

Effect of Fired Clay on the Physical and Mechanical Properties of Un-plasticized Poly (Vinyl Chloride) Composite

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ABSTRACT

The use of inorganic material to modify un-plasticized Poly (vinyl chloride) (PVC) was studied. Composites containing different amounts of clay with 0 to 80 parts per hundred part of PVC were prepared using compression molding press. It was discovered that the strength, toughness, elastic modulus of PVC/Fired clay composites increase with particle loading to 10% and decreases beyond that. PVC/Fired clay has higher Modulus of Elasticity at 10% particle loading. Results show that elongation at break decreased with increase in filler loading. Embrittlement test result showed signs of crumbling or flaking after 21 days with composites composition within 20 to 60 parts per hundred PVC while other composites composition of 70 to 100 parts per hundred PVC remained ductile throughout the time of study. Natural weathering and accelerated ageing of PVC/Fired clay, after 6 months of exposure, developed visual colour change. The modulus of elasticity, toughness and elongation at break, decreased initially then increased and finally leveled up with exposure time. Micrographs of the sample taken after 70 days of outdoor exposure show wearing a way of sample surfaces. There was a progressive increase in water absorption, density, hardness and conductivity of each sample tested.

KEYWORDS: Un-Plasticized, Poly (Vinyl Chloride), Composite, Fired Clay, Modification.

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I. INTRODUCTION

The word Polymer is derived from classical Greek *poly* meaning “many” and *meros* meaning “parts” thus a polymer is large molecules (macromolecule) build up by the repetition of small chemical units. They can be produced into finished article as it is in its pure (new) form. However, for the development of effective polymer products, polymer modification becomes very necessary, especially when one considers the major limitations in the unmodified polymer. These limitations may include low stiffness, low strength, and lack of stability of polymer to light, heat and ionizing radiation. To expand their applications in different sectors, especially in the current society, polymer composite development is the way forward so as to cope with the obvious limitations and give a new way to meet high performance polymer product.

A composite is a microscopic combination of two or more distinct materials having an identifiable interface between them^[1]. The material may be metal, ceramic or polymer.

Most common composite materials have been used by Man thousands of years, for housing and hunting purposes. Mud and clay were used to build wall. It was realized that chopped straw and strips or mats of bamboo canes or the like imparted higher strength, safety and durability to mud^[2]. Because of the enormous advantages obtained from composite, there has been research explosion on composite till date.

Development of composite material is running at the same rate with our civilization, as a result of this, special attention is paid to composite research to get new material. The use of these materials is found in every field of life; and involves virtually everything. E.g. sport, transportation, space craft and so on.

PVC is the third most widely produced plastic but difficult to process. Therefore, locally sourced fillers such as fired clay added to PVC may modify and possibly ease processing, reduce cost of production and upgrade its physical and mechanical properties.

Inorganic particles such as ground talc and clays, even though they improve some electrical properties, are classified as extenders, because they allow filling to high loadings without adversely affecting the physical properties^[3]. Recent studies have investigated clays absorption capacities in various applications, such as the removal of heavy metals from waste water and air purification^[4]

Clay is a chief material, a small amount of it incorporated in a matrix provide a high extent of improvement in physio-chemical properties of polymer. Many authors have reported independently on incorporating inorganic exfoliated clay minerals to polymer matrix ^{[5],[6],[7]}. It has been observed that Poly (vinyl chloride)/Kaolinite Nano-composites homogenously dispersed in PVC matrix ^[8]. Thermo gravimetric analysis also indicated that Clay introduction into polymer network resulted in an increase in thermal stability.

The aim of the study is basically to modify un-Plasticized poly (vinyl chloride) using locally sourced Clay as filler that will be suitable in applications where physical and mechanical properties are of interest such as in floor tiles, table tops, and so on.

II. EXPERIMENTAL

Un-Plasticized PVC with glass temperature 85°C, melting temperature 250°C, Particle size, less than 0.075mm, and viscosity number ISO/R174-1061(E): 128 and density 1.46 was supplied by BDH. The Clay, grey in colour was locally sourced from Bomo Village, Zaria.

2.1 Sample preparations

Un-Plasticized PVC was used as was supplied. The clay was cleaned, sun dried, oven dried and sieved to a grain particle size of 300µm, called the un-fired clay.

The locally sourced clay was fired at the Department of Fine Art Ahmadu Bello University Zaria, where the un-fired clay was molded and nestled together in a firing pit and covered with burnable materials to act as fuel during the firing process. The top of the pit was protected with metal baffles.

