

Electrical properties of graphene filled UPVC nanocomposites for mining pipe application

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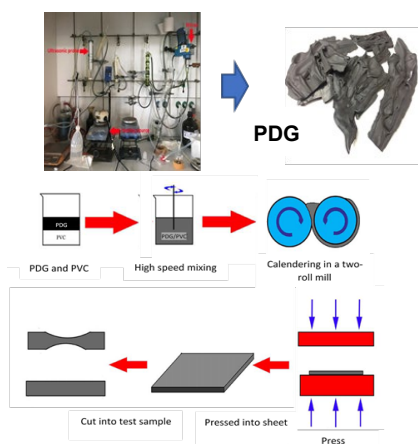
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Graphical abstract



Abstract

Graphene-filled UPVC nanocomposites is expected to be a promising material for mining pipe application. The main purpose of this study is to investigate the electrical properties of UPVC filled with graphene derivatives: graphene oxide (GO), reduced graphene oxide (rGO), and pre-dispersed rGO (PDG) in Fischer Tropsch wax (FT wax). Pre-dispersed rGO in FT wax (PDG) are prepared by defining melting method with ultrasonic probe. Test specimens were prepared according to different material formulations by dry-blend mixing, followed by two-roll milling and hot press molding methods. PDG showed the lowest volume resistivity thus indicating highest electrical conductivity. It was found that the presence of PDG can greatly increase the electrical conductivity at lowest percolation value of 0.75phr. At 1.5phr, comparable volume resistivity value comparable to commercial mining pipe formulation based on carbon black (CB) was achieved. This study also confirmed that optimum electrical properties of graphene filled UPVC nanocomposites can be achieved by maximizing the dispersibility of graphene within the PVC matrix. This level of conductivity opens the door for the PDG filled UPVC nanocomposites for mining pipe application.

Keywords: Carbon black (CB), Fischer Tropsch wax (FT Wax), graphene oxide (GO), reduced graphene oxide (rGO), pre-dispersed rGO (PDG), unplasticized polyvinyl chloride (UPVC), nanocomposites, melt-mixing method, volume resistivity (VR), dispersion, calcium zinc (Ca/Zn), Lead (Pb)

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INTRODUCTION

Polyvinyl Chloride (PVC) is the third most extensively produced synthetic plastic polymer after polyethylene (PE) and polypropylene (PP). It is widely used in many industries such as building and construction, electrical and electronics, automotive, packaging, and footwear due to its low cost, ease of processing and blending, high tensile strength, and flame-resistant properties. It is mainly available in two forms, namely plasticizing PVC (SPVC) and unplasticized PVC (UPVC). A typical insulating material, UPVC is primarily used in profile applications, in windows and doors, and construction (in the form of pipes). The stabilization of PVC pipes is commonly done using lead-based salts such as lead sulphate or lead stearate. Lead (Pb) is a heavy metal and it has been classified as toxic, whereas Calcium Zinc stabilization is recognized as an eco-friendly process and hence it paves the way in replacing lead-based stabilization.

Mining industry involves the transportation of clean water, fresh air, slurries, muds, as well as other infrastructures in and out from the quarry. Harsh surrounding in mining areas increase the chance of the piping network being damaged. Due to this particular reason, considering the possibility for corrosion, impact, abrasion, and ensuring electrical conductivity have been a challenge in designing mining pipe system with low cost. In the event of tunneling or underground mining operation, the ventilation system must be sufficed to dilute harmful exhaust pollutants where a single spark can lead to serious fire disasters

PVC pipes have high impact strength and flexibility together with the abrasion resistance required in slurry lines which makes it an ideal

material for the mining industry. Several methods had been developed over the years to enhance electrical conductivity of PVC materials [2-6], such as coating PVC with conductive layers and producing conductive polymer blend through the incorporation of inorganic/liquid anti-static. Unfortunately, PVC coated with conductive layers is easily peeled off due to poor interfacial bonding. Carbon black (CB) is one of the most extensively used conductive fillers due to its blending compatibility with PVC matrix and low production cost [7]. In order to achieve acceptable antistatic properties for mining pipe application, loading level up to 20wt. % is required which reduces the mechanical strength and processing performance of the CB filled UPVC composites. Carbon Nanotube (CNT) conductive fillers serve as a replacement for CB, but its usage is restricted in commercial applications due to its low dispersion and high production cost.

