Preparation of polypyrrole nanobowls and their effect for improving direct current dielectric properties of polyethylene

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Abstract

Polypyrrole (PPy) nanobowls were successfully prepared through a reactive self-degraded template polymerization and the morphology of PPy nanobowls was characterized by scanning electron microscopy (SEM). The nanobowls were uniform with diameters of about 100 nm. The low density polyethylene/polypyrrole (LDPE/PPy) nanocomposites were obtained by melt blending method. The structures of PPy nanobowls and the nanocomposites were studied by Fourier transform infrared spectrometer (FT-IR). Space charge distributions in LDPE/PPy nanocomposites with different PPy nanobowls contents were measured using the pulsed electroacoustic (PEA) method. The results indicated that PPy nanobowls doping with a small quantity exhibited excellent suppression performance of space charge accumulation in LDPE and the nanocomposites showed improved direct current (DC) electrical conductivity and breakdown characteristics.

Keywords: PPy; Nanocomposite; Space charge; Conductivity; Breakdown

1. Introduction

Space charge accumulated in polymer insulation can lead to the distortion of electric field and affect direct current (DC) electrical conductivity and breakdown characteristics, which greatly threatens the security of electrical apparatus and becomes a major obstacle for the development of polyethylene (PE) insulated high voltage direct current (HVDC) cables. Therefore, the key strategy to develop HVDC cables is to suppress the space charge injection and accumulation in polymer insulation. As a result, considerable attention has been focused on looking for effective methods to reduce the effect of space charge. Inorganic nanofillers such as MgO nanoparticles, carbon black and graphene due to fascinating size-controlled electrical properties in polymer matrix have been utilized to improve the distribution of space charge [1], the higher permittivity of the fillers is more effective and the conductive material is considered to have an infinite permittivity ideally [2].

Conducting polymers have not only the advantages of good processability, corrosion resistance and small density of traditional polymeric materials, but also good electrical conductivity and are attractive candidates for electronic devices, sensor, electrochemical energy storage and electromagnetic shielding application [3, 4]. The incorporation of conducting polymers and their composites into other polymer matrix brings about a series of distinctive characteristics. Polypyrrole (PPy) presents a significant action on retarding the oxidation of low density polyethylene (LDPE) under the irradiation of γ -rays by the scavenging peroxy radical after the formation of pyrrolyl radicals [5]. Low polyaniline (PANI) nanofibers doped with superfluous

dodecylbenzenesulfonic acid load (about 1 wt.%) can improve the tensile strength and elongation at break of the composites compared to pristine LDPE/EAA matrix [6]. Carbon black modified with PANI in LDPE resulted in a lower percolation threshold and excellent reproducibility of the resistivity-temperature curves during heating/cooling cycles [7]. However, the effects of nano-conducting polymers with nanostructure and high electrical conductivity on the space charge accumulation in the polymer matrix have been rarely reported. In this paper, PPy nanobowls were prepared and doped in LDPE by melt blending method. The obtained LDPE/PPy nanocomposites demonstrated excellent DC dielectric properties with low PPy doping amount by the measurement of space charge distribution, DC electrical conductivity and breakdown strength.

2. Experimental

2.1 Materials

Pyrrole monomer was purchased from Aldrich and stored at -4 °C before use. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), methylene orange, cetyltrimethylammonium bromide (CTAB) and ethanol were obtained from Tianjin Guangfu Fine Chemical Research Institute, China. All the above chemicals were analytical grade and used as received without further purification. LDPE (LD200BW) pellets with a density of 0.922 g/cm^3 and a Melt Flow Index (MFI) of 2.0 g/10 min were supplied by Beijing Yanshan Petroleum Co. Ltd., China.

2.2 Preparation of PPy nanobowls and LDPE/PPy nanocomposites

PPy nanobowls were synthesized via in situ chemical oxidative polymerization

directed by self-degradable templates. 0.324 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dispersed into 40 mL of 5 mM methyl orange deionized water solution at room temperature. Then 0.058 g CTAB and 115 μL pyrrole monomer were added sequentially into the above solution. The reaction mixture was stirred magnetically at room temperature for 30 h. The black product was centrifuged, washed with deionized water and ethanol several times, and then dried in a vacuum oven at 50 $^{\circ}\text{C}$ overnight.

