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SURVEY OF MICRO/NANO FILLER USE TO IMPROVE SILICONE RUBBER FOR OUTDOOR INSULATORS

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Abstract. Among the new insulating materials widely used in high-voltage outdoor insulation, silicone rubber has received the most attention. Indeed, silicone rubbers are gaining in popularity as an effective counter-measure to insulator contamination problems. However, pure silicone rubber shows little tracking and erosion resistance. So, some properties of silicone rubber need to be improved to extend service life. The fillers are added to the polymer to promote specific properties and also to reduce costs.

To improve the surface hydrophobicity, electrical conductivity, relative permittivity and thermal conductivity of polymeric materials, micro/nanofillers are added. In this review, we present the state of the art on the most common micro/nanofillers for dielectric applications. Special attention is put on the property modification of silicone rubber brought about by filler incorporation for outdoor insulation applications.

A need for comprehensive and exhaustive review of micro/nanofiller used in the area of outdoor insulator is being felt. This paper is intended to fulfil it. Literature surveys showed some filler as potential candidate for outdoor insulator application. However, much work is still needed to fully characterise and to optimise their property to establish for commercial application.

1. INTRODUCTION

Over past few years, polymer nanocomposites have attracted a great deal of attention. In contrast to conventional filled polymers, nanocomposites are composed of nanometer-sized fillers (nanofillers) which are homogeneously disturbed within the polymer matrix.

After review of the available data, polymer nanocomposite has been found to be promising as near-future advanced dielectric and electrical insulation from the viewpoint of its excellent properties [1]. In this paper we focused on the composite polymeric materials applicable for outdoor insulation.

Composite insulators have been very popular with utilities and equipment manufacturers all over the world since they first appeared in the 1960s. Among their advantages, composite designs offer lighter weight, less breakage, improved seismic performance and more flexibility in design than ceramic insulators. These features can translate into lower installation cost, greater durability and more aesthetically pleasing line design.

Composite insulator designs generally consist of:

i) a fibreglass rod or hollow core for mechanical strength,

ii) external weathersheds made from either silicone rubber (SIR), EPDM or EPR, and

iii) metal fittings for attachment (Fig. 1) [2-7].

For outdoor insulator application, silicone rubber showed better performance than most organic polymers such as EPDM [4]. Consequently, due to the relative importance of silicone rubber as base

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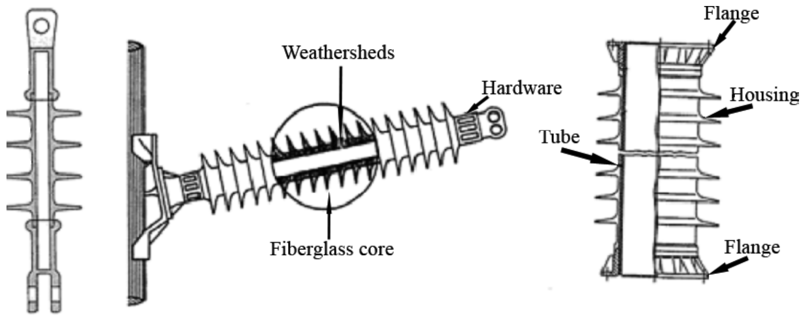

Fig. 1. Designs and types of composite insulators, see [2].

polymer for insulator applications, the present work focuses on silicone rubber materials.

2. SILICONE RUBBER

Polydimethylsiloxane (PDMS) is the basic polymer for silicone rubber (SIR), the hydrocarbon methyl groups being hydrophobic and water repellent (Fig. 2) [6,7]. Furthermore, SIR exhibits the ability to restore its hydrophobicity even after a pollution layer has built up on the surface, which can suppress the development of leakage currents, dry-band arcing and flashover [8,9].

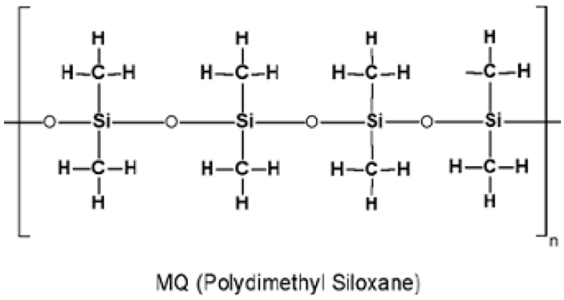

Fig. 2. Chemical structure of PDMS (Poly Di-Methyl Siloxane), the Low Molecular Weight component of silicone rubber.

The hydrophobic recovery property may be attributed at least in part to the transfer of low molecular weight (LMW) from bulk to surface and the subsequent adsorption process of LMW on the contaminant, either physical or chemical adsorption [10]. The microscopic diffusion of fluid serves to encapsulate contaminant particles and prevent moisture absorption (Fig. 3).

Besides the content of LMW in the bulk, the chemical properties of the polluting substance have much influence on the possibility and extent of hydrophobicity transfer [11].

However, SIR insulators suffer from loss of hydrophobicity, decreased tracking and erosion resistance, and degradation of their surface under wet atmospheric conditions such as heavy fog, drizzling rain and acid rain, etc. The loss and recovery of hydrophobicity in silicone rubber has been the subject of several research works [12-15]. According to these studies, the loss of hydrophobicity in polymeric insulators is influenced by three major factors:

i) Electrical discharge (partial arc, corona),
ii) Adsorption of pollution layers,
iii) UV radiation [14].

Currently, two forms of silicone rubber are widely used for outdoor high-voltage insulation, namely, high-temperature vulcanizing (HTV), used mainly as a weathershed; and room temperature vulcanizing (RTV), used mainly as hydrophobic coating on ceramic surfaces thus improving their contamination performance [12]. HTV is cured at high-temperature and pressure, catalyzed by peroxide-induced free radicals or by hydrosilylation. RTV is cured at lower temperature, i.e. around room temperature, by condensation reaction as one component system [3]. RTV contains cyclic LMW (5 wt.%) polydimethsiloxane while HTV has cyclic and linear LMW (3 wt.%) polydimethylsiloxanes [16].

The different properties of HTV and RTV may be attributed to the linear LMW in HTV, which diffuses better [16]. The maintenance of outdoor insulators is an art learnt through life-long experience. In this art, methods like high-pressure washing, silicone dielectric greases and RTV silicone coatings have been applied to porcelain and glass insulators. RTV silicone rubbers have proven to be more effective, offering much better long-term capacity to provide anti-pollution properties [17].

