Effect of Blend Ratio on Physico-Mechanical Properties of Agro Stone Composite Caulking Materials

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Abstract. This work aimed to study the effect of blend ratio on properties of Agro stone caulking materials. With the experiment, fixed ratio pumice filler and bagasse were used. Magnesia cement was used as binding material. Caulking were produced from different proportion of magnesium oxide and magnesium chloride brine solution (0.9:1, 0.95:1, 1:1, and 1.2:1, 1.32:1 kg per liter) with concentration of 28, 30, 33, 36 and 42 wt/wt % brine solution. The caulking materials were characterized by physical properties, mechanical properties, and free chlorine ions. After curing for 14 days and 28 days, the common mechanical properties tensile, compressive, and flexural bending strength was measured with the assistance of computerized testing machines according to testing procedures. The minimum and maximum water absorption capacities were 14 and 26.4% respectively. The optimum tensile, compressive and flexural bending strength of the experiments were 3.8 MPa, 25.8MPa, and 23.12MPa respectively with the ratio of caulking material 1:1 kg of MgO to a liter of MgCl2. The free chloride ion was reduced to 20% by adding 5%wt zeolite. The optimum mixing ratio was 1:1 with 36% of brine solution. The study shows the potential of high strength, and low corrosion biobased composite ecofriendly materials for the productions of agro stone composite caulking materials.

Keywords: Agro stone · Blend ratio · Bagasse · Brine solution · Caulking material · Water absorption

1 Introduction

The shelter is one of the three basic needs of a human being [1]. A wide range of construction facilities is required including in the area of residential, commercial, hospitals, schools, and transport infrastructure. Despite that, the construction industry is

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a major sector of the economy of most nations. However, this industry is a large consumer of factory-made building materials such as mineral-based materials ranging from aggregates, cement, bricks, and tiles to structural steel, glass, and ceramics. To overcome the common observed high construction cost, low-cost biobased composite materials are needed. Composite materials are made from two or more constituents with significantly different physical or chemical properties from each other. Biocomposites are materials in which one of their components is derived from biomass resources [2].

The major components of agro stone composite materials products are fillers such as (bagasse, pumice, wood, rubber [3], asbestos [2], fiberglass, and binder. Sorel s cement (SC) also known as magnesium oxychloride cement (MOC)was used as a binder for many years [4]. It is formed by a mixture of powdered magnesium oxide (MgO) and a brine solution of magnesium chloride ($MgCl_2$). Compared with Portland cement magnesium oxychloride cement has good resistance to oil, grease, superior mechanical properties, high fire resistance, fast hardening, low alkalinity, and high bonding ability [3]. The physical, mechanical, and chemical properties of the material which are made from Sorel s cement are significantly affected by the molar ratio of the reactants used in the formation process such as $MgO/MgCl_2$ or $H2O/MgCl_2$ [5]. The concentration of magnesium chloride significantly affects the strength, initial and final setting time. When the correct concentration of brine solution is not selected, this leads to the formation of magnesium oxide will react with water and form magnesium hydroxide, and also if its concentration beyond optimum the excess chloride ion cause corrosion problem [4].

The major commercial applications of magnesium oxychloride cement are industrial flooring, fire protection, grinding wheels, rendering wall insulation panels. Mostly it is limited for outdoor application this is because the prolonged contact with water results in leaching of $MgCl_2$, which leads to reduce the strength of the body. Most researchers devote themselves to improve the water resistance of magnesium oxychloride. It was found that some additives can greatly improve the water resistance of MOC cement, such as phosphoric acid and soluble phosphates, including the phosphates of alkali metals, alkali earth metals, iron, aluminum, and ammonia [6].

At present, Ethiopia has little experience within the utilization of various construction materials. The conventional materials are produced from mortar, gypsum, clay, limestone, and others excavated from the ground, however, it is unaffordable for everyone due to its high cost. Therefore it is important to focus on alternative building materials produced from raw materials like agro-industrial wastes, such as bagasse, wood rice husk. In recent years natural fibers have become the most interesting for reinforcement of composite material that Bagasse is cost-effective material used for the synthesis of agro stone composite materials. This is because it is a by-product of forestry and the agricultural industry. Compared with synthetic fiber natural fibers has an advantage such as widely available, good insulation properties, huge availability, cheaper and lightweight [7,8].