Graphene exhibits exceptional properties of high electrical and thermal conductivity; high modulus could be used as a viable and better cost performance alternative to substitute CNT [8-11]. Researchers had presented different methods for the production of graphene, which includes bottom up and top down methods such as mechanical/chemical exfoliation, GO and reduction, arc discharge, epitaxial growth, chemical conversion, and chemical vapor deposition (CVD). [6]. Graphene derivatives such as graphene oxide (GO), reduced graphene oxide (rGO), modified graphene oxide (MGO), graphene nanoplatelets (GNP) and multi-layer graphene (MLG) are widely used as functional fillers for polymer nanocomposites. Garmor, a company based in Florida relies upon new advances in milling technology to produce GO yielding only water as a by-product. Later,

the GO undergoes a reduction step using a suitable thermal, chemical and electrochemical route which is via microwave process. The reduced GO has an immaculate surface with almost no residual oxidation and no corrugation or damaged sp² orbital and hence conserves graphene's highly prized electrical, thermal and mechanical properties.

Notably, with the breakthrough of various graphene derivatives availability in the market with low costs [12], the method of preparing graphene filled polymer nanocomposites in a cost-effective way has been a critical issue to be explored and pushing its practical application forward. A more attractive and cost effective, GO has oxygenated groups (epoxy, hydroxyl, carboxyl) that can, in principle interact with the chlorine atoms in the PVC through halogen bonding and which serves as active sites to anchor functional groups to ensure GO compatibility with PVC. However, GO is electrically insulating which limit its application for conductive polymers. GO is electrically insulating but becomes conductive by the chemical reduction of GO into reduced graphene oxide (rGO), presumably by restoring the graphitic network sp² bonds. Nevertheless, rGO will easily aggregate due to high cohesive interaction making it difficult to disperse. This lack of homogeneous dispersion limits its ability to enhance mechanical, electrical, rheological, and thermal properties of graphene filled UPVC nanocomposites.

The improvement in electrical, mechanical, and thermal heat stability properties of PVC matrix with graphene derivatives has lately been reported in various literatures [4, 13-17]. Solution blending method had been used to prepare graphene filled PVC nanocomposite films. In the works of Vadukumpully et al. [4], it was reported that graphene filled PVC nanocomposites have high mechanical strength, thermal stability and good conductivity. Deshmukh and Joshi [16] prepared GO filled PVC nanocomposites films by colloidal blending method and reported an augmentation in the thermal stability because of the strong inter-linkage between PVC and GO. Pham et al. [13] produced graphene filled PVC nanocomposites by colloidal blending methods which exhibit a low percolation threshold of 0.4wt.%. and an electrical conductivity as high as 46.5 S/m corresponding to 4.0 wt. % of graphene loading. The Colloidal blending method was used to fabricate graphene filled PVC nanocomposites by Dang et al. [14] and achieved a threshold of 0.3 wt. %. while the best conductivity value obtained was as high as 38.5 S/m corresponding to 4 wt.% graphene loading. Ma et al. [13] observed an augmentation in electrical conductivity of graphene grafted with polyaniline filled PVC nanocomposites, and the works of Joshi et al. [14] confirmed that graphene filled PVC nanocomposites prepared by solution blending showcased high electrical conductivity properties. Referring to the few literature reviews [4, 13-17], it is worth pointing out that most preparation of graphene filled polymer composites are mainly by solvent or in situ process for conductive film application inevitably resulting in complicated procedures, high cost, and environmental pollution. Furthermore, this solution method is extremely difficult to be used for large-scale production of nanocomposites. As a contract, melt-mixing method is a conventional way to produce PVC pipe in a large-scale.

When it comes to the dispersion of graphene into PVC matrix, Renteria et al. [18] in their graphene dispersion research have selected a specific paraffin wax as a composite matrix medium for graphene dispersion which is intended to be used specifically in thermal phase change materials (PCMs) application. Fischer-Tropsch (FT) derived wax is a synthetic paraffin which consists largely of straight chain alkanes with a wide range of melting points and boiling points. The use of FT wax with low viscosity type SX 60 S is expected to have better compatibility, interaction, volume loading and degree of dispersion with rGO surface compared to FT wax with high viscosity SX 105 PW.