This maintenance practice imparts water repellence to the surface of porcelain insulators, thus limiting leakage current and suppressing flashover. Today, RTV coatings are gaining in popularity as an effective counter-measure to insulator contamina-

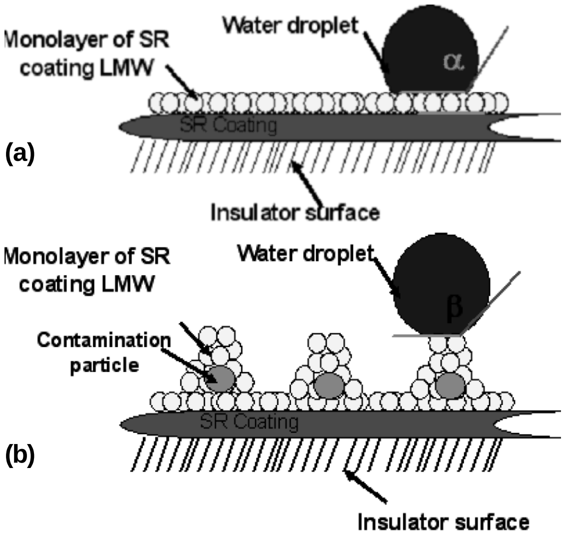

Fig. 3. Illustration of hydrophobicity recovery.

tion problems. This method is attractive because it reduces the need to replace insulators. The coating can be applied by dipping, painting, and/or spraying. The liquid polymer layer vulcanizes inside a flexible rubber layer when exposed to moisture in the air. However, the major problem with silicone rubber is its susceptibility to aging. The combined effect of electrical stresses (electric field and leakage current) and environmental stresses (UV, temperature, pollution and acid rain) will accelerate the aging process.

3. FILLERS

Pure silicone rubber shows little tracking and erosion resistance. In order to extend service life and improve service effect, some properties of silicone rubber need to be improved. The fillers are added to the polymer to improve specific properties and also to reduce costs. For a given material, the higher the filler content, the higher tracking performance will be, but this could hinder its hydrophobic properties [17,18].

Otherwise, the extent of nanocomposite property improvement depends on filler concentration, filler morphology, such as particle size and structure, the degree of dispersion and orientation in the matrix, and also the degree of adhesion with the polymer chains [18,19].

To improve particle dispersion, several techniques other than mixing are available [20]. This includes the surface modification of the micro/nanoparticles (micro/nanofillers) by physical and chemical methods using surfactants. Ramire et al. [21] examined the effect of surfactants on the electrical and mechanical properties of a two-part silicone rubber (SiR) matrix. They noted that surfactants greatly influence nanofiller dispersion. But there must be balance between matrix adsorption and the dispersion of the particles. A high concentration of surfactant in the matrix material can lead to reduced adsorption properties [21]. There are two types of fillers: reinforcing and extending. The reinforcing type can be used to improve tensile strength, modulus, tear strength and abrasion resistance. Common silicone rubber reinforcing fillers are fumed silica, aerogel silica, and carbon black. The extending filler is a semi-reinforcing or non-reinforcing material. It may be used to impart some desirable property and also extend the formulation. Common extending fillers are ground quartz, titanium dioxide, clay, whiting, alumina trihydrate (ATH), and zinc oxide.

Based on a literature survey, improvement in the surface hydrophobicity, electrical conductivity, relative permittivity and thermal conductivity of silicone rubber dielectrics make them useful for outdoor high-voltage insulation applications.

Below we discuss briefly the mechanism by which filler enhances the properties of silicone rubber dielectrics.

I. Surface hydrophobicity

If SIR had such surface properties as anti-adhesion, low surface energy and super-hydrophobicity, the adhesion of solid contaminations could be reduced, leading to what is termed a “self-cleaning” surface. Thereby, surface leakage currents and pollution flashovers due to contamination would also be suppressed efficiently.

Several methods, like plasma treatment, have been proposed to increase the hydrophobicity of silicone rubber. Recently Gao et al. [22,23] employed plasma treatment to modify the surface of silicone rubber. In particular, they utilised CF_4 radio frequency plasma to introduce fluorine groups onto the polymer surface. It is an effectual way to lower surface adhesiveness, surface energy and coefficient of friction, and thus create a super-hydrophobic surface. They achieved a super-hydrophobic silicone rubber with a water contact angle of 150° [22,23].

II. Electrical conductivity

Indeed, most polymers are usually electrical insulators but need to be conductive in some applications, especially for dissipating electrostatic discharges. Incorporating conductive filler particles into the polymeric medium is an interesting way to produce an electrically conductive polymer. At a given amount of conductive particles, called the percolation threshold, a continuous network of filler is formed

across the matrix and the material undergoes a sudden transition from insulator ($>10^{10}$ Wcm) to conductor ($<10^{5}$ Wcm) state due to the formation of a continuous filler network as the filler content increases (Fig. 4) [24,25].

III. Relative permittivity

Excessive electrical stress on insulators can cause local discharge, flashover or puncture, and further lead to the system failure. Several approaches such as grading rings, floating shields, resistive layers and high-permittivity insulation materials are essential to achieve stress control [26]. Among them, the use of high relative permittivity materials for stress relief in insulation systems is well known [27].

IV. Thermal conductivity

The heat generated by dry-band arcing is considered to be the primary source of material degradation [28,29]. Gorour et al. [30] concluded that material degradation is a function of the leakage current magnitude and dry band arcing time in a particular spot. The heat generated can bring the temperature on the insulator surface to 500 °C or higher, which is sufficient to cause the silicone rubber polymeric backbone to break into low chain polymers [30,31]. So the application of thermally conducting polymer seems to be an interesting solution to dry band arcing.

In this review, we present the state of the art on the most common fillers for dielectric applications. In particular, we report on the property modification of silicone rubber for outdoor insulation applications, brought about by filler incorporation. Theses fillers may be classified into four types: inorganic oxide materials, carbonaceous materials, organic materials and metals.

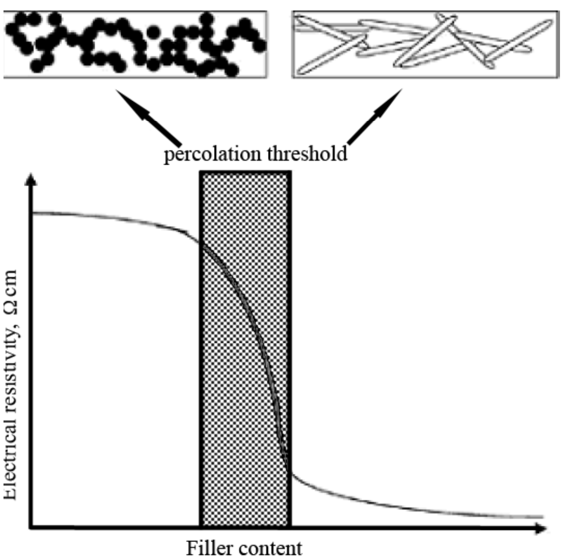

Fig. 4. Polymer resistivity relative to conductive filler particle content, replotted from [24].