Nowadays Ethiopia uses composite materials for interior partition, ceilings, and exterior walls of building structures. Caulking materials formulated from MgO, $MgCl_2$ solution, and fillers are widely used as an economical joint binder for different partition and ceiling boards. Despite excellent properties associated with MOC-based caulks, cracking at joints and corrosion have been common quality problems limiting customer s preferences. These characteristics quality is significantly sensitive to the relative proportion of components listed above and admixtures used during processing. Therefore the aims of this study were intended to determine the optimum mix design of components responsible to produce caulk material with maximum strength, stability, and corrosion resistance.

2 Materials and Method

2.1 Materials

The raw materials used in this study such as magnesium oxide (MgO) and magnesium chloride ($MgCl_2$), pumice, and bagasse were collected from the Bahir Dar Agro stone enterprise. Laboratory grade reagent such as hydrochloric acid, zeolite, nitric acid, Potassium chromate, and silver nitrate was collected from Faculty of Chemical and Food Engineering Bahir Dar Institute of Technology.

2.2 Fabrication of Mold

Metal molds were used in the production of the composite caulking samples. The mold used for this process was made of mild steel material with a thickness of 10 mm. The dimensions and shapes of cavities were made consistent with ASTM Standard D 63890 for tensile testing and ASTM Standard D 79097 for flexural (bending) testing (ASTM E290, 1990). The molds which were used for this work have a dimension of 150 * 150 * 10 mm for compressive strength test, 400 * 50 * 10 mm dimension for flexural strength test and 350 * 50 * 10 mm dimension for the tensile strength test.

2.3 Sample Preparation

Magnesium oxide powder and brine (magnesium oxychloride) were mixed according to the experimental mix design shown in Table 1 the mixing ratio which is used by the company was used as a reference. After the MOC was prepared the amount of filler, bagasse and pumice was determined based on the working consistency by using British standard as a reference. The size of bagasse filler that was used for this work was reduced with the help of laboratory cutters to a small size and sieved with a 1.7 mm laboratory sieve.

2.4 Setting Times Determination

The working consistency of the caulking sample was determined using the Vicat apparatus. This was repeated for all mixing ratios initial and the final setting time of paste was determined according to the following procedure.

2.4.1 1Initial Setting Time Determined by the Penetration Depth

The initial setting was determined by ASTM methods C 191 based on the principle of penetration resistance according to [8]. A fresh paste of normal consistency was prepared and filled into the Vicat mold. After 30 min the mold resting on a plate the needle was gently lowered and brought in contact with the surface of the paste and quickly released. Thirty seconds after releasing the needle the penetration was recorded. This was repeated every 15 min until penetration of 25 mm or less is obtained in thirty seconds.

Table 1. Experimental mix design

Code of sample	Brine ($MgCl_2$)[wt. %]	MgO powder/brine [Kg/Liter]
A1	28	0.9
A2	28	0.95
A3	28	1
A4	28	1.2
A5	28	1.3
B1	30	0.9
B2	30	0.95
B3	30	1
B4	30	1.2
B5	30	1.32
C1	33	0.9
C2	33	0.95
C3	33	1
C4	33	1.2
C5	33	1.32
D1	36	0.9
D2	36	0.95
D3	36	1
D4	36	1.2
D5	36	1.32
X1	42	0.9
X2	42	0.95
X2	42	1
X4	42	1.2
X5	42	1.32

2.4.2 Final Setting Time

For the determination of the final setting time the needle of the Vicat apparatus was replaced by Plunger. The paste was considered as finally set when the needle touches gently to the surface of the text block, only the needle makes an impression.

2.5 Water Absorption Test

The samples of the composite caulking material were dried by using an oven with a temperature of 105 ▯ for 6 h and cooled to room temperature. The weight of this dry sample was weighed. The dried specimens were immersed completely in clean tap water at room temperature for 24 h. The samples were removed and the excess water was wiped out by using a cotton cloth. Finally, the wet sample was weighed. The water absorption capacity of the sample was determined by Eq. 1 according to [9,8].

$$W(\%) = \frac{M2 - M1}{M1} * 100 \tag{1}$$

Where; W is the percentage of water absorption [%], M1 is a mass of the dried sample before immersion in water [g], and M2 is a mass of the sample after immersion in water [g].

