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Effect of Vinyltrimethoxysilane as a Coupling Agent on The Mechanical and Electrical Properties of Acrylic Rubber

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WHEN there is a need for enhancing the adhesion between a polymeric material and the filler, silane coupling agents are the best choice. in order to enhance the adhesion between acrylic rubber (acm) and silica, vinyl trimethoxysilane (vtms) can be used for this purpose. acrylic rubber was prepared by emulsion polymerization. vtms was added during the polymerization process to copolymerize with acm. vtms was added in different per cent; 0, 0.25, 0.5, 1.0 and 2.0 %. the effect of adding different percentages of vtms on the mechanical, thermal and mechanical properties was monitored. mechanical properties were significantly improved due to silane incorporation to the acrylic rubber matrix. the thermal stability of acrylic rubber increased due to silane addition. electrical measurements revealed that the volume resistivity, dielectric strength and breakdown voltage were also increased.

Keywords: Acrylic rubber, Silane, Rheometric characteristics, Sem, Mechanical and, Electrical properties.

Introduction

Acrylic rubber (ACM) is a copolymer of ethyl acrylate or other acrylates that have a small amount of cure site monomers which facilitates the vulcanization process. Being polar in nature, the backbone of these elastomers nominates them to be used in many applications such as automotive seal, hoses, belting and electrical cable jacketing [1,2]. To be cured and vulcanized, ACM needs cure sites such as; epoxy, chlorine and carboxylic cure sites. For safety matters, Carboxylic and epoxy cure sites are much better than chlorinated ones which were found to be toxic and corrosive.

Although they are polar in nature, ACM always shows incompatibility with fillers. This will obstruct the good dispersion of the filler particles within the acrylic rubber matrix. This incompatibility can be removed by surface modification surface treatment of fillers used in the rubber formulation. Surface treatment of fillers and reinforcements is often performed to improve the interfacial interaction [3,4]. It has been reported that the addition of silane coupling agents to rubber filled with silica or carbon black enhances the adhesion between fillers and polymer molecules. Being hybrids of silica and organic materials, silanes were recommended to improve bonding of polymers /glass fiber composites. Many studies reported the incorporation of silane coupling agents to enhance the adhesion between fillers and polymer molecules. It has been found that the addition of silane coupling agent leads to an improvement in the interaction between feldspar and polypropylene matrix and results in an increase in the tensile strength, tensile modulus, flexural strength, flexural modulus and impact strength [5]. Lyly et al found that silanes can affect the electrical properties of some composites. She studied the effect of

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using different types of silanes on the electrical properties of nanocomposites [6]. It was reported by Hashimoto and others that the use of coupling agents reduces the polymer viscosity leading to a better penetration of it into the reinforcing agent of the polymer matrix [7-9]. Silanes can also be used to modify the surface of nanofillers in order to get better properties.

Silver nanocomposite in epoxy nanocomposite with silane caused an improvement of the nanoparticle dispersion, electrical and flexural properties [10]. Shah studied in details the rubber modification by silane [11]. The rubber modification was carried out by grafting polymerization of the rubber surface with silane momomers. Grafting with silane may take place before mixing with other ingredients. Lee et al. added silane monomers during the mixing itself.

Recently, ACM was prepared via emulsion polymerization. Strictly speaking, emulsion polymerization can takes place in a system with only four components, a monomer that forms the structure of the polymer, water that acts as the continuous medium in which the polymer particles are dispersed, an initiator that produces free radicals which start and maintain the polymerization process, and surfactant that provides the initial site from which polymer particles subsequently grow and give stability to the growing particles [12,13]. In addition, most commercial recipes would normally include other ingredients to impart specific properties to the final polymer or emulsion, for example, a modifier to control the molecular weight of the polymer or a cross-linking agent to control the amount of gel [14,15]. Many researchers studied in details of the emulsion polymerization mechanism, factors Controlling the process itself [16-21] and the rate of emulsion polymerization [22,23].

In this study and in order to improve the properties of ACM composites, silane coupling agent was added during the emulsion polymerization of acrylic monomers. Different concentrations of VTMS were added to the mixture of ethylacrylate (EA) and methacrylic acid (MMA) as indicated and the effect of adding different silane percentages on the mechanical, thermal and electrical properties.

Experimental

Materials

Methacrylic acid (MMA) and ethylacrylate (EA) were supplied by Elf chem. Co., ATO, France. Trimethoxyvinylsilane (TMVS), Silquest A-171, was supplied from Momentive Performance Materials Inc., USA. The emulsifier, sodium laurylether sulfate (Glaxy LES 70), (conc. 68%) was supplied by Glaxy co., India. 1,3-di-o-tolylguanidine(DOTG) was brought from Alfa Aesar Gmbh & Co KG, Germany. Hexamethylenediamine carbamate (HMDC) was from DuPont Dow Elastomers, Freeport, TX. Precipitated silica ULTRASIL VN 3 GR was supplied by Evonik co., Germany. Other chemicals listed in the formulation were obtained as laboratory grade from indigenous sources.

Preparation of acrylic rubber samples

The preparation of ACM was carried out via emulsion polymerization. Two feed streams were fed to a 2 liter three-necked round bottomed flask. The first feed stream was the pre-emulsion solution. It was a mixture of 400 g of monomers (MMA, EA and VTMS), 9 g of Galaxy LES 70 and 249 g of distilled water. The ratio of EA % to VTMS % was varied as indicated in Table 1. Further increase in VTMS percent over 2% leads to a dramatic drop of some mechanical properties especially the elongation percent [24]. The mixture was stirred with a mechanical stirrer at 500 rpm and the temperature was kept constant at 85 °C for one hour. The second feed stream was the initiator solution. The initiator solution was prepared by dissolving 2 g of sodium persulfate in 98 g of distilled water. The temperature of flask contents was kept at 85 ˚C and stirring rate 200 r p m. The per-emulsion and initiator solutions were continuously and gradually fed to the three necked flask over a range of 2 hours. The reaction temperature was held constant at 85 °C for another 2hrs to ensure high percentage of monomers conversion and the flask was then cooled and filtered. A 1% NaCl solution was added to the filtrate to precipitate the acrylic rubber. The final product was washed and dried in an oven at 105˚C for 5 hrs.

TABLE 1. The per cent ratio of vinyl trimethoxy silane (VTMS) in acrylic rubber composites.

