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Carbon based conductive polymer composites

Wei Zhang · Abbas A. Dehghani-Sanij ·
Richard S. Blackburn

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Abstract Composite material has attracted increasingly remarked interest over the last few decades and set it apart in its own class due to its distinct properties. World annual production is over 10 million tonnes and the market has in recent years been growing at 5–10% per annum. Among these materials, one subgroup, conductive polymer composite, has figured out and its importance is increasing in years to come. When used as conductive material, it possesses the merits of light weight, ease of manufacturing and chemical resistance. This review focuses on the electrical properties of carbon based conductive polymer composites. Special emphases are placed on the percolation phenomenon, the factors that affect the percolation threshold as well as related theoretical research work. Then mechanisms of electric conduction and factors influencing conductive properties are addressed.

Introduction

The ability of polymers to act as electrical insulators is the basis for their widespread use in the electrical and electronic fields, the resistivity of which is generally around 10^{15} Ω m. However, material designers have sought to impart conduction to polymers by blending insulating polymers with conductive ingredients such as carbon blacks, carbon fibers, metal particles or conducting polymers such as polyaniline [1]. As a consequence, a range of so-called conductive polymer composite has come to existence since the 1950s [2] with the resistivity between metallic conductor (10^{-7} Ω m) and insulating materials (10^{15} Ω m) [3], which can find their applications in many fields such as floor heating elements, electronic equipment [4, 5], important strategic materials such as electromagnetic interference (EMI) shielding [6], apart from the conventional application of semi-conducting materials for dissipation of static electricity [7]. More recently conductive composites have been used for sensing components [8, 9]. Compared with metallic conductor, conductive polymer composites have the advantages of ease of shaping, low density, and wide range of electrical conductivities as well as corrosion resistance [10].

Nowadays, carbon black particles and carbon fibers are the most commonly used conductive components to incorporate conduction to polymer composite. The reason for this is that carbon black particles have a much greater tendency to form a conductive network due to their chain-like aggregate structures compared with other conducting additives such as metal powder. Whilst carbon fibers may be considered as chain-like aggregates of carbon particles having long chain length.

Percolation phenomena

Many conductive polymer composites exhibit percolation characteristic [8, 11–13]. The curve of conductivity versus filler concentration is S-shaped, which clearly demonstrates a relative narrow filler loading range during which a small increase in loading will result in a drastic increase in conductivity. This change implies some sudden changes in the

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W. Zhang (✉) · R. S. Blackburn
Green Chemistry Group, Centre for Technical Textiles,
School of Design, University of Leeds, Leeds LS2 9JT, UK
e-mail: texwzh@leeds.ac.uk

W. Zhang · A. A. Dehghani-Sanij
School of Mechanical Engineering, University of Leeds,
Leeds LS2 9JT, UK

dispersing state of conductive particles, i.e. the coagulation of particles to form networks which facilitates the electrical conduction through the composites. Put in another way, the composite exhibits an insulator to conductor transition. The critical amount of filler necessary to build up a continuous conductive network and accordingly to make the material conductive is referred to as the percolation threshold.

A critical aspect in the production of conductive polymer composites is the filler content, which must be as low as possible and still allows the composite to fulfill its electrical requirements, otherwise the mixture processing becomes difficult, the mechanical properties of the composite are poor and the final cost is high. There are several ways to decrease the percolation threshold of conductive filler concentration in polymeric matrices, which are mainly based on the use of additives, the optimization of processing conditions, as well as the size, distribution and porosity of filler [14, 15].

Factors influencing the percolation threshold

Polarity of polymer

Miyasaka and co-workers [16] investigated the effects of different types of polymer matrices on the conductivity of the composite with respect to percolation threshold. The results suggested that the polarity of polymer may be related to the critical content: the higher the polarity of a given polymer, the larger the critical content is. Combining the obtained results with the tension values of polymers available from others [17, 18] they have further revealed a correlation between the surface tension of the polymer and the critical carbon content: the larger the surface tension, the larger the critical content is. A strong correlation has also been demonstrated elsewhere in the enhanced conductivity of polymers with increasing polarity of the repeat unit [19–21]. However, Sau et al. revealed an opposite effect of polymer polarity on percolation threshold by studying the percolation characteristics of ethylene-propylenediene monomer rubber (EPDM)/acrylonitrile butadiene rubber (NBR)/their blends and acetylene black systems. In general, EPDM and NBR are considered as no-polarity and high polarity respectively. But EPDM exhibits the highest critical concentration, while NBR shows lower critical value. When short carbon fibers were employed as conductive filler in NBR/EPDM/(NBR/EPDM; 50/50) systems, their percolation thresholds differ quite marginally from each other [22].

