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STUDY ON THEORIES AND INFLUENCE FACTORS OF PTC PROPERTY IN POLYMER-BASED CONDUCTIVE COMPOSITES

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Abstract. Conductive polymer composites not only have the electrical conductivity of inorganic fillers and flexibility of polymers, but also have some new properties that a single phase doesn't possess. Certain conductive polymer composites have been paid more attention as positive temperature coefficient (PTC) material because of the advantages of low cost, excellent formability, flexibility and lightweight over the conventional inorganic ceramic PTC materials. Several conductive theories and their merits and demerits in polymer PTC conductive composites are summarized. The key factors that influence the PTC properties such as matrix material, kinds of conductive fillers, constructural composition and process technologies are analyzed in details. Some thoughts on the developing trend of this kind of materials are also presented in order to learn more about the intrinsical characteristics of them and improve their properties further.

1. INTRODUCTION

Conductive polymer composites (CPC) containing polymer materials incorporated conductive fillers have recently been the subject of intensive studies [1-10]. Semi-crystalline polymer filled with conductive particles usually exhibit two important insulator–conductor transitions. The first one corresponds to the dependence of resistivity (or conductivity) on the filler content, and the critical concentration of fillers is necessary to build up continuous conductive network referred as the percolation threshold [10,11]. The second one is related to the temperature dependence of resistivity, that is the composite usually shows a sharp increase in resistivity with temperature around melting temperature of the crystalline polymer, which is called positive temperature coefficient (PTC).

It is well known that PTC materials are generally made from two categories, one is based on ceramics such as doped BaTiO3 or V2O3 based compounds [12-14], the other is based on conducting polymer composite materials [15-17], which change their resistivity at the critical temperature by several orders of magnitude. Ceramic-based PTC materials show a large, reproducible increase in grain boundary resistivity over a small temperature interval just above the curie temperature (T_c), which is associated with a ferroelectric to paraelectric phase transformation [12-14]. Because of the commercial significance of such a temperature-activated switching feature, the PTC materials can be utilized in a wide range of industrial applications, such as self-regulating heaters, current protection devices, micro-switch sensors and other outdoor equipments [18-22]. However, the application of ceramic-based PTC materials is limited sometimes because of the brittleness, strict processing condition and costliness. Therefore, polymer-based PTC composites

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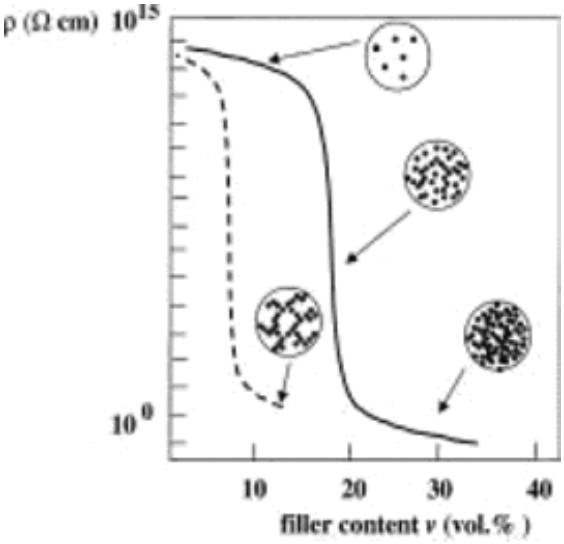

Fig. 1. Schematic sketch of the resistivity of a composite as a function of filler concentration for isotropic particles (full line) and CB (dashed line).

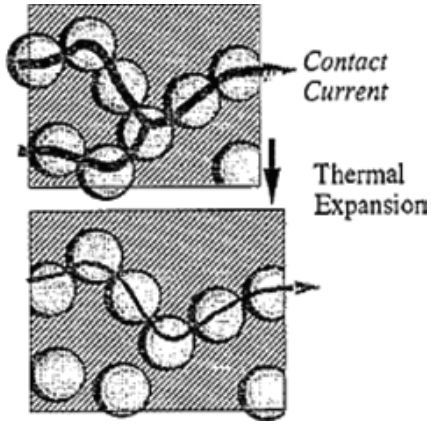

Fig. 2. Contact current mechanism for polymer PTC composite.

having been paid more attention because of the advantages of excellent formability, flexibility and lightweight over the conventional inorganic PTC materials, though they have some shortcomings, such as unstable electrical reproducibility and the negative temperature coefficient (NTC) effect phenomena when the temperature is above the melting temperature of the polymers.