2.6 Specific Gravity

The specific gravity of the magnesium chloride solution was determined by using a pycnometer. Its values were determined by using the following formula.

$$SG = \frac{M1 - MO}{M2 - M1} \tag{2}$$

Where; Mo is the mass of the pycnometer[g], M1 is the mass pycnometer and brine solution[g], and M2 is the mass of the pycnometer and water[g].

2.7 Mechanical Properties

The time effect on the physic mechanical properties such as bending, tensile, and compression strength of the product produced was determined. All properties were tested After 14 days and 28 days according to [10,11].

2.7.1 Compressive Strength Test

The compressive strength of the caulking material with different blend ratios was carried out in a compressive test machine before this analysis was carried out the sample was dried by air. Cubic samples were adjusted so that the load was applied perpendicularly to the direction of molding. The stress continued until the destruction of the samples was carried out. The compressive strength was calculated by using the following formula.

$$P = \frac{F}{Ac} \tag{3}$$

Where; F is maximum destructive force [N], P is Compressive strength [pa], and Ac is the cross-sectional area of the sample [m^2].

2.7.2 Flexural Strength Test

Modulus of rupture or bend strength was determined According to ASTM C473 with the dimension of width 50 mm, length 400 mm, and 10 mm thickness. It was calculated by using Eq. 4.

$$\sigma = \frac{3FL}{2bd^2} \quad (4)$$

Where; F is load [N], L is the length of the support span [m], b is Width [m], and d is the thickness of the material[m].

2.7.3 Tensile Strength Test

The tensile strength of each sample was determined According to ASTM C473, with a sample size of 5 mm width, 300 mm length, and 10 mm thickness specimen with the help of a computerized automated tensile testing machine.

2.8 Determination of Free Chlorine

The excess chloride of caulking material was determined by using ASTM C1152 procedure. The prepared caulk material was crushed by using a laboratory disk mill and sieved with a 0.545 mm sieve and 5 gm of the sample was placed in 250 ml beakers. Then 10% of nitric acid was added. Then the mixture was stirred with the help of a magnetic agitator to enhance the mass transfer. Finally, the chloride content was determined by titration by using silver nitrate as a titrant agent and the free chloride ion was determined according to the Bohr titration method. It was calculated by using Eq. 5 according to [12].

$$C1,\% = 3.545[(V1 - V2)N] * W \quad (5)$$

Where; $V_1$is volume of 0.05 N AgNO3 solutions used for sample titration [ml], $V_2$is volume of 0.05 N $AgNO_3$ solution used for blank titration [ml], N is normality of 0.05 N $AgNO_3$ solution, and W is mass of sample [g].

3 Results and Discussion

3.1 Magnesium Chloride Solution Specific Gravity

As shown from Fig. 1 the density of prepared brine/magnesium chloride solution increases with increases in the concentration of brine. Saltwater is denser than regular water, which suggests there's more mass during a certain volume of saltwater than there's within the same volume of normal water. Magnesium chloride is a highly hygroscopic salt this is easily soluble in water. It dissociates into two ions: a cation of magnesium (Mg^{2+}) and two anions of chloride (Cl^-). There are two reasons for the density of brine increase. One is just that the $MgCl_2$ is far denser than water due to its ions have more mass than the oxygen and hydrogen atoms within the water molecules. And also the ions bind nicely with the water molecules. The density of sample D with a weight ratio of 36%wt salt within this experiment was bigger. However, the density of solution (×5) which is already used by Bahir Dar agro stone enterprise is 1.23. The density of the solution was increase with salt content.