The filled pit was then set on fire and carefully tended at firing temperature of 1300°C overnight, until most of the inner fuel has been consumed. The pit was then allowed to cool before the fired clay object (red) was removed from it. The (red) non-toxic fired clay object was grinded, sieved to obtain a 300µm particle size.

TABLE 1: Composite Formulation

Composition	Sample								
	PF01	PF02	PF03	PF04	PF05	PF06	PF07	PF08	PF09
PVC %wt	100	90	80	70	60	50	40	30	20
Fired clay wt%	0	10	20	30	40	50	60	70	80

2.2 Compounding

The formulations on Table1 were picked one after the other and mixed with a Carvers Two Roll Mill at a processing temperature of 150-160°C within 7 minutes. The rollers speed for the rear and front were 48 and 5 revolution per minute (rpm) respectively. The compounded sample was then stored in a labeled black polythene bag.

The polymer matrix was placed first on the nip, the gap between the rolls and allowed to melt. When the polymer has sufficiently melted, the gap was then adjusted by closing the nip. This makes the melted PVC to accumulate at the nip forming a “bank”. The filler type picked, was then gently dispersed across the bank quickly to avoid excessive heating and possible degradation. With a help of a knife, the formed sample as it fold on the front roll, were scraped off and returned to the bank in a continuous manner until homogenous mixture was obtained. The speed of the rollers 48 and 5 for the rear and front, the temperature 150-160°C and time 7minutes of mixing for each formulation were the same. The compounding was done at Zaria-Nigeria atmospheric room temperature (27 °C).

2.3 Hot Press

A thin aluminum sheet was used as the mold. Each compounded formulation; 1.5g (in weight) was measured out and wrapped in a foil paper. The wrapped sample was then placed in between the aluminum mould, and placed on the moveable platens of the hot press. With the help of the hydraulic controlled ram, the lower platen moved up to the upper platen closing the mold and exerting molding pressure. The resulting film was compressed at a compression temperature and pressure of 170-185°C and 3 tons within 3 minutes respectively. After three minutes, the pressure was released with the lower platen falling by gravity. The mold was quickly removed and cooled by running water on it. The aluminum foil paper was carefully un-wrapped to remove the required film sample contained on it.

2.4 Tensile Properties test

The tensile test was carried out using a Hounsfield Tensometer (serial number: W3179), in the Strength of Materials and Heat Treatment Laboratory, Department of Mechanical Engineering, A.B.U Zaria. Parameters determined from tensile test include tensile strength, Modulus of elasticity, Ultimate strength, Elongation, Tensile Strain and Tensile stress.

2.5 Water Absorption of the composites Samples

Water absorption test was performed according to ASTM D570 by conditioning and weighing the sample. Samples were each immersed in distilled water in a transparent thermoplastic container and covered with the lid for 96 hrs at 27°C.

Excess water on the sample surface was wiped off with a filter paper before reweighing. The percentage increase in mass during immersion was calculated using the equation below:

$$\text{Increase in weight (\%)} = \frac{\text{weight after 96hrs} - \text{initial weight at 0hr}}{\text{initial weight at 0hr}} \quad (1)$$

2.6 Density Test

The density of the composite sample was measured according to ASTM Specification D792-00. The Specification describes the steps to calculate the density as in the equation below:

$$\rho_{cm^{-3}} = \frac{W_a \times 0.9975}{W_a - W_w - W_b} \quad (2)$$

Where ρ = the density of the composite material, in g/cm³

W_a = the weight of the specimen when hung in air

W_w = the weight of the partly immersed wire holding the specimen.

W_b = the weight of the specimen when immersed fully in distill water, along with the partly immersed wire holding the specimen

0.9975 = the density in g/cm³ of the distilled water at 23°C

2.7 Hardness Test

For every specimen, 3 readings were taken in accordance with Polymeric Matrix Composites (PVC) ASTM – 02240 – 97 for Hardness test. The hardness value was determined by the penetration of the Durometer indenter foot into the specimen.

The sample was placed on a flat surface on the pressure foot of the instrument. A calibrated spring in the Durometer applies a specific pressure to an indenter foot parallel to the surface of the specimen. The hardness value was read and recorded.