In this article, several conductive theories and their merits and demerits in polymer PTC conductive composites are summarized. The key factors that influence the PTC properties such as matrix material, kinds of conductive fillers, constructural composition and process technologies are analyzed. Some thoughts on the developing trend of this kind of materials are also presented in order to learn more about the intrinsical characteristics of them and improve their properties further.

2. CONDUCTION MECHANISM OF CPC

The conductivity of CPC depends critically on the volume content of the filler. For very low filler fractions, the mean distance between conducting particles is large and the conductance is limited by the polymer matrix (Fig. 1) [23]. When a sufficient amount of filler is loaded, the filler particles get closer and form linkages, which result in an initial conducting path through the whole material. The corresponding filler content is called the percolation threshold. In this concentration range, the conductivity can change drastically by several orders of magnitude for small variation of the filler content. At high filler loading, the increasing number of conducting paths forms a three-dimensional network. The conductivity is high and less sensitive to small changes in volume fraction.

Percolation theory gives a phenomenological description of the conductivity of a system near the metal-insulator transition [10]. In model percolation studies one starts with a large, preferably infinite regular periodic lattice. A site of this lattice is then assigned at a random filler content *f*. All sites are bonded to adjacent sites by a conductive bond. At a critical filler content, f_c, an infinite conducting cluster is first formed in the infinite lattice. This means that at an initial percolating path through the material the conductivity of the lattice changes from insulating to a finite value. Above f_c, the conductivity increase as

$$\sigma(f) \propto (f - f_c)^t \quad (1)$$

with a parameter *t* between 1.65 and 2 for three dimensional lattices [10]. f_c is called the critical or percolation threshold. The percolation behavior can be influenced by the shape of the filler. For random packing in three dimensions, f_c turns out to be about 16%.

3. THEORETICAL AND PHENOMENOLOGICAL BACKGROUND OF PTC EFFECT

It is generally believed that the PTC effect is caused by a break-up of the conductive network during

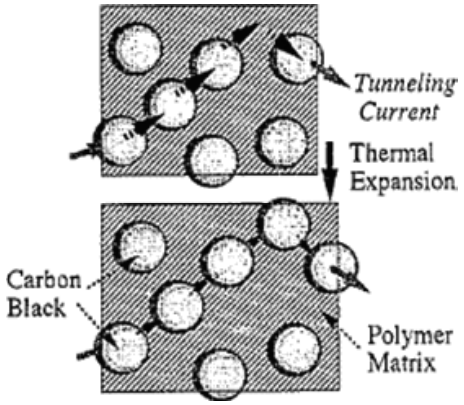

Fig. 3. Tunneling current mechanism for polymer PTC composite.

sample heating. Several theories have been proposed to elucidating the specific non-linear shift in resistivity with temperature parameter, such as thermal expansion, electron tunnel effect, electric field emission, as well as the inner stress and phonon-assisted tunnelling models. Nevertheless, these theories remain still in some problems and can not explain experimental results clearly, and the mechanism behind the PTC abnormality has not been well established.

3.1. Conducting chain and thermal expansion theory

Kohler first suggested that the PTC mechanism was a function of the difference of the thermal expansion coefficients between the matrix and the filler [24]. The sudden expansion, which took place at the melting point of the polymer matrix, resulted in the break-up of the conducting chains with a consequent anomalous increase in the resistivity (as shown in Fig. 2 [25], the schematica changes). However, this model was not able to explain the steep decrease in the resistivity above Tm (so-called NTC effect), when the volume of the matrix continued to increase with temperature.