The obtained PPy nanobowls were well dispersed in ethanol solution under sonication. Then, the LDPE and PPy suspensions were blended in torque rheometer at 110 $^{\circ}\text{C}$, the ethanol and H_2O inside the PPy nanobowls were evaporated absolutely and LDPE/PPy nanocomposites containing 0.2 or 0.5 phr (parts per hundreds of LDPE by weight) PPy nanobowls were obtained. LDPE, LDPE/PPy-0.2 and LDPE/PPy-0.5 indicated the nanocomposites with 0, 0.2 and 0.5 phr of PPy nanobowls, respectively.

The nanocomposites were hot compression moulded at 110 $^{\circ}\text{C}$ under a pressure of about 15 MPa for different tests. Aluminum electrodes were deposited on both sides of the tested specimens by vacuum coating system for the measurement of electrical characteristics.

2.3 Characterization

A Hitachi SU8020 scanning electron microscopy (SEM) was used to observe the morphology of PPy nanobowls. Infrared spectra of PPy nanobowls and LDPE/PPy nanocomposites were recorded on a Fourier transform infrared spectrometer (FTIR, SHIMADZU IR Pres-tige-21) with the wavenumber of 4000-400 cm^{-1} and a

resolution of 2 cm^{-1} ; For PPy nanobowls, the potassium bromide (KBr) wafer was used, and the weight percentage of PPy nanobowls in KBr was about 0.5-1%; For LDPE/PPy nanocomposites, the specimen with average thickness of $100\text{ }\mu\text{m}$ prepared by hot compression moulding was used directly.

2.4 Space charge measurement

The pulsed electro-acoustic (PEA) method was used to measure space charge distribution of the specimen with average thickness of $300\text{ }\mu\text{m}$. Silicone oil was used as acoustic coupling to achieve a better acoustic transmission. Calibration was conducted at a DC field of 3 kV/mm with a short period of voltage application for 5 min to minimize the influence on space charge accumulation. The evolution of space charge at different voltage application time was explored at 40 kV/mm at room temperature. Measurement signals were recorded from 1 to 40 min by a digital oscilloscope. The data were processed using calibration trace and a deconvolution technique to restore the original signal.

2.5 DC electrical conductivity measurement

To achieve relatively uniform electric field under measuring electrodes, the three-electrode system was adopted during DC electrical conductivity measurement. The test system and the specimen with average thickness of $200\text{ }\mu\text{m}$ were placed in a constant oven to control the test temperature at 30 and $70\text{ }^{\circ}\text{C}$ and to eliminate the interference of external signals. An adjustable high-voltage DC power supply (HB-Z103-2AC) was employed with the maximum output voltage of 10 kV and the current of 2 mA . Quasi-stationary currents at DC electric fields varying between 1 to

50 kV/mm under isothermal condition were recorded using EST122 picoammeter with a precision of up to 10^{-14} A.

2.6 DC breakdown strength measurement

For DC breakdown strength measurement, the specimen with average thickness of 100 μm was immersed in transformer oil to inhibit surface flashover discharging under cylindrical electrode at room temperature. The DC voltage was continuously increased at the rate of 3 kV/s until the specimen broken down. Ten breakdown tests were performed on each material to reduce the experimental errors. The two-parameter Weibull distribution was used to analyze the breakdown data statistically and this distribution has been found to be the most appropriate for the breakdown strength analysis [8]. The DC breakdown strength of the specimen was obtained.