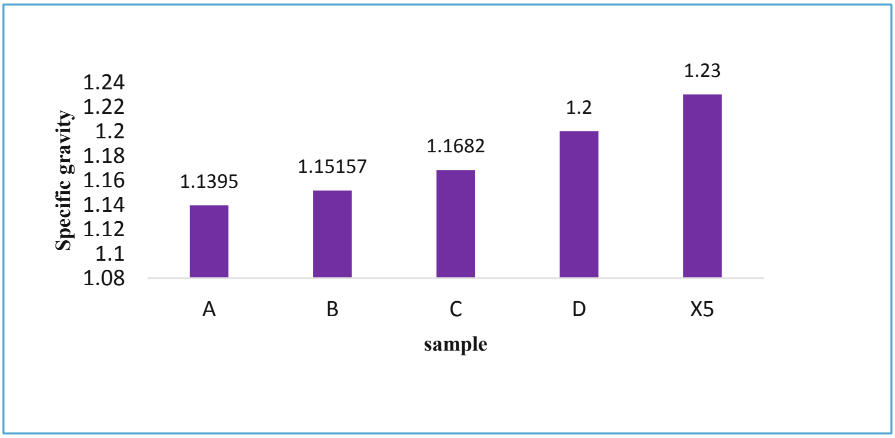

Fig. 1. The specific gravity of brine solution

3.2 Water Absorption

The water absorption test for oven-dried specimens was carried out for each caulking material in the different ratios of magnesium oxide to brine solution. As stated in the experimental design there are five ratios of magnesium oxide to magnesium chloride solution (0.9, 0.95, 1, 1.2 and 1.32, kg of MgO per liter of brine) and also the brine solution was between the ranges of 28 to 42% to make better magnesium oxy cement. As shown in Fig. 2 the water absorption of MgO caulking decreases from left to right which means the ratio of 0.9 to 1.32 is due to consumption of magnesium chloride increase. For all sample the water-resistance increase as a percentage of Sorel cement increase and by decreasing agro filler such as cellulose. The highest percentage of water absorption is observed in the A2 sample which means it is less reactive to admixture chemicals which help to impart the fiber hydrophilicity. And also it is highly porous. From the literature review, technical specifications and standards of Agro stone product's water absorption have to be less than 22% [13]. As shown in the result most of the sample's water absorption is below 22 it is good for water resistance. The water absorption ability of caulking material which is already used by the company was studied. The highest percentage of water absorption is observed on sample A2 with 26.4% which is above standard value. Since bagasse has a high amount of hemicelluloses. The water absorption capacity increase as the bagasse content increase in a caulking material. The structure of natural fibers and the chemical composition such as cellulose and hemicelluloses are responsible for hydrophilic behavior [8]. When the amount of pumice increases water absorption decreases this is due to the good interaction of pumice fillers with the binder makes better resistance to water than Bagasse filler. From the experiment sample, X5 has good water resistance (Fig. 3).

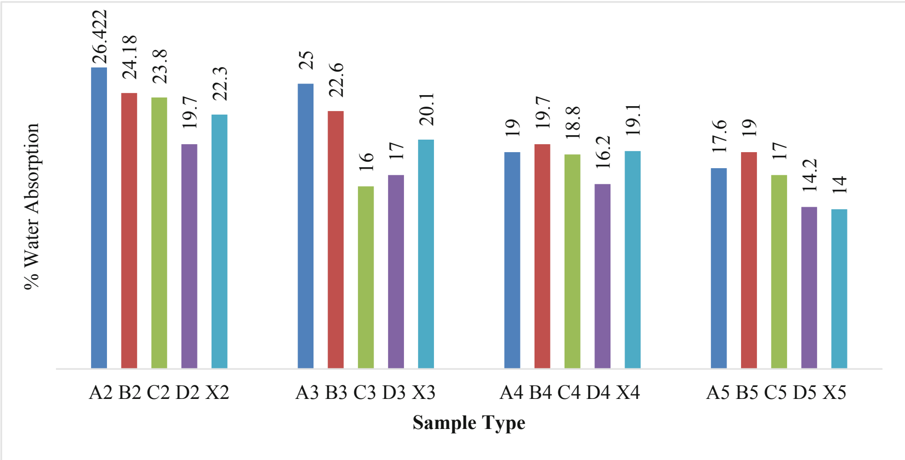

Fig. 2. Water absorption of magnesia cement composite caulking material

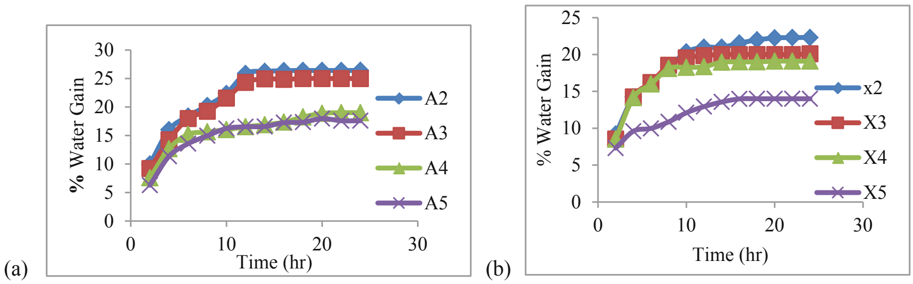

Fig. 3. Water gain of caulking materials a) 28% brine solution and b) 40% brine solution