Viscosity of polymer

The attainment of the percolation limit is also dependent on the viscosity of the polymer [23]. The higher the viscosity of the polymer matrix, the higher is the percolation limit. Because the structure of carbon black degrades owing to the high shearing action experienced during mixing. The higher the viscosity of the base polymer, the higher is the shearing force experienced by the black aggregates and thus the greater is the degree of structure breakdown of the black. Consequently, the formation of a conductive network throughout the matrix is delayed and occurs at a higher concentration. The similar trend is also true for carbon fiber filled systems [22]. The high viscosity of polymer will cause a pronounced drop of aspect ratio of short carbon fibers and block the formation of three-dimensional conductive networks. Thus, more fiber will be necessary to obtain a conductive composite.

Degree of polymer crystallization

The nature of the host polymer matrix is also important regarding the critical percolation concentration of the conductive filler, which is emphasized by Narkis and Vaxman [24] who studied the electrical resistivity of high-density polyethylene loaded with conductive blacks. In semicrystalline polymers the very fine carbon black aggregates tend to concentrate in amorphous regions. During the crystallization process a major part of the carbon black aggregates is rejected into interspherulitic boundaries and the rest may be located in amorphous regions within the spherulities. As a result, the threshold percolation concentration in semicrystalline systems is lower than in amorphous polymers.

Multiphase polymer matrices

Another approach to reduce the percolation threshold relies on the selective localization of carbon black particles in multiphase polymeric materials. Klason and Kubat [25] reported that a percolation threshold of 0.005 volume fraction of carbon black could be obtained by compression molding of a mixture of carbon black and polystyrene powders. In the absence of shear, the carbon black particles do not penetrate the polystyrene phase and remain essentially located at the interface between polystyrene particles. But this method suffers from poor mechanical properties and reproducibility. Gubbels et al. [26] reported that the percolation threshold can be efficiently decreased by the selective localization of carbon black particles in multiphase polymeric materials, i.e. in one phase or better at the interface of binary polyblends. Foulger proposed that the percolation threshold of the poly (ethylene-co-vinyl acetate) (EVA)/high density polyethylene (HDPE)/carbon black (CB) is at a significantly lower carbon content than the individually filled HDPE or EVA [19]. Analogous results have been observed for other ternary composites, such as poly (styrene)(PS)/HDPE/CB [27], poly (propylene) (PP)/poly(carbonate)(PC)/CB [28], and PP/Nylon/CB [29], emphasizing the tendency of filled immiscible blends to exhibit enhanced conductivities above that of the individually filled polymers.

This characteristic may arise from two phenomena. The first one is an increase of carbon black at the interface between the two immiscible polymer blends [19, 26, 30], which leads to a decrease of resistivity for the same CB percentage. The other one is the stress applied to the conducting network of CB-rich polymer phase by CB-poor polymer phase, as pressure is known to decrease resistivity [9, 31].

Types of conductive filler

Carbon black and short carbon fiber (SCF) also exhibit different behaviors in imparting conduction to the composites due to their differently inherent natures. In carbon black filled nitrile rubber composite, the threshold percolation lies in between 20 and 35 per hundred rubber (phr), while for short carbon fiber filled one it ranges from 10 to 20 phr [32]. Furthermore, the loading for onset of abrupt insulator to conductor transition is higher for the particle-filled composite. These differences can be attributed to the fact that the inherent fibrillar form of SCF has a higher tendency to form a three-dimensional network in the composites, ensuring better electrical response than the carbon black filler. In addition the carbon black surface generally comprises different chemically active groups containing hydrogen and oxygen, which are prone to capture electrons and reduce conductivity [33]. Whereas carbon fibers are generally devoid of such groups on their surface since they are subjected to high temperature during their manufacture. Sau et al. revealed that in acrylonitrile butadiene rubber (NBR)/ethylene-propylenediene rubber (EPDM)/(NBR/EPDM;50/50) and short carbon fiber systems, the percolation threshold is all about 14 phr, which is much lower that carbon black filled counterparts [22]. The similar trend was also realized by Flandin in ethylene–octene polymer matrix [34].

Physical properties of carbon black

As far as the carbon black particles are concerned, the aggregate structure, morphology and micro porosity of particles greatly affect the percolation threshold. The structures and properties of conductive fillers have significant roles to play with respect to reducing the critical limit for making conductive composite. Narkis and Vaxman [24] conducted a comparison of percolation thresholds between different types of carbon black filled polyethylene, namely, Ketjenblack EC, XC-72, Corax l6, Conductex 975 and Conductex 40-220. It is observed that the number of particles per aggregate and aggregate shape both affect the conduction level of aggregate/polymer composite systems. High structure, anisometric shape as well as high microporosity of carbon black are in favor of enhancing the electrical conductivity. By studying ethylene-octene-Conductex 975U/Printex 30/MS-TS systems, Flandin further confirmed this conclusion [34].