3. Results and discussion

The detailed morphology of PPy was presented using SEM in Fig. 1. Generously, PPy showed uniform bowl-like morphology with diameters of about 100 nm. Bowl-like structure can increase the specific surface area of PPy. FTIR spectra of PPy nanobowls, pristine LDPE and LDPE/PPy nanocomposites were depicted in Fig. 2. In the spectrum of PPy nanobowls, the broad band at $3300\text{--}3600\text{ cm}^{-1}$ could be attributed to N-H and C-H stretching vibrations of PPy. The peaks at 1554 , 1463 and 1044 cm^{-1} were related to the antisymmetric and symmetric stretching vibrations of the pyrrole ring, and C-H deformation vibrations, respectively. The peaks at 1194 and 920 cm^{-1} indicated the formation of PPy in its doped state [9, 10]. The characteristic bands of

LDPE at 2942-2844, 1467, 1373, 724 cm^{-1} assigned to $-\text{CH}_2-$ vibration peaks were observed [11]. The typical characteristic peaks of PPy and LDPE appeared in FTIR spectra of LDPE/PPy nanocomposites, although some peaks for PPy were not distinguished due to the low doping amount. And the relative vibration intensity of peaks for PPy increased with the doping amount increasing, indicating that PPy nanobowls have been successfully incorporated into LDPE matrix. Furthermore, the broad band at 3300-3600 cm^{-1} disappeared and the absorption peak at 1194 cm^{-1} was shifted to 1218 cm^{-1} for the nanocomposites compared to PPy, which may be caused by the interaction between PPy nanobowls and LDPE facilitating charge-transfer process between the components of the system and increasing the effective degree of electron delocalization [7].

Fig. 3 showed the space charge distributions in pristine LDPE and LDPE/PPy nanocomposites under a 40 kV/mm field for 40 min. The amount of space charges accumulated in pristine LDPE was larger than that in LDPE/PPy nanocomposites. As shown in Fig. 3(a), when the electric field continued for 1 min, a small amount of heterocharges appeared near the cathode in pristine LDPE, which may be arising from the ionization process of impurities in LDPE. Then the amount of space charges rapidly reached a maximum about 4.1 C/m^3 after stressed for 10 min. The inflection points close to the heterocharge packet were mainly induced by the homocharges. And with the increase of time, the amount of homocharges increased and the space charges were diffused towards the sample bulk and tended to be stable. Near the anode, a very small amount of homocharges injected from the anode was evident, and such space

charge development was minimal although the amount of space charges increased with the increase of time. When PPy nanobowls with different contents were filled in LDPE as shown in Fig. 3 (b) and (c), the magnitude of heterocharges adjacent to the cathode was dramatically reduced and the amount of charges increased slowly with time. Increasing the amount of PPy nanobowls resulted in the density of space charges at the cathode decreasing. After the field of 40 kV/mm was applied for 40 min, the amount of heterocharges reached about 2.3 and 1.5 C/m³ in the nanocomposites containing 0.2 and 0.5 phr of PPy nanobowls, respectively. And the transport of charges towards the bulk appeared to be suppressed in LDPE/PPy nanocomposites. This may be attributed to the nanostructure and high electrical conductivity of PPy. Nano-additives had a tremendously large surface energy and surface tension, which could improve the distribution of charges in the sample [12]. And it was reported that LDPE including inorganic nanofillers showed a good performance without space charge accumulation even under very high DC electric field and the higher permittivity of the fillers was more effective to reduce the accumulation [2]. The PPy was conductive material and considered to have an infinite permittivity ideally.

The electric field distribution in DC cable insulation depends on the electrical conductivity, and the electrical conductivity is significantly influenced by the temperature. Therefore, it is necessary to research the effect of the temperature on DC electrical conductivity in the development of HVDC cable XLPE insulation materials. Fig. 4 compared the dependence of the electrical conductivities of pristine LDPE and LDPE/PPy nanocomposites with 0.2 and 0.5 phr PPy nanobowls on the electric field