It should be noted that only alumina trihydrate, silica and nanoparticles of carbon have yet been incorporated into silicone rubber for outdoor insulator applications, but none of the other fillers.

3.1. Inorganic oxide materials

The use of silicone rubber compounds with inorganic oxide materials is widely studied. The most common inorganic oxide materials used as filler are described below, as found in the literature.

3.1.1. Alumina trihydrate and silica

Numerous studies have reported on the benefits of using alumina trihydrate (ATH) [32,33] and silica (SiO_2) [34,35] as fillers in silicone rubber, although one controversial study has indicated that ATH is not necessary to impart tracking and erosion resistance [36].

Typically, ATH is added to the silicone rubber as an anti-tracking agent and flame retardant. Han et al. [37] worked on the influence of the ATH content and high-temperature vulcanized silicone rubber (HTV) on the electrical insulation properties, tracking and erosion resistance. Their results showed that silicone rubber containing 130 phr (parts per hundred-rubber) of ATH significantly increases the arc resistance, tracking, and erosion resistance of the silicone rubber. This optimum amount of ATH can be widely used as housing material for high-voltage insulators [37]. Another study [38] showed that larger amounts of ATH to HTV lead to better erosion resistance but will result in declined mechanical properties.

Also, it has been reported that using ATH filler in the material formulation influences the electrical performance of the RTV silicone-rubber coating. Kim et al. [39] concluded that an optimum filler content may exist, which would ensure the desired performance and lifetime of a coating. At the same time, higher ATH filler levels slowed down the migration of the silicone fluid from the bulk to the surface of the coating. Other work done by Farhang et al. [40] showed that the best performance belonged to the sample with 70 pph ATH (70 parts of ATH in 100 parts of polymer). Adding 10 pph silica also improves the performance of coatings at ATH quantities between 35 and 70 pph, but replacing 10 pph ATH with the same amount of silica was not productively efficient.

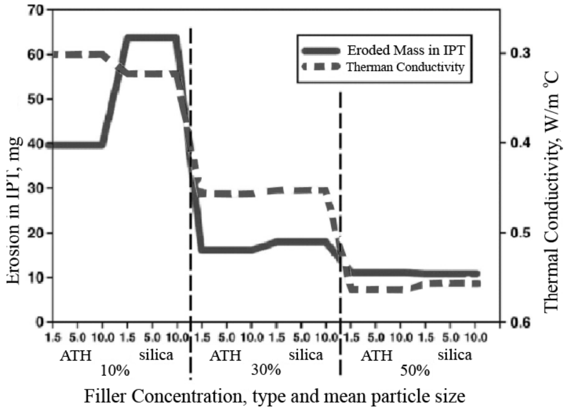

Fig. 5. Erosion and thermal conductivity relative to type and amount of filler, data from [43].

Dong et al. [41] showed that particle size may also influence filler performance. An optimum size of 4.5 μm has been recommended.

Silica, which is classified as a semi-reinforcing filler, improves the physical properties of silicone compositions through molecular bonding with the silicone polymer. But ATH filler (Al_2O_3 $3(H_2O)$) imparts slightly better thermal conductivity to silicone rubber compositions than silica (SiO_2) does [42]. Moreover, as the local hotspot temperature from dry-band arcing exceeds 220 °C, ATH begins to release water of hydration, which is generally recognized as an efficient way to cool the hotspots. However, hydrate release also causes surface roughness, which leads to further wetting and dry-band arcing [43]. The thermal conductivity of the composite material is dependent on the thermal conductivity, concentration, particle size, and bonding of the filler particles to the silicone matrix. The effects of the amount, particle size, and mixing mass ratio of the filler particles on the thermal conductivity and mechanical properties of silicone rubber have been analyzed [44].

Meyer et al. [43] and Sanaye-Pasand et al. [45] concluded that the thermal conductivity of the composite material is the main criterion governing material erosion. Meyer et al. [43] demonstrated that at low concentration the degree of protection is higher for the ATH filler. However, as the amount of filler increases, both of the ATH and silica fillers yield the same protection level, as seen in Fig. 5.

Generally, hydroxide fillers are considered to be the best flame retardants. The good erosion performance of the silicone rubber filled by magnesium dihydroxide (MDH) nanopartciles has been reported by Venkatesulu et al. [46]. They also compared the erosion resistance of nanofilled MDH (5 wt.%) and micron-filled ATH (5 wt.%) silicone rubber composites. Their results demonstrate the better performance of MDH in terms of eroded mass, depth, width and length at this filler concentration.

3.1.2. Zinc oxide

Zinc oxide (ZnO) is an important semiconductor material with a band gap of 3.3 eV at room temperature. Zinc oxide fillers increase the relative permittivity and also the thermal conductivity of the composite. The mechanical and thermal properties of silicone rubber incorporated with zinc oxide (ZnO) have been studied [47-49]. Sim et al. [49] showed that ZnO filled silicone rubber exhibited better thermal performance compared to Al_2O_3-filled silicone rubber [49]. ZnO is also a better reinforcement filler for improving the mechanical properties of the silicone-rubber compound than Al_2O_3 [47]. However, incorporation of ZnO fillers delays the curing process, whereas an enhancement in cure rate was observed for Al_2O_3 [47]. The percolation threshold has been reported to be 31.4% vol for ZnO filler loading [48].

3.1.3. Titanium oxide

In recent years, titanium dioxide has been extensively utilized in environmental applications such as self-cleaning, anti-bacterial and waste-water purification [50,51].

TiO_2 is a wide band-gap (3.2 eV) semiconductor which exhibits high photocataltic efficiency [52,53]. With its combined features, low cost and stable properties, TiO_2 makes a good candidate for polymeric material protection.

The use of TiO_2 as filler in polymeric materials also improves the thermal and electrical properties [54]. So, TiO_2 is a useful filler for achieving higher thermal conductivity and relative permittivity [27,52]

However, little has been published regarding the properties of TiO_2-filled silicon rubber for outdoor applications. Silva et al. [55] studied the improvement of the mechanical and photocatalitic characteristics of silicone rubber incorporated with TiO_2. Their results indicated that the thermal stability of PDMS/TiO_2 was enhanced by adding 10 phr of TiO_2. However, the further addition can accelerate the thermal degradation of the matrix [55]. Increasing the amount of TiO_2 also led to a decrease in the cross-linking density of the matrix, causing the rubbers to swell.

