

MOISTURE ABSORPTION OF COMPOSITES MADE FROM UNSATURATED POLYESTER FILLED WITH PULVERIZED SANDSTONE, DIORITE AND CORNSTALK.

IziesuOsiki^a, Timothy Thamae^{b#}

^{ab} *Department of Chemistry and Chemical Technology,
National University of Lesotho,
P.O. Roma 180,
Lesotho*

^a iziboyjesu@yahoo.com,

^b tm.thamae@nul.ls , thamaetm@gmail.com

Abstract

Moisture absorption of materials is one major concern in any engineering design. This is because moisture absorption is capable of leading to material degradation and ultimate failure. The purpose of this work is to study and compare the moisture absorption of composites made from polyester resin, reinforced with diorite, pulverized sandstone, and cornstalk. Moisture absorption was carried out using the long term immersion procedure based on the ASTM D 570 - 98 standards. Corn stalk-polyester composite was found to absorb more moisture than other composites. The diorite-polyester composite absorbed the least moisture and the moisture decreased with increasing amount of the diorite filler added. A brief review of efforts to commercialize the products is made.

Key words: Moisture absorption, diorite, sandstone, cornstalk, composite, polyester

1. INTRODUCTION

The area of composites is one major field which, although it has been explored widely in recent years, still offers many opportunities for improvements (Boukhoulda et al, 2006). This is because there is virtually no limit to the formation or design of composites as even scrap materials today have found profound use as components that make up a number of composite structures (Barbero, 1999). In developing countries particularly in Africa, this field is yet to be fully explored chiefly due to fewer researches conducted in this field of study. However, the composite design industry is believed to be potentially feasible if explored, as there is a number of inherent resources that if utilized are bound to bring about drastic development in the composite industry in Africa.

This research focuses on Lesotho as a case study of a developing country in Africa where natural resources can be explored for use in composite design. In developing countries such as Lesotho, composite design and manufacturing will require more than just the use of available natural resources, but proposed methods should reflect the economic situation of the country if they are to succeed and be beneficial to all stake-holders (Baillie, 2006, Medina, 2007).

Natural fibres in the form of corn and *Agave americana* are available in Lesotho. Natural fibres are fast emerging as potential alternatives to the already known synthetic fibres since they are considered inexpensive and are more environmentally friendly as opposed to synthetic fibres (Peijs et al, 1998). Introduction of natural

fibres into composite structures brings about reduction in product cost which is achieved by the replacement of a portion of the more expensive oil-derived polymer in composites. Furthermore, addition of natural fibres could improve the mechanical properties of the polymer matrix when they act as reinforcements. Common examples include timber by-products such as wood flour; saw dust and wood chips that are commonly used in composite board products (Deanin, 1975, White and Ansell, 1982).

One major factor impeding the application of natural fibres, particularly lignocellulosic materials is their known affinity to moisture (Thamae et al, 2009). This means that composites structures made from these materials will ultimately take up more moisture. The moisture affinity of Lignocellulosic fibres (hydrophilic behavior) is believed to be due to the presence of free hydroxyl groups on the chemical structures of these fibres that yield polarity which attract the already polarized water molecules (Thamae et al, 2009). Sreekala et al (1997) mentioned that the porous structure of these fibres is an additional factor that leads to increased moisture absorption owing to free movement of water molecules within the fibre structure. Other factors that could lead to increased water intake in natural fibre composites include indentions on fibre-matrix interfaces as suggested by Beg and Pickering (2008).

Diorite is another natural resource that is widely available in Lesotho and whose application as composite reinforcement still remains obliterate. The Diorite is a grey or dark-grey igneous rock which is composed mainly of plagioclase feldspar. It is reported to contain small amounts of quartz, microcline and olivine (Blatt and Tracy, 1996). One attractive property of the diorite is its hardness. Blatt and Tracy (1996) reported that the hardness of these rock types makes it easy for them to be polished and worked easily which results

in durably finished work. Another desirable property of diorites that should enhance their use as reinforcements is that they are slightly porous. Gul and Maqsood (2006) in their work on properties of diorite, found the porosity of diorites to be about 0.16 to 0.49 weight percent. This low porosity of diorites is one reason they would serve as good reinforcements even in hygro-environments.