Mix	Bo	B1	B2	B3	B4
EA (%)	95.0	94.75	94.5	94.0	93.0
MAA (%)	5.0	5.0	5.0	5.0	5.0
TVMS (%)	0.0	0.25	0.5	1.0	2.0

Mixing Procedure

Mixing was accomplished on a laboratory mill; 170 mm diameter and 300 mm working distance. The speed of the slow roll is 24±0.5 rpm and the ratio between the slow and the fast rolls is 1:1.4. The mill has the facility of roller temperature control. Mixing starts with Mastication of the prepared ACM for 5 minutes. They were passed through the mill repeatedly till the rubber became plastic enough to receive the other ingredients. All other ingredients shown in Table 2 were then added to finish mixing. Test specimens for the cure meter and the tensile testing machine measurements were taken and the rest of the batch was then passed through the mill into sheets. Vulcanized sheets (from which standard dumbbell shape samples were cut) were produced by molding in an electrically heated platen press at 180°C at the time estimated for each sample from the rheometer measurements. The postcuring of test specimens of all mixes was carried out in an oven at 180°C for 4 h.

TABLE 2. Formulations of acrylic rubber mix ingredients and Rheometeric properties.

Mix	B_o	B_1	B_2	B_3	B_4
Ingredients (phr)					
Acrylic Rubber	100	100	100	100	100
Precipitated Silica	30	30	30	30	30
Stearic Acid	1	1	1	1	1
6PPD	1	1	1	1	1
DOTG	2	2	2	2	2
HMDC	1	1	1	1	1
Rheo. Characteristics					
M_L (kg.cm)	0.1	0.2	0.3	0.4	0.4
M_H (kg.cm)	3.5	4.4	4.7	5.3	5.6
ΔM (kg.cm)	3.4	4.2	4.4	4.9	5.2
t_{S1} (min)	2.5	2.5	2.4	2.1	2.1
t_{S2} (min)	5.3	5.1	4.6	3.6	3.5
t_{90} (min)	12.2	13.4	13.5	13.8	13.3
Cure Rate Index (CRI)	14.6	12.0	11.2	11.1	10.3

Characterization

Rheometric Data

The cure characteristics of the rubber mixes were determined at 180 °C according to the technical procedures of the ASTM D 2084-11. The cure characteristics were measured using the oscillating disc rheometer, MRD 2000, Alpha Technology, UK. Rheometery was run at 180°C to determine the scorch time after two (t_{S2}) the cure time (t_{90}) minutes, , the minimum torque (M_L) and maximum torque (M_H) of each composite and Delta torque ($\Delta M= M_H - M_L$) in kg.cm and Cure Rate Index.

Mechanical Properties

Tensile specimens were punched out from the molded sheet using ASTM Die and the mechanical testing was carried out as per ASTM D 412-15a in a universal Zwick Tensile Testing Machine Z 010/TH2A, Germany, at a crosshead speed of 500 mm/min at 25°C. The average value of five tests for each sample is reported here.

Hardness Shore A

Hardness testing measurements were carried out according to ASTM D 2240-15. Hardness determinations were made using a Zwick Hardness Tester 3150, Germany. Test specimens used were cylindrical in shape whose thickness and diameter were 6.00 ± 0.2 mm and 14.00 ± 0.2 mm respectively.

Crosslink Density Calculations

The stress–strain relationship was expressed according to the statistical theory of rubber like elasticity relating the force F per unit area A required for stretching a perfectly elastic network at small extension value λ is given by:

$$\frac{F}{A} = \frac{\rho RT}{Mc}\left(\lambda - \lambda^{-2}\right) = 2C_1\left(\lambda - \lambda^{-2}\right) \qquad (1)$$

Where, ρ is the density of rubber, T is the absolute temperature, R is Boltzman's constant and M_c is the number average molecular weight of the network. This is sometimes known by molecular weight between two crosslinks. The C_1 is known by conventional elastic constant at a given temperature. The crosslink density υ can be calculated from the following equation:

$$\upsilon = \frac{1}{2Mc} \qquad (2)$$

Compression set

The compression set test was done under a constant strain of 25% according to ASTM D 395-16 at 150°C for 72 h. The compression set per cent can be calculated from the following equation:

$$Compression\ Set = 100 \times {}^{(t_o - t_f)}\!/_{(t_o - t_s)} \qquad (3)$$

Where, t_o is the original thickness, t_f is the final thickness, t_s is the spacer height.

FT-IR

FT-IR (JASCO 430 FT-IR, ATR) spectra were carried out, in the 4000-400 cm-1 range. UV-visible spectra were recorded on JASCO UV-visible spectrometer, V-650 model. Absorption spectra were recorded at ambient temperature using 1 cm path length cells.

SEM

The microstructures of all samples were observed using a JEOL scanning electron microscope JSM-5500, Japan. The samples were coated with gold by a gold sputter coater (SPI - module).

Thermal Gravimetric Analysis (TGA)

Thermal Gravimetric Analysis (TGA) of all acrylic rubber samples carried out using Shimadzu-50 Thermogravimetric Analyzer in presence of air at a rate of 10 °C/min, using temperature range of 25 °C to 600 °C. Degradation temperature of the composites was studied through this analysis.

Electric Properties

The breakdown voltage was measured by putting a circular sample with diameter 5 cm and 2mm thickness as sandwich between two electrodes at room temperature under an AC voltage ramp of 750 V/sec. The ac voltage was increased with a rate of 750 V/Sec. until breakdown occurred. Dissipation factor or loss tangent (Tan δ) and insulation resistance were measured directly using Agilent E4980A LCR meter. The dielectric constant, Dissipation factor and insulation resistance were measured at three frequencies 1, 10 and 100 kHz. Dielectric constant was also measured by using the same sample dimensions. The dielectric breakdown measurements were performed using AC Dielectric Test Set. The samples were sandwiched between two electrodes and tested at room temperature under an ac voltage ramp of 750 V/sec. The AC voltage was increased with a rate of 750 V/Sec until break down occurred. The equivalent parallel capacitance (Cp) was measured directly from the apparatus then, the dielectric constant was calculated from the following equation:

$$\epsilon_r = \frac{C_p\, t}{\epsilon_o\, A} \qquad (4)$$

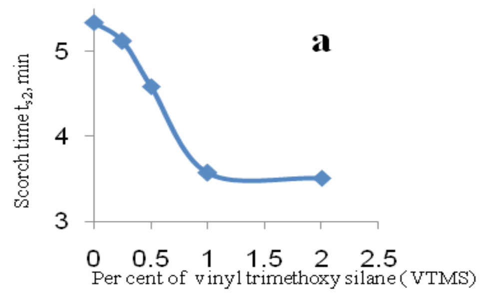
Where, E_0 = 8.854 × 10 - 12 F/m is the permittivity of free space, *t* is the thickness of the samples and *A* is the area of electrodes.