Physical properties of carbon fiber

As for carbon fiber, the aspect ratio dependence of conductivity has been observed. Narkis and Vaxman [24] commented that carbon fiber performance in polymer composite is highly dependent upon the fiber aspect ratio; the higher aspect ratio, the higher conductivity it can impart. So it is easy to come to the conclusion that fiber attrition during compounding and fabrication should be minimal. However, it should also be pointed out that the uniform dispersion of fiber in polymer matrix is another issue that must be taken into account. To achieve uniform dispersion results, the fibers usually experience shear forces which leads to drop of aspect ratio. Thus the fabrication should be a combination of keeping high aspect ratio with homogenous dispersion. Additionally, Pramanik [32, 35] suggested that the greater the surface-to-volume ratio of the carbon fiber, the more likely is interparticle contact which will give rise to higher conductivity and result in reduction of percolation threshold. In this aspect, carbon fibers have advantage over carbon black.

Theoretical research of percolation phenomenon

It is well known that percolation theory has been successfully used for interpreting the electrical conductivity of random mixtures of conductors and insulators [36]. Quite often in these systems, volume resistivity decreases gradually with increasing conductive content under the percolation threshold, which has been speculated to be a quantum mechanical result, where the increase in conductivity arises from an elevated propensity of electrons to effectively tunnel between isolated conductive filler domains with diminishing separation distance [37]. When the conductive contents greater than the threshold, a significant increase in conductivity with increasing levels of conductive fillers is exhibited. This change in conductivity (σ) beyond the percolation threshold can be expressed in following form, as developed by Kirkpatrick [36] and Stauffer [38].

$$\sigma = \sigma_0 (P - P_c)^t$$

where P_c is the critical or threshold probability of formation of a conducting network, P is the probability of finding the conducting phase which is equivalent to the volume fraction of conducting phase above the critical concentration, σ_0 is the pre-factor and t is the conductivity exponent.

Various expressions and values have been proposed for the conductivity exponent t. Balberg and Bozowski reported that in stick-like carbon polyvinylchloride system the conductivity exponent lies in the range from 1.5 to 2.1 [39]. This value is fairly good agreement with that was reported by Stinchcombe [40] and Abeles et al. [41] as well as the theoretical value ($t = 1.7$) [42]. Clerc et al. related the exponent t to the dimensionality of the system, t being equal to 1.9 in 3D systems and 1.3 in 2D systems [43]. Based on experimental data, Gabbels concluded that in polystyrene (PS)/polyethylene (PE)/carbon black (CB) system t is 2.0, when CB is dispersed within the amorphous phase of pure PE, while t is equal to 1.3 when CB is at the interface of a PE/PS blend with dual-phase continuity [44]. It can be seen that experimental data support theoretical model very well.

However it is worth mentioning here that the classical percolation theory applied to conductive-filler-polymer systems must meet some definite conditions. The theoretically predicated value shows reasonable agreement with the experimental one only when the following perquisites are fulfilled: the particles must be spherical, monodisperse and have an isotropic conductivity. If one or all these conditions are not fulfilled, the theoretical value will deviate far from the realistic one. Although in some cases, it is unclear which condition is disobeyed.

Carmona et al. reported that in short fiber-epoxy resin composites a fit of experimental data to a power law dependence gives the exponent $t = 3.0 \pm 0.6$ when the length of fibers ranges between 1.15 mm and 2.85 mm, which is significantly higher than the universal value [44]. From publications, it seems that conductivity exponents should have to be associated to fiber-like conducting heterogeneities in an insulating medium, although no definite criteria, thus far, has been reported.

More recently, Foulger [19] found that in poly (ethylene-co-vinylacetate)/high density polyethylene/carbon black system t is equal to 3.6. Levon et al. [45] reported the dependence of critical exponent for multiple percolation system (t_{eff}) with n levels of percolation has been estimated to be $t_{\mathrm{eff}} = nt$, where t is the exponent of single percolation. As one can expected quite often t_{eff} is larger than the magnitude for percolation system [46], in which t is about 2. On basis of aforementioned equation, t_{eff} should be 4 in this ternary system. But it should be pointed out that this agreement seems fortuitous since the morphology of the ternary composites does not resemble the idealized hard sphere systems on which the theoretical values are based. Nonetheless, the similarity between the theoretical and experimental results of rapid increase in conductivity with filler content via the critical exponents highlights the viability of the multiple percolation approach in generating conductive systems with low levels of conductive filler.