2.8 Embrittlement Test

Films were tested for embrittlement daily after exposure to both outdoor weathering and UV-light. Strips of rectangular shape of approximately equal thickness were taken on the hand, bending to an angle of 180° on both sides, that is, bending toward the person holding the film and bending away from the person holding the film^[9]. Breakage/crumbling/flaking/cracking indicates brittleness.

2.9 Conductivity Measurement

A Pico Ammeter (KETHLEY487) machine at Center for Energy Research and Training (CERT), Zaria- Nigeria was used to carry out resistivity test. The instrument, allows a constant voltage of 20 volt to pass through each sample of constant length, and the current which passed between the lengths was read. The equation of calculating resistivity is as shown below:

$$\text{Resistance } (\Omega) = \frac{\text{Volt (V)}}{\text{Current (Amp)}} = \frac{V}{I} = R \quad (3)$$

$$\text{Resistivity} = \frac{\text{Area} \times \text{Resistance}}{\text{Length}} \quad (4)$$

2.10 Natural Weathering of Polyvinyl Composites

The natural weathering of poly (vinyl chloride) was done by exposing the test films outside in the open air in accordance with ASTM D1435 Standard.

2.11 Ultraviolet Irradiation

Sample films were mounted between two cardboard papers in which holes of approximate dimensions were made similar to the ones exposed to the natural weather. The sample was placed over the hole on one side of the cardboard paper while another cardboard paper was placed on top. The cardboard paper was labeled according to the composition of the film. A masking tape was used to hold the two cardboard together. The system was then placed under the UV-lamp. (36.50Nm). Samples were picked at regular interval of time and their mechanical properties tested.

2.12 Morphology of the composites

Photographic Visual Metallurgical Microscope Model Number NJF-120A was used to view the Micrographs of sample processed after compounding, hot press and after exposure to outdoor weathering. The Sample was placed on the flat surface under instrument called Binocular viewing head. Through the eyepiece, sample photographs snapped were transferred to the screen where they were seen. Micrographs of compounded samples were taken, before and after exposure to both UV-lamp and outdoor weathering.

III. RESULTS AND DISCUSSION

“Fig”1a shows the complete stress-strain curves for all the composite formulation (table 1). For clarity of view of the effect of the formulation on PVC, “Fig” 1b was extracted from “Fig” 1a.

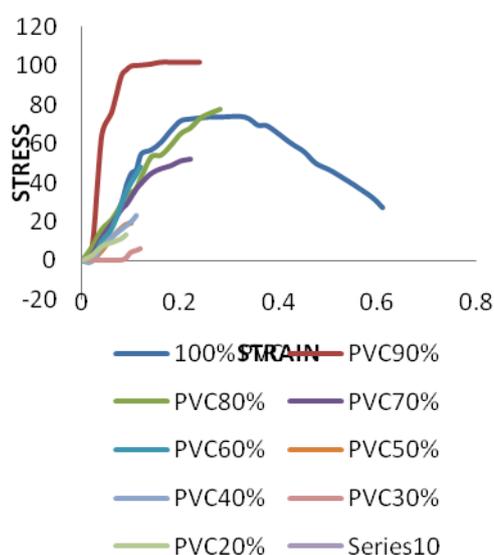


Figure 1a : A Stress-Strain plots for all PVC/Fired Clay ratios.

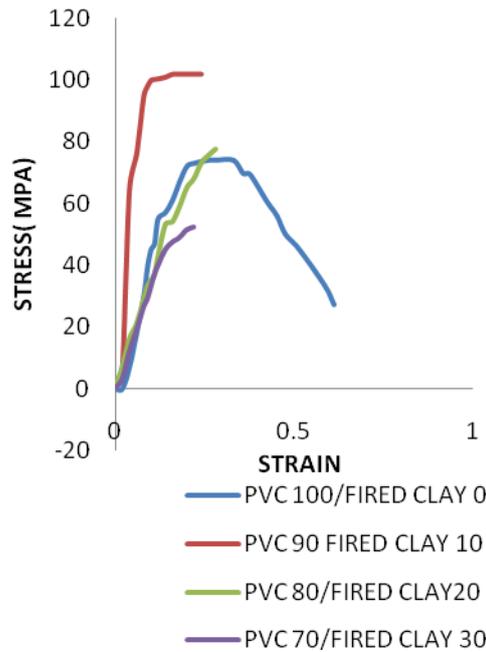


Figure 1b: A stress-strain plots of PVC/Fired Clay ratios.