3.2. Tunneling current mechanism

In contrast, the model proposed by Ohe and Natio assumed that a more uniform distribution of interparticle gaps and the gaps width is small enough to allow intensive tunneling to take place at low temperature [26]. The distribution of the gaps become more random when temperature near melting point (Tm), and a significant number of interparticle gap was too large to allow appreciable electron tunneling, although the average gap width did not change considerably (as shown in Fig. 3 [25]). This resulted in the elimination of many conductive paths with a consequent rise in the resistivity. The influence of the matrix on the PTC effect and the increasing randomness of the inter-particle gaps as T_m was approached were unexplained. The NTC effect, which usually took place immediately above the melting point of the matrix, also remained unexplained.

The tunneling model was further modified by Meyer taking the effect of change in crystalinity into consideration [27]. Meyer proposed that the conductive particles existing only in amorphous regions being separated by crystalline films, which has been assumed to be more conductive than amorphous ones. Thus he suggested that the anomalous rise in resistivity near the melting point can be attributed to the melting of the crystals. He also suggested that the NTC effect might be attributed to the immigration of carbon black particles, which resulted in the formation of new conductive chains of the filler particles.

Although Meyer's model can explain PTC and NTC phenomena, he has not mentioned the effect of crystalline change and the NTC effect.

3.3. Mechanism of congregation and migration changes of filler particles

Klason explained the PTC and NTC effects on the basis of changes taking place in the carbon congregation structure with temperature [28]. Although they suggested that the NTC effect was due to the formation of the new networks of the conductive particles, this process was not explained in detail. On the other hand, Voet attributed the PTC effect to the large volume expansion of the polymer in the melting range, as well as the migration of the carbon black to the previously carbon black-free crystalline region as mentioned above, which further diluted the concentration of the filler in the matrix and increased the resistivity [29].

3.4. Electric field emission mechanism

Based on the above viewpoints, H.K Allak proposed that contact resistance between particles is important in the case that the filler volume concentration exceeds the percolation threshold, and charge transport through the filler phase takes place via direct contact between the particles. On the contrary, when a thin, insulating polymer layer separates the

filler particles, conductivity is dominated by charge transport via tunneling effect [30].

Additionly, the dynamic factor resulting in re-aggregation of CB particles has been considered as the attraction between them (such as Van der Waals interaction or covalent bands between them), which is too weak to overcome the separation resulting from the vigorous macromolecular movement at temperatures over T_m, so NTC effect is caused by a decrease of elastic modules of the polymer at high temperature.

3.5. Internal stress mechanism

During curing of the thermoset matrix or cooling of the thermoplastic matrix in polymer composites, internal stresses appear [31]. These stresses increase the pressure between adjacent particles, give the contact pressure and decrease the contact resistance. Hence, internal stresses in the polymer matrix caused by shrinkage, external mechanical actuation or thermal expansion play an important role for the conductivity of composites. A shrinkage of the polymer during processing can induce high internal stress. This reduces the interparticle resistance. Instead, the observed strong resistivity change is caused by a release of particle-particle contact pressure and a change in gap distance. Polymer and the conducting filler particles are in a state of close packing with intimate contact to next neighbors, forming conducting paths throughout the composite. During heating, the polymer expands much more than the filler particles themselves. The contact pressure between adjacent filler particles is reduced leading to a moderate resistivity increase.

3.6. The percolation theory and the PTC effect

According to the percolation theory and the above PTC theories, the PTC effect of polymer composites strongly depends on the filler content. The PTC curve practically coincides with that of the percolation curve. Conductive particles agglomerate in the composite as clusters. As the size and number of the clusters increases with increasing filler content, at some critical content, that is called the percolation threshold, the cluster becomes infinite and makes a contribution to the composite conductivity. The agglomerates of particles in the infinite cluster can be abruptly separated and the composite become dielectric by thermal expansion of polymer matrix. So the greatest PTC effect usually takes place in composites with moderate filler content.

In summary, because these theories cannot be observed by experimental techniques, there has been difficulty in finding a comprehensible explanation for the effect, and thus most of mechanisms still remain controversial.

