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Improvement on temperature-sensing property of low-density polyethylene based PTC composites with static magnetic field treatment

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Abstract. A stable magnetic field was applied during hot press molding of low-density polyethylene (LDPE)/carbon black (CB)/ carbon nanotube (CNT) composites and HDPE/CB/nickel powder composites. The effect of magnetic field treatment on the temperature-sensing property of LDPE-based positive temperature coefficient (PTC) composites was investigated. Experimental results indicate that the magnetic field treatment can lead to an alignment of CNT and nickel powder in LDPE along the direction of the applied external magnetic field. The alignment of these filler particles can endow the composites with low room-temperature resistivity and high PTC intensity when the concentration of CB is decreased. The alignment also can significantly improve mechanical property and processability of the composites. Compared with CNT, nickel powder with strong magnetism has more sensitive response to external magnetic field and is much easier to align in LDPE. Addition of nickel powder is beneficial for developing PTC composites with excellent comprehensive properties.

Introduction

Polymer-based positive temperature coefficient (PTC) composites are fabricated by adding conductive fillers (e.g. carbon fillers, metal powder and metal oxides) into organic polymers (e.g. polyolefine, epoxy and rubber). Because polymer-based PTC composites have such advantages as good flexibility, easy process, simple preparation technology, low production cost, and good applicability in low temperature situation, they have got more and more application in recent years [1-4].

CB is one of the typical conductive fillers for fabricating polymer-based PTC composites. Significant amount of researches had proved that polymer-based composites filled with high-structure CB have no PTC property, while those containing low-structure CB exhibit good PTC property [5]. When the concentration of CB is close to the percolation threshold, the high PTC intensity can be obtained. However, these composites have high room-temperature resistivity [6]. In order to develop PTC composites with low room-temperature resistivity, a high concentration of low-structure CB is needed. However, addition of the CB at high concentration will cause a decrease of PTC intensity and mechanical properties, an increase of brittleness and a deterioration of processability of the composites. The authors had verified that magnetic field treatment can change the orientation and distribution of fillers in polymer, thus improving the electric property of the composites [7-9]. Therefore, the aim of this study is to develop new PTC composites with low room-temperature resistivity and high PTC intensity when the concentration of CB is cut down. Small concentration of carbon nanotube (CNT) and nickel powder, which are sensitive to magnetic field, are respectively added into the low-density polyethylene (LDPE) containing lower concentration of CB. A stable external magnetic field is applied during hot press molding of the LDPE/CB/CNT and LDPE/CB/nickel powder composites to make an alignment of CNT and nickel powder in the composites. The effect of magnetic field treatment on the temperature-sensing property of the two types of PTC composites is systematically investigated.

Experimental material and methods

Experimental materials and equipments. The raw materials used include LDPE (18D) with a density of 0.920g/cm^3, acetylene CB with particle size of 35~45nm, CNT(Aligned-MWNT-1020) with diameter of 10~20nm and length of 5~15μm, and nickel powders with particle size of 2~5μm. Main experimental equipments include polarization microscope, magnetic field generator, digital teslameter, plate vulcanization machine, open mixing roll, picoammeter, multimeter, DC power supply and drying cabinet. The magnetic field generator is a dual-conjugate single-tuned electric magnet as shown in Fig.1.

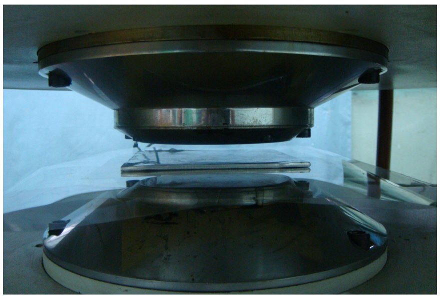

Fig.1 Pole heads of magnetic field generator

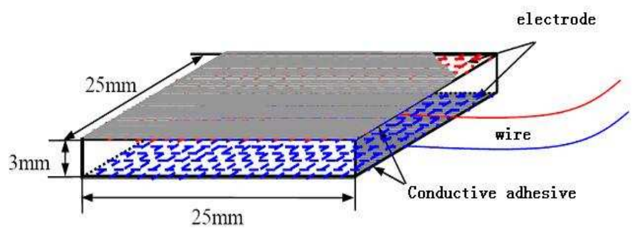

Fig.2 Diagram of sample structure for temperature-sensing property testing

Preparation method of samples. The preparation process of the PTC composite samples without magnetic field treatment can be summarized as six steps. Step 1: weight LDPE and fillers in proportion; Step 2: mix LDPE with fillers in an opening mixing roll at a temperature of 125~130ºC; Step 3: put mixture into molds with length, width and height of 2.5cm, 2.5cm and 3mm respectively; Step 4: put stainless steel mesh at upper and lower sides of molds; Step 5: perform thermoforming processing under a temperature of 165ºC and a compressive stress of 10MPa; Step 6:keep compressive stress stable and cool down below 50ºC at a rate of 2ºC /min.

