PREPARATION OF ELECTRICALLY AND THERMALLY CONDUCTIVE TRYMETHYLGLYSINE DOPED POLYPYRROLE / CHLOROPRENE RUBBER NANOCOMPOSITE

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Abstract

Polypyrrole (PPy) is a conjugated polymer that can be conductive electrically and thermally due to its electron delocalization. PPy was prepared by chemical oxidative polymerization in the presence of ammomiun persulphate (APS) and trimethylglycene (TMG) as an oxidant and a doping agent respectively. The composite of TMG doped PPy / chloroprene rubber (CR) and TMG doped PPy / CR with thermally conductive agents; Aluminum Nitride (AlN), Aluminum Oxide (AlO) and Magnesium Oxide (MgO) were prepared by using colloidal dispersion method. Electrical conductivity was measured by using high frequency impedance spectroscopy, whereas thermal conductivity analyzer was used to measure thermal conductivity of the composites. Results obtained showed improvement in electrical conductivity with high weight percentage of PPy in the composites. Thermally conductive agents AlN, AlO and MgO were found to increase the electrical and vary the thermal conductivity of the composites.

Keywords: polypyrrole; conductivity; composite; thermally conductive agent; colloidal dispersion

Introduction

Heat dissipation problem in microelectronic packaging is becoming increasingly important as the demands in denser and faster circuits intensify. The incorporation of highly thermally conductive ceramic materials in polymers in order to improve the thermal conductivity of encapsulates or substrate has long been studied (Ishida & Rimdusit 1998). Heat generated by electronic devices and circuitry must be dissipated to improve reliability and prevent premature failure. Techniques for heat dissipation include heat sinks and fans for air cooling, and other forms of cooling such as liquid cooling (Dong et al. 2005). Thermal management such as heat removal from integrated circuits is a critical problem for the electronic industry that limits potential miniaturization, speed and reliability (Bar-Cohen 2001).

The continuing increase in electronic packaging density has resulted in a need for materials with high thermal conductivity. In addition, to minimize thermal stresses that can cause component or solder failure, packaging materials must have coefficients of thermal expansion (CTEs) matching those of ceramic substrates and semiconductors. Furthermore, low density is desirable in many applications, including portable systems such as lap-top computers, handphones and avionics. Reducing weight also minimizes potentially damaging stresses resulting from shock loads that can occur during shipping and from other causes. Low cost is also a key consideration. As traditional materials used in electronic packaging do not meet all of these requirements, new composite materials have been and are continuing to be developed (Zweben 1998; Park et al. 2015; Si et al. 2018).

Composites of electrically conductive particles in non-conducting polymer matrix are materials with increasingly important for a variety of practical applications (Vilčáková et al. 2004). This includes Chroloroprene Rubber (CR). CR has been known for its adhesiveness, ease to undergo composite preparation and light weight. For this reason, CR is also a good matrix to overcome the brittleness of conducting polymers, such as polypyrrole (PPy).

Electrically conductive thermoplastic composites are a class of materials that consist of conductive filler supported by an insulating polymer matrix. These composites have several advantages over other conductive materials including processability, flexibility, ability to absorb mechanical shock, light weight,

corrosion resistance, ability to form complex parts, parts consolidation and conductivity control (Norman 1970).

PPy is one of the heteroatomic conducting polymers that has good environmental stability, relatively high electrical conductivity and ease to synthesis (Omastová et al. 2003, Yan et al. 2017). However, because of their poor processability, conducting polymers are usually investigated in combination with other polymers or inorganic materials. PPy can be prepared by electrochemical or chemical oxidation of pyrrole (Py) in various organic solvents or in aqueous solution. Polymer films with conductivity of about 10² Scm⁻¹ can be produced electrochemically, however, their size is limited by the working area of the electrodes. Therefore, the simplest method for the synthesis of conducting polymers is chemical oxidation in aqueous solution in the presence of FeCl₃ as oxidant has an electrical conductivity of about 10 Scm⁻¹. Further improvement of PPy electrical conductivity can be achieved by the addition of anionic surfactants into the aqueous reaction solution during the synthesis. The electrical conductivity, morphology and other chemical as well as physical properties of PPy are influenced by the method of preparation, the conditions of polymerization, as well as the solvent, the oxidant, and the various additives used (Omastová et al. 2003, Utami et al. 2016).