Sandstone is another natural resource available in Lesotho which is also being explored for its possible use as composite reinforcement. Sandstone is a common sedimentary rock whose formation takes place in many environments such as those having rivers and oceans. Sandstones have properties that are similar to those of diorite in that they are easy to work through and are still relatively strong, and this combination of properties has made them useful even as building and pavement materials. The use of sandstones in composites is a relatively new phenomenon which is likely to gather pace in the near future. Recently, quartz rich sandstones have been used in engineered stone products (Lam dos Santos et al, 2011, Hamoush et al, 2011). Generally sandstones are very porous rocks (David et al, 1993), which is one drawback that would ultimately be encountered in their outdoor applications. The presence of pores in sandstones allows them to absorb moisture from the environment. However the polymer matrix, known to be highly moisture and solvent resistant is expected to reduce their moisture absorption capabilities in the composite.

Recently, greater emphasis is being placed on production of more viable materials which have better and improved qualities and properties. If a holistic approach is adopted in this regard, composite materials are bound to take an even more important role in the near future in Lesotho and the rest of Africa. However, this work is the first step aimed at

developing low cost composite materials made from pulverized sandstones, diorites and cornstalks as fillers following a processing procedure that would be of low cost for Lesotho. A brief account of the efforts to commercialize the materials being developed is given.

2. METHODOLOGY

2.1. Materials

2.1.1 Sandstone

The sandstone was obtained from the Roma Mountains, a walking distance from the National University of Lesotho, in Lesotho, Southern Africa. This stone is found in the regional geological formation known as Clarens formation. Previously known as cave sandstone because of the many cave overhangs it makes, this formation lies just below Lesotho formation and its mineralogy vary between quartzose and feldspatic sandstones with calcareous matrices. Properties such as physical texture as well as colour were the main criteria used in selection of sand stones. This was necessary because properties of sandstones used as reinforcements in composites could vary depending on the physical property of the sandstone in use.

2.1.2 Diorite

Diorite was obtained from a company called Lesotho Funeral Services. The company manufactures tombstones using this material, creating a lot of waste stone in the process. The waste is currently used in low cost applications such as concrete used in building construction despite being a more valuable material.

2.1.3 Corn stalks

The corn stalks were supplied by local farmers who sell the product as animal food. The corn stalks used were harvested in bulk, which was thereafter delivered to the Department of Chemical Technology in

the University for further Analysis. Again care was taken in the selection of the stalks, to ensure that those with desired corn stalk fibre were harvested

2.1.4 Mould

A silicone rubber mould was used for the casting of all composite materials. The making of the silicone rubber mould followed appropriate mixing of silicone rubber (silicone mold max 30) with silicone hardener (silicone catalyst MM30) in the ratio of a hundred parts to ten parts respectively; this was then allowed to set at room temperature. The moulds had dimensions of 3.7×8.7×1.2 mm following the ASTM D 570 – 98 standards.

2.1.5 Matrix (Resin)

The matrix material used, was polyester resin (UPE 1685LV). In Table 1, properties of the resin are shown. UPE 1685LV is described as a pre-accelerated, unwaxed, non-thixotropic, rigid, medium-low reactivity DCPD (Dicyclopentadiene)-orthophthalic unsaturated polyester resin (Cray valley Resins data sheet). The aforementioned characteristics mean it has:

- Low exotherm, which means it is suitable for bulk casting
 - Pre-accelerated, which means it requires only addition of hardener
 - DCPD based, which means it has low styrene emission, superior filler and pigment wet-out, and high filler loading.
- In this work, UPE 1685LV will be simply referred to as polyester resin.

2.2. Composite Fabrication

All filler raw materials (sandstone, diorite, and cornstalk) had to be prepared for use in composites. This preparation included drying in an oven, crushing, grinding, and sieving. Crushing and grinding of the sandstone and granite was done manually with the aid of a sledge hammer, this was done to reduce the particle size of the

sandstone and diorite samples to aid further processing. Corn stalk samples were milled using Russell Hobb's grinder. Sieving of all materials was done using a sieving machine. Pulverized materials were then hand mixed with polyester resin and the mixtures cast on silicone rubber molds and cured in ovens at 80 °C for 3 hrs. Complete preparatory steps are presented in Figure 1. Weight fractions used were different for different materials,

based on their bulk properties. All the weight fractions are referred to in percentages. For instance, more bulky cornstalks flour would accept lower weight fractions (up to 30 %) while denser diorites could only be used at higher weight fractions (close and up to 80 %) to achieve meaningful filler distributions in the composites.

