Structure and Applications of CB/Crystal Fluoride Resin Alloy in Self-Regulated Heating Cables

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ABSTRACT: A conductive composite was prepared by blending carbon black with a modified crystal fluoride resin alloy. The formulation and the processing technology were optimized, and the positive-temperature-coefficient (PTC) characteristics under different conditions were studied by SEM, WAXD, and DSC. Relationships between the proper-ties and the structures are illustrated, and applications of this composite in high-grade temperature self-regulating heating cables (135°C) are suggested. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2664–2669, 2003

Key words: alloys; structure; conducting polymers; matrix

INTRODUCTION

Self-regulation heating cables are one of the best electric heat-saving devices in the world. They are ideal energy-saving devices used for pipeline and other heat-saving engineering. The conductive polymer material employed has a positive-temperature-coefficient effect (PTC) effect;[1–3] and the electric resistance of the PTC material is proportional to temperature: the higher the temperature, the greater the electrical resistance. The output of the cable can, therefore, be corrected with the environmental temperature, and the cable can be self-controlled in a desired temperature range. Self-regulating heating cables have many unique properties. They are used in pipelines, for melting snow and warming homes, etc.

Self-regulating heating cables were first made and marketed by the Raychem Company in the United States in the 1970s. After that, the technology and the formulations were continuously improved to satisfy the request of different end users. Now, most of the studies of PTC materials are focused on a low temperature grade, from 65 to 85°C. Cables used for high temperatures, such as 135°C, have seldom been reported up to now. Our research was focused on blends of carbon black with the matrix of a crystal fluoride resin. These composites were used in the self-regulating heating cables for high temperature grade (135°C). The application effects were successful.

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EXPERIMENT

Raw materials

Materials include: crystal fluoride resin, MI = 10–20; special elastomer; modification agents; acetylene style carbon black; electric conductive carbon black: 20–30 nm.

Preparation of the sample

Roll mill

The material was put through a two-roll mill; model SK 160, made in Shanghai. The temperature of the front roll was 230 ± 5°C, the temperature of the rear roll was 210 ± 5°C, rolling speed was 2 : 1, with a 1.2-mm roll distance. The feed weight was 200 g at one time.
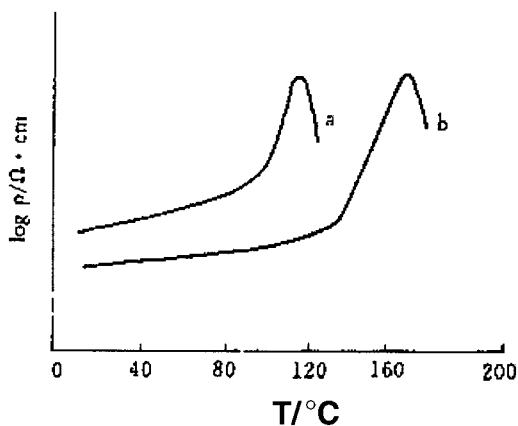
Mix

Using a HAKKE Buchler Mixer (System-40), with a mixing temperature at 230°C, each component was premixed and added in at the same time. The feed weight was 65 g at one time.

Compress

A 45-ton plant vulcanization machine made by the Shanghai rubber mechanical plant was used in two steps. The mold compression temperature was 240 ± 5°C. The mold was preheated 4 min. The hot compression time was 9 min, with a pressure of 16 MPa. The cool compression time was 6min with a pressure of 10 MPa.

Figure 1 PTC curves for different matrices. (a) PE, (b) crystal fluoride resin.

Preparation cables

Cables were prepared by extruding after mixing or blending the material. Cables were heat treated in a temperature maintaining stove at 60–210°C after extruding. Cooling time was less than 1°C/min.

Tests

An electrode system was designed according to ISO 3915–1981(2) and attached with a temperature maintaining system. The thickness of the sample was 1mm and the diameter was 10.5 mm. The surface of the sample was covered with a thin layer of conductive Ag gel to join the electrode system and the sample. Samples 1meter long were kept at 70°C for 8 h before testing. Testing temperature was from room temperature to 200°C with a heating speed of 2°C/min.

SEM: using Cambridge S-250; working volt was 20 kV.

DSC: using Dupont 1090. Heating speed was 10°C/min, from room temperature to 250°C. Sample weight was 10 mg.

WAXD: using D/MAX- RB rotating target X-ray instrument. Scan speed was 4°/min in the range of 3–50°, 40 kV, 40 mA. Thickness of the sample was 0.1 mm.