The conductivity of a conjugated polymers, such as PPy, is strongly dependent on the doping agents (dopant) with electron donating or withdrawing abilities. The doping process can even transform an intrinsically insulating conjugated polymer to a near-metallic conductor (Lee et al. 2006). The doping agents are incorporated during the redox polymerization reaction. The conduction mechanism is generated by the carrier movement from the energy band gap (HOMO-LUMO). When the energy band gap is small, it is easier to have high conductivity (Sasso et al. 2008).

In order to enhance further the thermal conductivity of the polymer, fillers (such as diamond, boron nitride, aluminium nitride, silicone carbide and alumina) (Song et al. 2019) which are thermally conductive but electrically insulating are used. The transport of heat in non-metals occurs by phonons or lattice vibration. This thermal transport is associated with various types of phonon scattering process; such as phonon-phonon scattering, boundry scattering and defect or impurity scattering. To enhance the thermal conductivity, these phonon scattering processes must be minimized. Phonons travel at the speed of sound. The scattering of phonons in composite materials is mainly due to the interfacial thermal barriers resulting from acoustic mismatch and flaws associated with the filler-matrix interface (Xu et al. 2001).

Colloidal system or colloidal dispersion is a heterogeneous system which is made up of dispersed phase and dispersing medium. In colloidal dispersion one substance is dispersed as very fine particles/droplets in another substance called dispersing medium. In case of dust, solid particles are dispersed in air as dispersing medium. Dispersed phase and dispersing medium can be solid, liquid or gas. Depending upon the state of dispersed phase and dispersing medium, eight different types of colloidal dispersions can exist that include emulsion of PPy and CR, where the PPy is greatly dispersed in the colloidal dispersion of CR (Balci et al. 1995).

Materials and Methods

Synthesis of TMG doped PPy

PPy was synthesized by chemical oxidation polymerization. Py (0.6 mol; Sigma Aldrich) was purified by passing through a column of activated basic alumina and stored in a refrigerator at about 4 °C prior to polymerization. Py and doping agent, TMG (0.08 mol, Fluka) were dispersed in 900 mL of distilled water in a 1 L beaker with magnetic stirring at 400 rpm. The mixture was then cooled to 0°C. APS (0.2 mol, Merck) which was dissolved in 100 mL of distilled water was then added dropwise into the mixture while stirring. The polymerization was carried out for 4 hours at 0°C with magnetic stirring at about 400 rpm. The mixture was then poured into methanol to terminate the polymerization. The resulting black powder of TMG doped PPy was washed with distilled water and dried in vacuum oven at 60 °C for 24 hours.

Preparation of TMG doped PPy /CR composites

Toluene and sodium dodecylsulphate (SDS) were used as medium of emulsion and surfactant, respectively. Emulsions of PPy and CR were prepared separately with magnetic stirring (400 rpm) for 1 hour. Then both emulsions were mixed and stirred for 3 hours at 400 rpm. Composite was percipitated into methanol and

dried in fume hood. There were 5 sets of TMG doped PPy / CR composites; 0:100, 10:90, 20:80, 30:70 and 40:60 (weight ratio).

Preparation of TMG doped PPy /CR composites with conductive agents: AlN, AlO and MgO

Conductive agents; AlN, AlO and MgO (5%) were added to the composite and stirred overnight at 400 rpm. Composites of TMG doped PPy / CR with conductive agents; AlN, AlO and MgO were percipitated into methanol and dried in fume hood.

Measurement of conductivity

Electrical conductivity of PPy was measured by using high frequency impedance spectroscopy model Solartron 1255 (SOLARTRON Schlumberger) in the range of 1 Hz to 10 MHz. Sample of PPy (0.2g) was compressed into pellets, 13.0 mm in diameter,d and 1.5 mm thickness, t. Whereas, samples of composites were pressed by hot press into cake-shape, 25.0 mm in diameter, d and 5.0 mm thickness, t. Thermal conductivity was checked by thermal analyzer TCI C-THERM. The PPy sample was compressed into pellets, 25.0 mm in diameter and 5.0 mm thickness, t while samples of composite were pressed by hot press into cake-shape, 25.0 mm thickness, t.

Results and Discussion

Figure 1 (left) showed Field Emission Scanning Electron Micrograph (FESEM) of TMG doped PPy. TMG doped PPy appeared as loose clusters of fine particles with size of below 50nm. The clusters were found to easily break into smaller clusters, especially when incorporated into CR matrix. However, the size of TMG doped PPy particles remained more or less the same, as indicated by the FESEM micrograph presented in Figure 1 (right).