Although there is no satisfactory theory to explain the PTC and NTC phenomena, all of these models suggest that the volume expansion plays an important role in the PTC behavior, and the explanation based on the tunneling effect is widely accepted. According to this mechanism, electrons pass through the thin gaps between adjacent CB particles, aggregates and agglomerates at a practical magnitude of the electrical field. The rapid expansion near the melting point of the polymer matrix increases the width of the gaps, and thus hinders the process of electron tunneling. On the other hand, negative temperature coefficient (NTC) effect is presumably due to the reaggregation of the conductive particles in the polymer melting state and therefore the reparation of disconnected conductive pathways.

4. INFLUENCE OF THE POLYMER MATRIX ON THE PTC EFFECT OF COMPOSITES

The polymer is the framework of a composite, and the melting expansion is the main role in the PTC effect. Therefore the conductivity of polymer composites is sensitively influenced by the characteristics of polymer matrix such as chemical structure, thermal property, morphology, crystallinity and processing conditions.

4.1. Influence of the polymer crystallinity on PTC effect

Many semi-crystalline polymeric composites exhibit a PTC effect. The amorphous polymer PTC composites are hard to obtain great PTC effect because the volume thermal expansion of amorphous polymers is too small to produce significant resistivity change. This has led some scientists to suggest that crystallinity has an influence on the electrical conductivity [32-34]. However, this has been questioned by others. Some experiments do not support a correlation between PTC intensity (the ratio of peak resistivity to the room temperature resistivity) and crystallinity [35-37]. It is reported to prepare an amorphous polymeric PTC composite with PTC intensity of about 10^3, using polyurethane (PU) as matrix, CB as conductive filler and by adding reactive low molecular crystals stearic acid as crys-

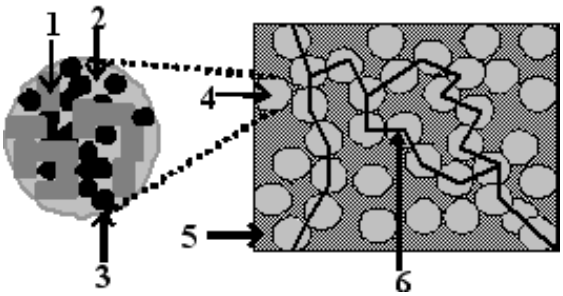

Fig. 4. Schematic picture showing a clear microstructure of the CB-PP/PVDF composite, where number 1, 2, 3, 4, 5, and 6 stand for the crystalline phase of PP, the amorphous phase of PP, the conductive filler CB, the conductive CB-PP phase, the PVDF host phase and the conductive networks in the CB-PP/PVDF composite, respectively.

talline phase into polymers [35]. As the stearic acid could melt and expand rapidly in a very narrow temperature range around the melting point, the volume fraction of CB could consequently reduce sharply, which results in the disconnection of conductive channels and cause the amorphous rubbery composite to produce PTC effect. Comparing to crystalline PTC plastics, the amorphous rubbery PTC material can easily form crosslinking to prevent NTC effect while it still have rubbery toughness, processability and mouldability. The electrical conductivity near the melting point of the polymer matrix, at this temperature the polymer matrix also has its largest thermal expansion coefficient. Therefore, it was assumed that the PTC effect is due to the difference of the thermal expansion coefficients between matrix and filler.

4.2. Influence of melting temperature of the polymer on PTC critical temperature

Polymers can show three significant reversible structural transitions, which are thermally induced: crystallization and melting in a semi-crystalline phase and a glass transition in the amorphous phase. All three transitions are related to a relative large volume change or to a pronounced change in the thermal expansion.

According to the mechanism mentioned above, the PTC transformation is triggered by the melting of crystalline phase, therefore, the critical transformation temperatures are near the melt points of these polymers and difference with the variation of polymer. In literature the highest critical transformation temperature was reported to be 170 °C [38-40]. The critical transformation temperature of polymer-based composites can be adjusted by adding low molecular crystals with different melting points, or intermixture immiscible polymer blends to obtain two resistivity jumps which designated as the double PTC effects. For example, for CB-filled ETFE/HDPE composite, the large thermal expansion owing to the melting of HDPE and ETFE crystallites is responsible for the first and second critical transformation temperature [21].