3.3 Mechanical Properties

3.3.1 Compressive Strength

As shown in Fig. 4 different samples with different mix ratios of magnesium oxide to magnesium chloride with various brine concentrations in the range of 28 to 42 wt% have different compressive strengths. Sample D3 and X3 with a ratio of 1:1 magnesium oxide to magnesium chloride at brine concentrations of 36 and 42 wt % withstand greater loads as compared to others. For the production of MgO caulking material or board, the major raw materials to form magnesium oxychloride MOC cement are magnesium oxide and magnesium chloride. As shown from the results a ratio of 0.9:1, 0.95:1, 1.2:1, and 1:1.32 withstand a lower load than that of 1:1 kg of magnesium oxide to the liter brine solution. This is due to the reason that the former two ratio magnesium oxide are limiting reactant consumed before brine solution, therefore, there is unreacted brine this cause defect and decrease the ability to withstand load and also water resistance as depicted in Fig. 2. For the latter two ratios, the reason for decreasing compressive stress is brine solution is a limiting reactant has consumed before magnesium oxide this unreacted MgO causes a defect and leads to decrease compressive strength of the caulking materials. Therefore 1:1 ratio (with 36 wt/wt % of brine solution) is the optimum from this experiment to obtain good MOC. For all samples, compressive strength was increased from 7 days to 28 days. This is because as stated from literature reviews there is a different form of magnesium oxychloride but among

