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BATCHING METHOD AND EFFECTS OF FORMULATION AND MECHANICAL LOADING ON ELECTRICAL CONDUCTIVITY OF NATURAL RUBBER COMPOSITES FILLED WITH MULTI-WALL CARBON NANOTUBE AND CARBON BLACK

K. HEMKAEW[a], C. DECHWAYUKUL[b], P. AIYARAK[c], R. J. SPONTAK[d], W. THONGRUANG[b*]
[a]*Department of Mining and Materials Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Thailand 90110*
[b]*Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University,*
Hat Yai, Thailand 90110
[c]*Department of Computer Science, Faculty of Science, Prince of Songkla University, Hat Yai, Thailand 90110*
[d]*Department of Chemical Engineering and, also, Department of Materials Science & Engineering, North Carolina State University, Raleigh, USA 27695*

Method, formulation and mechanical load variation on electrical conductivity of natural rubber composites filled with multi-wall carbon nanotube and carbon black have been investigated. These nanometer-scale fillers were used due to their good dispersion in the rubber matrix together with their good electrical conductivity. Samples were prepared using five conventional methods involving internal and open-mill mixers, and molding using hot compression machine. Desirable high conductivity and well defined flexure was found best from compounding employing internal mixer which rendered better control in the mixing of chemicals. Two formulations of carbon black were studied: Ketjen Black and Vulcan Black; mixture of the two yielded better conductivity and response to loads than that of Vulcan Black alone, and that the higher the filler content, the better. Conductivity responses to mechanical loading were analyzed at three loading conditions: compression, shear, and combinations of the two. Conductivity of the composite subjected to pure compressive stress and that subjected to loading at different angles similarly behaved nonlinearly; increasing with the angle with respect to normal strain. With respect to shear strain, conductivity increases with decreasing loading angle.

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1. Introduction

Pure polymers, unlike metals, are generally electrical insulators in their nature, so they are applied as electricity insulating materials. Conductive polymers, however, hold many advantages over metallic conductors: they can be easily shaped using low cost technologies; are light weight; corrosion resistant, and thus offer a wide range of electrical conductivity applications.

Numerous fillers can be compounded into polymer insulating matrix in order to achieve different conductivity ranges. In electrical conductive polymers, formation of conductive networks

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[*] Corresponding author: twiriya@me.psu.ac.th

depends mainly on filler concentration and its geometry (particularly shape and size) [1-3]. Appropriate filler has to be chosen in an application since it also affects other functional properties besides conductivity.

From the abovementioned outlines, flexible polymers have been increasingly chosen as base materials for sensor elements while conductive fillers, which can detect stress and/or stimuli electrically, are compounded into the polymers to make filler/polymer composites [4–15]. In a composite, the gap between the included conductive fillers decreases with increasing filler content. When gaps are small enough, contact effect and tunneling effect occur, leading to formation of local conductive paths [4–6].

When compressive stress is applied on a composite, the filler elements further approach one another to form new conducting paths, leading to drastic conductivity increase of the composite. Complementarily this means that the amount of compressive stress applied can be estimated by detecting the strength of electrical signals, i.e., a composite can work as a tactile or force-sensor material [7–15].

As earlier stated, electrical resistance of conductive polymers and rubber composites changes with external pressure and hence these materials are widely used for sensitive components of elastic force-sensors [16-19]. Piezoresistive characteristics of the composite are generally the key to improve performance such as in measuring range, sensitivity and repeatability of flexible force sensor [20-24]. Wang [20] studied changes in volume fraction of carbon black (CB) that affects changes in resistivity of the composite by applying pressure. Works by Zhang et al. [21] and Yi [22] confirmed that the mean distance between conductive particles that decreases with pressure leads to the decrease of composite resistance. Piezoresistive phenomenon of conductive particle networks for short carbon fiber composite with polyolefin was explained in their formations and destructions under pressure [23, 24]. This, however, may not be applicable for CB composites employing natural rubber. Song et al. [24] investigated the piezoresistive characteristics of silicone rubber/CB composites with carbon black/silicone rubber mass ratio in ranges of 0.10 to 0.14.