3.1.4. Calcium carbonate

Although a number of studies have been devoted to the analysis of silica or carbon-black-filled elastomer networks, little work has been done on the reinforcement of $CaCO_3$-filled elastomer networks. With the development of nanotechnology, nano-sized calcium carbonates have attracted more and more interest due to the abundance of these raw materials, low cost compared with fumed silica, and the generation of activity by surface treatment. The nano size, larger surface area and active sites of nanocalcium carbonate make it feasible for use as reinforcing agent, just like carbon black or silica [56].

Furthermore, $CaCO_3$ is a wide-band gap insulator 6.0±0.35 eV [57] with rhombohedral unit cell and dielectric constant 8.19 [58,59].

Great improvement of the mechanical, rheological and flame retarding properties of PDMS reinforced by nanocalcium carbonate has been reported [60, 61]. According to a study conducted by Peng et al. [56], PDMS filled with 80 phr nano-$CaCO_3$ showed enhanced mechanical properties.

Recently, Yang et al. [62] prepared superhydrophobic films by means of mulberry-like $CaCO_3$/SiO_2 composite particles and self-assembled PDMS. This surface is superhydrophobic with a water contact angle (WCA) above 160° and sliding angle (SA) below 10°. This excellent hydrophobicity may be attributed to the synergistic effect of micro–submicro–nano-meter scale roughness (fabricated by composite particles) and the low surface energy (provided by polydimethylsiloxane) [62].

3.1.5. Barium titanate

Barium titanate ($BaTiO_3$) has been extensively employed as a ceramic filler [63-68]. It presents a high dielectric constant and high electrical breakdown strength [66-68].

Adding $BaTiO_3$ nanoparticles to polyimide also results in better thermal stability of the composites. Increasing the $BaTiO_3$ content led to higher decomposition temperature. More importantly, the dielectric constants could be controlled by the content of $BaTiO_3$, as they increased with increasing $BaTiO_3$ content [67,68].

The control of Polyetherimide /$BaTiO_3$ dielectric properties was examined by Choudhury et al. [67]. They obtained good dielectric constants as high as 37 (at 1kHz) for the composite containing 50% vol of $BaTiO_3$ particles [67]. As yet there has been no study regarding the properties of $BaTiO_3$-filled silicone rubber for outdoor insulator applications.

Table 1. Role of most common inorganic fillers used in dielectric applications.

Filler	Property Modification
Al_2O_3	Thermal conductivity, anti-tracking & erosion
SiO_2	Thermal conductivity, anti-tracking & erosion
TiO_2	Relative permittivity, thermal stability, photocatalytic
ZnO	Electrical conductivity, relative permittivity, thermal conductivity, mechanical property
$CaCO_3$	Flame retarding, hydrophobicity
$BaTiO_3$	Relative permittivity, thermal stability

The influence of some inorganic oxide fillers on composite properties is summarized in Table 1.

3.2. Carbonaceous materials

Conducting polymer composites filled with carbonaceous materials such as carbon black, carbon fibre, graphite and carbon nanotube have been widely studied over the past few decades. It has been observed that the combined electrical, mechanical, and thermal properties are strongly influenced by filler type, size, shape, content, distribution, and also the processing methods of these composites. An S-shaped curve of electrical conductivity occurs with increasing filler content in all these composites. However, a sharp decrease in mechanical properties occurs when a higher contents (usually > 15 wt.%) of filler were loaded.

3.2.1. Carbon-black particles

Carbon black is widely used as conductive filler in polymer materials. Conductive filler particles mixed into a polymer matrix form a network that can carry an electrical current as well as a mechanical load [69,70]. Reviews of most of these studies were reported in [71].

The electrical properties and rheological behaviour of carbon black/PDMS matrices were examined by Rwei et al. [72]. Significant increases in electrical conductivity, form 10^{-9} to 10^{-4} $(\Omega.cm)^{-1}$, were observed.

Silicone rubber incorporated with carbon nanoparticles was used as a coating for high-voltage porcelain insulators by Liao et al. [70]. These

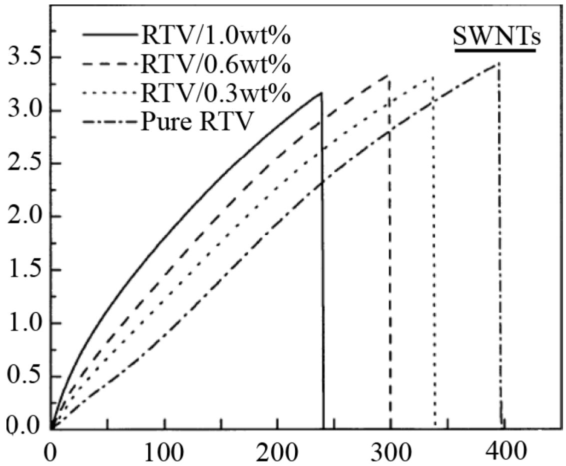

Fig. 6. Stress-stain curve for RTV/SWNT composite, data from [85]. The stress is the engineering stress and the strain is the true strain.

coatings behaved as semiconducting glaze and the results are encouraging. The semiconducting glazed insulators are known to perform well in polluted conditions [73] due to the surface drying effect of the Joule heating generated by the current flowing through the surface and the uniform voltage distribution along the surface.

They demonstrated experimentally that a semiconducting RTV coating on insulators delays ice formation and reduces the amount of ice by as much as 50 wt.% [70]. Flashover occurred at higher voltages on coated insulators than on uncoated insulators [70].

3.2.2. Graphite and expanded graphite

Natural graphite exhibits excellent electrical and thermal conductivities. Graphite is a layered material composed of several alternating carbon layers. The carbon atoms are in-plane covalently bonded while graphite layers are bound by much weaker van der Waals forces, which makes intercalation possible. Expanded graphite is obtained by intensive heating of graphite intercalation compound (GIC), as described elsewhere [74]. Because of big pores and groups like —OH and —COOH, expanded graphite has good miscibility with both non-polar and polar molecules [75].

Over the past several years, a number of papers have studied material preparation and characterization of various polymer nanocomposite systems reinforced with expanded graphite (EG) [41,75,76]. Some results on the improvement of electrical and mechanical properties of silicone rubber filled with graphite nanosheet were presented by Chen et al. [77].

Mu et al. [78] studied the effect of EG content and preparation methods of silicone/expanded graphite (EG) composites on the thermal conductivity of composites.

They stated that the increase of EG content greatly improves the thermal conductivity of silicone/EG composites. They also showed that the solution intercalation method has better effect than the melt-mixing method for improving the thermal conductivity of composites.

3.2.3. Carbon nanotubes

Great interest has been shown for carbon nanotubes since their discovery in 1991 [79], as they exhibit exceptional electrical and mechanical properties, such as:

a. Electric-current-capacity 1,000 times greater than copper
b. Thermal conductivity twice as high as diamond
c. Tensile strength 10-100 higher than steel [80].