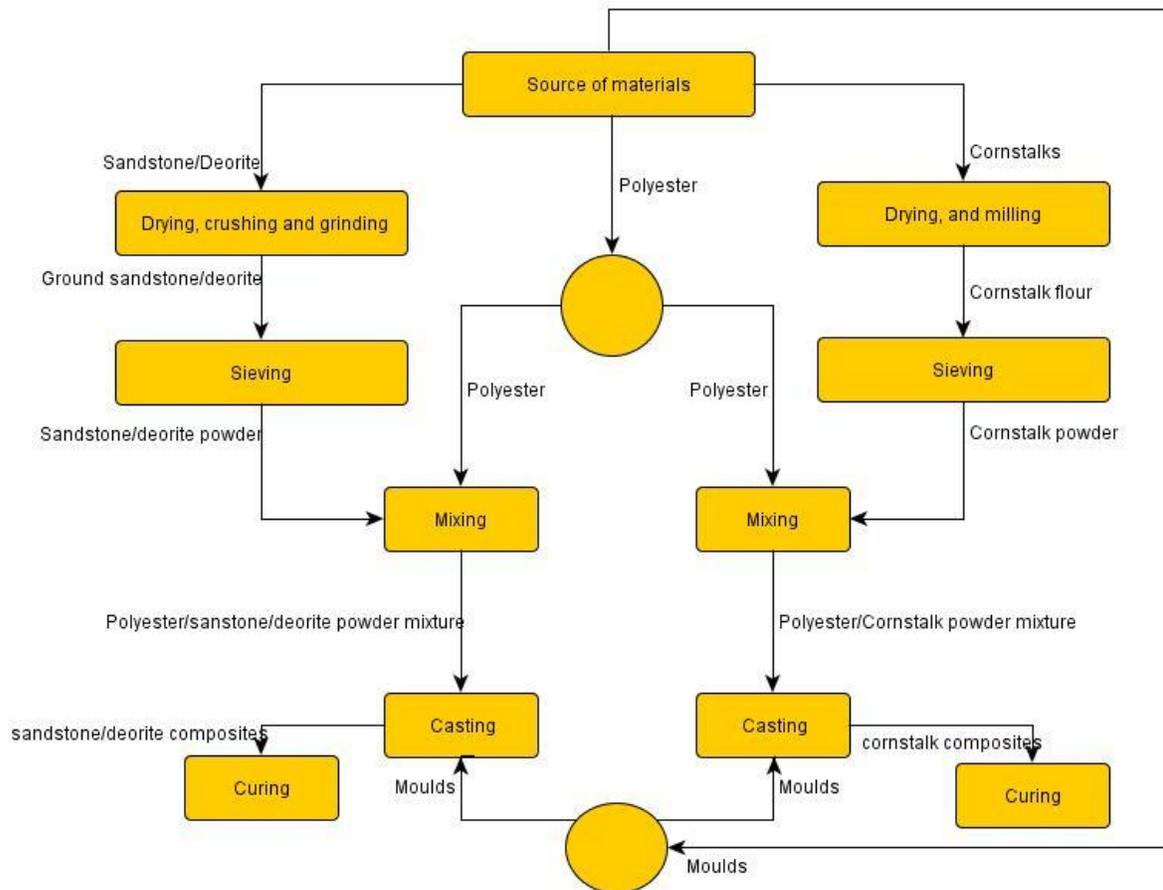


Figure 1: Flow chart showing preparation of the composites

2.3. Material testing

2.3.1 Moisture absorption

Conditioning of materials

For conditioning of the materials, five samples per variable from each of the three types of composite materials were

weighed, then placed in an oven at about 70°C for 24 hours, after which the final weight was measured to the nearest 0.001g.

Moisture absorption test procedure

The long term immersion procedure based on the ASTM D 570-98 standard was used in the moisture absorption test.