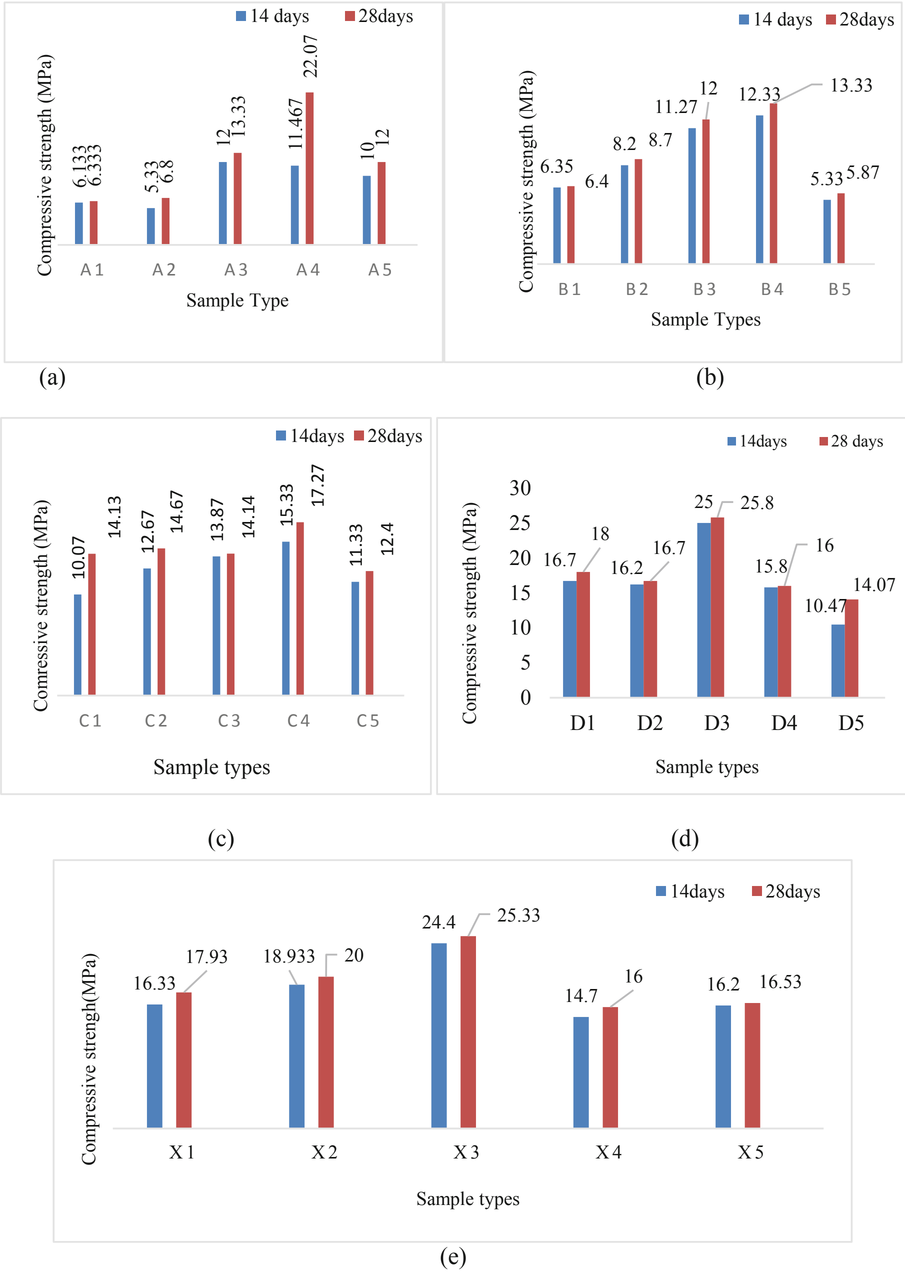

Fig. 4. Results of compressive strength of caulking material: a) 28%, b) 30%, c) 33%, d) 36% and, e) 42% by mass of brine solution

that 5-phase and 3-phase are stable at room temperature. 5-phase MOC withstands superior mechanical properties. As stated from literature kinetic experiments observed that the 5-phase is formed quickly, but the kinetics is not complete for several days this causes increasing in strength within an increasing day [4].

3.3.2 Flexural Strength

Figure 5 illustrates the different bending strength in X, D, C, B, and A specimen values due to varying the mixing ratio of the binder and the drying period of the sample. Therefore bending strength is found to be the highest in X5 followed by C5, D3, X1, D2, B5, D4, and from the rest of the other specimens. The bonding strength between the magnesium chloride and magnesium oxide is very strong in the X5 specimen which has a mixing ratio of 1.32 kg of magnesium oxide per liter of 42% magnesium chloride solution. It can be understood that specimen X5 has good resistance of the force applied due to proper magnesium chloride and magnesium oxide mixing ratio from the rest of the other specimens that leads to the maximum bending strength. In this particular case, defects are carefully minimized and the values seen can tell us that the maximum magnesium oxide and maximum magnesium chloride ratio as well as good MOC solution increase the ability to resist the downward force applied on the specimen which leads to maximum bending strength.

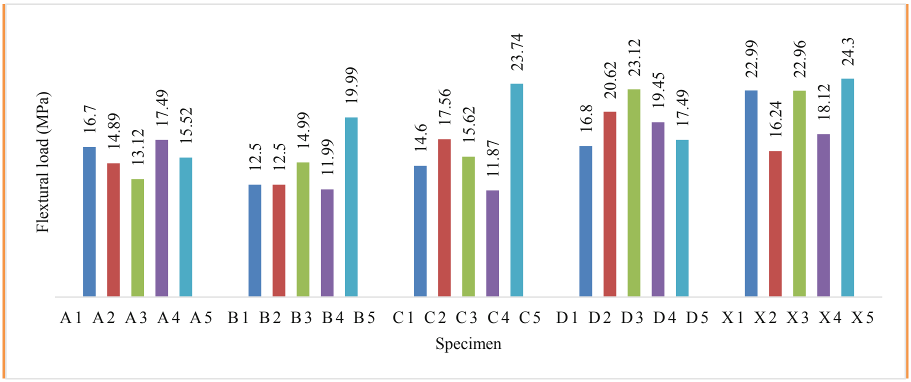

Fig. 5. Flexural stress result after 28 days

3.3.3 Tensile Strength Test

Figure 6 clearly shows that different samples that designated as A, B, C, D, and X with 28% 30% 33% 36% and 42% respectively of different magnesium chloride solution which has different tensile strength. As shown tensile strength increases with $MgCl_2$ solution from 28% to 42%. Compared with other samples D and X withstand greater tensile strength. From the ratio of the samples A to C**,** magnesium oxide is the limiting reactant and $MgCl_2$ solution in excess which will lead to absorb the moisture from the atmosphere that causes the surface of the cement to expand slightly or otherwise become irregular. Similarly, the amount of MgO of the samples D and X is excess and $MgCl_2$ solution is a limiting reactant especially for sample X there is unreacted MgO.