Their exceptional electrical and mechanical properties are expected to impart major enhancements in various properties of polymer composites at relatively low filler loadings (< 10 wt.%) [81].

Nevertheless, poor dispersion and poor interfacial bonding limit the full utilization of carbon nanotubes for reinforcing polymeric media [80,82].

Carbon nanotubes can be visualized as graphene layers rolled into cylinders consisting of a planar hexagonal arrangement of carbon-carbon bonds. Their outstanding properties are a consequence of this unique bonding arrangement combined with the topological defects required for rolling up the sheets of graphite into cylinders. During growth, depending on the synthesis methods, they can assemble either as concentric tubes (multiwall nanotubes, MWNT) or as individual cylinders (single-wall nanotubes, SWNT). Their diameters range from about one nanometre to tens of nanometres with lengths ranging from several micrometers to millimetres or even centimetres [82]. The influence of carbon nanotubes on the mechanical, electrical and thermal properties of composites will be discussed further below.

3.2.3.1. Mechanical properties

The high and reversible deformability of elastomers is of great industrial importance. Typically however, the initial modulus and durability of such materials are low, and an additional reinforcing phase is required for practical use.

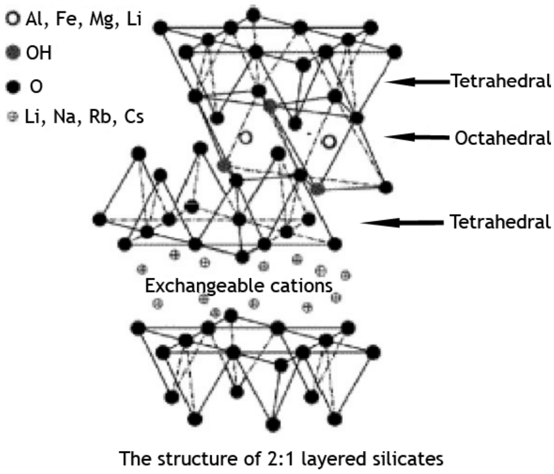

Fig. 7. Schematic structure of MMT, replotted from [100].

Significant improvements in mechanical properties of polymeric matrices by adding CNT have been reported [17,83,84]. Allaoui et al. [84] found that the incorporation of 1 wt.% of MWNTs into an epoxy matrix results in an increase in the Young's modulus and in the yield strength by, respectively, 100% and 200%, compared to the pure matrix. However, few studies about the behaviour of silicone rubber/CNT are found in the literature.

Tensile tests performed on a RTV silicone rubber/SWNT exhibit dramatic improvement in mechanical properties as a function of filler content, as shown in Fig. 6 [85]. Also, the initial modulus increase has been shown to be approximately linear with weight fraction, with a slope of 200%/ wt.%.

The mechanical properties of PDMS/MWCNT composites were analyzed by Wu et al. [86]. They reported that MWCNT yields significant improvements in the mechanical properties of silicone rubber (PDMS).

3.2.3.2. Electrical properties

In addition to improving mechanical properties, carbon nanotubes impart conductivity to low-resistivity elastomeric matrices. Carbon materials provide electrical conduction and lead to a change in resistivity with increasing filler volume fraction in the polymer matrix [81].

Carbon nanotubes with quasi-one-dimensional structure can be metallic or semiconducting, depending on their structural parameters. This makes the CNT a core element in the composite materials for many electronic applications. It turns out that the MWCNT composites had a lower electrical percolation threshold than SWCNT [87].

It has been generally accepted until now that the electrical conductivity of the composites is significantly raised as the CNT loading increases. Much effort has been devoted to exploiting the electrical properties of polymer/CNT composites by controlling the orientation of CNT to make an ultra-low electrical percolation threshold plausible.

Sometimes electrical insulating properties are demanded from high-performance polymer–CNT composites. For this purpose, enhanced electrical conductivity as a result of CNT incorporation may be disadvantageous. However, to the best of our knowledge, no paper has been published to describe the control and constraint of the electrical conductivity of polymer–CNT composites. A novel method to functionalize CNT sidewalls with a SiO_2 layer is reported to provide a flexible way for preparing materials with controlled electrical conductivity as well as enhanced mechanical properties [88].

Jiang et al. [89] studied the dielectric properties of MWNT/VMQ composites. They reported a huge dielectric constant of composite as the concentration of MWNT was near a low percolation threshold.

Significantly enhanced electrical conductivity using the modified carbon nanotube was also observed by Jiang et al. [90]. They surface treated the MWNT with c-aminopropyltriethoxy silane. In this case, the electrical conductivity of the composite becomes 7 orders of magnitude larger than that of silicone rubber [90].

3.2.3.3. Thermal properties

Thermal conductivity of SWNT/epoxy composites was studied by Biercuk et al. [91]. Samples loaded with 1 wt.% non-purified SWNT showed 70% increase in the thermal conductivity at 40K, and 125%

Table 2. Role of carbonaceous materials used as filler for dielectric application.

Filler	Property Modification
Carbon black	Electrical conductivity, mechanical properties
Expanded graphite	Thermal conductivity, electrical properties, mechanical properties
SWNT	Mechanical properties, thermal conductivity
MWNT	Dielectric constant, electrical conductivity, mechanical properties

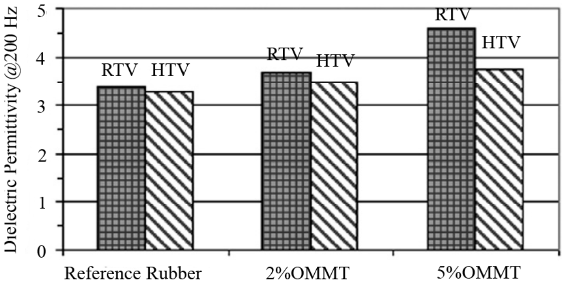

Fig. 8. Role of OMMT on the dielectric permittivity of RTV and HTV silicone rubbers measured at 200 Hz, replotted from [109].

increase at room temperature. Commonly, CNT-filled nanocomposites have higher thermal conductivity, compared with polymer composites embedded with carbon fibres of larger diameter such as vapour-grown carbon fibres (VGCF) [92].

However, the relatively high cost of SWNTs and MWNTs has precluded their widespread application as fillers for polymer nanocomposites. Table 2 lists the carbonaceous fillers incorporated into composites and their effects on composite properties.

3.3. Metallic materials

Numerous studies have shown the interest of using metallic particle fillers in the polymer matrix [93]. It has been found that the addition of metal particles, e.g. nickel [93], iron [94], copper [93, 94], zinc [95], and aluminium [94,96] into polymer results in an increase of both electrical and thermal conductivities of the composites. The effect of iron, silver and zinc powder on the mechanical properties of composites was also studied in [95,97,98]. The work of Singh et al. [99] reports on how aluminium powder improved the dielectric constant of epoxy composites.