- *Twenty-four hour immersion:* The conditioned samples of each kind of material were placed in a container filled with distilled water. Care was taken to ensure that all material samples were completely immersed in the distilled water. At the end of the twenty-four hour duration each of the samples of the different kinds of materials, were removed from the water, wiped dry, and immediately weighed to the nearest 0.001g.
- *Long-term immersion:* In determining the total amount of water absorbed when substantially saturated, the conditioned samples of the different kinds of composites were tested as previously

described, except that at the end of a one-week period, the samples were removed from water, wiped dry and weighed to the nearest 0.001g, and then placed back into the distilled water. This procedure was then repeated for an interval of two weeks until an observable saturation point was reached over a number of weeks.

Calculations

The moisture absorption over time was reported as percentage change in weight of the materials during immersion, and was calculated to the nearest 0.01% as shown in equation 1:

$$\text{Moisture content(\%)} = \frac{\text{weight after immersion} - \text{oven dry weight}}{\text{oven dry weight}} \quad [1]$$

3. RESULTS AND DISCUSSIONS

3.1. Diorite polyester composites

Figure 2 shows the moisture absorption of diorite polyester composites. Moisture absorption decreases with increased addition of the diorite filler in the range of 0-70% resin. This could be due to the nearly lack of porosity in diorites as shown by Gul and Maqsood (2006), which make the composites moisture resistant. However, a large deviation from this general trend was observed at 80% diorite filler. At this point, the composite possibly became porous due to poor filler matrix interface as the 20% polyester could not completely encapsulate the filler particles. Only in the processing of engineered stone products using state-of-the-art vacuum-vibro-compression machines are such filler loadings (up to 94 % for commercial

products) possible. Thus while the moisture intake peaked at around 0.8% at 70 % filler loading, it suddenly increased to a peak of nearly 4.3% at 80% filler loading.

Significant decline in weight after the composite with 80% filler loading composite reached the peak could be due to leaching, which, aided by higher porosity, resulted in the leached minerals leaving the composite overtime. Similar behavior can be observed in other filler loadings but after a longer period and to a smaller extent. Generally, the diorite composites show very low values of moisture intake even at high filler loadings.

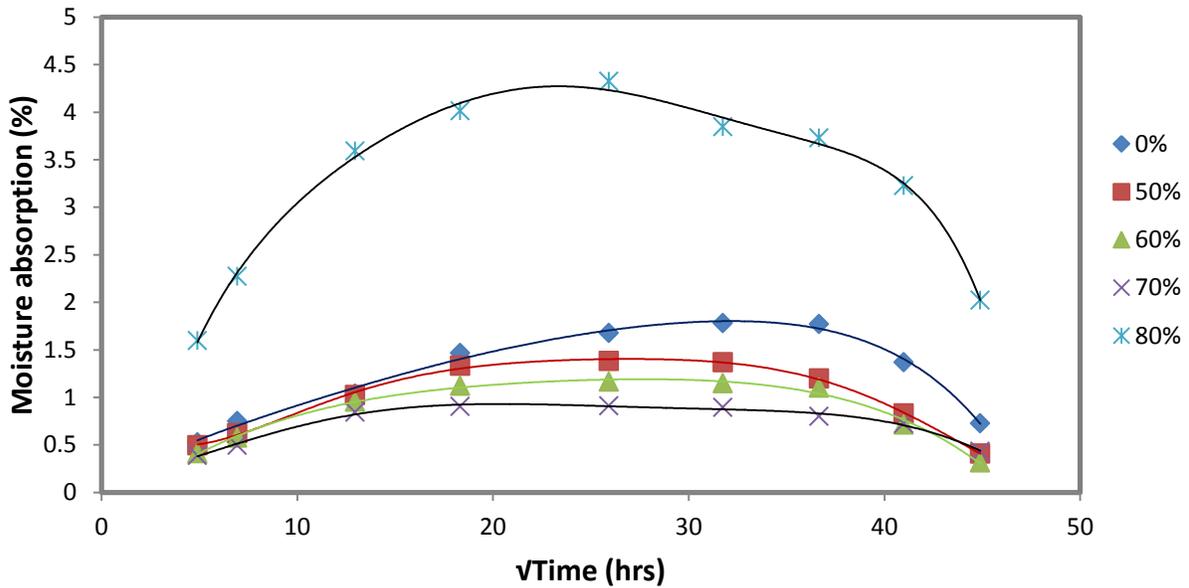


Figure 2: Moisture Absorption Behavior of Diorite-Polyester Composite (all percentages refer to filler loading)