This will tend to combine with water and forms Mg $(OH)_2$, there will be excess water which must evaporate, slowing the curing time of cement and Mg $(OH)_2$ has no cement bonding properties with $MgCl_2$ and water. From the literature, the preferable range of specific gravity for the $MgCl_2$ solution is in the range from SG=1.179 to SG=1.218 which gives adequate strength. The specific gravity of samples D and X is SG=1.1682 and SG=1.2 respectively which is found in the acceptable range. Since compressive strength is the main parameter to be tested, which is sample X3 has the best compressive strength; as a result, sample D at 36% of $MgCl_2$ solution with a tensile strength of 3.8 MPa is preferable to the other.

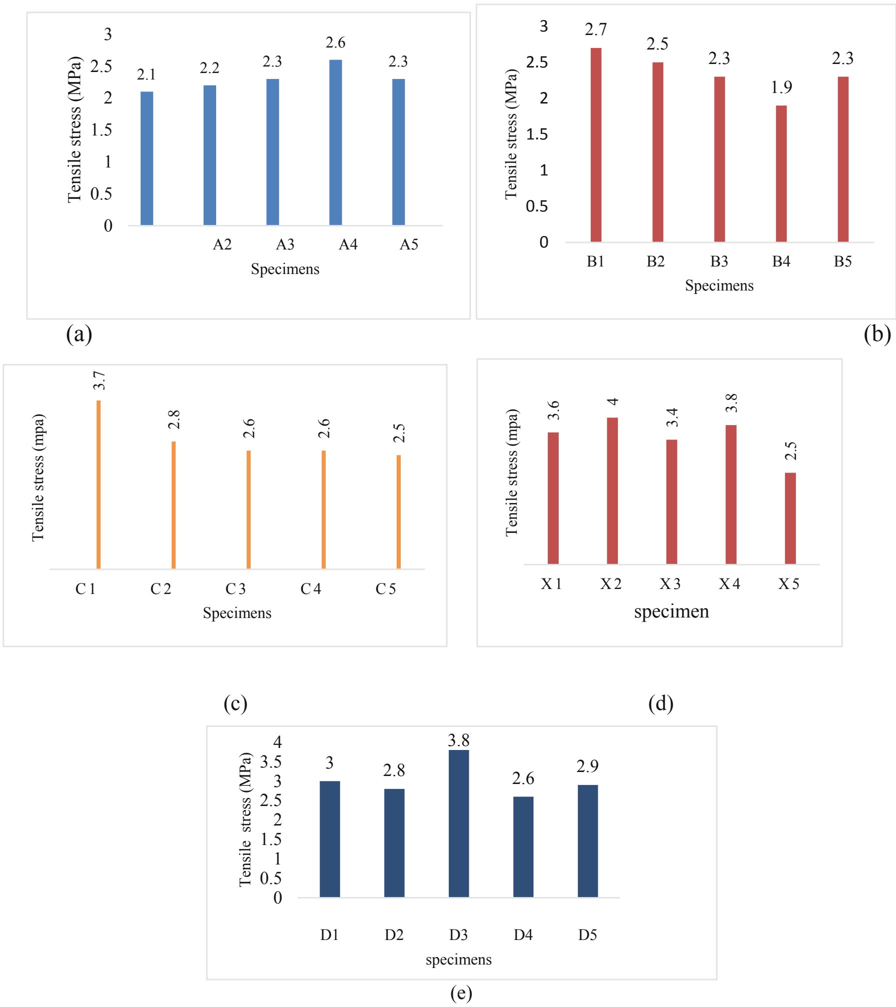

Fig. 6. Results for tensile strength of magnesium chloride after 28 days a) 28%, b) 30, c) 33, d) 42%, and e) 36%