The stress and strain curves (figure 1b) at the stress of 0 to 60 MPa increase approximately with a linear relationship for all the composites. The ratio of stress-strain is constant obeying Hooke’s Law. Above the stress point of 60MPa, the stress-strain straight lines curve deviating from Hooke’s law. This indicates that the strain increases faster than the stress, causing permanent deformation on the composites. The sample is therefore reacting plastically to any further increase in stress above 60 MPa. However, composite PVC70/fired clay 30 in this figure fractured before the yield point which shows that the sample is brittle. The most ductile composite was PVC100/Fired clay 0, which shows a maximum strain value of 0.6; this was so because its intrinsic properties have not been affected. The minimum strain value (0.08) was found in PVC 20/Fired clay 80 composite as shown in figure 1a. This was the maximum permissible fired-clay content that can be accommodated by the PVC/fired-clay composites. Generally, as the fired clay is added to the PVC, the fired-clay/PVC intercalation gradually decreases to a minimum. At minimum interaction, the hardness and brittle nature of fired clay might have imparted its rigidity to the ductile PVC. PVC 90/Fired clay10 (figure 1b) shows the maximum stress value of 102MPa, meaning that fired clay-PVC adhesion is well bonded here, with the rigidity of the fired-clay effectively transferred to the PVC in the composite. It can therefore be concluded that the PVC 90/Fired clay10 and PVC 80/Fired clay 20 composites have superior mechanical property than the remaining composites. Hence, they have successfully modified the PVC. Beyond this, that is, from PVC70/Fired clay30 (figure 1a), as the fired clay content is being increased, there is a progressive decrease in fired clay-PVC intercalation, reducing the mechanical quality of the composites.

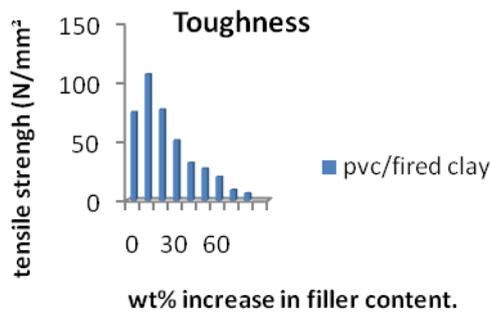


Figure 2: Plots of tensile strength against percentage increase in filler type

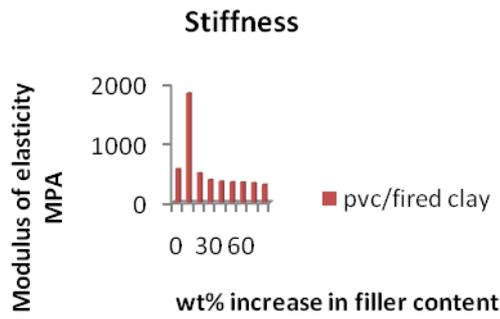


Figure 3: Plots of Modulus of elasticity of composite formulation for PVC/Fired clay

From “Fig” 2 and 3 the highest value of Tensile Strength (107N/mm²) and Modulus of elasticity (1864.8MPa) occurs at 10% filler content. At 10% and 20% increase in filler content the composites have higher toughness and better stiffness than pure PVC (with 0% filler content), thus enhancing the mechanical properties of the PVC/fired clay composite.

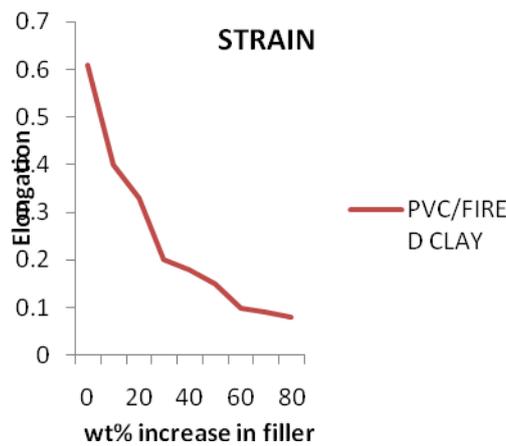


Figure 4: Plots of strain against percentage increase in filler

The strain of PVC as represented in Figure 4 decreases with increase in the composition of fired clay in all the PVC/Fired clay ratios. The figure provides an indication of how visible overloading the PVC with fired clay gradually damages its elasticity to the point of fracture which occurs at 80% filler content.