4.3. Influence of binary-polymer blends on percolation threshold of composites

It should be strongly stressed that most past investigations on the PTC and NTC effects of CB-filled polymer composites were focused on the composites containing CB and a single semicrystalline polymer. However, it is often difficult to reach a suitable conductivity by adding the amount of CB small enough to preserve the mechanical properties of the polymer and to reduce as much as possible the cost of the final composite. Few studies were conducted on the PTC and NTC effects of CB-filled immiscible semicrystalline polymer or multiphase polymeric blends [20-22,39,41]. The purposes include: (1) to obtain a conductive composite with a very low percolation threshold; (2) to provide a new approach to eliminate the NTC effect even at temperatures much higher than the melting point of the polymer.

The selective dispersion of CB in one phase or at the interface of two polymers causes a decrease of the percolation threshold to a very low level, which contributes to being processed with ease, preserving the mechanical properties of the polymer and reducing as much as possible the cost of the final composite. It is proposed that the heterogeneous distribution of CB in immiscible polymer blends is mainly due to the difference in affinity of CB particles to each component of polymer blends, i.e., the difference in the interfacial free energy of the polymer/ filler [as shown in Fig. 4, the schematic picture of CB-filled binary-polymer blends polyvinylidene fluoride (PVDF) and polypropylene (PP)] [41]. Gubbels *et al.* reported the two-step percolation in the LDPE/EVA composite filled with CB [42]. They thought that CB particles were predominately dispersed in LDPE first due to lower interfacial free energy and then began to be localized at the LDPE/EVA interface when the CB content in LDPE had approached a saturation limit. Di *et al.* proposed that the high viscosity of UHMWPE melt will minimize the migration of carbon particles into the polymer matrix and deformation of the polymer

particles during the hot compaction [20]. This provides the possibility of reducing the percolation threshold by favoring the heterogeneous distribution of CB particles, and eliminating the NTC effect by hindering the movement of CB particles in the UHMWPE melt.

5. INFLUENCE OF THE CONDUCTIVE FILLER ON THE PTC EFFECT OF COMPOSITES

The conventional method of preparing conductive polymer composites is to disperse the conductive filler such as carbon black (CB), carbon fiber (CF), graphite and metal particles, throughout the polymer matrix. The conductivity of polymer composites depends not only on the characteristics of polymer matrix but also on the properties of fillers such as particle size, concentration, dispersion state and aggregate shape, et al. Clarifying the role of all these factors enable us to choose the suitable processing method for obtaining the composites and to improve the electrical characteristics of these systems.

5.1. The kinds of conductive filler

The usual conductive fillers used can be classified as carbon system such as carbon black (CB), carbon fiber (CF), graphite and metallic system such as nickel, copper, zinc. The superconduct materials can act as a potential filler to be used in PTC materials.

5.1.1. Carbon system filler

An increasingly important use for CB is as the filler in polymers in order to enhance the electrical conductivity of the polymer. CB varies greatly in their structure. The structural characterization of these materials is difficult because of the very small particle size in the materials. In general, the structures are described as being either a high structure or a low structure. A high structure CB usually consists of many primary particles of CB fused together in an aciniform aggregate structure. A low structure CB consists of a small number of CB particles fused together in an aggregate, generally with a larger primary particle size. The use of CB of different structures will affect the conductivity in a given polymer system to varying extents. Normally a polymer loaded with a high structure CB or a CB with a small particle size, will have a lower electrical resistivity than a CB which possesses a low structure or large particle size, at the same CB concentration in a composite [43,44].

Natural graphite is a well-known material with good electric conductivity, and has been extensively applied to make polymer/graphite composites [45]. The use of expanded graphite in polymer/graphite composites will greatly enhance their electrical conductivity. In addition, it is interesting to note that graphite has different conductivities at different directions.