Results and Discussion

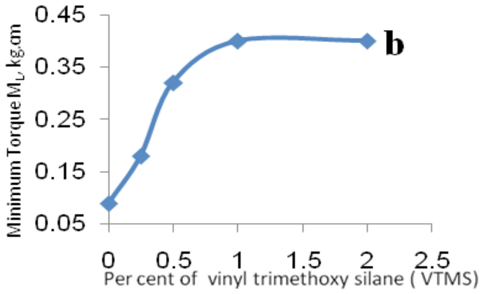
Rheometric Data

Cure curves of the acrylic rubber compounds having different percentages of VTMS are shown in Fig. 1 (a-f). Scorch time (ts_2) is a measure of time when the premature vulcanization of the material occurs. From Fig. 1-a, it can be seen that scorch time decreased with the increasing percent of VTMS. This decrease is maximum for the acrylic rubber mixes containing 1 and 2 % of VTMS. This may be attributed to the viscosity increases with the increase of percent of VTMS in acrylic rubber mixes. Therefore, a shorter time was required for the beginning of the vulcanization process for the acrylic rubber compounds reflecting the effect of the silane addition to acrylic rubber. The minimum torque (M_L) is a measure of stiffness of the unvulcanized test specimen taken at the lowest point of the cure curve. It can be seen from Fig. 1-b that the minimum torque increased with increasing the silane percentages. This is because of the viscosity increase due to crosslink formation before curing. In addition to being physically compatible with acrylic rubber, the silane with its vinyl group can covalently bonded with the acrylic rubber matrix giving rise to the increase in crosslink density before curing [27]. The maximum torque (M_H) is a measure of stiffness or shear modulus of the fully vulcanized test specimen at vulcanization temperature. In other words, it is also an indicator for the crosslink density of rubber; the higher the M_H value, the higher the crosslink density [28]. Both the maximum torque and the difference of delta torque between the maximum and minimum torque (ΔM) increased with the increase of the silane as a result of the increased formation of crosslinks between the macromolecular chains, leading to the increase in the viscosity of the fully vulcanized acrylics, specilally for those of higher per cent of silane. The effect of adding silane is very clear for the smallest silane percent (0.25 %). Th cure time (t_{90}) increases with the increase of the silane per cent. This increase in the cure time is due to the more time needed for formation of more crosslinks as the silane per cent increase. Further addition of silane percentages has a slight effect on the cure time. This is due to the fact that the silane can act as a compatlbilizer leading to that slight change in cure time [29].

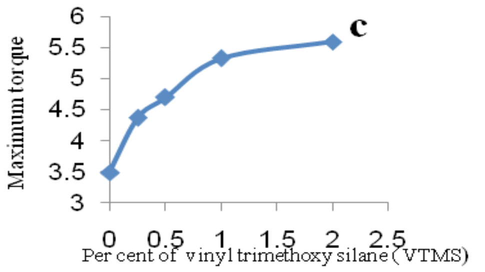
The Cure Rate Index (CRI) of all acrylic rubber composites was calculated according to



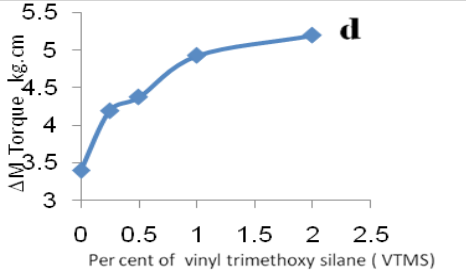
Effect of adding Diferent per cent of VTMS on Scorch time of acrylic rubber composites.



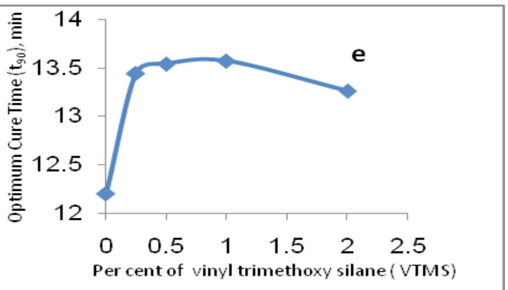
Effect of adding Diferent per cent of VTMS on Minimum Torque of acrylic rubber composites



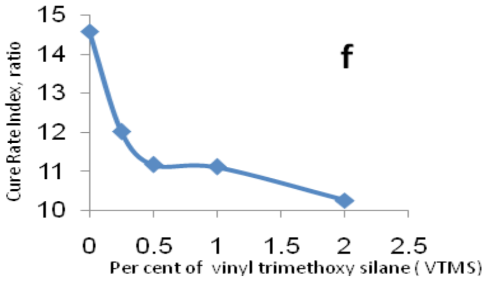
Effect of adding Diferent per cent of VTMS on Maximum Torque M_H of acrylic rubber composi



Effect of adding Diferent per cent of VTMS on Torque difference (ΔM)of acrylic rubber



Effect of adding Diferent per cent of VTMS Optimum Cure Time (t_{90}), min of acrylic reuuer composites



Effect of adding Diferent per cent of VTMS Cure Rate Index of acrylic reuuer composites

Fig. 1. Rheometric curves of acrylic rubber composites containing different per cent of vinyl trimethoxy silane (VTMS).

the following formula [17]:

$$\mathrm{CRI} = {}^{100}\!/_{(t_{90} - t_{S2})} \qquad (5)$$

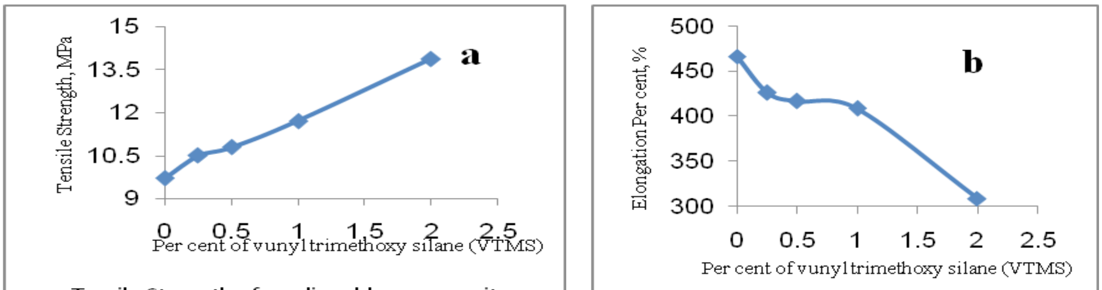
Data of the cure rate index (CRI) of the rubber recipe at different VTMS percent contents showed that CRI decreases with the increase of VTMS reflecting the role of silane in enhancing the vulcanization rate and showing a cure acceleration effect of VTMS at higher percent levels.

Generally, the addition VTMS to acrylic rubber during emulsion polymerization lead to the increase of the values of torque, and cure rate. This increase is maximal for the Mix B4 that has 2 % of VTMS. B4 possesses the maximum number of the functional silane that can link more and form more crosslinks leading this mix to have the lowest CRI. In fact B4 acrylic rubber composite represents the best rheometric data obtained among all other mixes.