Mechanism of electric conduction

Depending upon the types of filler and their concentration, various mechanisms of conduction have been proposed which include simple inter-aggregate conduction, field emission, tunneling of electrons. We herein discuss the conduction mechanism briefly on basis of three distributions of the conductive particles, namely separate, adjacent and touching.

Separate

Maxwell [47] studied the conductivity of an insulating medium with evenly dispersed conducting spheres and obtained a relationship which has proved valid up to 10% volume of conducting component. Bruggeman [48] proposed a relationship valid up to some 50%, but it is to be noted that even with this proportion of conducting component the resistivity had only been reduced to about one-fifth of that for the insulation.

Adjacent

In narrow insulating gaps between conducting areas of electrically conductive fillers, especially when the adjacent particles approach closely enough so that the interval distances between them are within a few nanometers, very high field strength can be expected. Thus the internal field emission may account partially for some conductive behaviors of conductive filler-polymer systems. According to electric field radiation theory it is assumed that an emission current is caused to flow by the high electric field being generated by a gap of a few nanometers [49].

A special case of internal field emission is the tunneling effect. In the electron tunneling theory, the electrical conduction is believed to take place not only by interparticle contact but also by electrons being able to jump across a gap or tunnel through energy barriers between conducting elements in the polymer matrix. Tunneling is a quantum mechanical process, which is expected to operate when the distance between conductive components within the insulating matrix are close to a threshold value, usually a few nanometers. From the conduction viewpoint, these gaps are equivalent to interparticle contact [50]. The basic difference between this theory and conduction path theory lies in the fact that the percolation limit is more probable at lower concentrations of conductive filler than that in conductive path theory.

Many researchers have ascribed some conductive behaviors of conductive filler-polymer systems to tunneling effect mechanism theoretically and some observed experimental results also support this theory. Beek investigated the internal field emission phenomenon in carbon black-loaded natural rubber vulcanizates and suggested that the occurrence of electron tunneling is concerned with types of filler, filler concentration, degree of filler's dispersion, temperature as well as externally applied voltage. It is noteworthy that in some cases the electron tunneling can even happen over insulating gap widths of 2 and 2.5 μ [51, 52]. Sheng reported a tunneling conduction mechanism of tunneling with potential-barrier modulation by thermal fluctuations based on carbon-polyvinylchloride composites. High temperature and large size of the conducting carbon aggregates will aid the happening of electron tunneling [53, 54]. These can be interpreted as due to the following reasons. At high temperature, the tunneling current increases because the thermal fluctuations decrease the potential barrier between carbon aggregates. Whilst as a direct consequence of the large size of the conducting carbon aggregates is that the charging energy required to remove an electron from a neutral aggregate is completely negligible, in sharp distinction to conduction in granular metals where the charging energy plays the dominant role [55, 56]. Connor et al. [57] found that at high temperature (from 45 K to room temperature) the conduction can be ascribed to thermal fluctuation induced tunneling of the charge carriers through the insulating layer of poly (ethylene terephthalate) separating two carbon black aggregates, which is a temperature dependent process, whereas at low temperature (lower than 45 K) conduction becomes temperature independent [58], processing by tunneling through a potential barrier. That is to say conventional tunneling conduction would replace fluctuation-induced tunneling.

Touching

The conductive filler forms a few continuous chains (conductive network) in the polymer matrix. Through this continuous network, charged species (electrons) move from one end to the other under an applied electrical field. This movement of electrons causes the phenomenon of electrical conduction. This is the basis of the well-known conduction path theory. Thus the formation of a conductive network through physical contacts of conductive particles or their aggregates is essential and therefore the formation of a conductive network is more probable above a critical value, i.e. percolation limit [59].

Grekila and Tein considered the probability of forming conducting paths through a regular geometric array as the proportion of conductive component was increased [60]. The distribution of chains through a lattice was the subject of thorough investigations by Flory [61] and Gibbs and Di Marzio [62, 63]. All these theories are based on statistical method to predict the formation of conducting chains in a mixture and the resultant conduction and the conductive path is treated as a discrete one. But in fact multiple contacts between chains exist, forming shunts both between an along chains and making it impossible to assign a definite value to the number of conductive paths formed. Based on the theories of liquid structure [64] in which basic volume elements are considered to be distributed in a random manner so that there is no long-range order in the structure, which leads to properties on the microscale being independent upon the effects of nearest neighbors around any individual element, while properties observed for the bulk material represent the average individual situations, Scarisbrick [3] derived a relationship between resistivity and the volume proportion of conductive material for a mixture in which conducting particles are considered to be touching, in which the shape, size and orientation of the particles were also taken into account.