On the mixing of rubber compounds, these are traditionally carried out in batch-wise equipment, particularly roll mills (open mixers) and the later-on developed internal mixers for large scale mixing [25-27]. Although normal internal mixer requires higher mixing energy [28], the discontinuous-mixing equipment has high flexibility regarding different recipes and mixing orders. However, a major disadvantage of this process is that it could lead to differences in mixture quality from one batch to another [29-30].

In case of rubber compounds with fillers, agglomerates are broken down into smaller aggregates and primary particles. Another major part in mixing is thus the dispersion of the filler particles; the higher the dispersion, the better the material properties. Nevertheless, good dispersion depends partly on particle size of the filler, and an optimum size is important in getting the optimum final rubber properties [31].

Carbon black (CB) fillers have been widely used as conductive mixes to polymers. These consist of spherical-shaped, nano-sized particles, which usually aggregate in agglomerates with low or high structures. Among the CBs, Vulcan black and the higher-grade Ketjen Black are prevalently used. Ketjenblack EC600-JD, used in our experiment, has higher porosity and surface area than Vulcan XC-72 [32]. The former also has ultrahigh conductivity due to its highly branched and fibrillous structures. Its distribution of particle and aggregate size is exceptionally broad, which may also contribute to strong network formation, and thus high conductivity. The primary particle size is less than 30 μm, and the size of the aggregate is about 100-300 nm [32], and is considered one of the optimum filler sizes.

From these brief reviews, the initial objectives of this research are to single out one best method of mixing and to investigate carbon black fillers efficiency and their appropriate combination. Ultimately the research proposes an idea of “effective conducting paths” to study the destruction, formation and/or reformation of the paths during compression and shear, or combinations of both. The experimental results and models were evaluated to explain the phenomena of composites subjected to various types of loading involving compression and shear which cause changes in resistance of the conductive rubber composite.

2. Experimental

2.1 Materials

Natural rubber (NR; STR5L) used as the matrix in the experiments was supplied by Chana Latex Industry Co., Ltd. (Thailand). Two types of carbon black (CB), Vulcan XC-72 (V) and Ketjenblack EC600-JD (K), were chosen as conductive nano-fillers. Carbon black V was supplied by Cabot India Ltd., while K was obtained from Akzo Nobel Chemicals Pte Singapore Ltd. The multiwall carbon nanotube (MWCNT), supplied by Chengdu Organic Chemicals Co., Ltd. China, was used for bridging and enhancing conductivity purpose. Other chemicals associated with curing of the NR were supplied by Kitpyboon Limited Partnership and Polymer Innovation Co., Ltd. Thailand, and is detailed in Table 1 together with their quantities. Selected compounding methods and steps of mixing were shown in Table 2 in Article 2.2.

Table 1 The natural rubber composite compound formulation.

Constituent	phr
Natural Rubber (STR5L)	100
Zinc oxide (ZnO)	5
Stearic acid	3
CB: Vulcan (V), Ketjen (K), or both	vary
MWCNT (M)	7
Mercaptobenzo thiazole (MBT)	1.5
Tetramethylthiuram disulfide (TMTD)	2.5
Paraffinic oil	30
Sulphur (S)	0.5

Note: ‘phr’ designates ‘parts per hundred parts of rubber’

2.2 Sample preparation

Master batches of NR and CB (except for Method 2 in the five compounding methods employing different mixing procedures, chemical ingredients and composition mixing sequence detailed in Table 2) were mixed in an internal mixer (YFM Dispersion mixers 3 L, Yong Fong Machinery Co., Ltd.) at 70-80°C for 45-60 minutes. After cooling, each mixture was further compounded with the rest of the constituents, shown in Table 2 (except for Method 3) on an open two-roll mill. The Efficient Vulcanization (EV) of low sulphur content was used in this study. MWCNTs were also added onto the two-roll mill in Methods 1 and 2 for compounding. The total mixing time in this stage was about 40-50 minutes. The compounds were vulcanized using a hot-compression molding machine under conditions of 3,000 psi and 150°C. Duration for vulcanization was obtained from a Moving Die Rheometer (MDR 2000). Vulcanizates were stored for 24 hours at ambient temperature for maturing purposes before the test.

