolidone generates silver NWs in 0.5-2 min. Uniform set of silver nanowires with diameter of 75 nm 500 nm could be observed by SEM. Morphology of silver nanowire is highly dependent on the microwave heating time and Na_2S:$AgNO_3$ ratio. Silver nanowire/epoxy nanocomposites have been developed via incorporating as-prepared silver nanowires into the epoxy matrix. The nanocomposites with silver nanowire volumes content of 15% showed an up to 20% increase in thermal stability. The initial decomposition temperature and glass transition temperature of could be elevated simultaneously by this method.

1. Introduction

Incorporation of metallic nanoparticles and nanowires into polymer matrix offers enormous possibilities for the design of functional materials with significant technological applications. Metal-polymer nanocomposites can be applied for the development of embedded-capacitor technology, antibacterical materials, etc. [1] Among the different metals, silver nanowires have gained a significant amount of research attentions because of their excellent electrical and thermal properties [2], especially in embedded-capacitor applications. Properties of metal-polymer nanocomposites mostly depend on the dispersion status of metallic nanoparticles or nanowires in polymer matrix and interfacial compatibility toward polymeric molecules. [3]

Several approaches have been developed for preparation of silver nanowires with controllable sizes. The most commonly used methods are various chemical routes, such as polyol process [4], wet chemical synthesis [5], the hydrothermal method [6], electrochemical techniques [7], template techniques [8] and microwave-assisted method [9]. Among these methods, the polyol process is an effective route to synthesize silver nanowires, especially by introducing microwave irradiation into the polyol synthesis method. Comparing with traditional hydrothermal method, microwave-assisted method has the advantage of shorter reaction time. Nanocomposites containing silver nanostructures including nanoparticles and nanowires have an intense potential to be useful in future electronic applications such as high charge-storage capacitor, electrical sensors and electoactive materials [10]. These conductive metal/polymer mixed composite could form conductor-insulator percolative systems and achieve high dielectic constant [11]. Recently, one-step synthesis of silver nanoparticles and preparation of silver/epoxy nanocomposites were started in our group. The results show that thermal properties of the composite could also be improved.

In this study, we report a convenient, rapid synthesis of silver nanowires by introducing microwave irradiation into the polyol synthesis method by reducing silver nitrate with ethylene glycol and using PVP as an adsorption agent. The synthesized silver nanowires were dispersed in epoxy resin matrix to develop high dielectric constant materials. Moreover, thermal properties of the silver-epoxy nanocomposites are also important for potential application related to integrated circuit, which were characterized by dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA). The dependence of the thermal and mechanical properties of composites on the morphology of the nanowires was also discussed.

2. Experimental part

2.1 Materials

Silver nitrate (99.9%) was purchased from Shanghai Shenbo Chemical Reagent Co., China. Ethylene glycol, Poly(N-vinylpyrrolidone) (PVP) with molecule weight of 40000 and sodium sulfide (Na_2S) were purchased from Nanjing Chemical Reagent Co., China. A commercial epoxy resin DER 383 from Dow Chemical Co. and 4,4'-diaminodiphenylsulfone (DDS) from Shanghai Aladdin Reagent Co. were cured as polymer matrix. Water used in experiments was purified with a JL-RO 100 Milipore-Q Plus equipment till the specific resistance reached the value of 18.0 MΩ cm^{-1}. All solvents and other chemicals were of analytic grade or better.

2.2 Preparation of silver nanowires

Into a 250 ml conical flask with oil heat, magnetically stirring and syringe pump, 50 ml ethylene glycol solution of $AgNO_3$ was charged. Then a mixture of 50 ml ethylene glycol solution of 0.2 mmol/L Na_2S and 0.15 mol/L PVP was injected into the flask at a speed of 1ml/min. The mixture in the flask became dark red colored because of the formation of Ag_2S. Afterward, the flask were moved into a microwave-equipped oven and heated for 40 seconds with power of 400W. After the reaction was completed, the solution were allowed to cool down to room temperature in air. Silver nanowires were separated from ethylene glycol by addition of a large amount of ethyl alcohol, followed by sonication and centrifugation for five times then dispersed in acetone.

2.3 Preparation of silver nanowires/epoxy nanocomposites

The acetone dispersion of silver particles were mixed with epoxy resin DER 383 and then placed in vacuum over at 50 ℃ to remove the solvent. The silver-blended epoxy resin and curing agent DDS were mixed in 1:1 equivalent ratio and cured on hot plate at 120 ℃for 1 h, 180 ℃for 1 h, 240 ℃ for 2h. The cured composites were cooled slowly down to room temperature to get the required specimens for DMTA and TGA measurements.

2.4 Characterization

The morphologies of the silver nanowire specimens were determined by Scanning Electron Microscopy (SEM) at 10 kV (JSM-6510, JEOL Co. Japan) and Transmission Electron

Microscopy (TEM) (JEM-2100, JEOL Co. Japan). Thermogravimetric analysis was performed on a Netzsch STA 409 PC thermal analyzer at a heating rate of 10 ℃/min under nitrogen atmosphere to investigate the thermal stability of silver nanowire/epoxy composites. Dynamic mechanical thermal analysis was carried out with a TA DMA Q800 instrument using 2 mm × 10 mm × 35 mm rectangular samples at a programmed heating rate of 3 ℃ /min from 50 ℃ to 300 ℃ at a frequency of 1Hz under air atmosphere.