Sometimes, for one system it is difficult to reconcile the substantial disagreement that exists in the conduction theories put forward by various authors. It seems that the actual conduction mechanism is quite complex in nature and the net result may be due to a combined effect of different mechanisms.

Factors influencing conductive properties

Effects of processing parameters

Processing parameters, especially those involving considerable shear of the polymer/filler mixture, have a profound effect on the conductive properties of the ultimate conductive polymer composite. Since there are two conflicting effects that should be balanced when mixing the conductive polymer composites. (i) To ensure the conductive fillers are dispersed uniformly throughout the polymer matrix, the composites should be stirred sufficiently, that means severe and long-time stirring will produce a positive effect on the improvement of conduction; (ii) on the other hand, however, this severe mixing conditions will generate greater shearing forces and lead to heavy breakage of the carbon black aggregate or short carbon fibers, which will reduce their tendency to form conductive paths in the polymer matrices and consequently the resistivity will increase. Care should be taken when the processing parameters are selected. There is no doubt that an excellent mixing process must be combination of homogeneous dispersion of conductive filler and good conduction improvement. Several authors have observed that during mixing the composite, mixing time, temperature and order of addition of materials will affect the resistivity of the composite to a high degree [22, 65–67].

During mixing, polymer-filler bonds are formed and there is a net reduction of filler-filler bonds. If prolong the mixing time, better filler dispersion results may be expected. But the negative effect on conduction can not be negligible due to the shearing forces that the filler experiences during this process. The more severity of the mixing technique and the higher viscosity of the composite, the more severity is the degradation of the filler. In the meantime, different properties of filler and various mixing machines and methods complicate this problem even more. Thus, the type and structure of carbon black, type of short carbon fiber and its initial aspect ratio should also be a consideration when selecting the mixing time. To date, there are no definite rules and optimizing results can be achieved only by trials and errors.

Of more importance than mixing time are the effects of breaking the normal milling period and interposing periods of (i) standing at room temperature, (ii) standing at high temperature or (iii) hot milling [68]. Abdel-bary [69] observed that remilling the carbon black loaded styrene-butadiene composites, which were left at room temperature for different periods of time, will increase the resistivity. Because the agitation and thorough blending of the polymer-filler mix tend to break down the filler aggregates, resulting in higher resistivity of the composite. In addition, thermal-oxidative aging of such vulcanized composite will also decrease the conductivity. This may be due to the reactive sites produced in rubber chains, which in turn react with active sites of carbon black. This interaction leads to an increase in hardness as well as a decrease in conductivity [70].

Martin and Parkinson [71] investigated the effect of mixing temperature and maturing cycles on the resistivity of an HAF black block. Two batches were mixed at 120 °C and 190 °C respectively. They found that increasing the mixing temperature results in an increase in resistivity when the sample are mixed in air, while the effect is small and slightly reversed if the mixture is carried out under nitrogen. Khastagir [22, 67] also emphasized that the resistivity is a function of mixing temperature and therefore in comparison experiments, this parameter should be keep identical in order to avoid its effect on resistivity. However no detailed values have been provided.

Agari et al. [72] measured the effects of different mixing methods on the electric conductivity of polyethylene filled with graphite particles. The improved conductivity of composites follows the decreasing order of powder mixture > solution mixture = roll-milled mixture > melt mixture. In the roll-milled mixture aggregates of graphite particles could not be sufficiently broken by milling because the viscosity of molten polyethylene was very low. In the solution mixture, graphite particles were able to surround the crystals of polyethylene that were separate in the solution. Thus the formations of conductive chains in the roll-milled mixture and in the solution mixture are considered to be easier than in the melt mixture. In the powdery mixture, since graphite particles were arranged to surround powdery polyethylene structure, the formation of conductive chains can be considered the easiest and therefore the conduction was improved much pronouncedly. Jana et al. found that the resistivity of short fiber filled polychloroprene rubber by conventional mill mixed is higher than that by the cement method. This is because by cement method wherein carbon fibers are mixed with the rubber-solvent (chloroform) mixture prior to being passed through the mixing mill, the breakage of carbon fiber is reduced drastically and high aspect ratio of fibers are remained, which is preferred for the formation of conductive network and results in lower resistivity. The analyses of scanning electron micrographs corroborate this explanation [73].