Table 2 Compound methods according to mixing procedures used.

	Compound Method									
	1		**2**		**3**		**4**		**5**	
	Constit	**phr**	**Constit**	**phr**	**Constit**	**phr**	**Constit**	**phr**	**Constit**	**phr**
Master batch (internal mixer)	NR	100	-	-	NR	100	NR	100	NR	100
	CB	50	-	-	CB	50	CB	50	CB	50
	-	-	-	-	M	7	M	7	M	7
	-	-	-	-	-	-	Oil	30	-	-
Internal mix (internal mixer)	-	-	-	-	Stearic acid	3	-	-	-	-
	-	-	-	-	ZnO	5	-	-	-	-
	-	-	-	-	MBT	1.5	-	-	-	-
	-	-	-	-	TMTD	2.5	-	-	-	-
	-	-	-	-	Oil	30	-	-	-	-
Open mix (two-roll mill)	Stearic acid	3	NR	100	S	0.5	Stearic acid	3	Stearic acid	3
	ZnO	5	Stearic acid	3	-	-	ZnO	5	ZnO	5
	M	7	ZnO	5	-	-	MBT	1.5	MBT	1.5
	MBT	1.5	MBT	1.5	-	-	TMTD	2.5	TMTD	2.5
	TMTD	2.5	TMTD	2.5	-	-	S	0.5	Oil	30
	Oil	30	CB	50	-	-	-	-	S	0.5
	S	0.5	M	7	-	-	-	-	-	-
	-	-	Oil	30	-	-	-	-	-	-
	-	-	S	0.5	-	-	-	-	-	-

Note: Constit = Constituents; other abbreviation meanings can be found in Table 1

2.3 Testing

NR composite specimens were prepared in forms of 2-mm thick, 15.5-mm dia. disc. Electrical conductivity responses to loadings were observed by placing each specimen between the copper-wired electrodes mounted on a universal testing machine (Instron, 8872) and connected to a programmable automatic RCL meter (Fluke PM-6306), as shown in Fig.1. The setups for measuring responses to mechanical loadings (compressive, shear, and combined compressive-shear) are diagrammatized in Fig. 2. The RCL meter measuring frequency was set at 1 MHz. The conductivity data reported was obtained from the average of three specimens at same corresponding position from the compounding batch.

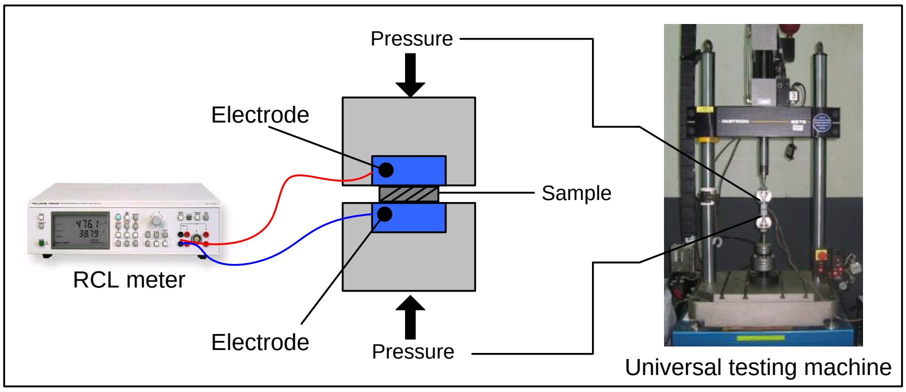

Fig.1 Schematic diagram for electro-mechanical study on the specimen.