3.2. Corn stalk polyester composites

In contrast to moisture intake behavior of diorite polyester composites, cornstark composites' moisture absorption increases with increasing amount of cornstark filler added, although at lower filler loadings than in the previous situation (0 - 30%)(Figure 3). This was expected and had been confirmed by other authors (Thamae, et al, 2010; White and Ansell, 1983). The enhanced moisture uptake in cornstark polyester composites (up to 14% intake at 30 % fibre loading) can be attributed to the hydrophilic nature of the cornstark fibres due to the presence of hydroxyl groups that attract water molecules and bind with them through hydrogen bonding. This can partly be due to the fact that at higher fibre content, there are more hydroxyl group sites which lead to increases in moisture absorption.

Higher moisture intake could also be due to the porous nature of cornstark fibres

which would allow for more free movement of water. Any exposure of fillers on the surface in natural fibre composites is alleged to be a gateway through which water penetrates the materials (Thamae, et al, 2010). Also, natural fibres such as those of cornstark increase the interfacial area of the fibre-matrix (due to the often assumed cylindrical nature of natural fibres which offers more surface area for interfacial interaction) and allow water to be absorbed along the fibre-matrix interfaces (White and Ansell, 1983).

Furthermore, milled cornstalks contain a parenchyma tissue called pith. Importantly, cornstark particles contain some components of the pith which are believed to add to the water retention abilities of the composites (Thamae et al, 2010).

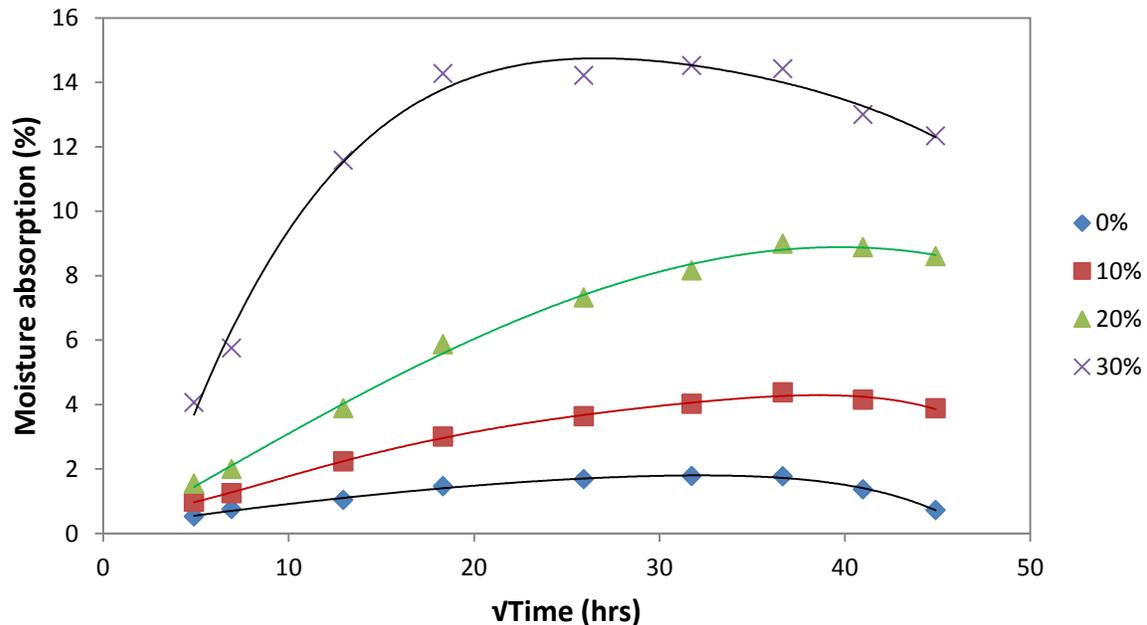


Figure 3: Moisture Absorption Property of Cornstalk fiber-Polyester Composites (all percentages refer to filler loading)