Vulcanization processing parameters also generate influence on the electrical conductivity. The time and temperature of vulcanization have a considerable effect on the electrical conductivity of composite. Gul et al. [74] studied the variations of resistivity of carbon black filled phenol-formaldehyde (hardening at 150 °C) and epoxide (hardening at 80 °C) systems during the hardening process. The resistivity of both the systems drops great within the first 10 min of hardening process and then reduces slightly with the prolonged hardening time. In carbon black loaded styrene butadiene system, at 140 °C the major change in electrical conductivity occurs at the first 2 min of vulcanization process, followed by a slight decrease of electrical conductivity, then reaches a constant after 20 min [75]. This may arise from two effects: (i) the formation of new chemical bonds between the resin molecules leads to the reduction of large particles of carbon black to fine particles. Thus the number of fine particles increases and consequently the probability of the carbon black particles coming into contact and forming chain and network structures are increased, which results in the increase of conductivity, (ii) the hardening process, which is carried out at high temperature, is accompanied by the evaporation of solvent and low-molecular fractions, and also by a decrease in volume as a result of crosslinking. The decrease in volume also increases the carbon-carbon contact and consequently the electrical conductivity. In the latter stages of hardening when the resin is very viscous, the conductivity remains substantially constant.

The nature of the vulcanized network may also result in differences in the electrical properties. Jana et al. [73] summarized that the resistivity values of thermo-vulcanized and conventionally vulcanized composites and found that at a given filler loading, thermo-vulcanized composites show higher resistivity than conventionally vulcanized ones. This phenomenon can be ascribed to the following reason: the convention vulcanized composite possesses a higher crosslinking density, as compared to the thermo-vulcanized systems; the higher crosslinking could result in a conductive network [76, 77].

Effects of polymer matrix

Although some information is available regarding the effects of different types of polymer upon the resistivity of conductive rubber, it must be realized that the relationship cannot be precise since [78]: (1) In general, different polymers will contain different ingredients and another assortment of base formulae might give different relative effects. (2) The mixing techniques, even if nominally similar, will differ in fact, since at any stage in the process the mechanical reaction to the same operation depends on the type of polymer. (3) One polymer may give a higher resistivity than a second at given concentration of a given type of carbon black, but a lower resistivity than the second at another concentration or with a different type of carbon black. (4) There is little information about the effect of the deformation and heat treatment on the resistivity of synthetic rubbers and thus alteration of conditioning treatment may also affect the relative values of resistivity.

Due to aforementioned reasons, it seems unlikely to make a definite conclusion regarding the effect of polymer matrix on conductivity that can be applied to various conductive filler-polymer systems. But many researchers do relate the conductivity to polymer matrices with respect to the presence of polymer groups, polymer surface tension and different blends of polymer. Their influence on conductivity follows the similar trend as they affect percolation threshold which has been discussed in previous section and will not be addressed here.

One influencing factor that has not been dealt with is the compatibility of polymer matrix with conductive filler, which does have a substantial effect on conductivity. Gul et al. reported that [11] carbon black filled phenol-formaldehyde system has higher conductivity than carbon black epoxide resin system at the same filler loading. The poor compatibility of epoxide resin with the carbon black can account for this phenomenon. In the case of the epoxide resin there is a definite separation into two components, epoxide resin containing a small quantity of carbon black and a mixture of the filler with a small quantity of resin. A direct result is large aggregates of the filler is formed, which hinders the formation of chain structures and increases the resistivity. While phenol-formaldehyde system is more compatible with carbon black and carbon black is uniformly dispersed in the matrix, which will facilitate the formation of conductive network through the matrix. This can find its support in scanning electron micrograph studies.

Effects of the types of filler, their concentration, geometry and morphology

Carbon black is the most widely used conducting filler. However, short carbon fiber also has its own characteristics due to its high conductivity in polymer matrix. It is of great importance when high conductive system is required. By studying electrical conductivity of high density polyethylene-carbon fiber composites mixed with different concentrations of carbon black, Calleja and co-workers recognized that carbon fibers provide charge transport over a large distance and carbon black particles improve inter-fiber contacts [79]. As stated previously, the conductivity of conducting filler loaded polymer depends largely on the content of fillers. Both carbon black and short carbon fiber systems exhibit percolation phenomenon. There is a critical content at which the system experiences an insulator to conductor transition. Below this critical concentration, the fillers are just dispersed in the matrix as isolated individuals and there is no obvious conductive network existing through the matrix due to the large widths between the fillers. Thus the conductivity of the system depends mainly on the conductivity of the polymer matrix, which is generally non-conductive in nature, so the whole system appears as an insulator. In this region, increasing the filler content does not generate considerable effect on conductivity. At critical content, conductive networks in the matrix will suddenly form and a minor increase in filler content will result in a large increase in conductivity. This change of macroscopic properties reflects the variation in microscopic structure. Beyond this critical value, the conductivity of the system will mainly depend on the conductive networks formed by the fillers. Since conductive networks already exist, further increase in filler loading is similar to increase the diameter of a conductive wire, thus the conductivity will increase marginally against the increase of filler content. It is worthwhile that the content to obtain the conductive network is much lower for short carbon fibers than that for carbon black particles. This can be ascribed to the fibrous nature of short carbon fibers, which will aid the formation of the conductive network [22].