The main objective of this research was to develop a graphene-based PVC composites with suitable electrical properties for mining pipe application. Pre-dispersed reduced graphene (rGO) in Fischer-Tropsch wax (FT wax) filled UPVC nanocomposites is expected to be a promising material for mining pipe application and can be manufactured using conventional melt-mixing method. The main scope was to develop a method to pre-disperse rGO in FT wax to ease dispersion and compatibility within PVC. Scanning Electron Microscopy (SEM) is used to study the morphology of the pre-disperse

rGO in FT Wax filled UPVC composites. Later-on, the effect of different types and loading levels of graphene derivatives: GO, rGO, and pre-dispersed rGO in Fischer-Tropsch wax (FT wax) filled UPVC nanocomposites on electrical properties was investigated. The electrical properties of Carbon Black (CB) UPVC composites based on commercial formulation were determined as comparison

EXPERIMENTAL

Method of preparing pre-dispersed rGO with FT wax

rGO (Garmor, USA) and SX 60 S (Shell, Malaysia) were chosen for the preparation. rGO was dried at 80°C for 2 hours prior to use. Fig. 1 illustrates that the FT wax was melted on a hot plate. The temperatures (80°C and 120°C) at which the FT wax was melted were maintained throughout the process. The more appropriate temperature among the two was taken as a final processing temperature for the melt mixing process. Also, continuous whisking with the help of a stirrer was performed throughout the whole pre-dispersing process. When the wax was melted, rGO was slowly added into the wax portion by portion as long as the FT wax-rGO mixture remains to be in a liquid/gel like state. An ultrasonic probe was used to ensure good dispersion of FT wax-rGO throughout the process in order to breakdown any agglomeration of rGO that might occur during the pre-dispersing process. Once the FT wax-rGO mixture was observed to be homogeneously mixed, the stirrer and the ultrasonic probe were stopped, and the mixture was allowed to cool. After cooling, the solidified FT wax-rGO mixture was ground into powder form using the micron-miller.



Fig. 1 Experimental setup for pre-dispersed of rGO-FT wax.

Preparation of graphene filled UPVC nanocomposites

Commercial formulation for mining pipe stabilized with Pb and 20phr carbon black was used as a benchmark for the entire formulation design. Basic PVC formulation based on Ca/Zn stabilizer with 1, 1.5, 2, 3, and 5phr GO or rGO content was employed to investigate the loading effect. The novelty pre-dispersed rGO is expected to be much more effective and designed to have lower loading level of 0.5, 0.75, 1, 1.25 and 1.5phr. Proper calculation is essential to ensure total content of FT waxes to be balance in each formulation. As a control, the blank formulation base on Pb and Ca/Zn was prepared.

The weighed PVC dry-blend was mixed together to reach 120°C by using a high-speed mixer, and then discharged into the cool mixers for cooling to around 40°C. The dry-blend from the mixing process goes into two-roll milling to melt, homogenize and shape into a uniform thickness mill sheet. The rate at which PVC goes through the feed train is determined by the roller mill. Mold was designed and fabricated for compression molding of sample with hot press machine.

Scanning Electron Microscopy (SEM)

The structure and morphology of pre-dispersed rGO filled UPVC nanocomposites in the form of two-roll mill sheet were examined by scanning electron microscopy (SEM, Hitachi SU1510 at 15kV).

Testing of Electrical Conductivity (ISO 14309:2011)

Volume resistivity tester (Amtest, 1865+ Digital Megohmmeter I/R Tester) was used to determine the effect of electrical properties of the different type and loading level of graphene derivative filled UPVC nanocomposites. Pressed sample were cut into the dimensions according to BS ISO 14309:2011 standard and the average thickness of each shape piece was recorded before resuming to the volume resistivity test. Fig. 2 presents the setup of VR tester. The average value of volume resistance (R_v) was recorded and volume resistivity (ρ_v) is calculated using the formula given below:

$$\rho_v = \frac{\pi \times D1^2 \times R_v}{4t} \text{ (ohm-cm)}$$

where,

D1= diameter of the guarded electrode (cm)

t = thickness of the test piece (cm)



Fig. 2 Setup of Volume Resistivity Tester.