3. Results and discussion

3.1 Morphology of silver nanowires

Silver nanowires were prepared from the reduction of silver nitrate. The proper concentration of Na_2S facilitates the formation of silver nanowires. When Na_2S ions were added into the ethylene glycol solution of silver nitrate, Ag_2S colloids formed as a warehouse of silver ions. The silver ions from these colloids are released to the solution for maintaining the equilibrium concentrations, which has the similar effect of syringe pump to keep a slow and continuous supply of free silver ions. This allows for the continuous growth of silver nanowires.

Figure 1 shows the SEM and TEM images of the silver nanowires. Straight silver wires could be observed and few silver structures with spherical or quasispherical shape were found. The diameters of the synthesized silver nanowires ranged from 150 nm to 300 nm.

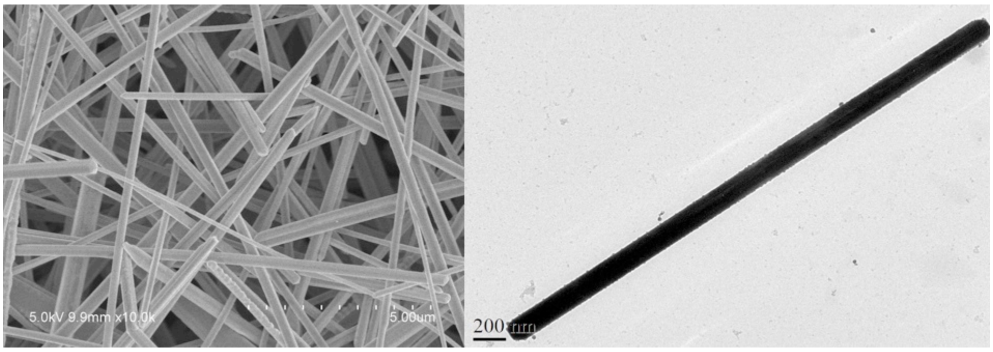

Figure 1. SEM and TEM images of silver nanowires.

3.2 Thermal properties of silver nanowire/epoxy nanocomposites

Dynamic mechanical observations were performed to analyze the dynamic elastic modulus and the occurrence of molecular mobility transitions such as glass transition [12]. The DMTA scans of silver nanowire/epoxy nanocomposites with different volume fraction are shown in Figure 2. The peak temperature of tan was taken as the glass transition temperature (T_g). The DMTA measurement showed that T_g of the silver nanowire/epoxy nanocomposites rise with volume fraction of silver nanowires. TGA is the most favored technique for rapid evaluation in thermal stability and degradation behaviors of various polymers or polymer based composites. To study the relation between thermal stability of silver nanowire/epoxy nanocomposites, specimens similar to DMTA test with different silver volume fraction were prepared. The initial decomposition temperature in TGA curve is the main parameter to evaluate thermal stability of the specimen. In order to succinctly compare thermal stability of silver-epoxy composites, 5 wt% degradation temperature ($T_{5\%}$) and 10 wt% degradation temperature ($T_{10\%}$) as well as T_g from DMTA were listed in Table 1. The silver containing epoxy composite exhibited higher thermal stability than neat epoxy resin even 5 vol% silver nanowires loaded. However, thermal stability of the composite isn't improved significantly with the increase of silver nanowire loading.