The preparation process of the samples with magnetic field treatment is as following. Step 1: put the fabricated samples without magnetic field treatment between the two pole heads under a temperature of 165ºC (as shown in Fig.1); Step 2: adjust the distance between the two pole heads until the sample is compressive; Step 3: adjust the current in the pole coil to achieve a magnetic field strength of 2.5T; Step 4: keep temperature, compressive stress and magnetic field strength stable for 20min; Step5: cool down below 50ºC at a rate of 2K/min under the stable pressure stress and magnetic field strength ; Step6: take out the samples and paint conductive glue at their upper and lower surfaces; Step7: put the samples into the drying cabinet and cure them for 30min under a temperature of 80ºC; Step8: take out the samples and keep them at room temperature for 24h before they are tested.

Measurement method of PTC property. The temperature-sensing property of the samples is measured as following. Step 1: put the samples into the drying cabinet; Step 2: weld wire with stainless steel mesh at upper and lower surfaces of the samples and lead out the wires outside the drying cabinet (as shown in Fig.2); Step 3: raise interior temperature of the drying cabinet step by step and measure resistance of the samples at different temperatures; Step 4: calculate conductivity of the samples at different temperatures and draw PTC property curves.

Results and discussion

Effect of magnetic field treatment on distribution of CNT in LDPE. CNT are easy to generate tunneling and field emission effects due to their high aspect ratio and small tip curvature radius. Addition of CNT can significantly enhance the conductive capability of composites and decrease their percolation threshold [10,11]. Previous researches have proven that the unique hexagon and curly hollow cylinder structures of CNT make them sensitive to magnetic field effect, thus generating induced magnetic moment. Therefore, CNT will be subject to magnetic field force in a magnetic field.

Fig.3 gives the electrical conductivity of the composites, containing different concentrations of CNT, with and without magnetic field treatment. It can be seen from Fig.3 that magnetic field treatment can significantly improve the electrical conductivity of LDPE/CNT composites. The improvement effect increases with the concentration of CNT. These results indicate that magnetic field force can adjust the distribution of CNT in the composites and strengthen the orientation trend of CNT along the magnetic field direction.

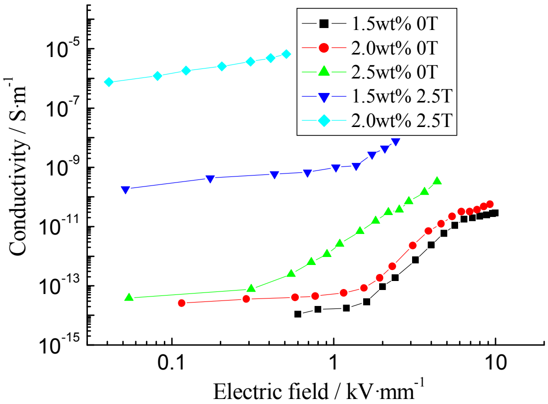

Fig.3 Relationships between conductivity and electric field of LDPE/CNT composites

Effect of magnetic field treatment on distribution of nickel powders in LDPE. Fig.4 gives optic microscope photos of LDPE containing 5.0 wt. % nickel powders with and without magnetic field treatment. As shown in Fig.4, nickel powders are uniformly dispersed in the composites prepared without magnetic field treatment, while they exhibit line alignment in local area of the composites prepared with magnetic field treatment. The electrical resistivity of the composites prepared without magnetic field treatment is about $10^{14}\Omega$•cm, but it is about $10^{3}\Omega$•cm for the composites prepared with magnetic field treatment. This outstanding improvement on conductivity of the LPDE/nickel powder composites results from the strong magnetism of nickel powders. Nickel powders are magnetized under magnetic field, so that they suffer from stronger magnetic field force. The stronger magnetic field force will lead to a movement of nickel powders in the melting LDPE and an ordered arrangement along the direction of the magnetic force line, thus improving electrical conductivity of the composites.

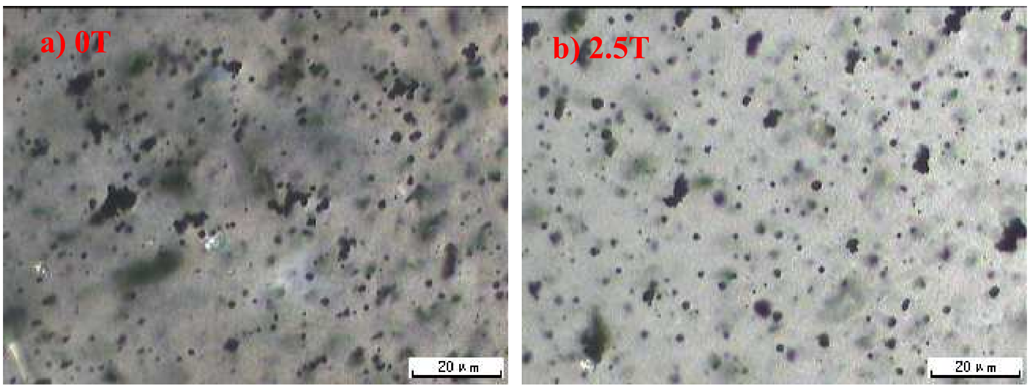

Fig .4 Optics microscope photos of LDPE/Nickel powder composites with/without magnetic field treatment