RESULTS AND DISCUSSION

Pre-dispersed reduced (rGO) with Fischer-Tropsch wax (FT wax)

The pre-dispersion process of rGO in FT wax was conducted a few times with different loads to understand the optimum loading level of rGO. To determine the optimum loading level of rGO, initially, 20% of rGO was added and observed to assess if more quantity of rGO can be added before viscosity of the mixture reaches a point after which the homogeneous mixing cannot be achieved. The mixture was observed to be viscous above 30% of rGO loading.

While deciding the loading level the temperatures starting from 80°C were also studied to determine the best temperature to perform the melt processing. At 80°C, it was observed that the mixture was highly viscous and hence the temperature was increased to 100°C and 120°C to observe the viscosity. From this study 120°C was determined to be the best temperature for conducting the process of melt mixing (refer to Fig. 3). At 80°C the mixture displayed, varying viscosities and such behavior is referred to as a non-Newtonian behavior which means that the viscosity of the fluid was dependent on the shear rate. With the increase in the shear rate the viscosity of the fluid increases, hence the fluid becomes shear thickening. Such behavior of the fluids is referred to as non-Newtonian behavior. This kind of behavior in fluids is a result of various factors, most of them being in relation to the structural reorganization due to the flow of fluid molecules. At 120°C the mixture exhibited a Newtonian behaviour where the viscosity of the mixture remained constant irrespective of its flow i.e. it is independent of shear rate. The mixtures or fluids exhibiting Newtonian behavior generally consist of small isotropic molecules whose properties and shape are symmetric and not oriented by the flow. However, such behavior is also possible with the anisotropic molecules. The Newtonian behavior in cases where the rate of shear is low along with plateau is referred to as the region of zero shear viscosity. From the study, it was determined that the optimum loading level of rGO to allow well dispersion into FT wax is 30% at 120°C. The 30% pre-dispersed rGO (PDG) developed will be further used to analyze the effect of electrical properties.

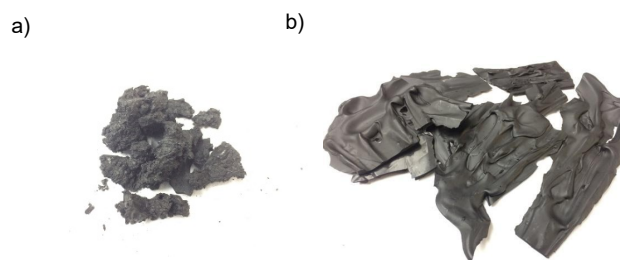


Fig. 3 (a) Pre-dispersed rGO in FT wax prepared at 80°C in flake form and (b) 30% Pre-dispersed rGO in FT wax prepared at 120°C in flake form.

SEM morphology analysis

SEM analysis was conducted on the PDG filled UPVC nanocomposites at 0.5phr and 1.5phr loading level to study the morphological structures under various magnifications (1000X, 2000X, 5000X). Unfilled UPVC stabilized with Ca/Zn stabilizer was used as reference sample. Based on Fig. 4, magnification 1000X shows the presence of calcium particles which was used for stabilization over the surface. Increased magnification (X2000 and X5000) of calcium blank samples helped to visualize the white-irregular shaped particles in the samples. These white particles can be defined as calcium carbonate as part of the PVC formulation. At the magnification of X1000 milled sheet samples, of 0.5phr 30% PDG and 1.5phr PDG the rough surface over the samples was confirmed. Higher magnification (X2000 and X5000) confirmed the presence of mixed rGO in a dotted structure on the complete upper surface of prepared test samples.

Magnification	Milled Sheet Samples		
	Calcium Blank	0.5phr 30% pre-dispersed rGO	1.5phr 30% pre-dispersed rGO
X 1000			
X 2000			
X 5000			

Fig. 4 SEM images unfilled UPVC VS 30PDG 0.5phr and 1.5phr.