Mechanical Properties

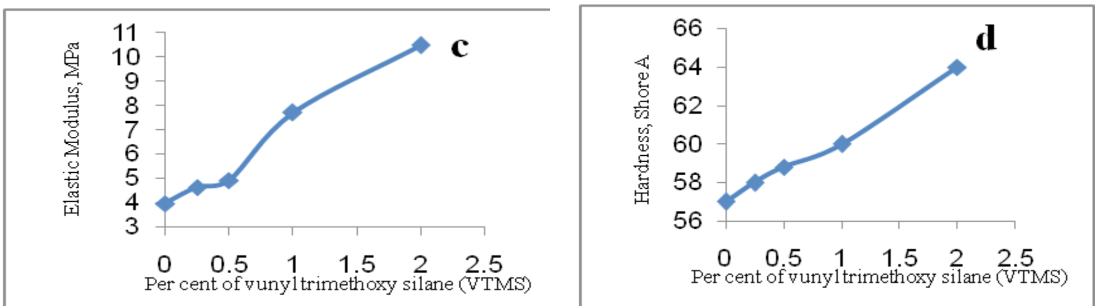
The mechanical properties of acrylic rubber mixes, such as toughness, impact strength, elongation at break, etc., determine their potential applications by stress-strain behavior. The changes in values of tensile strength, elongation modulus and hardness as the silane % increases from 0 to 2% are given in Fig. 2 (a-d). From these stress-strain curves, it is clear that the tensile strength increases with the increase of the VTMS percent reaching a maximum value at 2 % and resulting in an increase of more than 40 %. This improvement reaches its maximal levels when the VTMS percent is 2 %. Similar trends were seen with respect to the elastic modulus of the acrylic rubber mixes. The modulus of all vulcanizates is increased with raising VTMS percent from zero to 2 %, giving a raise in elastic modulus values of about 300 % compared to zero percent mix. This is due to the increase in the crosslink density of the vulcanizates at higher percentages of VTMS. These results are in good agreement with the results of the measurements of the crosslink density and the maximum torque from rheological measurements results as well. The case was reversed with regard to the elongation % at break, it showed a regular decrease approaches about 30% at higher VTMS %.

It is important to note that the hardness value



Tensile Strength of acrylic rubber composites containing different per cent of VTMS

Elongation Per cent of acrylic rubber composites containing different per cent of VTMS

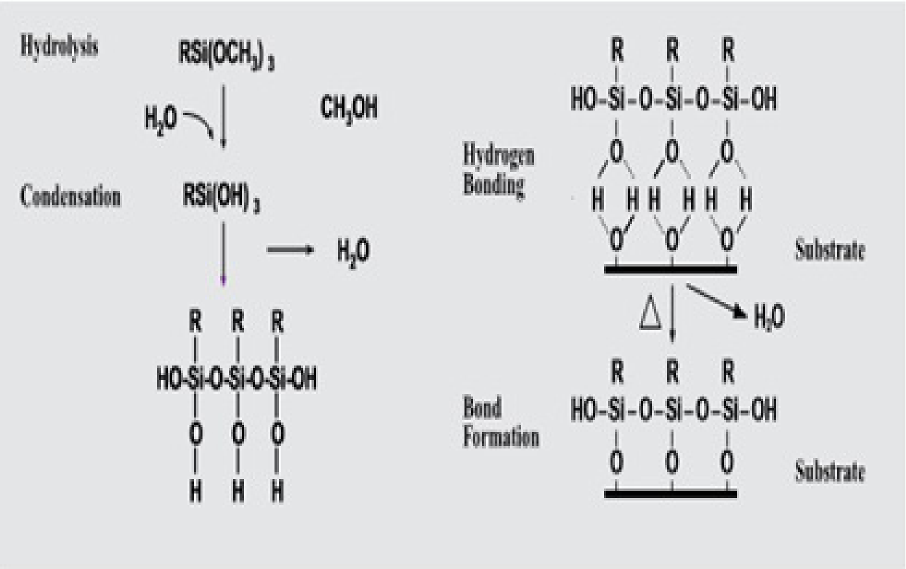


Elongation Modulus of acrylic rubber composites containing different per cent of VTMS

Hardness of acrylic rubber composites containing different per cent of VTMS

Fig. 2. Mechanical properties of acrylic rubber composites containing different per cent of vinyl trimethoxy silane (VTMS).

of the vulcanizates indicates also the same trend as the modulus values. The enhancement of the mechanical properties and hardness with the increase of VTMS per cent is due to the fact that the addition of VTMS which is tightly held to the skeleton of the acrylic rubber is also bonded well to the hydroxyl groups on the silica surface. The methoxy groups on silicone hydrolyze to silanols, either through the addition of water or from residual water on the inorganic surface. Then the silanols coordinate with metal hydroxyl groups on the inorganic surface to form an oxane bond and eliminate water. This mechanism is shown in Scheme (1), where R group represents the acrylic rubber molecule. A similar trend is observed for elongation modulus reaching its maximumal levels at 2 % of VTMS (Mix B_4). The modulus of all acrylic rubber vulcanizates are increased with increasing the percentage of VTMS. It is important to note that the hardness value of the vulcanizates indicates also the same trend as the modulus values. These results can be explained on the basis of results obtained by crosslink density calculations showing higher values for the mix that has the highest per cent of VTMS.



Scheme 1. Coupling of silane with substrate containing hydroxyl group.

Crosslink density

Table 3: Crosslink density and molecular weight between two crosslinks of acrylic rubber composites containing different per cent of VTMS