at different temperatures. The electrical conductivities of pristine LDPE and LDPE/PPy nanocomposites increased with the electric field and temperature. A significantly lower electrical conductivity in the whole temperature region was found for LDPE/PPy nanocomposites compared to pristine LDPE and the electrical conductivities of all the materials at 10 kV/mm were as low as 1×10^{-14} S/m, which met the demand of insulation materials for HVDC cables. The internal molecular motion of polymer chain segments in the nanocomposites was hindered by the presence of PPy nanobowls due to the interaction between the PPy nanobowls and the matrix [13, 14], and the addition of the nanofillers reduced the electronic carrier mobility in the amorphous regions [15]. Therefore, the electrical conductivities of the nanocomposites reduced. At 30 °C, the increase of PPy nanobowls content led to a small increase of the electrical conductivity, which can be ascribed to the formation of a more-developed conductive network. At the fillers content of 0.5 phr, the hindering effect of PPy nanobowls for molecular motion of polymer chain was overruled by the high electrical conductivity of PPy. At 70 °C, the electrical conductivities of LDPE/PPy nanocomposites decreased with the increase of the fillers content. Overall, the electrical conductivities of LDPE/PPy nanocomposites were less affected by the temperature.

Fig. 5 showed two-parameter Weibull plot for DC breakdown strengths of pristine LDPE, commercially available XLPE manufactured by American Dow Chemical (Dow-XLPE) and LDPE/PPy nanocomposites containing 0.2 and 0.5 phr of PPy nanobowls at room temperature with derived parameter values. In this, α is the scale

parameter that represents Weibull DC breakdown strength at the cumulative failure probability of 63.2% while β the shape parameter that represents the inverse of data scatter. For pristine LDPE, the DC breakdown strength was 250.3 kV/mm. The DC breakdown strength of LDPE/PPy nanocomposite with 0.2 phr PPy nanobowls (about 266.1 kV/mm) was close to that of pristine LDPE without reduction, and comparable to the commercially HVDC insulation materials of Dow-XLPE (about 257.6 kV/mm). However, the addition of 0.5 phr PPy nanobowls reduced the DC breakdown strength to 196.2 kV/mm. The drop of DC breakdown strength was pronounced when PPy nanobowls load increased. The agglomeration effect could lead to the reduction of DC breakdown strength of the nanocomposites [16].

4. Conclusions

In conclusion, we have successfully prepared PPy nanobowls with uniform bowl-like morphology of about 100 nm in diameters through a reactive self-degraded template polymerization and added them into LDPE to obtain LDPE/PPy nanocomposites by melt blending method. The addition of a small quantity of PPy nanobowls could considerably improve the distribution of space charge in LDPE. The amount of the heterocharges close to the cathode in LDPE/PPy nanocomposite containing 0.2 phr PPy nanobowls was reduced to 1.5 C/m³ from 4.1 C/m³ compared to that in pristine LDPE stressed at 40 kV/mm DC. And the transport of charges towards the bulk appeared to be suppressed in LDPE/PPy nanocomposites. Compared to pristine LDPE, the electrical conductivities of LDPE/PPy nanocomposites containing 0.2 and 0.5 phr nanobowls reduced significantly in the whole temperature

region and were as low as 1×10^{-14} S/m at 10 kV/mm. When the content of PPy nanobowls in the nanocomposite was 0.2 phr, the DC breakdown strength was not reduced and comparable to the commercially used HVDC insulation materials manufactured by American Dow Chemical. So, we propose that the LDPE/PPy nanocomposites are promising to be used as HVDC cable insulation materials.

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Figure Captions

Fig. 1 SEM image of PPy nanobowls

Fig. 2 FTIR spectra of LDPE (a), LDPE/PPy-0.2 (b) and LDPE/PPy-0.5 (c) at different wavenumber region

Fig. 3 Space charge distributions during polarization in LDPE (a), LDPE/PPy-0.2 (b) and LDPE/PPy-0.5 (c)

Fig. 4 Dependence of the conductivities of LDPE, LDPE/PPy-0.2 and LDPE/PPy-0.5 on the electric field at different temperatures

Fig. 5 Weibull plot for DC breakdown strengths of LDPE, Dow-XLPE, LDPE/PPy-0.2 and LDPE/PPy-0.5 at 30 °C

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5