RESULTS AND DISCUSSION

Crystal fluoride resin alloy/CB system

Polymer matrix

As shown in Figure 1, PTC effects were greatly different in various polymer matrixes. These differences were also shown in T_s, T_{max}, and the strength of PTC effects. (T_s was switch on temperature, T_{max} was the temperature with the maximum PTC strength). In the PE matrix, T_s was 85°C, T_{max} was 120–130°C; but in the crystal fluoride resin, T_s was 135°C, T_{max} was

TABLE I
Mechanical Properties of Crystal Fluoride Alloy Resins

Rubber content (Wt.)	0	0.1	0.2	0.3	0.4
Tensile strength (MPa)	44	37	20	13	10
Extension at break (%)	50	120	150	200	250

160–170°C. So crystal fluoride resin was suitable for the matrix of 135°C grade heating materials.

Polymer alloys

Special rubber was used in the matrix in order to modify the crystal fluoride resins. The tensile strength and extension ratio at break are listed in Table I. PTC curves of alloys with different content of special rubber and with a acetylene carbon black content of 0.08 (wt.) are shown in Figure 2.

As shown in Table I and Figure 2, the toughness of the alloy was optimized and the PTC curve remained constant when the alloy contained of 10% special rubber.

CB content

Compared acetylene CB with conductive CB, acetylene CB got better result, which was similar as reported.[7] So acetylene CB was chosen in the alloy.

Figure 3 shows SEM photos of the freeze-broken surfaces that content different amounts of CB. Relationships between electric resistively and components were relied on to form a conductive network. For samples content 0.03 CB, it was difficult to form the conductive network because the CB particles were dispersed in the matrix and the electric resistance ratio of the composite relied on the conductivity of the matrix. More CB content, more CB particles are involved in one unit volume. The nearer the particles were, the more opportunities of particles to join each other. When the CB content reached 0.08 (the first
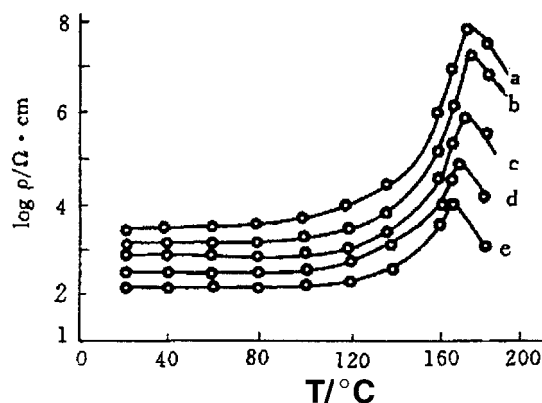
Figure 2 PTC curves of CB/crystal fluoride alloy resin. Rubber content: (a) 0%, (b) 10%, (c) 20%; (d) 30%, (e) 40%.
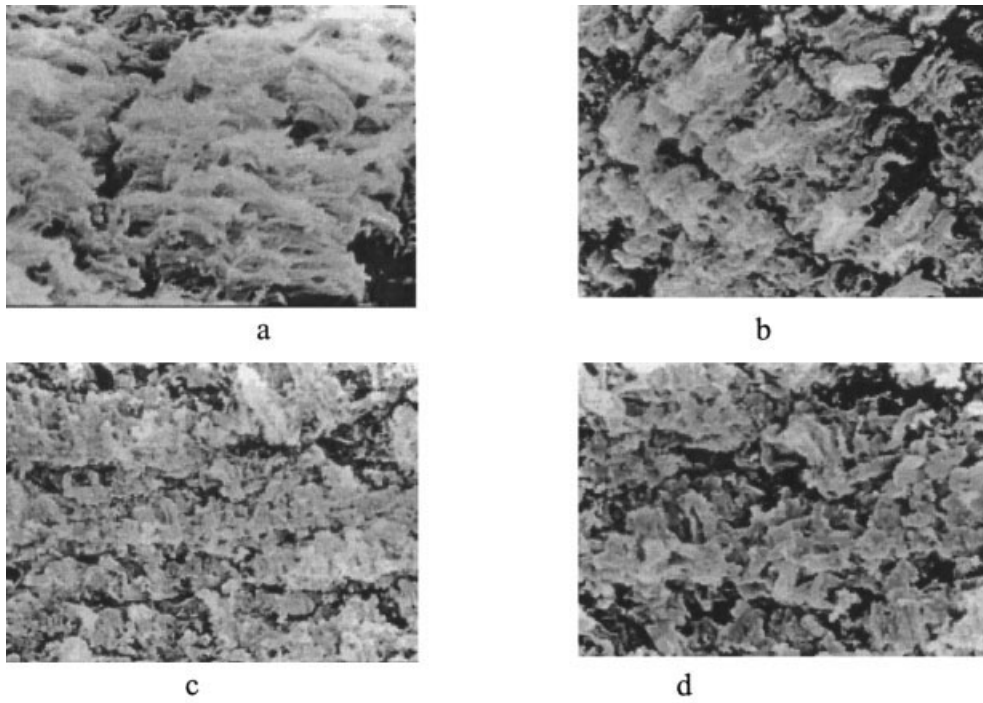
Figure 3 SEM of the composites with different CB content. CB% (wt.): (a) 3%, (b) 8%, (c) 12%, (d) 20%.