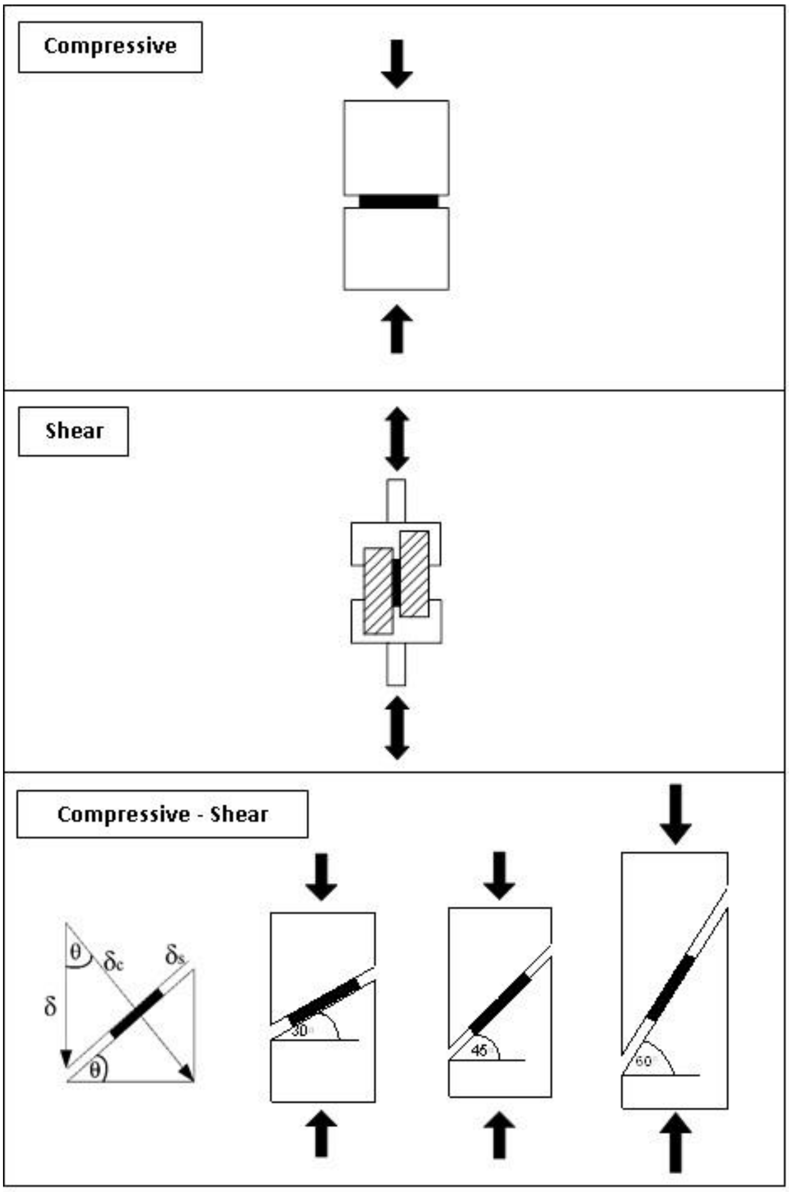

Fig. 2 Test setup for electrical response investigation to mechanical loading.

3. Results and discussion

Changes of conductivity versus applying strain (10-50%) on the specimen derived from the five compounding methods are shown in Fig. 3. All methods were prepared at same content of conductive fillers of 50 phr CB (V) and 7 phr (M). Method 2, which was not prepared as a master batch and had all ingredients compounded on the two-roll mill, exhibited inconsistent results of conductivity-strain compared with other methods due to non-uniform dispersion of chemicals and uncontrollable losses during mixing. Among the mixing methods, compounding from Method 3 showed superior results than all others, both in conductivity level and characteristics. In addition, it was found in the case of paraffinic oil mixing into the compound that the sequential steps of mixing needed to be strictly adhered; oil could prevent mixing of chemicals to the rubber if steps are shuffled – as was confirmed in the conductivity result of Method 4 being less than that from Method 3. It was also found that mixing of oil into the rubber/fillers in the internal mixer prior to mixing of other chemicals, such as that conducted in Method 4, did not adversely affect conductivity as that of mixing of oil and chemicals in the open mill mixer (Methods 1 and 5). Mixtures of high oil content employing open mill mixer must have reduced much shear during mixing, resulting in poor distribution of conductive fillers, and hence less conductivity.