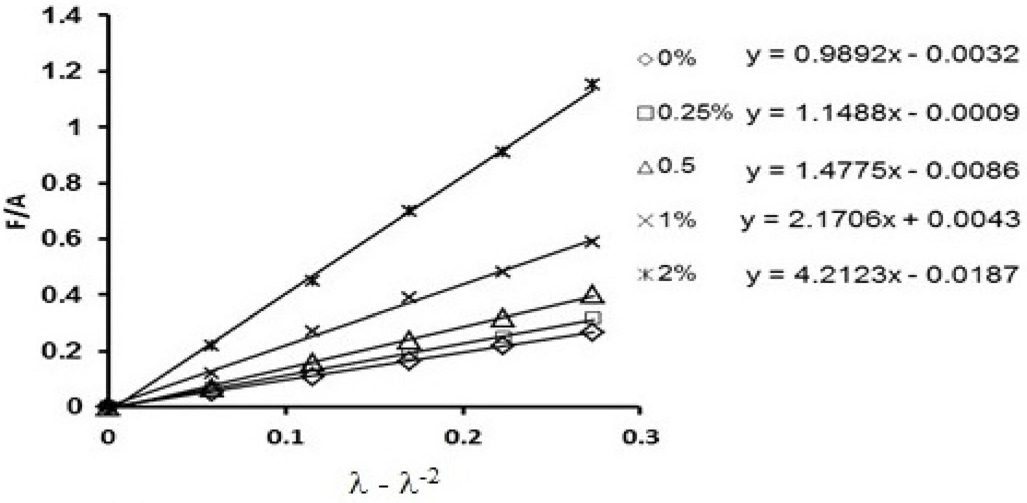
The crosslink density for all mixes was calculated from stress-strain measurements. For each extension ratio λ the value of $(\lambda - \lambda^{-2})$ was calculated and plotted against the applied stress F/A. The stress strain curves showed almost straight lines as shown in Fig. 3. Figure 4 and Table 3 represent behavior of acrylic rubber composites having different percentages of with respect to the molecular weight between two crosslinks (M_c) and the crosslink density (υ). The molecular weight between two crosslinks increases with the increase of the VTMS per cent, while the crosslink density increases. The increase of crosslink density with increasing of VTMS is may be due to the condensation between silanols groups to form oxane bonds between acrylic rubber composite chains [30, 31].

TABLE 3. Values of crosslink density of different mixes containing different TMVS%.

Mix	Mc(g.mol^{-1})	υ (g-1.mol)*10^5
B_o	2679.50±195.20	18.66±1.33
B_1	2359.38±37.86	21.19±0.34
B_2	1833.83±100.87	27.27±1.5
B_3	1248.19±28.67	40.06±0.92
B_4	643.09±9.10	77.75±1.1

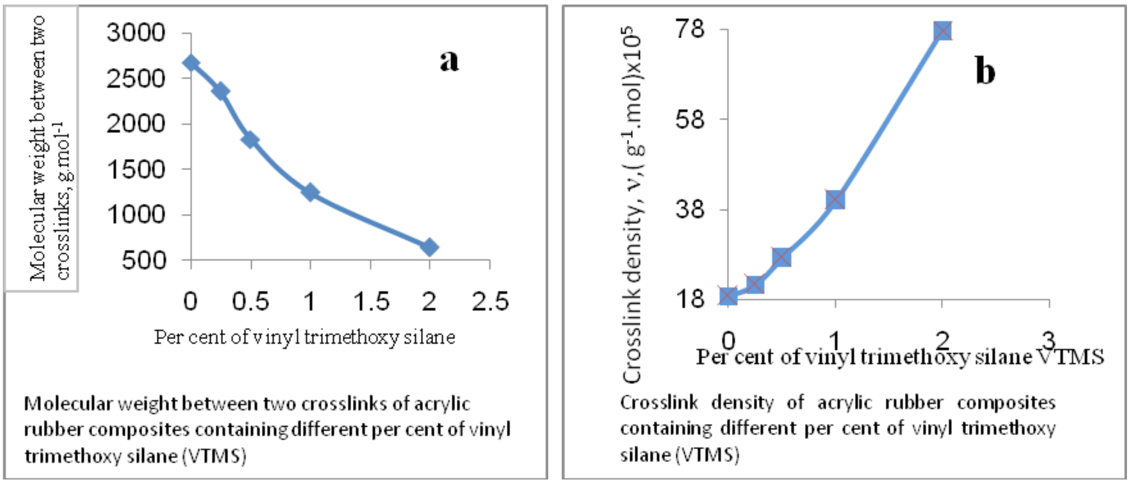
Compression set %

To improve the compression set, it is necessary to prevent chain slipping. Chain slipping could be decreased by chemically bonding between polymer and filler. TMVS was used in this study to bond polymer and filler chemically. In our study TMVS was copolymerized with acrylic rubber's monomers to produce silane modified ACM. Silanol groups of Silane can react with the hydroxyl groups of silica as mentioned before.



where, F/A is the force per unit area and λ is the value of a small extension

Figure (3): Stress strain curves of acrylic rubber composites containing different per cent of vinyl trimethoxy silane (VTMS)



Molecular weight between two crosslinks of acrylic rubber composites containing different per cent of vinyl trimethoxy silane (VTMS)

Crosslink density of acrylic rubber composites containing different per cent of vinyl trimethoxy silane (VTMS)

Fig. 4. Crosslink density and molecular weight between two crosslinks of acrylic rubber composites containing different per cent of vinyl trimethoxy silane (VTMS).

Table 4 and Fig. 5 show the effect of silane modification on the compression set value of acrylic rubber composites. The compression set of ACM composite improved as the TMVS increased, where Fig. 5 showed a linear relation between TMVS % and compression set. The improvement of compression set resulted from TMVS modification may be due to the increase of crosslinking and the chemical bonding between ACM and silica [32,33]. Figure 6 shows there is a gradual decrease in compression set value with increasing of crosslink density.

TABLE 4. Values of compression set of different mixes containing different TMVS %.

Mix	Compression set
B_o	42.3±1.2
B_1	42.0±0.7
B_2	41.0±1.3
B_3	37.5±0.9
B_4	33.3±1.1

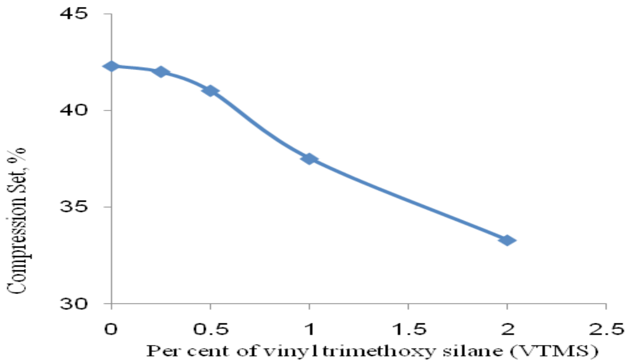


Figure 5: Cpmpression Set of acrylic rubber composites containing different per cent of vinyl trimethoxy silane (VTMS)

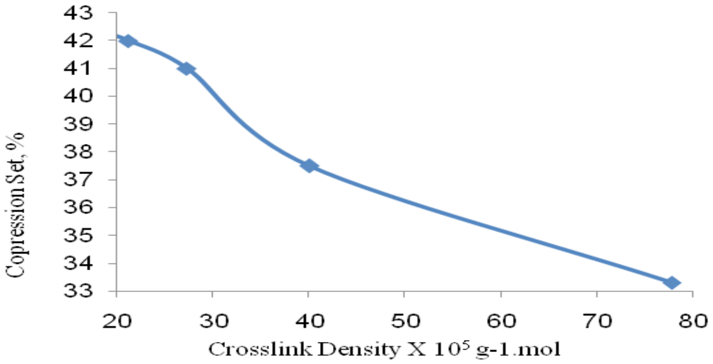


Figure 6: Relationship between cmpression set % and crosslink density of acrylic rubber composites containing different per cent of vinyl trimethoxy silane (VTMS)