sudden change in the electric resistively to the components curve) there were so many CB particles connected each other that the pore on the broken surface was dispersed closely and evenly, which indicated the formation of the conductive network. When the CB content was 0.12 (the second sudden change in the electric resistively to components curve), cavities in the cross section were more slight and even. There were much more CB particles connected to each other, and the primary conductive network was formed more perfectly. Therefore, the conductivity of the composite was decided by the perfectibility of the conductive network. When the CB content reached 0.20, the

conductive network was so perfect that the electric resistance was approximate to CB particles.

Figure 4 shows the relationships between electric resistance and temperature in composites of different CB contents. When CB content was 0.08, the curve can be obviously divided into three different stages: smooth region, sudden increase region, and sudden decrease region. P [the strength of PTC effects of the composite $P = \log\rho(\max/T)$] was even higher than 3.0 in such a sample. When CB content was 0.20, the curve also has three different changing stages, but P was now less than 1.0. When CB content was 0.30, there were no sudden change stages in the smooth curve.

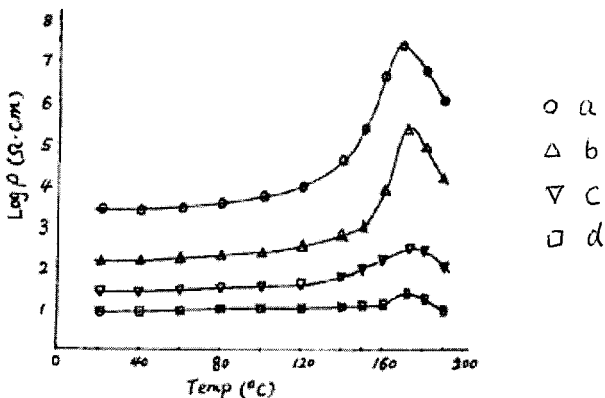As shown in Figure 5, P shows a sudden change

Figure 4 Electric resistance–temperature curves of the composite with different CB content. CB: (a) 8%, (b) 12% c) 20%, (d) 30%.
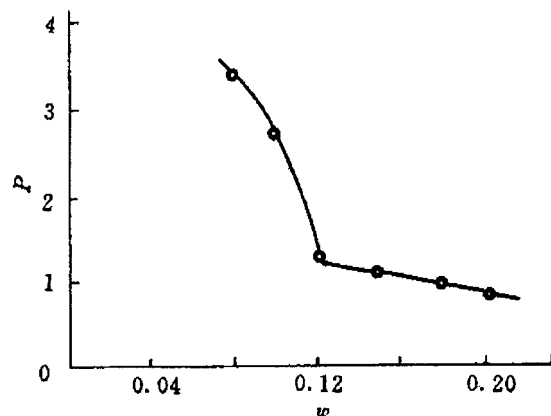

Figure 5 Relation of P (PTC strength of CB/crystal fluoride resin)–CB content.
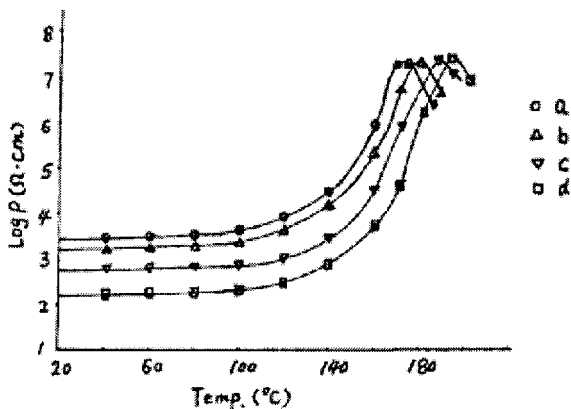
Figure 6 Influence of heat-treatment temperature on PTC characteristics (annealing time 8 h): (a) unannealed; (b) annealed 130°C; (c) annealed 150°C; (d) annealed 170°C.

with the variety of CB content. P is much higher at low CB content. When CB content is more than the critical amount and is involved in the noncritical zone, the PTC strength suddenly decreases to 1.0 and stabilizes. Only when P was over 3.0 and the CB component was in the critical component zone, has the composite acceptable application value, and the CB content should, therefore, be controlled in the critical component zone.