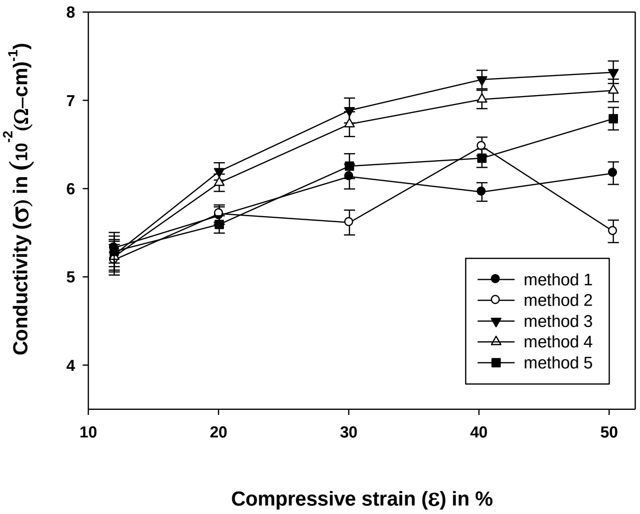

Fig. 3 Conductivity vs. compressive strain of the five compounding methods.

It is evident now that mixing equipment and mixing step for compounding affect electrical conductivity outcome of the composite. Method 3 compounding, by preparing a master batch of conductive fillers in the internal mixer to control the quality and quantity of mixing, was found to be most appropriate. Uniform distribution of fillers and chemicals in the rubber via this method had led to a good conductivity response to the strain as desired.

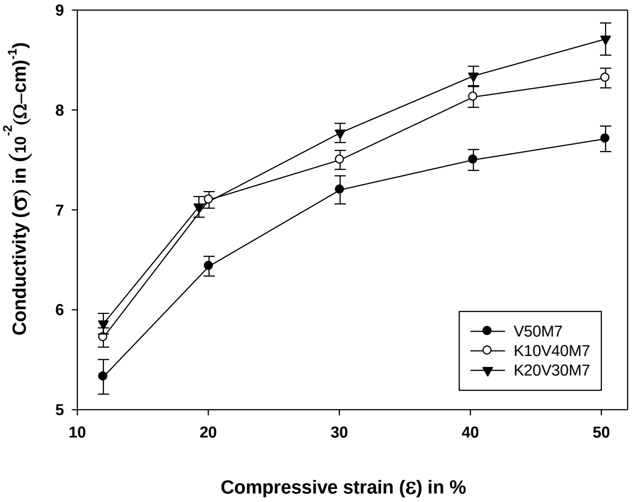

Fig. 4 Conductivity vs. compressive strain in compounding from three different experimental filler contents (the numeric following the character refers to that particular character's content in phr unit).

In Fig. 4, comparisons of conductivity employing same total amount of CBs at 50 phr plus a constant amount of 7 phr MWCNT were made. Altogether, three mixes were investigated: one with pure Vulcan Black (V) at 50 phr; one with 40 phr V and 10 phr Ketjen Black (K); and one with 30 V and 20 K. The latter two were mixed for synergy and complement purposes.

At the same total amount of 50 phr CB, it is clear that more amount of K in the rubber enhances better conductivity. This result is in accordance to other studies such as [33] which investigated 50/50 blends of HDPE and TPU filled with K of 1 wt% and reported that volume resistivity of the blend filled with K (4.13×10^3 Ω.cm) was very much less than that blend filled with V (6.47×10^{11} Ω.cm). This is most probably due to the greater surface area of K, up to 1,400 m^2/g [34], than that of V at 267 m^2/g [35]. In addition, K has a higher pore volume and structure resulting in more connections of the conductive path that lead to higher conductivity [36]; the K porous volume of 4.80-5.10 cc/g was reported by [37] while a lower V porous volume of 0.46 cc/g was published in [38]. Thus in general, the use of Ketjen Black do provide a better conductivity than Vulcan Black at same concentration, albeit a little costly.