FT-IR

FT-IR analyses were used for the detection of chemical reactions leading to chemical coupling of the polymer and filler. To facilitate the understanding of the following discussion, the relevant spectra of the prepared acrylic rubber (A) and acrylic rubber containing VTMS (B) are presented in Fig. 7. As seen in this figure, Acrylic rubber shows its characteristic peaks starting from the broad peak at 3340 cm^{-1} which represents the OH vibration of the –OH in the carboxylic group –COOH. The strong absorption peak at 1726 cm^{-1} shows the stretching vibration of carbonyl (C=O). Absorption peaks at 1446 cm^{-1} and 1380 cm^{-1} result from the asymmetric stretching vibration and symmetric bending vibration of the –C–H– in the methyl group, respectively. The peak at 1155 cm^{-1} is due to the vibration of C-O in the ester group. Peaks at 1166, 972, 840, and 808cm^{-1} result from vibration of the rocking of -CH_3 and –CH_2 and the stretching of CH–CH_2 and CH–CH_3 [34-36]. The spectral curve of acrylic rubber containing TMVS (B) possesses two peaks, the first at 1060/1040 cm^{-1} assigned to the linear Si-O-Si linkage and the second is a relatively small rather sharp peak at 950 cm^{-1} representing the Si-OH of vinyl trimethoxy silane [37,38]. These two peaks indicate the incorporation of VRMS into the acrylic rubber matrix.

SEM

The SEM micrograph images of acrylic rubber composites with and without VTMS are shown in Fig. 8(a-e). The micrograph gives a proof on the effect of silane on the morphological structure. It is clear that the control sample (Bo) showed a surface roughness due to the heterogeneity of the polymer matrix and resulting in a detrimental effect as indicated by the values of the torque, Hardness and mechanical properties of this polymeric mix. The SEM photograph of Fig. (8-b) showed a significant enhancement of the surface morphology with the contribution of a small percent of 0.25 % of VTMS (B1). This positive impact continued to increase and became maximum at Fig. (8-e) using 2 % of VTMS which gave rise to smoother surface indicating a complete miscibility of the silica filler and acrylic rubber showing one phase rubber blend. Thus, VTMS has been proven to be more effective in improving the filler–matrix interaction in one hand and enhancing the rubber miscibility and mechanical properties on the other hand. The use of larger amounts of silane is believed to be responsible in promoting the compatibility between silica and ACM rubber and forms a dispersible network within the rubber blend matrix which enhances the rubbers miscibility with each other [39,40].

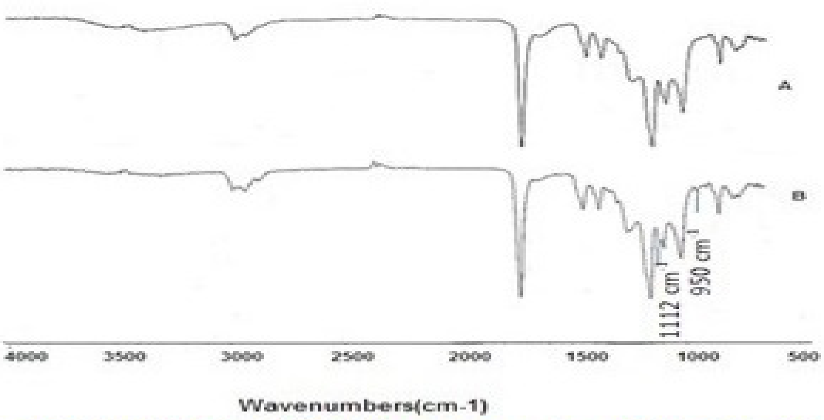


Figure (7): FTIR of acrylic rubber composites; (A) without and (B) with VTMS

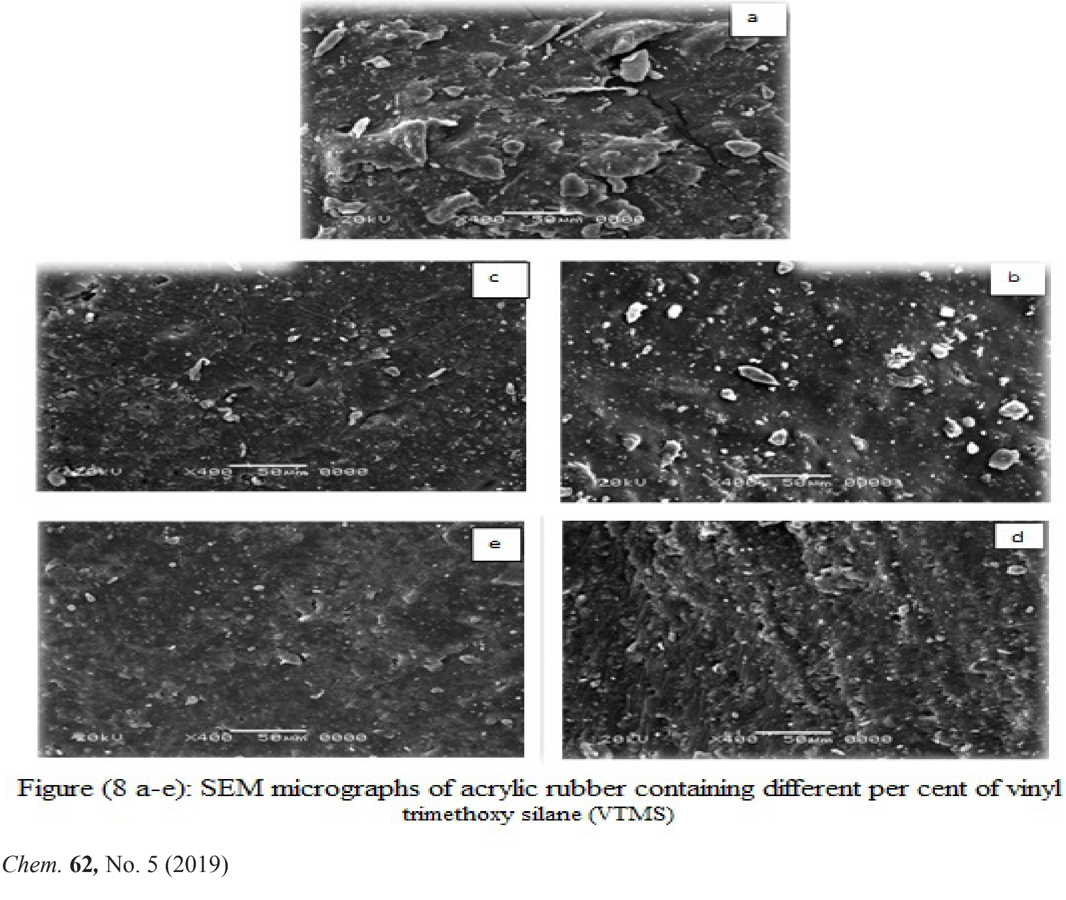


Figure (8 a-e): SEM micrographs of acrylic rubber containing different per cent of vinyl trimethoxy silane (VTMS)