The electrical conductivity of CF or CNT is between the CB and graphite. The high aspect ratio of CF or CNT would affect the physical and mechanical properties of the synthesizing polymer composites. But the higher cost limits the usage of CF or CNT. It can be considered as the second conductive filler, which are considerably longer than the CB particles to bridge distant and unconnected CB particles and which are more likely to form conductive pathways within the polymer blend [7-9, 46-48].

5.1.2. Metal system filler

Polymer composites filled with conductive metal particles are of interest for many fields of engineering [49-53]. The interest arises from the fact that the electrical characteristics of such composites are close to the properties of metals, whereas the mechanical properties and processing methods are typical for plastics. It was observed experimentally that the electric conductivity and the PTC effect of metal–polymer composite predominantly depend on the electric conductivity, the particle shape and size, and the volume fraction and the spatial arrangement of the metal particles. In the present studies, aluminium, nickel, iron, zinc and copper powders with essentially different particle shapes (irregular, dendritic and almost spherical), as well as the compounds such as TiB_2, TiC, NbB_2, WSi_2, $MoSi_2$, V_2O_3, VO_2 were used as conductive fillers.

However, the usage of metallic fillers in PTC composites is limited to some extent because of the easy oxidation of the surface and the surface oxide layers formed may decrease the conductivity. Moreover, the high cost of the metallic fillers is another reason for limiting the widely application. Since carbon black is relatively cheap and only small amounts of powder are necessary to produce a conducting composite, it is widely used.

5.2. Effect of the grain size and morphology of the filler on conductivity of composite

Polymer materials in their pure state are excellent electrical insulators, which can also become con-

ductors when filled with various kinds of conductive particles. In general, the electrical conduction process in conductive polymer composites is complicated and dependent on a large number of parameters, mainly on filler concentration. In addition to the amount of loading, filler particle size and morphology structure, filler matrix interactions, and processing techniques are key factors in the determining the physical properties [54,55].

5.2.1. Effect of filler size

Experimental data supported that the composite loaded with the larger average filler size exhibit a higher PTC intensity and room temperature resistivity than those composites with the same filler content. The reason for this difference in the PTC intensity lies in the fact that the entanglement between the particles and polymer chains increases and the number of conductive pathways is smaller, the resistivity of the composite is sensitive to even a small decrease in the number of the conductive paths. For example, the degree of entanglement between a large-size CB and the polymer chains is much higher than that between a small-size CB and the polymer chains, thus the movement of the polymer chains caused by thermal expansion due to the melting of the crystallites may introduce a major deformation of the conductive network structure and break up a large number of the conductive paths. Therefore, composites with a larger particle-size CB show a higher PTC intensity, but their room temperature resistivity is usually higher. This is a major disadvantage for the use of large CB particles in many industrial applications. A balance between the PTC intensity and the room temperature resistivity is then attempted by using a mixture of large- and small-sized CB particles in the composites.

5.2.2. Effect of filler shape

In the previous sections, spherical particles were always assumed in modeling the composites. In practice, however, fillers are often used which have a shape very much different from a sphere. Examples are aluminum flakes, stainless steel fibers or carbon fibers. The percolation threshold can be drastically reduced for particles with an aspect ratio larger than one. One can easily apperceive that fibers with high aspect ratio can drastically increase the connecting paths and reduce the percolation threshold. Carbon fibers with an aspect ratio of 1000 need only 1.0 vol.%, whereas fibers with an aspect ratio of 10 need a volume fraction of about 10% in order to achieve the same resistivity [46].

5.2.3. Effect of filler distribution

The conductive properties depends strongly on the distribution of filler particles in a composite, and the distribution state of filler particles is mainly influenced by the chosen processing technique. For industrial production, extrusion or injection molding processes are used quite often. Using fibers, flakes or carbon black, the high shear forces occurring at the nozzle both methods cause an alignment of the filler particles in the flow direction. Hence, the orientation of the fibers or flakes in the final part depends strongly on the form of the mold and the flow of the polymer.