It could be noted in Fig. 4 that the two mixtures involving K yielded higher conductivity than that only with V, as reasoned earlier. As for the two K mixes, they exhibited subtle differences at compressive strain of less than 20%. Beyond this value it was found that conductivity started to increase differently; the more at the more K, due to better connections within the rubber matrix as earlier described. Mean distance between particles in aggregate or agglomerate forms decrease as filler concentration increases. Nevertheless, there appears to be an upper limit to include K, whereas there is no restriction on the amount of V; mixing difficulty with K is one reason, and a seemingly asymptotic efficiency is another [39].

Subjected to stresses, some networks might have been destroyed during deformation [40] but new network formations appeared to be dominant in our case. Fig. 5 contains sketches to clarify this understanding.

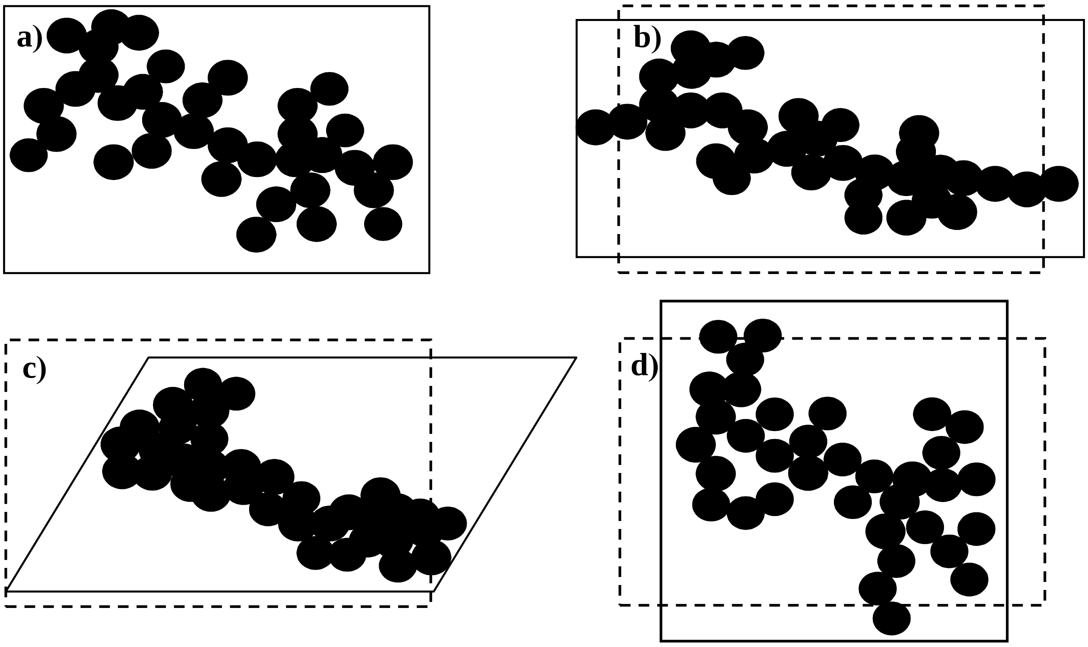

Fig. 5 Model Sketches showing conductive CB pathways for: a) sample at rest; b) sample under pure compression; c) sample under compression and shear; and d) sample under pure shear.

As can be seen from part of Fig. 6, conductivity of the composite subjected to pure compressive stress increases nonlinearly with normal strain (ε_n). This is similar to the conductive behaviors of the composite subjected to combined loadings at different angles of 30, 45, and 60 degrees in the Figure. At same normal compressive stress, increasing inclined angles resulted in higher conductivity. It is understood that after shear is applied to very high conductive filler composites the shear force causes forming of new 3D conductive networks of aggregates rather than breaking of existing networks; similar results to calculated works published in [41-42].

As schematically illustrated in Fig. 5, position change from at-rest status (Fig. 5a) from deformation of conductive particles increases with vertical compressive displacement (Fig. 5b) and the applied angle (Fig. 5c) resulting in a decrease of the mean distance between conductive aggregates which lead to formation of new closer secondary conductive networks. In Fig. 5d under pure shear (i.e. under zero normal compression) the mean particle distance reverted back close to that under at-rest condition and yielded the least desirable conductivity comparing with other conditions of loading. However, it still gave a little improvement over the undisturbed condition since its particle arrangement is such that the connecting paths are a little longer and also in the more perpendicular direction.