Analysis of electrical properties

To evaluate the electrical properties of the graphene filled UPVC nanocomposites, the electrical conductivity test was conducted on the sample to determine the effect of loading level and different graphene derivatives: GO, rGO and 30% pre-dispersed rGO in FT wax (PDG). Besides, the commercial formulation for mining pipe filled with CB is based on Pb stabilizer. Due to health and environmental issues, Ca/Zn stabilizer which is more environmentally friendly had been used in this study. Thus, it is interesting to understand if Pb and Ca/Zn stabilizer systems will have any effect on electrical properties. The effect of Pb stabilizer and Ca/Zn stabilizer on the volume resistivity of the unfilled UPVC is illustrated in Fig. 5. It can be inferred from the figure that the unfilled UPVC with Pb stabilizer (PVC/Pb/BL) has a higher volume resistivity when compared to the unfilled UPVC stabilized with Ca/Zn stabilizer (PVC/Ca/BL). The higher the volume resistivity, the lower the conductivity. Hence, adding a Pb stabilizer decreases the

conductivity while the Ca/Zn stabilizer increases the conductivity. However, the increase in conductivity for Ca/Zn stabilizer is minimum compared to Pb stabilizer at same magnitude value of $\times 10^{13}$ thus, can be negligible. The reason Ca/Zn system lowers the volume resistivity compared to Pb stabilizer is mainly due to the increase of hydrophilic ingredients such as Zinc chloride (Lewis Acid) during dehydrochlorination of PVC.

throughout PVC matrix, exhibiting more significant decrease in electrical resistivity of the rGO filled UPVC composites.

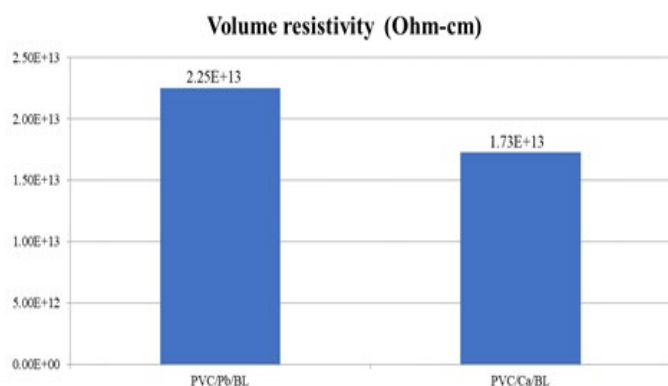


Fig. 5 Effect of Pb and Ca/Zn stabilizer on volume resistivity.

Fig. 6 shows the volume resistivity of different content of GO filled UPVC nanocomposites (PVC/Ca/GO). It is shown that the volume resistivity of GO filled PVC nanocomposite decreases with the increase GO content thus improving the electrical conductivity. The addition of GO gradually decreases the volume resistivity with a linear trend from loading level 1 to 5phr. However, the improvement is still at the same orders magnitude of $\times 10^{13}$ comparable to the baseline PVC/Ca/BL, which is not significant enough for the PVC composites to transit from electrical insulator to semi-conductor.

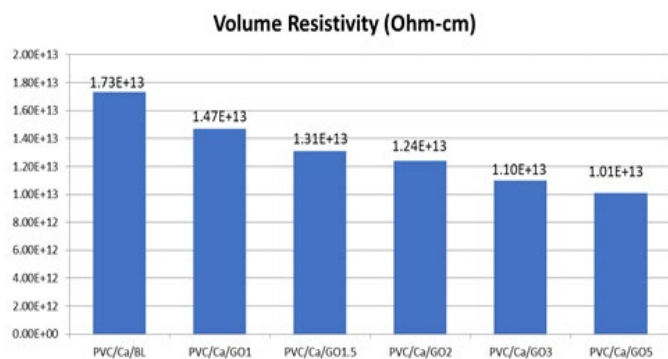


Fig. 6 Effect of different GO content on volume resistivity.