To the best of our knowledge, there have been no studies regarding the properties of powder-metal-filled silicone rubber for outdoor applications. Table 3 shows the most common powder metals used as filler for dielectric application.

Table 3. Role of most common powder metals used as filler for dielectric applications.

Filler	Property Modification
Nickel	Electrical conductivity, thermal conductivity
Iron	Electrical conductivity, thermal conductivity, mechanical properties
Copper	Electrical conductivity, thermal conductivity
Zinc	Electrical conductivity, thermal conductivity, mechanical properties
Aluminium	Electrical conductivity, thermal conductivity, dielectric constant
Silver	Mechanical properties

3.4. Organic materials

In recent years, rubber/layered silicate nanocomposites such as montmorillonite (MMT) have received particular attention because they often exhibit unexpected properties, especially mechanical properties as reinforcing fillers. They are even approaching commercialization in certain application areas.

MMT is a hydrated alumina-silicate clay composed of units of two silicate tetrahedral sheets with a specific alumina octahedral sheet (Fig. 7). The silicate layers of MMT are planar, stiff and about 10 Å in thickness, and 1,000 to 2,000 Å in length and width [100,101].

Currently, among several fillers used in the silicone rubber industry, aerosilica is the most used reinforcing agent. Because it is expensive, conglomerates easily, and is a health hazard for workers, researchers have recently focused on the development of other reinforcing fillers such as organic montmorillonite (OMMT) to replace aerosilica [102]. These organophilic montmorillonite (OMMT) clays with lower surface energy polymer molecules, which make them more compatible with organic polymers, may be able to intercalate within the galleries, under well-defined experimental conditions [103]. Much effort has been directed at improving the mechanical properties of silicone rubber using montmorillonite clays [103-108].

In particular, an interesting study was conducted by Yang et al. [107] on the mechanical and flame retardant properties of silicone rubber/montmorillonite composites. Using magnesium hydroxide (MH) and red phosphorus (RP) as synergistic flame retardant additives, they obtained a flame-retardant MVMQ/montmorillonite composite. This nanocomposite shows higher thermal stabilities, flame-retardant properties and excellent mechanical properties compared with an MVMQ basal polymer matrix [107].

For MVMQ/OMMT composites containing 1 wt.% montmorillonite, the decomposition temperature is higher (129 °C) than that of MVMQ as basal polymer matrix [107]. This kind of silicone rubber nanocomposite could be considered to be a promising flame-retardant composite.

The effect of organically modified montmorillonite (OMMT) on the dielectric properties of silicone rubber was examined by Razzaghi et al. [109]. OMMT was added to this rubber in two concentration levels, 2 wt.% and 5 wt.% [109]. The results are summarized in Fig. 8.

Their results also showed that the order of organoclay layers in the less dispersed structure of the clay imparts an additional ionic polarization and higher dielectric permittivity compared to clay layers that are more dispersed and have lost their order.

Kaneko et al. compared the effect of natural MT and organically modified MT clays on some properties of PDMS [110]. Both clays enhanced the thermal stability and the mechanical properties of PDMS with regard to tensile strength and modulus.

4. SUMMARY

In this review, the researches carried out on nanofillers reinforced silicone rubber are presented. After a brief description of the silicone rubber compound and the aging process, the most common fillers used for dielectric application are listed and discussed. In particular, the role of these fillers on the property modification of silicone rubber dielectrics, such as surface hydrophobicity, electrical conductivity, thermal conductivity, and permittivity are mentioned.

Among the fillers used, ATH and silica are most often used by industrial manufacturers for outdoor insulator applications. Numerous studies have examined the effectiveness of these fillers for improving the tracking and erosion resistance of silicone dielectrics for outdoor insulators. Nanoparticles of carbon black were recently incorporated into RTV silicone rubber to produce a semiconducting coating on the porcelain insulator. The effectiveness of this coating was demonstrated.

A literature survey suggests using a composite of nano, micron and sub-micron fillers to increase the hydrophobicity of insulators. The importance of well-dispersed nanoparticles on the improvement of the mechanical and electrical properties of polymers is also emphasized. However, one of the problems encountered is that the nanoparticles agglomerate easily because of their high surface energy.

Applying semiconducting materials like the nanoparticles of carbon, TiO_2 and ZnO are expected to play a role as innovative insulating materials. In particular, the semiconducting feature shows great promise for the development of outdoor insulators for use in cold regions.

This review provides a good perspective on the application of nanofillers in insulating materials. Further study is ongoing in this field.

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REFERENCES

[1] C. Sumereder and M. Muhr // *Proc. 19 CIRED* **19** (2007) 594.

[2] R.S. Gorur, E.A. Cherney and J.T. Burnham, *Outdoor Insulators* (Phoenix, Ariz, USA, 1999).

[3] M. Amin, M. Akbar and S. Amin // *Sci. China. Ser. E: Technol. Sci.* **50** (2007) 697.

[4] R Hackam // *IEEE Trans. Dielectr. Electr. Insul.* **6** (1999) 557.

[5] J.K. Kim and IN-HN. Kim // *J. Appl. Polym Sci.* **79** (2001) 2251.

[6] J.P. Reynders and I.R. Jandrell // *IEEE Trans. Dielectr. Electr. Insul.* **6** (1999) 620.

[7] S. H. Kim, E.A. Cherney and R. Hackman // *IEEE Trans.* Elec *Insul.* **27** (1992) 610.

[8] G.G. Karadv, F.M. Shah and R.L. Brown // *IEEE Trans. Power Delivery.* **10** (1995) 965.

[9] J. Kim, M. K. Chaudhury and M.J. Oweny // *J. Colloid. Interface. Sci.* **226** (2000) 231.

[10] H. Homma, T. Kuroyagi, K. Izumi, C.L. Mirley, J. Ronzello and S. Boggs // *IEEE Trans. Dielectr. Electr. Insul.* **6** (1999) 370.

[11] S. Wang, X. Liang, Z. Cheng, X. Wang and Z. Li, *Hydrophobicity changing of silicone rubber insulators in service* (The project of NSFC (50025720) supported the research).

[12] J.W. Chang and S.R. Gorur // *IEEE Trans. Elec. Insul.* **1** (1994) 1039.

[13] Y. Zhu, M. Otsubo, C. Honda and S. Tanakav // *Polym. Degrad. Stab.* **91** (2006) 1448.

[14] M. Amin, M. Akbar and S. Amin // *Rev. Adv. Mater. Sci.* **16** (2007) 10.