Effect of heat treatment

Influence of heat treatment temperature on PTC characteristics: Figure 6 shows the electric resistance–temperature curves at different heat treatment temperatures. As shown in Figure 6, heat treatment temperature influenced PTC characteristics very much. When the heat treatment temperature varied from 130 to 170°C, P obviously increased and reached the maximum about 7.0 at 170°C. Heat treatment also influenced the temperature at which the maximum electric
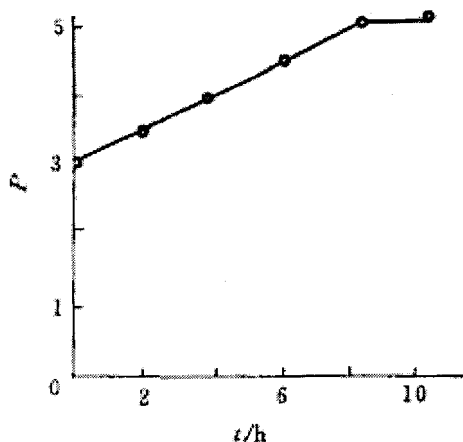

Figure 7 Effect of annealing time on PTC characters (annealing temperature: 170°C).
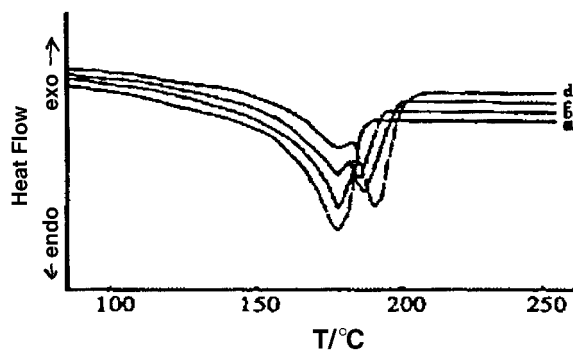

Figure 8 DSC of the composites (annealing time: 8 h): (a) unannealed; (b) annealed 130°C; (c) annealed 150°C; (d) annealed 170°C.

resistance appeared, T_{Max} was 5°C higher after cables were heat treated at 170°C.

At higher levels of crystallinity, the higher temperatures the critical zone shifted. Therefore, cables must be heat treated before marketing for the stability. If cables are not annealed beforehand, the working temperature range will increase slowly instead of remaining constant.

Effect of heat-treatment time on PTC characteristics: relationships between annealing time and PTC strength are shown in Figure 7; the periods of heat treatment time are different, and the temperature is at 170°C. PTC strength increases with an increase of heat treatment time up to 8 h, then levels off.
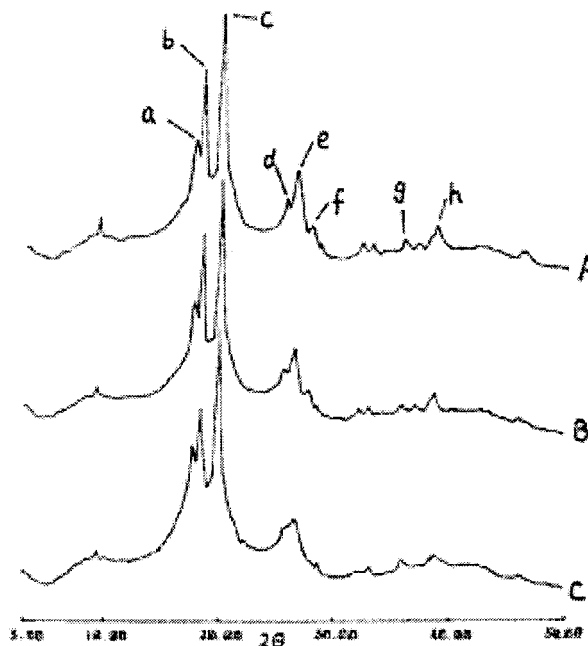

Figure 9 X-ray diffraction of the composite (annealing time: 8 h): (A) annealed 170°C; (B) annealed 150°C; (C) unannealed; (a) α-phase (100); (b) α-phase (020); c) α-phase (110); (d) α-phase (120); (e) α-phase (021); (f) α-phase (111); (g) β-phase; (020); (h) γ-phase (201).
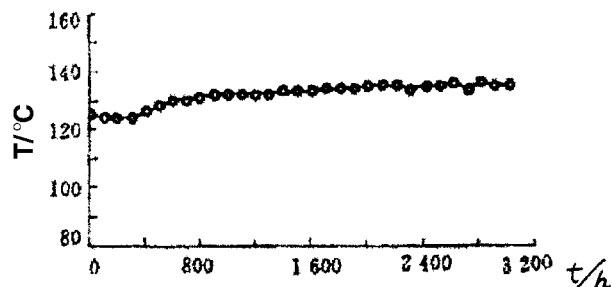
Figure 10 Cable temperature vs. time.