Figure 1. FESEM micrographs of TMG doped PPy (left) and TMG doped PPy / CR composites (30:70)

Table 1 showed the electrical conductivity of TMG doped PPy / CR and TMG doped PPy / CR composites with thermally conductive agents; AlN, AlO and MgO.

Samples	TMG doped PPy / CR	Electrical conductivity (Scm ⁻¹)
PPy	100/0	1.262 x 10 ⁻⁵
Composite 1	10/90	4.744 x 10 ⁻⁷
Composite 2	20/80	3.818 x 10 ⁻⁷
Composite 3	30/70	2.835 x 10 ⁻⁶
Composite 4	40/60	6.203 x 10 ⁻⁶
Composite 5	30/70 + AIN (5%)	4.825 x 10 ⁻⁷

Table 1. Electrical conductivity of Composites

Composite 6	40/60 + AIN (5%)	3.641 x 10 ⁻⁶	
Composite 7	30/70 + AlO (5%)	5.279 x 10 ⁻⁷	
Composite 8	40/60 + AlO (5%)	1.089 x 10 ⁻⁵	
Composite 9	30/70 + MgO (5%)	2.290 x 10 ⁻⁷	
Composite 10	40/60 + MgO (5%)	2.655 x 10 ⁻⁶	

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The calculation of electrical conductivity for polymer and composites is based on equation (1) and (2), where Z_i is the value of low infinite frequency data, Z_{∞} is high frequency infinite data, A is the surface area of the pellet and R_s is the resistance (Phang 2005).

$R_b = R_s \left(Z_i - Z_\infty \right)$	(1)
	(2)
$\sigma = R_b x A$	

The values of electrical conductivity were all in the same range which is in the semiconducting range (Le et al. 2017). The electrical conductivity for TMG doped PPy is 1.262 x 10⁻⁵ Scm⁻¹. TMG is a zwitterionic surfactant that contains both positive and negatively charged hydrophilic headgroups in the molecule and show anionic property at high pH and cationic property at low pH (Yoshimura et al. 2005). The values of electrical conductivity of the composites of TMG doped PPy / CR increased with increasing amount of PPy in the composites. This is likely attributable to the increasing extent of electron delocalization within the samples as the amount of doped PPy increased (Le et al. 2017). These values were still in the semiconducting range.

After the addition of thermally conductive agents; AlN, AlO and MgO, the values of electrical conductivity become higher. The higher the amount of agents added, the higher the electrical conductivity obtained, which is in agreement with reports by other researchers (Bujard et al. 1999).

Table 2 showed the value of thermal conductivity for PPy that is 0.623 W/mK. This value is higher than values of thermal conductivity of composites. The presence of CR in composites decreased the thermal conductivity, however, the conductivity increased as the amount of of PPy increased in composites.

Table 2. Thermal conductivity of composites			
TMG doped PPy / CR (weight ratio)	Thermal conductivity (W/mK)		
100/0	0.623		
10/90	0.373		
20/80	0.386		
30/70	0.446		
40/60	0.468		
30/70 + AIN (5%)	0.406		
40/60 + AIN (5%)	0.425		
30/70 + AlO (5%)	0.410		
40/60 + AlO (5%)	0.414		
30/70 + MgO (5%)	0.392		
40/60 + MgO (5%)	0.406		

As shown in the Table 2, the thermal conductivity of composites with thermally conductive agents is lower as compared to those without thermally conductive agents, and values of thermal conductivity varied with different thermally conductive agents (Dong et al. 2005). The particle size of PPy and thermally

conductive agent were too different, and thus electron hopping is not facilitated, infact the electron hopping became poorer. This will ultimately lead to poor heat conductivity (Xu et al. 2006). The morphology of thermally conductive agents also gives variation in values of thermal conductivity of composites. The lower the total surface area of thermally conductive agent the lower the thermal conductivity (Abdullah 2004, Xu et al. 2001).

However, the more the thermally conductive agents added, the higher the thermal conductivity obtained (Bujard et al. 1999). Out of all the results obtained, AlN gives the higher thermal conductivity, followed by AlO and MgO.

Conclusion

In conclusion, TMG doped PPy / CR composites showed good electrical and thermal conductivities. The electrical conductivity increased and thermal conductivity varied with the addition of conductive agents; AlN, AlO and MgO. The increase of electrical conductivity depends on the amount of PPy and thermally conductive agents present in the composites. The higher the percentage of PPy, the higher the electrical and thermal conductivity.

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