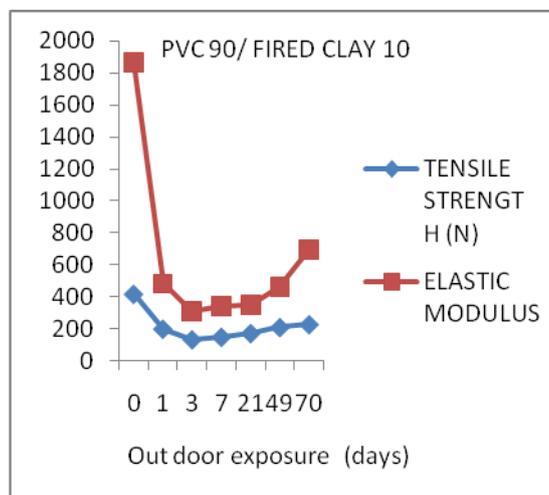


Figure 5: Plots of Tensile strength (T.S) and Modulus of Elasticity against time of exposure.

The tensile strength and modulus of elasticity (“Fig” 5) dropped as the duration of outdoor exposure increases. The Modulus in the sampled composite (PVC90/fired clay 10) dropped sharply from 1864.8 MPA to 483.225 MPA on the very first day of outdoor exposure then stabilizes for the next 48days. There was an attempted gain in modulus after 21days exposure from 350 MPA to 696.3 MPA on exposure for 70days. The tensile strength on the other hand was relatively stable with a small drop from 417 N/mm² to 133.5 N/mm² before stabilizing.

The loss of strength and modulus is an indication of degradation taking place. The development of colour on the samples which was observed (plate 2) a few days after exposure is a criteria of PVC degradation.

The effect of continuous exposure of composite to outdoor weather leads to wearing a way of the surface of the composite as shown in plate 2. Continues exposure might make it difficult to improve the stability of PVC for outdoor use.

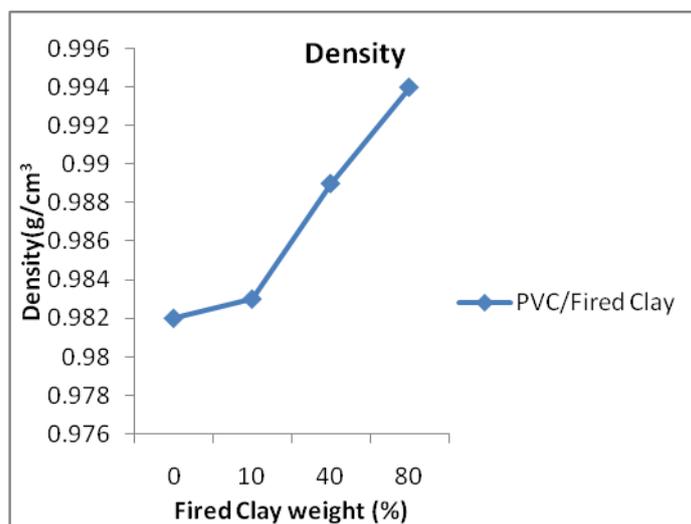
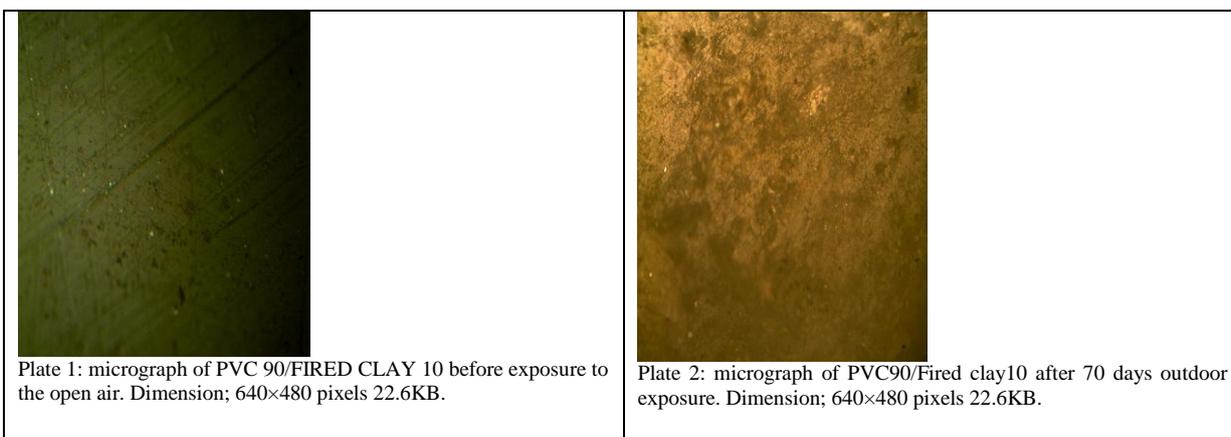


Figure 6: Plots of density against percentage increase in filler .