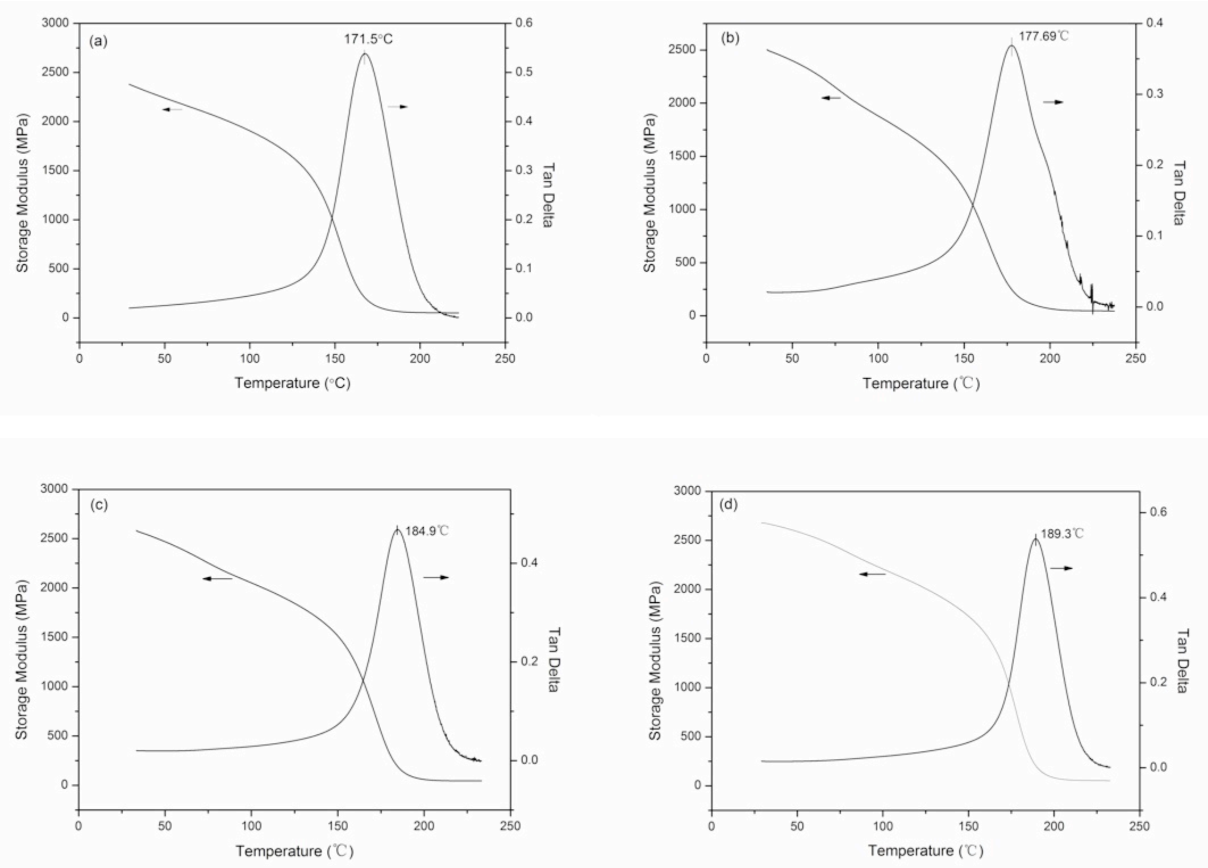

Figure 2. DMTA curves of silver nanowire/epoxy nanocomposites with different volume fraction. (a) neat epoxy;(b) 5%; (c) 10%; (d) 15%

Silver nanowires Loading*, vol.%	Nitrogen atmosphere		Air atmosphere		T_g, °C
	$T_{5\%}$, °C	$T_{10\%}$, °C	$T_{5\%}$, °C	$T_{10\%}$, °C	
0	341.2	354.0	327.6	346.1	171.5
5	371.2	397.5	359.2	387.1	177.7
10	394.7	401.9	361.8	389.6	184.9
15	402.1	411.7	367.9	393.2	189.3

Table 2. TGA results and Tg of the silver nanowire/epoxy nanocomposites

4. Conclusions

Silver nanowires with a diameter between 150 nm and 300 nm have been synthesized via microwave-assisted polyol process to enhance physical properties of epoxy composites. The silver nanowire/epoxy nanocomposites with different silver loadings were prepared to evaluate thermal properties including glass transition temperature and initial decomposition temperatures. The results show that volume fraction of silver nanowires in the epoxy matrix plays a significant role in determining thermal properties. With 15 % silver loading, the glass transition temperature increases by 17.8 ℃ compared to neat epoxy resin. These pronounced properties make the silver nanowire/epoxy nanocomposites a promising candidate for embedded capacitor applications.

References

[1] L. Qi, B.I. Lee, S. Chen, W.D. Samuels and G.J. Exarhos, *Adv. Mater.* 17, 1777-1781, 2005.
[2] D. Chen, X. Qiao, X.Qiu, J. Chen and R. Jiang, *J. Coll Int. Sci.* 344, 286-291, 2010.
[3] H. REN, S. Tang, J.A. Syed and X. Meng, Mater. Chem. Phys., 137, 673-680, 2012.
[4] S.E.Skrabalak, B.J. Wiley, M.Kim, E.V. Formo and Y.N. Xia, *Nano Lett.* 8, 2077-2082, 2008.
[5] P.S. Mdluli and N. Revaprasadu, *J. Alloys Compd.*, 469, 519-523, 2009.
[6] J.Xu, J.Hu, C.J. Peng, H.L. Liu and Y. Hu, J. Colloid Interf. Sci., 298, 689-693, 2006.
[7] M. Mazur, *Electrochem. Commun.*, 6, 400-407, 2004.
[8] S. Berchmans, R.G. Nirmal, G. Prabaharan, S. Madhu and V. Yegnaraman, *J.Colloid Interf. Sci.* 303, 607-611, 2006.
[9] A. Pal, S. Shah and S. Devi, *Mater. Chem. Phys.* 114, 530-536, 2009.
[10] A. Facchetti, M.H. Yoon and T. J. Marks, *Adv. Mater.* 17, 1705-1725, 2005.
[11] H.W. Choi, Y.W. Heo, J.H. Lee, J.J. Kim, H.Y. Lee, E.T. Park and Y.K. Chung, *Appl. Phys. Lett.* 89, 132910, 2006.
[12] H.Ren, J.Z. Sun, Q. Zhao, Q.Y. Zhou, Q.C. Ling, *Polymer*, 47, 8309-8316, 2008.