Also, there is a notable transition of interest that can be clearly observed in Figure 3, where there is a rapid change in the moisture absorption at 30% filler loading. Thamae et al (2010) observed this behavior using a thermoplastic matrix, and concluded that at higher filler loadings, chances of particles forming agglomerates are increased, which in turn, increase moisture absorption. It has then been suggested that there is a 'critical cornstalk fibre content' at which agglomerates formed results in clusters that serve as passages for water movement in the particles (Wang et al, 2006). It is at this critical point that the composite water uptake increases rapidly to levels higher than those observed for all other samples. This behavior could be due to the increased difficulty in mixing at higher filler loadings leading to agglomerates and fibre exposure.

3.3. Clarens sandstone polyester composites

Sandstone polyester composites do not show any specific trend in the range between 0-60% as observed in Figure 4. The behavior could reflect that variability in chemistry and porosity of the stone may have resulted in inconsistent moisture intake. Further tests are needed for the sandstone composites to confirm this theory. However, another outstanding moisture intake at 70% filler loading was observed which may also be due to factors discussed in similar behavior above.

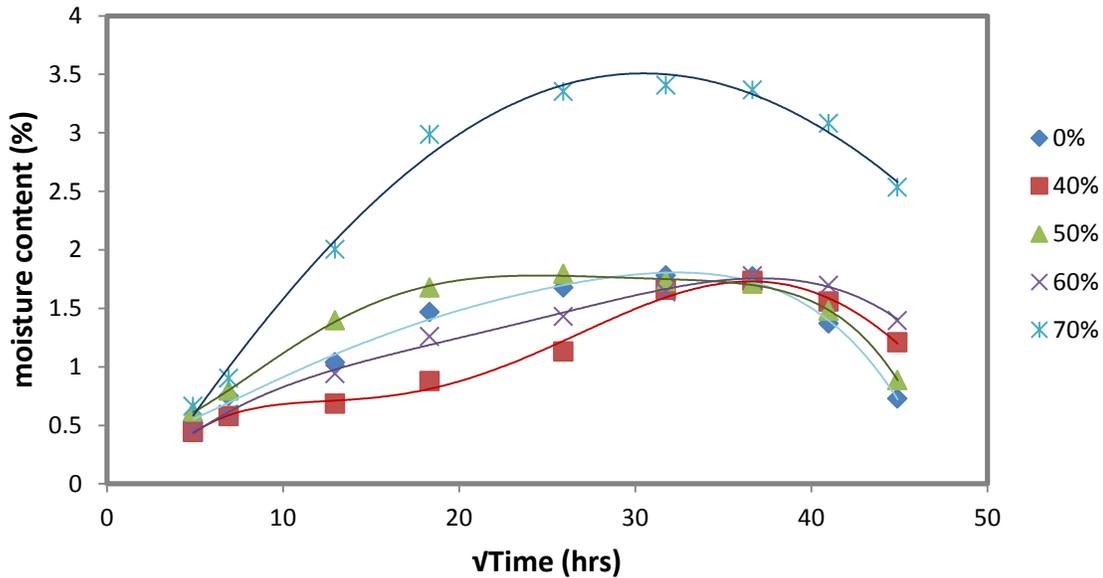


Figure 4: Moisture Absorption property of Sandstone-Polyester Composite (all percentages refer to filler loading)

4. EFFORTS TO COMMERCIALIZE SOME OF THE PRODUCTS

4.1. Research collaboration with “Triple T”

As a result of research coming from this work, The National University of Lesotho and a local sandstone company called “Triple T” have signed a research contract to develop and commercialize composite materials based on locally available Clarens Formation sandstones as fillers in thermosetting resins. In the collaboration, the National University of Lesotho will be helping the company to make complete use of the stone by finding alternative uses for all the waste stones and dust produced during brick production. The present prototypes are those of indoor cladding.