[15] H. Hillborg and U.W. Gedde // *IEEE Trans. Dielectr. Electr. Insul.* **6** (1999) 703.

[16] J.P. Renders, I.R. Jandrell and S.M. Renders // *IEEE Trans. Dielectr. Electr. Insul*. **6** (1999) 620.

[17] E.A. Cherney // *IEEE Electr. Insul. Mag.* **11** (1995) 8.

[18] Y.S. Song and J.R. Youn // *Carbon* **43** (2005) 1378.

[19] H. Deng, E.A. Cherney and R. Hackam // *IEEE Electr. Insul. Dielectr. Phenomena Conference* (1993) 598.

[20] M.Z. Rong, M.Q. Zhang and W.H. Ruan // *Materials Sci. Techn*. **22** (2006) 787.

[21] I. Ramirez, E.A. Cherney, S. Jayaram and M. Gauthier // *IEEE Trans.* Elec. *Insul.* **15** (2008) 228.

[22] S.H. Gao, K.S. Zhou, M.K. Lei and L.S. Wen // *Plasma Chem. Plasma Process* **28** (2008) 715.

[23] S.H. Gao, K.S. Zhou, M.K. Lei and L.S. Wen // *Appl. Surf. Sci.* **255** (2009) 6017.

[24] L. Bokobza // *Vib. Spectrosc*. **51** (2009) 52 .

[25] J.Y. Yi and G.M Choi // *J. Electroceram*. **3** (1999) 361.

[26] H. J. Wei, S. Jayaram and E.A. Cherney // *J. Electrostat.* **63** (2005) 273.

[27] E.A. Cherney // *IEEE Trans. Dielectr. Electr. Insul.* **12** (2005)1108.

[28] S. Kumagai and N. Yoshimura // *IEEE Trans. Dielectr. Elect.r Insul.* **8** (2001) 203.

[29] T. G. Gustavsson, S. M. Gubanski, H. Hillborg, S. Karlson and U.W. Gedde // *IEEE Trans. Dielectr. Electr. Insul.* **8** (2001) 1029.

[30] R. S. Gorur, E. A. Cherney and R. Hackam // *IEEE Trans. Power Delivery* **3** (1988) 1892.

[31] L.H. Meyer, S.H. Jayaram and E.A. Cherney // *IEEE Trans. Dielectr Electr. Insul.* **11** (2004) 424.

[32] E. Wendt and H. Jahn // *Insulator News and Market Rep. Conf. Proc.* (2000).

[33] S. H. Kim and E. A. Cherney // *IEEE Trans. Power. Delivery* **5** (1990) 1491.

[34] J. Mackevich and S. Simmons // *IEEE Elect. Insul. Mag*. **13** (1997) 10.

[35] J. Mackevich, S. Simmons, M. Shah and R.J. Chang // *IEEE Elect. Insul. Mag.* **13** (1997) 25.

[36] R. Chang and L. Mazeika // *IEEE Trans. Dielectr. Electr. Insul*. **6** (1999) 342.

[37] D.H. Han, D.J. Kang, D.P. Kang and K.E. Min // *Polym. Bull***. 61** (2008) 611.

[38] F. Su, J. Zhidong, G. Haifeng and G. Zhicheng, *2007 annual report conference on electrical Insulation and dielectric Phenomena*.

[39] S.H. Kim, E.A. Cherney and R. Hackam // *IEEE Trans. Power. Delivery*. **6** (1991) 1549.

[40] F. Farhang, M. Ehsani and S.H. Jazayeri // *Iran Polym. J.* **18** (2009).

[41] K. Siderakis // *IEEE Trans Power Delivery.* **23** (2008) 2631.

[42] K. Siderakis, D. Agoris and S. Gubanski // *J. Phys. D: Appl. Phys.* **38** (2005) 3682.

[43] L. H. Meyer and E. A. Cherney // *IEEE Elect Insul Mag*. **20** (2004) 13.

[44] W. Zhou, S. Qi, C. Tu, H. Zhao, C. Wang and J .Kou // *J Appl. Polym. Sci.* **104** (2007) 1312.

[45] M. Sanaye-Pasand, A. Naderian Jahromi, A.H. El-Hag and S.H. Jayaram // *Int. J. Emerg. Electr. Power. Syst.*, Doi: 10.2202/1553-779X.1477, (2008).

[46] B. Venkatesulu and M. Joy Thomas, *2008 annual Report conference on electrical Insulation Dielectric Performance.*

[47] L.C. Sim, C.K. Lee, S.R. Ramanan and H. Ismail // *Polym. Plas.t Technol. Eng*. **45** (2006) 301.

[48] Q.Mu, S. Feng and G. Diao// *Polym Compos*. **28** (2007) 125.

[49] L.C. Sim, S.R. Ramanan, H. Ismail, K.N. Seetharamu and T.J. Goh // *Thermochimica Acta* **430** (2005) 155.

[50] C.H. Kwon, H. Shin, J.H. Kim, W.S. Choi and K.H. Yoon // *Mater. Chem. Phys.* **86** (2004) 78.

[51] A.A. Belhekar, S.V. Awate and R. Anand // *Catal. Commun.* **3** (2002) 453.

[52] A. Laachachi, A.M. Cochez, M. Ferriol, J.M. Lopez-Cuesta and E. Leroy// *Mater. Lett.* **59** (2005) 36.

[53] C.Y. Chang, K.S. Yao, J.H. Lee and C.H. Chen // *Environmental information archives.* **5** (2007) 655.

[54] A. Dey, S. De, A. De and S.K. De // *Nanotechnology* **15** (2004) 1277.

[55] V.P. Silva, M.P. Paschoalino, M.C. Goncalves, M.I. Felisberti, W.F. Jardim, and I.V.P. Yoshida // *Mater. Chem. Phys.* **113** (2009) 395.