Study [43] reported, however, that at high filler content no change in inter-particle distance is to be expected, as had been visualized in this study. Our argument is that under high shear at same normal strain, formation of secondary conductive networks is more dominant than destruction of conductive pathways, especially at very high conductive filler concentration. Results from our study confirmed that shear deformation do exert enhancing effect on conductive network structures in high-filler-content composites.

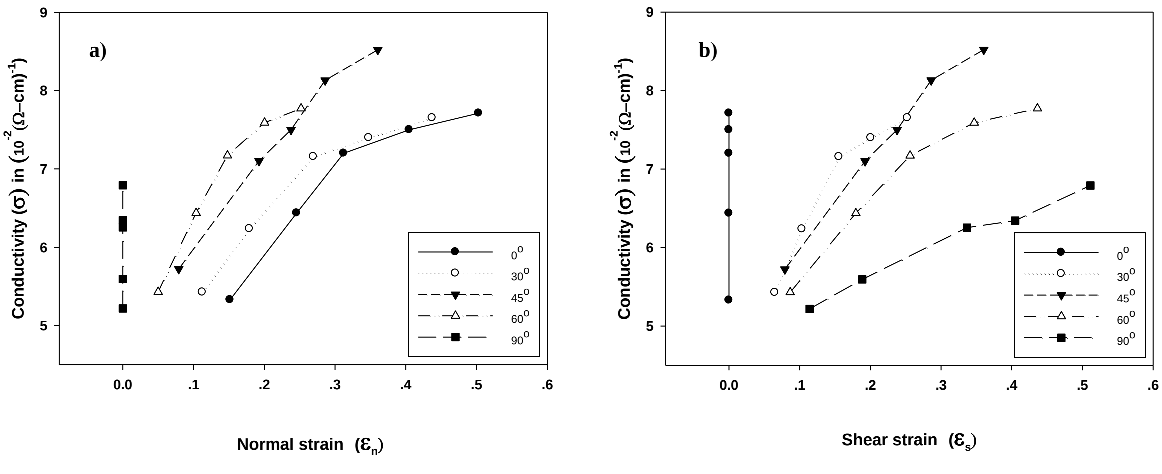

Fig. 6 Conductivity vs. a) normal strain and b) shear strain, at varying loading conditions, i.e., compression (0°), shear (90°), and combinations of compression and shear (30°, 45° and 60°).

4. Conclusions

Five methods of composite compounding involving natural rubber/multiwall carbon nanotube/carbon black (NR/MWCNT/CB) were investigated. One method (Method 3) conducted with an internal mixing machine rendered better conductivity characteristics than other four methods due to better controls on quality and quantity during compounding. Mixing of paraffinic oil into the compound needs to be of great concern since improper sequencing of oil input would hamper mixing of other chemicals. However, mixing of oil into rubber/fillers prior to mixing of other chemicals employing internal mixing machine would not adversely affect sample conductivity as much as that employing an open mill mixing machine.

In the filler study involving Vulcan black and Ketjen Black and their proportions, introduction of Ketjen Black filler rendered better electrical characteristics and better trait of conductivity response under compressive loading than that employing pure Vulcan black, and in general the more Ketjen Black, the better the result. However, a limit should be observed on the use of Ketjen Black since too much of this ingredient leads to a diminishing return, and this is not to mention its higher cost.

Under mechanical loading, electrical conductivity of the composite increases nonlinearly with normal compressive strain (ε_n). Similar trends were observed in specimens subjected to loading at different angles of 30°, 45° and 60°. At a fixed normal compressive stress on a very high filler composite (K20V30M7 in this study), a greater inclined angle (leading to a larger shear effect) resulted in higher conductivity - most probably attributable to formation of new conductive networks of the aggregates rather than breaking of existing ones. Decreased mean distance between conductive particles under load, except in pure shear scenario, could be one good reason that new closer secondary conductive networks are formed. Our experiments have confirmed that shear deformation has an enhancing effect on the conductive network structures of the high filler content composites.

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