4.2. Research collaboration with “Lesotho Funeral Services”

The National University of Lesotho and “Lesotho Funeral Services” have signed a research contract to develop and commercialize engineered stone based on

diorite and other quartz based rocks. The company already has factories making tombstones from granite. However, large quantities of waste resulting from the tombstones are not fully utilized. The envisaged engineered stone products will be used for tiles and tabletops. With an average of 600 000 (500×500mm) tiles a month envisaged by the company, the project is likely to be a welcome boost for local economy.

5. CONCLUSION

The moisture absorption property of the differently reinforced composites has been successfully studied. Following tests carried out for the moisture absorption property, it has been established that the corn stalk reinforced composite has the highest moisture absorption capabilities as described in previous sections of this report. The diorite reinforced composite however, absorbed the least amount of moisture over time, having a moisture content of 0.7% at 70% of the diorite-filler loading in the composite. These results proffer interesting trends for the future of

engineering materials, particularly composites.

6. ACKNOWLEDGEMENTS

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REFERENCES

- ASTM D5229/5229 M, Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials, American Society for Testing and Materials, ASTM International, United States, 2004.
- Baillie, C. (2006). Engineers within a local and global society (1st edition), Morgan and Claypool publishers, San Rafael.
- Barbero E.J, (1999), composites for construction: *Introduction to composite material design*, Taylor & Francis, Philadelphia.
- Beg, M. D. H. & Pickering, K. L. (2008). Reprocessing of wood fibre reinforced polypropylene composites. Part II: Hygrothermal ageing and its effects, *Composites Part A: Applied Science and Manufacturing*. Volume 39, Issue 9, Pages 1565-1571.
- Blatt, Harvey and Robert J. Tracy (1996). *Petrology: Igneous, Sedimentary and Metamorphic*, 2nd ed. W.H. Freeman, New York.
- Boukhoulda B.F, Adda-Bedia E, and Madani K (2006), The effect of fiber orientation angle in composite materials and material degradation after hygrothermal ageing, *Composite Structures*, volume 74, issue 4,
- Cray Valley Resins, Material Data Sheet. South Africa
- David, C, Darrot, M and D. Jeannette, (1993), Pore structure and transport properties of sandstone, *Transport in Porous Media*, Volume 11, Pages 161-171.
- Gul, H.I., and A. Maqsood (2006), Thermophysical properties of diorite along with the prediction of thermal conductivity from porosity and density data, *International Journal of Thermophysics*, Vol. 27, No.2
- Hamoush S, T. Abu-Lebdeh, M Picornell, S Amer (2011), Development of sustainable engineered stone cladding for toughness, durability, and energy conservation, *Construction and Building Materials*, Volume 25, Issue 10, Pages 4006–4016
- Lam dos Santos J.P., L.G. Rosa, P.M. Amaral (2011), Temperature effects on mechanical behaviour of engineered stones, *Construction and Building Materials*, Volume 25, Issue 1, January, Pages 171–174
- Leaman, D.E. 1973. *The Engineering properties of Tasmanian Diorite, with particular reference to the route of the Bell Bay Railway*. Tech. Rep. Dep. Mines Tasmania. 16:148-163.
- Medina, M. (2007). Waste picker cooperatives in developing countries. In M. R. Chen, R Jhabvala, R. Kanbur & C Richards (Eds.), *Membership based organizations of the poor* (1st edition, 105-121), Routledge, London.
- Peijs, T, Melick, H.G.H, Garkhail, S.K., Pott, G.T., and C.A. Baille (1998) *Proceedings of the European Conference on Composite Materials: Science, Technologies and Applications*, Woodhead Publishing, pp. 119–126.

Sloane, D.J. 1991. *Some Physical Properties of Diorite*. Rep. Dep. Mines Tasmania. 22:1-5.

Thamae T, Vaja.S, Yiyi. S, Finoro. C, Stefano N. and Baillie. C (2010). Green Composites: Properties, design and life cycle assessment: *Mechanical and absorption properties of corn and wheat flour composites for developing countries*, Nova Science Publishers, New York.

Wang, W, Sain, Mand P.A. Cooper (2006), Study of moisture absorption in natural fiber plastic composites, *Composites Science and Technology*, Volume 66, Issues 3-4, Pages 379-386.

White, N.M and M.P. Ansell (1983), Straw-reinforced Polyester Composites. *Journal of Materials Science*, Volume 18, Pages 1549-1556.