Care must be taken if composite parts are made by compression molding of polymeric and conductive powders. The carbon black particles are much smaller than the polymer particles. This results in a core-shell structure. The polymer particles are surrounded by shells of carbon black, forming a percolating network. The percolation threshold of a core-shell structure is considerably lower than that of homogeneous composite. A controlled orientation of filler particles and an anisotropic conductivity can be achieved by applying electric or magnetic fields during the processing. This can serve not only for relative high conductivity at low filler content, but also for unidirectional conductivity.

5.3. Influence of binary-fillers on percolation threshold of composites

To pursue the relatively low loading levels needed to achieve desired conductivities and further improvement on PTC properties, a lot of efforts have been done and then the introducing a second conductive filler into the CB filled polymer composites is considered as one of the effective ways. The purpose of the second filler is to span across insulating regions and further connect existing conductive pathways. In this manner, the second filler serves to bridge the network and enhance the net conductivity of the composite. In a separate study, it is found that mixtures of conductive fillers (e.g. G and CF) in a single polymer matrix can be used to enhance the electrical conductivity of conductive polymer composites [56,57]. This observation reflects an overall improvement in the conductive pathway established by particles differing in size and shape. High-aspect-ratio carbon fibers (CF) or carbon nanotubes (CNT) were considered to be better used as the second conductive filler, which are considerably longer than the CB particles to bridge distant and unconnected CB particles and which are more likely to form conduc-

tive pathways within the polymer blend [as shown in Fig. 5, the schematic image of CB/CF or CB/CNT mixture filled polymer blend]. In this case, discrete CB-rich channels are connected by CFs or CNTs.

Utilization of ceramic materials, such as $BaTiO_3$, as reinforcers in polymer composites is also an effective solution to the challenge of developing new polymers for specific sets of properties and applications. With the increasing by numerous applications of these materials, more and more knowledge is needed to gain a better understanding of their filler matrix interaction, which can give them different physical properties. Ceramic is an important material for high-temperature PTC applications because of its high melting point, hardness, elastic modulus and electrical conductivity as well as its relatively low coefficient of thermal expansion. As far as we know, no experimental work had been reported in the open literature on polymer filled synchronously with conductive filler and ceramic particle. The investigation of the effect of ceramic particles on the network structure, electrical and thermal properties of polymer PTC composites has a potential significance in discovering new PTC materials.

6. THE OTHER EFFECTIVE WAYS TO IMPROVE THE PTC PROPERTIES OF COMPOSITE

Research and development activities on PTC materials have brought successful industrial applications, and an enormous amount of knowledge has been accumulated in this field. Nevertheless, many problems are not solved yet. Polymer PTC composites have some shortcoming, such as unstable electrical reproducibility due to irregular structure changes in heating/cooling cycles, NTC phenomena and the slow response rate of PTC effect associated with an adverse effect on desired switching properties. Several ways which include crosslinking, filler treatment and polymer blends are introduce to increase stability of PTC materials.

6.1. Surface modification of conductive filler by coupling agents

The conductive filler, especially for CB produces large cohesive strength between the individual fine particles, which leads to aggregates of particles, having diameters of not less than several microns. Therefore, it is extremely difficult for the CB to be dispersed on the order of submicrons in the medium. So it is very necessary to make a suitable modification on the CB surface in order that it can be more evenly dispersed in the matrix and the interfacial interaction between CB and polymer can be strengthened. Relevant developments in polymer blends based on CB with surface modification such as grafting crosslinking, plasma sputtering, gasification etching, emulsion polymerization have shown very efficient in improving dispersion behavior and morphological stabilization [43,58,59], yet the common dispersants would only have a reaction with surface of fillers and not with the molecule of polymers. Grafting a coupling agent to the CB surface can be considered as one of the options to deal with these problems. The coupling agent such as titanate coupling agent (NDZ-102), silane coupling agent (KH550) has two quite different chemistry reactive groups in the molecule structure, which can react with inorganic filler forming the firm chemical bonds and synchronously link with the organic polymer molecules through physical entanglement or chemical crosslinking, respectively, bridging the filler and polymer tightly together. Fig. 6 shows the schematic image of chemical reaction mechanism of NDZ-102 on the interface of CB and polymer [58]. That is, the filler can be soaked better in the polymer to improve the compatibility of the composite.