There was a gradual increase in density with increase percentage filler in the composite as observed in “Fig” 6. The filler being heavier than the matrix may be responsible for this observation.

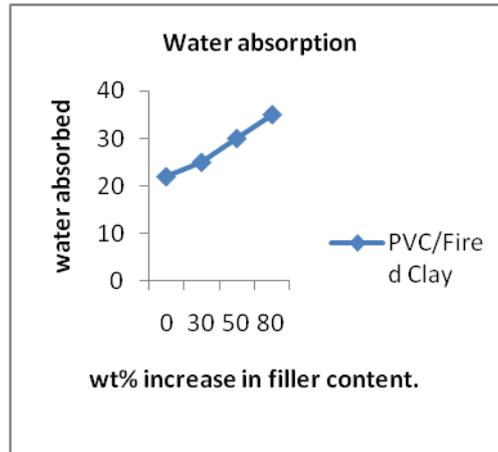


Figure 7: Plots water content against percentage increase in fired clay

There was a general increase in absorption rate with increase in fired clay content ("Fig" 7). This behavior might be due to the presence of void spaces in the matrix which could have been formed during compounding of composites. The void spaces in the matrix accommodates the water absorbed.

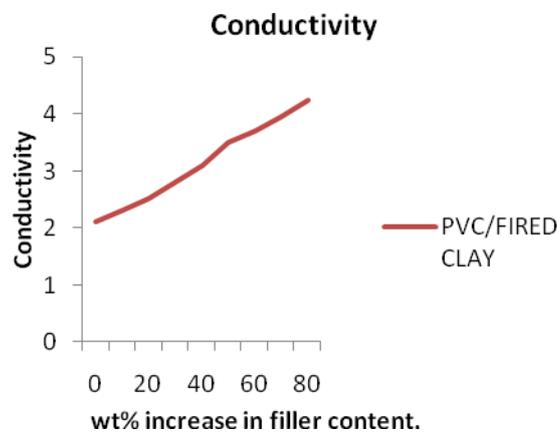


Figure 8: plots of Conductivity against percentage increase in filler.

A gradual increase in conductivity was observed as the percentage of the filler is increased ("Fig" 8). It shows that the fired clay do conduct electricity to some extent being that the PVC is a non-conductor of electricity.

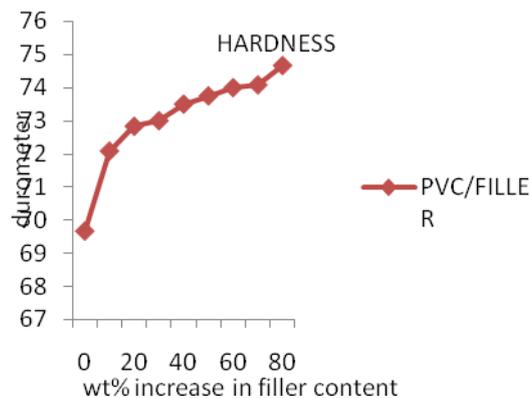


Figure 9: Hardness against percentage increase in filler.

The hardness of the composites increase with increase in filler content (“Fig”9). This correlates well to other mechanical properties such as modulus of elasticity & tensile strength of the composites tested.

IV. CONCLUSION

The use of the fired clay as PVC filler gave an improved mechanical and physical property of unplasticized poly (vinyl chloride) by 38%. The results show that the stress-strain is constant, obeying Hooke’s Law up to 60MPa beyond which permanent deformation of the composite occurs. The fired clay has acted as a plasticizer to the unplasticized PVC. The mechanical properties of the PVC/fired clay composites are enhanced at 10% and 20% increase in filler content. The highest value of Tensile Strength (107N/mm²) and Modulus of elasticity (1864.8MPa) occurred at 10% filler content which resulted in higher toughness and better stiffness than the pure PVC. The tensile strength and modulus of elasticity dropped as the duration of outdoor exposure increases. However, prolong exposure of the matrix to damp/moist atmosphere leads to its degradation. Hence, the product can be used as a table top and floor tiles.

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