In particulate fillers the important geometrical and morphological aspects are the particle size, structure and porosity on which the formation of individual aggregates. It has been reported that small particle size leads to the formation of more conducting paths per unit volume [80, 81]. The smaller particles coalesce to form small aggregates, but their greater number results in a smaller gap between the aggregates, which aids the electron flow by electron hopping or tunneling. Abdel-Bary [82] observed the particle size dependence of conductivity of styrene-butadiene rubber (SBR) systems. It is found that, in some case, an increase of conductivity of five orders of magnitude arises from the particle size reduction. Furthermore, good surface chemistry, high aggregate shape and structure as well as high surface area will facilitate the formation of three-dimensional conductive networks, thus giving rise to high conductivity.

As for carbon fiber fillers, the fiber length, aspect ratio and distribution of fibers in the rubber matrix are important factors in controlling electrical properties of conductive composites. The fiber length to be mixed with polymer matrix should have a certain value: it should not be too long or it may act against proper dispersion due to fiber-fiber entanglements; very short fibers may adversely affect electrical properties leading to the formation of discontinuation among the continuous conduction paths responsible for high conductivity. But it is not easy to control the fiber length, since breakage will occur during mixing process due to the brittle nature of carbon fiber, the severity of which will depend on its initial aspect ratio and stress it experiences during the process [65].

Effects of temperature

For conductive polymer composite, temperature dependence of resistivity is a ubiquitous but complicate phenomenon, which has been the topic of many authors. According to the rate of increase in resistivity against temperature, we here categorize this behavior into two groups: gradual variation and abrupt variation.

Gradual variation

In many composites, the resistivity changes gradually with increased temperature. Depending on different polymers, different types, concentrations and properties of fillers as well as their interactions, the temperature coefficient of resistance may be positive (PTC), negative (NTC) or zero, which is the combined result of several processes that the composites undergo at high temperature. One is the difference of thermal expansion of conductive fillers and polymer matrix. Usually the polymer matrix will expand more than the conductive filler due to their different physical properties. This uneven thermal expansion results in an increase of distance between conductive fillers, thus making electron tunneling more difficult. Apparently, this effect leads to the increase of resistivity at high temperature. By contrast, a few other phenomena are operative in the system simultaneously, which cause an increase in conductivity. These processes include: the flocculation of particulate filler, leading to formation of further conductive networks during heating; high temperature electron emission between two ends of black aggregates which are separated by a smaller gap; and aerial oxidation leading to the formation of polar group. Therefore the temperature dependent behavior of conductive composite is mainly determined by the predominant process.

When the thermal mismatch between fillers and polymers prevails, the resistivity of composite will increase at high temperature, i.e. PTC effect [83]. If the processes that increase conductivity govern the electrical properties of composite, the resistivity will decrease at high temperature, i.e. NTC effect [57, 75]. This means the increase of the conductivity with increase in temperature more than compensates for the PTC effect. If the increase in resistivity just counterbalances the decrease with increasing temperature, i.e. the processes of destruction and reconstruction are almost equally probable and lead to a stable state of conductivity, the composite will exhibit temperature independent properties.

The nature of polymers, the filler and its concentration have a marked influence on the composite's temperature dependency of resistivity behavior. By studying acrylonitrile rubber (NBR), ethylene-propylene diene rubber (EPDM) and 50/50 NBR/EPDM loaded with short carbon fiber, Sau found these composites exhibit PTC properties and this trend is influenced by the polymer matrix, NBR-carbon fiber composite shows the smallest increase in the same temperature range at the same filler concentration [22]. For different blends of carbon fiber and carbon black loaded nitrile rubber composites, Pramanik et al. [66] related the resistivity variation with temperature (higher than 40 °C) to the blend ratios: carbon fiber-rich composites shows PTC behavior, whilst carbon black-rich composite undergoes NTC process. Abdel-Bary reported that different types of carbon black loaded styrene-butadiene rubber (SBR) systems show PTC, NTC and zero behaviors depending on filler type and concentration. Heavily loaded SBR in its temperature dependence of resistivity shows PTC effect, while lower filler content exhibits NTC effect. Zero temperature effect arises from the carbon black which has a tendency to form aggregates [82]. For PTC effect, increasing the concentration of conductive filler will decrease the effect progressively and sometimes the resistivity may become temperature independent [73]. This is because higher loading have a greater number of continuous conductive networks in the insulating polymer matrix compared to that of the composites with lower filler loadings; moreover the average interparticle gap is also lesser, which will improve the conduction of composite and partially counteract the increase of resistivity arising from mismatch of thermal expansion [13]. Sometimes increasing the filler content also reduces the NTC effect, although the reason is still unclear [23].