The effect of different contents of rGO on volume resistivity is shown in Fig. 7. Addition of rGO from 1 to 1.5phr reduces the volume resistivity gradually, thus improving the electrical conductivity compared to unfilled UPVC (PVC/Ca/BL). Further increase of rGO content improves the electrical conductivity. At an rGO content of 2phr the volume resistivity of the filled UPVC composite begins to decrease significantly by 1 order magnitude from 1.36×10^{13} to 8.0×10^{12} , implying a percolation threshold of 2phr for the rGO filled UPVC composites. A further increase of rGO content up to 5phr give only moderate increase in conductivity. Percolation threshold is the minimum filler content in the polymer matrix after which there is no significant change in electrical properties of the composites. When the rGO loading is lower than the percolation threshold, the rGO filled UPVC composites exhibit high electrical resistivity because these not well dispersed rGO by nature will have higher tendency to aggregate and isolate thus cannot form optimum conductive pathways at lower dosage. When the rGO loading reaches 2phr, the rGO begins to contact with each other, and consequently forms conductive pathways

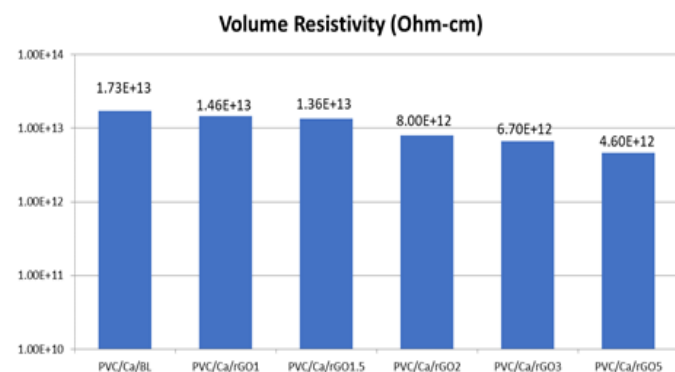


Fig. 7 Effect of different rGO content on volume resistivity.

The variation of different content of Pre-dispersed rGO (PDG) on the volume resistivity is shown in Fig. 8. Adding 0.5phr of PDG slightly decreases the volume resistivity thus indicating no significant improvement in electrical conductivity compared to unfilled UPVC (PVC/Ca/BL). However, at 0.75phr PDG content, volume resistivity of the filled UPVC nanocomposites decreased drastically from 1.61×10^{13} to 9.70×10^{11} . The percolation threshold of the PDG filled UPVC nanocomposites is at 0.75phr, which is much lower percolation value than the rGO filled UPVC composite at 2phr. A further increase in content level of PDG gave rise to a sharp increase in the conductivity. Subsequent increase in content level to 1, 1.25 and 1.5phr led to a decrease of volume conductivity to 8×10^{10} , 8.6×10^7 and 9×10^5 , respectively. At 1.5phr of PDG, the volume resistivity of the filled UPVC nanocomposites is already approximately 8 orders of magnitudes lower than the unfilled UPVC (PVC/Ca/BL).

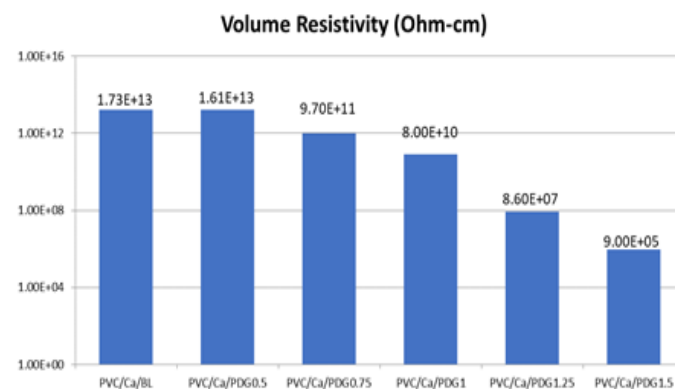


Fig. 8 Effect of different PDG content on volume resistivity.

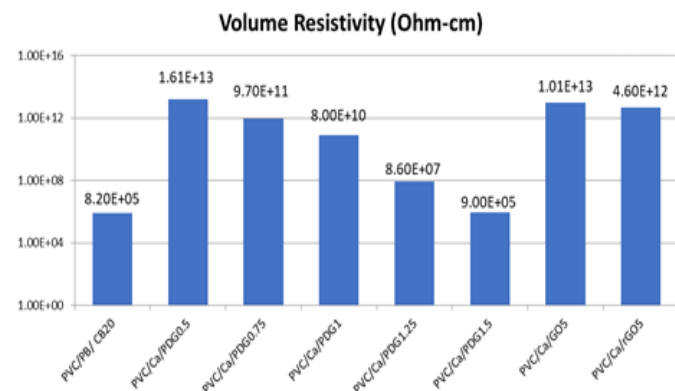


Fig. 9 Comparison between commercial CB-filled UPVC composite vs GO, rGO and PDG filled UPVC nanocomposites on volume resistivity.