Thermal Properties

High temperature thermal analysis (TGA) (50-600°C) curves for the samples are shown in Fig. 9 and Table 5. (T_i) represents the temperature at which the degradation of the acrylic rubber mixes starts, (T_{20}) is the temperature at which 20% degradation occurs and (T_{Max}) is the temperature at which Maximum degradation of rubber takes place. (Residue %) is the percent of the remaining weight after at the end of degradation. All these parameters were summarized in Table 5. The initial temperature of the acrylic rubber mix containing a low percent of VTMS (0.25 %) was shifted to higher temperature reflecting an increase in the thermal stability of the mix due to silane effect. This raise continues with increasing VTMS % in the other mixes. The increase in thermal stability is maximal for rubber mix containing 2.0 % of VTMS. A similar trend was seen for the residue % at 600 °C. As the temperature of all rubber mixes increases, degradation starts showing more stability of acrylic rubber samples containing higher percentages of VTMS. This increase in temperature levels is due to the fact that C-C bond energy is less than that those of C-Si and Si-O bonds. Therefore, with an increase in the VTMS per cent, the networks formed by VTMS increased with more C-Si and Si-O bonds, and the weight loss of the sample decreased reflecting an increase in the thermal stability of acrylics having high concentrations of VTMS [41].

Electric Properties

TABLE 5. Thermal parameters of acrylic rubber composites containing different per cent of vinyl trimethoxy silane (VTMS).

Mix	T_i, °C	T_{20}, °C	T_{50}, °C	T_{Max}, °C	Residue % at 600 °C
B_o	325.39	333.44	366.78	366.78	3.90
B_1	340.92	354.40	391.92	393.54	4.30
B_2	345.96	355.67	392.26	394.75	4.22
B_3	354.92	361.26	393.78	396.69	8.22
B_4	363.16	367.50	400.36	401.50	8.19

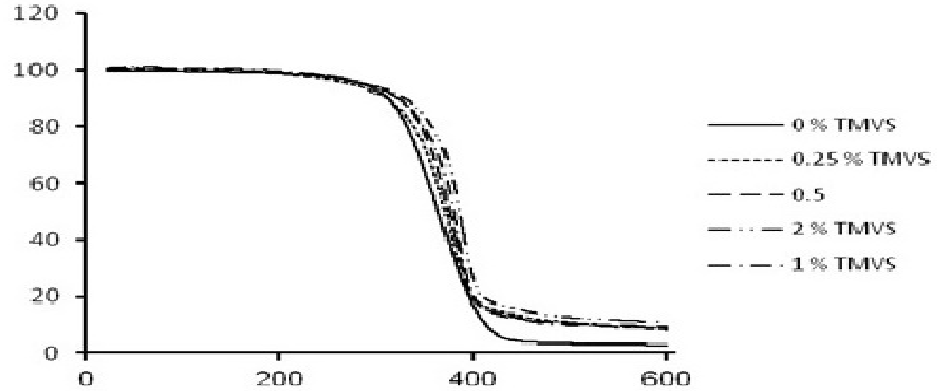


Figure (9): TGA curves of the acrylic rubber composites containing different per cent of vinyl trimethoxy silane (VTMS)

Volume Resistivity

Results of the electrical properties are all tabulated in Table 6. Resistivity studies are crucial for insulating materials since the most desirable characteristic of an insulator is its ability to resist the leakage of the electric current. The resistivity of all acrylic rubber mixes are plotted against the silane percent concentration at 100 KHz frequency. Figure 10 shows the variation of the volume resistivity (ρ_v) of acrylic rubber mixes having different percentages of TVMS. The results showed an appreciable increase in the volume resistivity of the acrylic rubber with the increase of the VTMS percent ratio followed by a remarkable increase in the volume resistivity at higher percent ratios. This is due to the increase in the cross-linking density for mixes having higher percent ratios of VTMS. The presence of much more cross-linking points in the rubber can be considered as barrels to prevent the charge movement between rubber chains and thus increase the volume resistivity of the crosslinked mix [42-44].

TABLE 6. Electric properties of acrylic rubber mixes having diffper cent concentrations of silanes.

Mix	ε_r	tan δ	$\rho\times10^8$, Ω.mm	Dielectric Strength, kV/mm	Breakdown voltage, kV
B_o	$7.55\pm1*10^{-4}$	$0.0498\pm1.7*10^{-6}$	$5.03\pm12*10^{-5}$	12.63±0.37	22.55±0.67
B_1	$7.76\pm1.9*10^{-4}$	$0.0510\pm1.4*10^{-6}$	$5.13\pm16*10^{-5}$	12.74±0.68	22.67±1.22
B_2	$7.69\pm0.7*10^{-4}$	$0.0520\pm2.8*10^{-6}$	$5.18\pm12*10^{-5}$	13.08±0.59	22.88±1.06
B_3	$7.5\pm0.8*10^{-4}$	$0.0488\pm1.7*10^{-6}$	$5.81\pm13*10^{-5}$	13.20±0.25	23.07±0.46
B_4	$7.57\pm1.5*10^{-4}$	$0.0483\pm1.8*10^{-6}$	$5.88\pm19*10^{-5}$	13.50±0.36	24.29±0.66

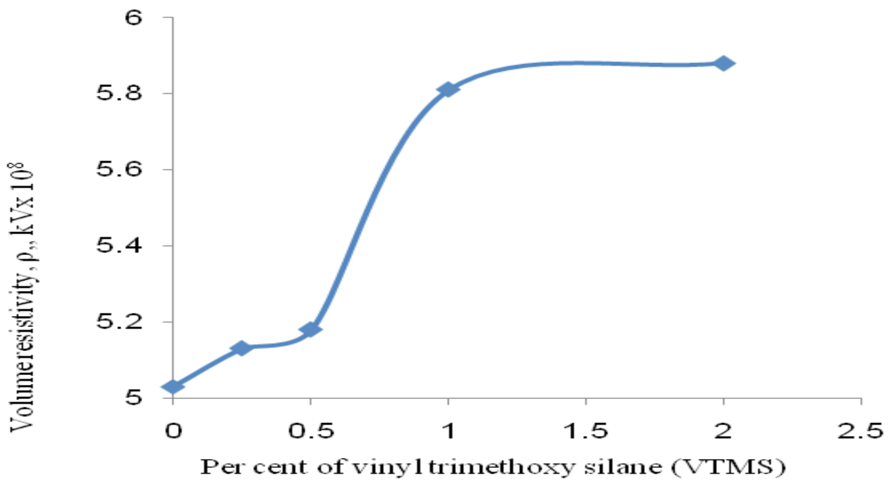


Figure (10): Volume resistivity of acrylic rubber composites having different per cent of vinyl trimethoxy silane (VTMS)

This is in agreement with the Kolesov study [45] in which he described the influence of molecular weight on morphological and electrical properties of PE, he also has shown that the increase of the molecular weight leads to an increase in the volume resistivity. Also Marsacq et al. [46] have shown that the increase in molecular weight leads to an increase in charging ability of PE, i.e. the growth of a number of traps in material which prevent the charge movement inside the polymeric material and hence increase the electrical resistance.