Several authors have observed the hysteresis phenomenon for the conductive composite, that is to say heating and cooling curves in the variation of resistivity with temperature do not follow the same path resulting in a hysteresis loop. The hysteresis decreases with increasing filler loading [73] and heating/cooling cycles [19, 23]. Increasing heating/cooling cycles diminishes temperature dependence of resistivity can be interpreted in the light of the following fact: after the composite experiences the heating/cooling cycle, a somewhat stabilized electrical network is formed; during next cycle, the effect of temperature on resistivity becomes relatively marginal and this trend is gradually intensified by increasing cycles. Thus, the more cycles the composite undergoes, the little hysteresis it exhibits.

Abrupt variation

In some conductive composites, the resistivity suddenly changes by several orders of magnitude in the vicinity of the polymer transition region, usually a small temperature interval centered on the crystal melting temperature. This behavior is referred to as thermoelectric switching properties, which may find its use in temperature self-regulation applications.

Bueche [84] found that carbon black-hydrocarbon wax ($C_{36}H_{74}$) system exhibits an abrupt increase in resistivity when temperature is elevated to about 73 °C. This may be explained in terms of the sudden change in volume. Since the wax melts at 73 °C with a consequence increase of volume of about 22%, the volume fraction of black drops precipitously as the temperature is raised above 73 °C, which will hinder the formation of conducting network and occurrence of electron tunneling due to the increased particle gaps and therefore bring about high resistivity. Narkis and Vaxman [24] investigated the behavior of resistivity with the variation of temperature in different types of carbon black/carbon black-carbon fiber loaded polyethylene systems. The thermoelectrical behavior was also observed for these systems; however, this only happened when the conductive filler concentration was low. It seems unlikely to achieve significant switching characteristic coupled with high conductivity. As is expected since only at low filler concentrations filler contact and overlap are broken during the system's expansion step accompanying the melting process, while this effect becomes insignificant for high filler loading. Another phenomenon should be noticed is a rapid resistivity decrease closely followed the sharp resistivity increase for most of the systems, which is considered to be associated with the changing distribution of conductive filler during the melting process of the semicrystalline polymer although this has not been scientifically supported. From point of view of application, it is an obvious drawback, since the switching properties will lose their significance once followed by a distinguished decrease in resistivity. Feller et al. [85] reported that by addition of poly (butylene terephthalate) to poly (ethylene-co-ethyl acrylate)-carbon black composite, the NTC effect can be eliminated but the PTC effect also diminishes and the composite becomes temperature stability, which obviously reduces the self-regulating heating ability of the composite.

Another disadvantage that prevents the practical applications of switching properties is the lack of electrical reproducibility due to irregular structure changes upon heating/cooling cycles. Narkis et al. [86] reported that by crosslinking, carbon black filled polyethylene system showed good electrical reproducibility after the first run and the resistivity decrease following the sharp increase disappeared. But these methods are still insufficient to eliminate all the undesired properties for practical application.

Conclusions

In recent years, significant progress has been made in manufacture and application of conductive polymer composites by blending conductive component with polymer matrices. To achieve high conductivity, several issues must be kept in mind during designing and manufacturing processes. Processing parameters must be tailored in order to eliminate the processing induced degradation of carbon black and carbon fiber; low viscosity and multiphase polymer matrices favor an increase of conductivity; for carbon black, small particle size, high structure, anisometric shapes and high microporosity are preferred; for carbon fiber, moderate fiber length and high aspect ratio aid the improvement of conductivity; additionally high compatibility of polymer matrix with conductive filler and uniformity of dispersion of conductive filler in polymer matrices contribute positively to the conductive property.

Meanwhile, carbon based conductive polymer composite is not without undesired characteristics. These materials are generally lack of temperature stability accompanied with hysteresis phenomenon during heating/cooling cycles which excludes them from consideration in many cases, especially in temperature variation environment. Further, sometimes these materials are incapable of providing enough conductivity required. As a result, many metal loaded composites have come into existence. Apparently, to resolve these problems completely will see an even more proliferation of carbon based composites.

Attempting to achieve conductive composites with improved service properties, silica-carbon-epoxy resin nanocomposites have been prepared. It is observed that the conductivity of composites is high dependent on not only the content of carbon black but also silica concentration [87]. The conductivity of composites is governed by the conductive network developed by carbon black particles. The introduction of silica to the composites will facilitate or block the formation of conductive paths and consequently impose effect on the conductivity of composites. Further work is still ongoing.

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