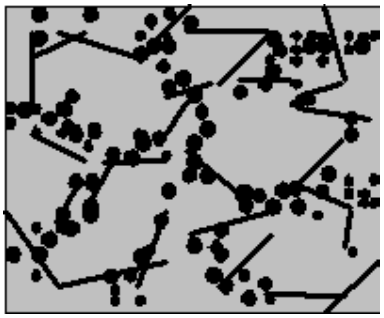

Fig. 5. Schematic image showing the CB/CF or CB/CNT mixture eventually forming a bridged network. In this case, discrete CB-rich channels are connected by CFs.

6.2. The crosslinked polymer composites to eliminate the NTC effect

It is well known that when the temperature is above the melting point of semicrystalline polymers, non-crosslinked CB-filled semicrystalline polymer composites exhibit a NTC effect. Researchers have pro-

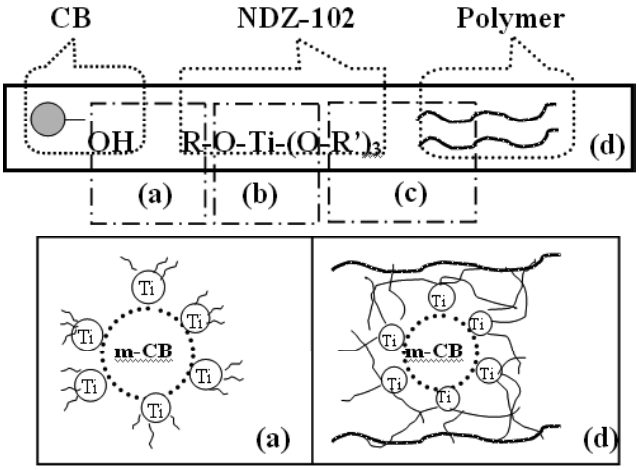

Fig. 6. Schematic image of chemical reaction mechanism of NDZ-102 on the interface of CB and polymer (a) chemical bond of R groups in NDZ-102 with hydroxyls in CB to form a single molecule layer of coupling agent on CB surface, (b) crosslinking action of NDZ-102 with CB and polymer through conversion reaction of lactones groups, (c) physical entanglement and chemical crosslinking of R' with polymer molecules, and (d) the enhanced interface between CB and polymer.

posed and developed many methods to eliminate the NTC effect of polymer composites. Among these methods, the first approach used is to crosslink the semicrystalline polymer matrix by a crosslinking agent [60-63]. For instance, Narkis successfully used a peroxide to crosslink CB-filled high-density polyethylene (HDPE) composites without sacrificing the PTC intensity [64,65]. In addition to the use of a crosslinking agent, Gamma and electron beam radiations have been used to crosslink polymer composites [66,67]. It was mentioned that a third filler could be used to stabilize the polymer matrix and eliminate the NTC effect. Even though crosslinked composites have been used as thermistors and self-regulating heaters in the industry for many years, the mechanism for eliminating the NTC effect has not been fully understood. However, the absence of the NTC effect in the crosslinked polymer composites is related to an increase in the viscosity of the polymer matrix, leading to a significant reduction in the mobility of the CB particles in the composites. Based on this idea, it is possible to use a very high viscosity semicrystalline polymer matrix to eliminate the NTC effect.

6.3. Heat treatment of the composite

The crystallization process and crystallinity of the polymer matrix and its morphology have a very important effect on PTC characteristics of a composite. Heat treatment and annealing can improve the crystallization of polymers and enable the fillers to arrange more regularity, so they are good means of improving PTC characteristics of a polymer composite [19,68].

7. SUMMARY

Several conductive theories and their merits and demerits in polymer PTC conductive composites are summarized. The key factors that influence the PTC properties such as matrix material, kinds of conductive fillers, constructural composition and process technologies are analyzed in details. Some thoughts on the developing trend of this kind of materials are also presented in order to learn more about the intrinsical characteristics of them and improve their properties further.

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