Fig. 9 displays that the PDG from 0.75phr to 1.5phr exhibited lower volume resistivity thus implying the highest conductivity compared to the GO and rGO with lower percolation value of 0.75phr. It is worth noting that to accomplish electrical conductivity properties there is a need to have percolation, an interconnected graphene network throughout the composite which is accomplished at 0.1vol% theoretically. However, in practice, it can vary from ~0.1 to 3 vol. % [19].

rGO exhibited lower volume resistivity compared to GO filled UPVC composite at 5phr loading level. The fact is that GO made by a mechanochemical process yields edge-oxidized graphene oxide composed of a few layers of graphene. This mild oxidation process preserves only partly the carbon sp^2 orbitals on the surface of the flake, which affects its conductivity. In order to erase the functional group, GO is subjected to a reduction step. As the GO material is edge functionalized, it is more readily reduced. A suitable thermal, chemical and electrochemical route has been identified for the reduction conversion, where the rGO is created through a microwave process. This is a very clean process that does not leave any chemical residue and produces the same high-quality material as those produced through thermal treatments, presumably by fully restoring the graphitic network sp^2 bonds as pristine graphene. However, rGO will easily aggregate due to high cohesive interaction making it difficult to disperse. Although this lack of homogeneous dispersion limits its ability to enhance electrical properties of graphene filled UPVC nanocomposites but better result was yielded compared to GO which is close to the insulator.

The PDG filled UPVC composite exhibited significant improvement in the electrical conductivity because of the homogeneously dispersed rGO in PVC matrix [20]. The PDG is considered better than GO and rGO since the latter requires higher quantity of nanomaterial for improving the electrical conductivity while the former requires a very small quantity of nanomaterial and the reduction in the volume resistivity is also high. This PDG allows the formation of optimum conductive pathways at lower dosage due to well disperse rGO without aggregation. In general, an increase in the concentration of the nanoparticles in the polymer matrix will yield effective conductive network. However, higher dosage is required if rGO aggregates without being well dispersed. The nanofillers would stick to each other, resulting in the formation of micro particles since the surface area is high. The graphene sheets are also susceptible to restacking because of the strength of interaction among the particles and their high aspect ratio [21].

Fig. 9 also provides a comparison of the volume resistivity behavior between CB-filled UPVC Composite and PDG. From these results, it can be observed that the addition of 1.5phr PDG (0.45phr content of rGO) provides value of 9.0×10^5 Ohm-cm which is comparable to the electrical conductivity in comparison with the commercial CB filled UPVC composite use to produce mining pipe application at 8.2×10^5 . This level of conductivity opens the door for the pre-dispersed UPVC nanocomposites for mining pipe application.

CONCLUSIONS

A PDG (pre-dispersed rGO in FT wax) filled UPVC nanocomposites was developed by using conventional melt-mixing methods and has the potential to be used in mining pipe application. Some of the important conclusions drawn from the study are discussed in this section.

It was found that the addition of graphene derivatives reduced the volume resistivity thus improving the electrical conductivity. Increasing the graphene content resulted in lower volume resistivity. From the results it can be observed that the PDG is a better option compared to GO and rGO since it gave the lowest percolation value of 0.75phr and at 1.5phr (0.45phr rGO content) and achieved a comparable volume resistivity value than the commercial CB filled UPVC composite for mining pipe application. Hence, it can be concluded that the dispersibility of graphene should be maximized within PVC matrix to achieve optimum electrical properties of graphene filled UPVC

nanocomposites. This level of conductivity opens the door for the pre-dispersed UPVC nanocomposites for mining pipe application.

On the other hand, the pre-dispersed rGO filled UPVC composites can greatly improve processing with lower machine torque, produce greater length per kg due to lower density and finally lower production cost compared to commercial filled UPVC composite for mining pipe application which is closely associated with much lower loading level of PDG.

A proper measure of work has been performed and significant inferences have been drawn. However, a research is an endless process, future works can possibly be carried out such as to investigate the effect on mechanical, thermal and rheological properties of the PDG filled UPVC nanocomposites.

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