[56] Y. Peng, R.N. Du, F. Qiang and Y.L. Wang // *Chin. J. Polym. Sci.* **23** (2005) 411.
[57] C.T. Dervos, J.A. Mergos and A.A. Iosifides // *Mater Lett.* **59** (2005) 2842.
[58] S. Roberts // *Phys. Rev.* **76** (1949) 1215.
[59] S.K. Medeiros, E.L. Albuquerque, Jr. Maia, E.W.S. Caetano and V.N. Freire // *J. Phys. D.: Appl Phys.* **40** (2007) 5747.
[60] Y. Zhou, S. Wang, Y. Zhang, X. Jiang and D. Yi // *J. Appl. Polym. Sci.* **101** (2006) 3395.
[61] T. Kaully, A. Siegmann and D. Shacham // *Polymer compos.* **29** (2008) 396.
[62] J. Yang, P. Pi, X. Wen, D. Zheng, M. Xu, J. Cheng and Z. Yang // *Appl. Surf. Sci.* **255** (2009) 3507.
[63] J.W. Liou and B.S. Chiou // *J. Phys. Condens Matter.* **10** (1998) 2773.
[64] I. Vrejoiu, J.D. Pedarnig, M. Dinescu, S. Bauer-Gogonea and D. Bäuerle // *Appl. Phys. A* **74** (2002) 407.
[65] Y. Bai, Z.Y. Cheng, V. Bharti, H.S. Xu and Q.M. Zhang // *Appl. Phys. Lett.* **76** (2000) 3804.
[66] D.H. Kuo, C.C. Chan, T.Y. Su and B.Y. Lin // *J. Eur. Ceram. Soc.* **21** (2001) 1171.
[67] A. Choudhury // *Mater. Chem. Phys*. **121** (2010) 280.
[68] S.H. Choi, I.D. Kim, J.M. Hong, K.H. Park and S.G. Oh // *Mater. Lett.* **61** (2007) 2478.
[69] Y.W. Wong, K.L. Lo, and F.G. Shin // *J. Appl. Polym. Sci.* **82 (2001) 1549.**
[70] W. Liao, Z. Jia, Z. Guan, L. Wang, J. Yang, J. Fan, Z. Su and J. Zhou // *IEEE Trans. Dielectr. Electr. Insul.* **14** (2007) 1446.
[71] J.C. Huang // *Adv. Polym. Technol.* **21** (2002) 299.
[72] S.P. Rwei, F.H. Ku and K.C. Cheng // *Colloid. Polym. Sci.* **280** (2002) 1110.
[73] O. Elsasser, K. Feser and F. Messerer // *Electrical Insulation and Dielectric Phenomena, 2000 Annual Report Conference*, pp. 203-206.
[74] G. Chen, D. Wu, W. Weng and W. Yan // *Polym. Eng. Sci.* **41** (2001) 2148.
[75] Y.C. Li and G.H. Chen // *Polym. Eng. Sci*. **47 (2007)** 882.
[76] W. Zheng, X. Lu and S.C. Wong // *J. Appl. Polym. Sci.* **91** (2004) 2781.
[77] L. Chen, L. Lu, D. Wu and G. Chen// *Polymer composites* **28** (2007) 493.
[78] Q. Mu and S. Feng // *Thermochim. Acta.* **462** (2007) 70.
[79] S. Iijima // *Nature* **354** (1991) 56.
[80] E.T. Thostenson, Z. Ren and T.W. Chou // *Compos. Sci. Technol.* **61** (2001) 1899.
[81] L. Bokobza // *Polymer.* **48** (2007) 4907.
[82] M. Moniruzzaman and K.I. Winey // *Macromolecules* **39** (2006) 5195.
[83] A. Fakhru'l-Razi, M.A. Atieh, N. Girun, T.G. Chuah, M. El-Sadig and D.R.A. Biak // *Compos. Struct.* **75** (2006) 496.
[84] A. Allaoui, S. Bai, H.M. Cheng and J.B. Bai // *Compos. Sci. Technol.* **62** (2002) 1993.
[85] M.D. Frogley, D. Ravich and H. Daniel Wagner // *Compos. Sci. Technol.* **63** (2003) 1647.
[86] C.L. Wu, H.C. Lin, J.S. Hsu, M.C. Yip and We. Fang // T*hin Solid Films* **517** (2009) 4895.
[87] A. Moisala, Q. Li, I.A. Kinloch and A.H. Windle // *Compos. Sci. Technol*. **66** (2006) 1285.
[88] G.X. Chen, H.S. Kim, B.H. Park and J.S. Yoon // *Carbon* **44** (2006) 3348.
[89] M.J. Jiang, Z.M. Dang and H.P. Xu // *Appl. Phys. Lett.* **90** (2007) 042914.1.
[90] M.J. Jiang, Z.M. Dang and H.P. Xu // *Eur. Polym. J.* **43** (2007) 4924.
[91] M.J. Biercuk, M.C. Llaguno, M. Radosavljevic, J.K. Hyun and A.T. Johnson // *Appl. Phys. Lett.* **80** (2002) 2767.
[92] J.K.W. Sandler, J.E. Kirk, I.A. Kinloch, M.S.P. Shaffer and A.H. Windle // *Polymer* **44** (2003) 5893.
[93] Ye.P. Mamunya, V.V. Davydenko, P. Pissis and E.V. Lebedev // *Eur. Polym. J.* **38** (2002) 1887.
[94] A. Qureshi, A. Mergen, M.S. Erolu, N.L. Singh and A. Güllüolu, // *J. Macromol. Sci, Part A: Pure Appl. Chem.* **45** (2008) 462.
[95] M. Rusu, N. Sofian and D. Rusu // *Polym. Test.* **20** (2001) 409.
[96] I. H. Tavman // *J. Appl .Polym. Sci.* **62** (1996) 2161.
[97] A. Gungor // *Materials and Design* **28** (2007) 1027.
[98] K. Chosh and S.N. Maiti // *J. Appl. Polym. Sci.* **60** (1996) 323.
[99] V. Singh, A.R. Kulkarni and T.R. Rama Mohan // *J. Appl. Polym. Sci*. **90** (2003) 3602.
[100] A.P. Kumar, D. Depan, N. Singh Tomer and R. Pal Singh // *Prog. Polym. Sci.* **34** (2009) 479.
[101] S.S. Ray and M. Okamoto // *Prog. Polym. Sci*. **28** (2003) 1539.

[102] J. Wang, Y. Chen and Q. Jin // *Macromol. Chem. Phys*. **206** (2005) 2512.

[103] J. Wang and Y. Chen // *J. Appl. Polym. Sci.* **107** (2008) 2059.

[104] S. Wang, C. Long, X. Wang, Q. Li and Z. Qi // *J. Appl. Polym. Sci.* **69** (1998) 1557.

[105] J. Wang, Y. Chen and Q. Jin // *J. Adhesion Sci. Technol.* **20** (2006) 261.

[106] J. Wang, Y. Chen and J. Wang // *J. Appl. Polym. Sci.* **111** (2009) 658.

[107] L. Yang, Y. Hu, H. Lu and L. Song // *J. Appl. Polym Sci*. **99** (2006) 3275.

[108] J. Wang, Y.Chen and Q. Jin // *High. Perform. Polym.* **18** (2006) 325.

[109] M.Razzaghi-Kashani, N. Gharavi and S. Javadi // *Smart Mater. Struct.* **17** (2008) 065035.

[110] M.L.Q.A. Kaneko and I.V.P. Yoshida // *J. Appl. Polym.* **108** (2008) 2587.