Figure 11 Relationshps of heating power to environment temperature.

Annealing perfects the crystal and eliminates recrystallization, so stablizing cables during working process. The result can also be proven by DSC and WAXD before and after annealing.

DSC curves are shown in Figure 8. The nonheat-treated sample had a lower melting point and a wider melting temperature region than the annealed sample because the annealed sample had a much more perfect crystallization and the crystallinity was increased, which can be seen by the area of the peaks.

In WAXD(Fig. 9), the ideal peaks became sharper after annealing and indicated the crystallization was more perfect. Division of peaks showed an increase of crystallinity, which was indicated similar to DSC results.

Applications of self-regulation heating cables

Electrification experiment

Figure 10 shows the relationship of the working temperature on the cables to continuous power for 3000 h.

Heating power and working temperature before and after power on for a 3000-h run are listed in Table II. The relationship is fairly stable (within 20%), so application requirements can be satisfied.

Relationship of heating power and environmental temperature

As shown in Figure 11, as the environmental temperature increased, electric resistance of the cables increased, and the heating power of the cables was lower. Therefore, the temperature of the heating cables was self-controlled. When the environmental tem-
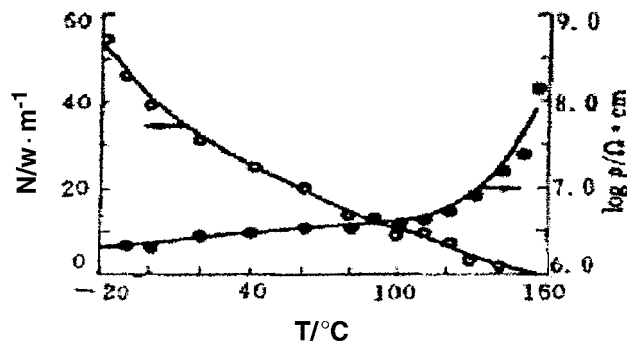
perature is up to 155°C, the heating power will turn to zero, so destruction of the cables at high temperature was avoided.

On-off cycles

For one cycle, voltage across samples is 220 volt, with power on 45 min, following a 15-min off. The Influence of the cycle number on the working temperature and electric resistance are shown in Figure 12.

After 500 cycles, the working temperature remained constant, electric resistance increased at the beginning, then stabilized at the end. Therefore, electrification on-off cycles almost did not influence the temperature control characters of the cables.

CONCLUSIONS

1. Crystal fluoride resin/CB composite is suitable for high-temperature grade self-regulating heating cables. Application requirements can be satisfied.
2. Acetylene CB is suitable for this system. The optimum CB amount is 8%.
3. Self-regulating heating cables should be heat treated before using. The suitable heat-treatement condition is 170°C, 8 h.
4. All the experiment results (3000 h working experiments, on-off experiments, heating power, and environment temperature experiments) satisfy the international standard.

TABLE II
Working Temperature and Heating Power of the Cables before and after Electrification on 3000 Hours

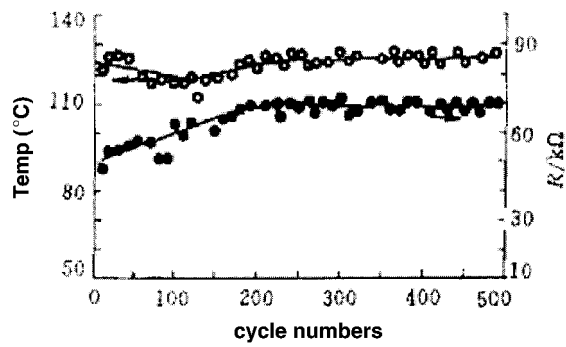| Cable No.	TRT (°C)	T3000 (°C)	T(%)	NRT (W/m)	N3000 (W/m)	N (%)
HT35-1	127	137	7.9	29.9	35.2	17.7
HT35-2	124	135	8.9	27.9	33.0	18.6
HT35-3	120	134	11.7	27.9	34.1	22.2
HT35-4	124	136	9.7	29.3	33.4	14.0
HT35-5	132	139	5.3	31.7	36.3	14.5
Average	125.4	136.2	8.6	29.3	34.4	17.4

Figure 12 On-off recycles of the cables.

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