Improvement of magnetic field treatment on temperature-sensing property of LDPE/BC/CNT PTC composites. Fig.5 gives the relationship curves between temperature and volume resistivity of the HDPE/CB/CNT composites with different intensity of magnetic field treatment. It can be seen from this figure that, although the total concentration of conductive fillers in samples B is less 2.5wt% than that of samples A, the average room resistivity of samples B is 100 times higher than that of samples A. When the samples are treated by magnetic field, their average room-temperature volume resistivity is close to that of the samples without magnetic field. This is because that the orientation of CNT along the magnetic field direction forms more conductive paths in the composites, which has equal effect with increase of CB concentration. In addition, the tensile strength, the elongation at break and fusant flow rate of samples A are 8.5 MPa, 65% and 10.5g/10min respectively, while those of samples C are 12.8 MPa, 130% and 17.3g/10min respectively. This indicates that the mechanical and fusant flow performances of samples C are remarkably enhanced.

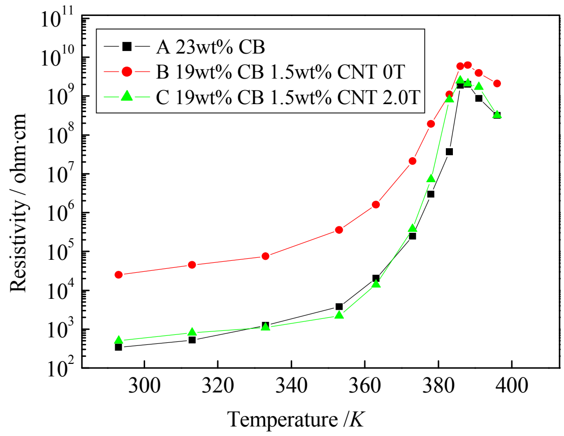

Fig.5 Relationship between temperature and resistivity of LDPE/CB and LDPE/CB/CNT composites

Improvement of magnetic field treatment on temperature-sensing property of LDPE/BC/nickel powder PTC composites. Fig.6 gives the relationship curves between temperature and volume resistivity of the LDPE/CB composites and the LDPE/CB/nickel powder composites with and without magnetic field treatment. A comparison of Figs.5 and6 indicates that the resistivity and PTC intensity of samples D are respectively 1500 times higher and much lower than that of samples A, as the concentration of CB decreases from 23 wt. % to 19 wt.%. When the samples (samples E) are treated by magnetic field, their room-temperature volume resistivity and PTC intensity are close to that of the samples (samples A) without magnetic field. Moreover, the tensile strength, the elongation at break and fusant flow rate of samples E are 15.3MPa, 188% and 22.3g/10min respectively, which are much better than that of samples A. Additionally, it can be observed from Fig.5 with Fig.6 that, although the volume concentration of CNT is 3.3 times that of nickel powders, the improvement of nickel powders on electrical resistivity of composites is obviously better than that of CNT. This is because nickel powders have more sensitive response to magnetic field than CNT.

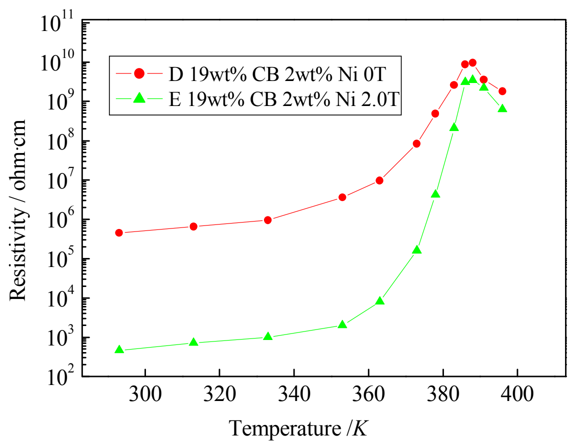

Fig.6 Relationship between temperature and resistivity of LDPE/CB and LDPE/CB/nickel powder composites

The above experimental results indicate that addition of a small quantity of conductive fillers, which are sensitive to magnetic field, can increase the comprehensive properties of PTC composites and decrease the concentration of conductive fillers when external magnetic field are applied during hot press molding of the LDPE-based composites.

Conclusions

(1) Stable magnetic field treatment can lead to an alignment of CNT and nickel powders, thus increasing conductivity of the composites along the direction of external magnetic field.

(2) When the concentration of CB in LDPE/CB composites is appropriately decreased and a small quantity of CNT or nickel powders are added into the composites, magnetic field treatment can endow the composites with low-temperature resistivity and high PTC intensity and significantly improve mechanical and fusant flow performances of the composites. The PTC composites prepared with magnetic field treatment exhibit good comprehensive properties.

(3) Addition of the conductive fillers that strongly sensitive to magnetic field effect is beneficial for improving comprehensive properties of the composites when magnetic field treatment is used to aid the preparation of PTC composites.

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