Dielectric Strength

Figure 11 shows the relation between the VTMS percent ratio and the dielectric strength. The dielectric strength increases linearly with the percent ratio giving the highest value for acrylic rubber containing 2 % of VTMS. This is results from the effect of increasing the crosslinking density as mentioned before.

Breakdown voltage

The dielectric strength of an insulating material is defined as the maximum voltage required producing a dielectric breakdown. Dielectric strength is expressed in volts per unit of thickness such as V/m. All insulators allow a small amount of current to leak through or around themselves. The small leakage generates heat, providing an easier access to more current. The process slowly accelerates with time and the amount of voltage applied until a failure in terms of dielectric breakdown, or what is known as puncture, occurs. The higher the breakdown voltage is, the better the quality of an insulator will be. The breakdown voltage is measured by increasing the voltage from zero to breakdown at uniform rate (the rate of rise is generally 100, 500, 1000, or 3000 V/sec until the failure occurs) [47-51]. Figure 12 represents the breakdown voltage of all acrylic rubber mixes having different concentrations of VTMS. Results showed that the electric insulation behavior is upgrading steadily till 1.0 % followed by abrupt increase at 2.0% percent of silane. This is because that mix possesses higher percent of silane and gives rise to a higher crosslink density and molecular weight as well and hence providing more resistance before complete breakdown starts.

Conclusion

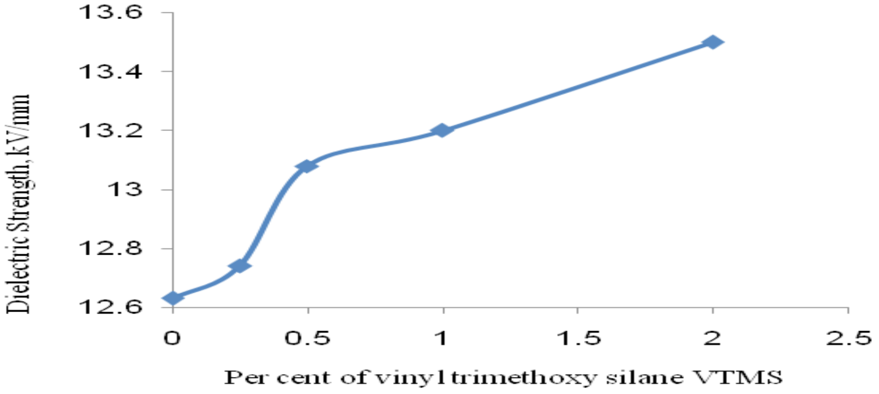


Figure (11): Dielectric dtrength of acrylic rubber composites containing different per cent of vinyl trimethoxy silane (VTMS)

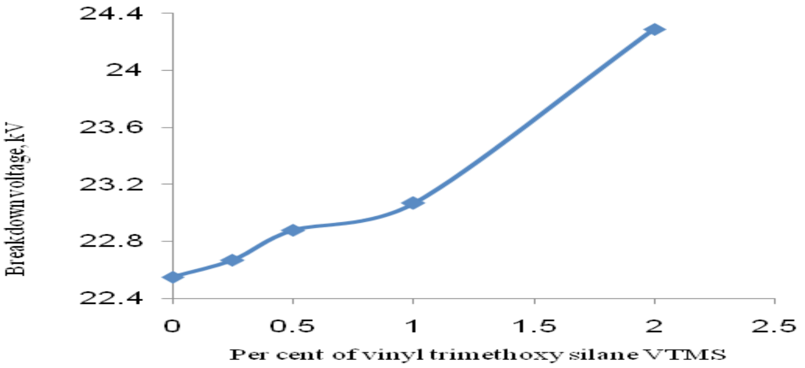


Fig. 12. Breakdown voltage of acrylic rubber composite containing different per cent of vinyl trimethoxy silane (VTMS).

FT-IR curve of acrylic rubber composite containing VTMS shows the presence of two peaks indicating formation of links between silica and trimethoxy silane. This observation was also seen from SEM images that show a complete miscibility of the acrlic rubber matrix with all ingredients including vinyl trimethoxy silane. The incorporation of silane to the acrylic rubber matrix is accompanied by an enhancement of the mechanical properties and an improvement in the thermal stability of composites. The achievement is maximal for acrylic rubber composite having 2% silane. Results of the electrical properties were satisfactory and showed that the addition of silane to acrylic rubber improves the electrical insulation of acrylic rubber/silane composites.

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تأثير فينيل ثلاثي الميثوكسي سيلان كعامل مزدوج على الخواص الميكانيكية والكهربية لمتراكبات مطاط الأكريليك

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عند الرغبة فى تحسين الإلتصاق بين البوليمر والمادة المالئة، يكون إختيار عوامل إقتران من السيلان، ومن الممكن إستخدام فينيل ثلاثي الميسوكسي سيلان (VTMS) بغرض تحسين الإلتصاق بين مطاط الأكريليك والسيليكا. ويتم تحضير متراكبات مطاط الأكريليك من خلال بلمرة المستحلب، حيث يتم إضافة VTMS بنسب: ٠, ٠,٢٥, ٠,٥, ١,٠ and ٢,٠ ٪ أثناء عملية البلمرة، ويتم دراسة تأثير إضافة السيلان بنسب مختلفة على الخواص الميكانيكية، الحرارية والكهربية. وقد أظهرت النتائج تحسن الخواص الميكانيكية بصورة ملحوظة نتيجة لإضافة VTMS إلى متراكبات الأكريليك بالإضافة إلى تحسن الثبات الحرارى لها. كما أظهرت نتائج قياسات العزل الكهربي للمتراكبات المحتوية على VTMS إرتفاع مستويات المقاومة الحجمية وجهد الإنهيار الكهربي.