3.4 Results of Free Chloride in Caulking Material

As shown in results from Fig. 7 when the ratio of magnesium oxide to magnesium chloride increases the free chloride decrease this is due to the excess reactant of MgO. At the ratio of 0.9:1 kg of MgO to a liter of $MgCl_2$, the free chloride ion is higher in both D1 and X1 because MgO is a limiting reactant. Chloride that causes corrosion was reduced by adding a corrosion resistance agent of 5% zeolite [14]. It reduced a free chloride ion of 20% with a ratio of 1:1. Zeolite can be added to 15% but it harms strength and water resistance. The Free Chloride ion of sample X is higher than sample D with the same ratio since the concentration of brine is higher.

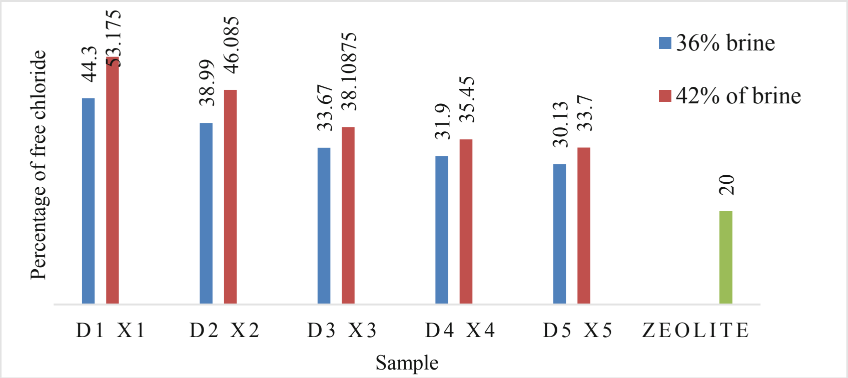

Fig. 7. Results of free chloride ion that cause corrosion

4 Conclusion

It can be concluded that the production of construction material from composite material is important. Magnesium oxide board is a composite material that acquired a significant role owing to fire resistance. Magnesium oxide is found to form a good and compatible formula in the production of composite material for partition boards and ceilings. Despite the strength and good fire resistance of magnesium boards, the caulking material used to join boards faces problems like cracking and corrosion. This study focused on the analysis of this problem. The physical properties (water absorption), mechanical properties (tensile stress, bending strength, and compressive strength), and the free chloride ion that causes corrosion of caulking material were studied. The water absorption of caulking material decreases as the ratio of magnesium oxide to brine solution increases this is due to the consumption of magnesium chloride increase. A mixing ratio of 1:1 magnesium oxide to magnesium chloride (magnesium oxychloride) at brine concentration of 36 and 42% wt withstand greater loads as compared to others. Therefore 1:1 ratio is the optimum for this experiment to obtain good MOC. The corrosion problem of caulking material was reduced to 20% by incorporated zeolite admixture.

5 Recommendation

- Further researches have to be done to analyze fire resistively, and sound insulation, of the caulking material.
- To improve water tightness and corrosion resistance of agro stone caulking materials further research have to be done by incorporating additive for instance various alkali metal phosphates; such as Magnesium mono or dihydrogen phosphate, Magnesium Stearate Aluminum Sulfate or Magnesium Sulfate for water resistance and nitrites, and other novel additives for corrosion resistance.
- The effect of weather conditions or season on caulking material should be investigated.
- The structure of the product should be analyzed with the help of a scanning electron microscope and also the porosity with the help of BET machines.

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References

1. Ali, M.M.: Design and development of cost-efficient houses the challenges and prospects of affordability. In: Technical Report of the Housing Development & Management, Lund University, pp. 120 (2009)
2. Hasmadi, M., Noorfarahzilah, M., Noraidah, H., Zainol, M.K., Jahurul, M.H.A.: Functional properties of composite flour: a review. Food Res. **4**(6), 18201831 (2020). https://doi.org/10.26656/fr.2017.4(6).419
3. Jin, F.: Magnesium oxychloride cement. Magnesia Cem., 2974 (2020). https://doi.org/10.1016/b978-0-12-391925-0.00009-1
4. Karimi, Y., Monshi, A.: Effect of magnesium chloride concentrations on the properties of magnesium oxychloride cement for nano SiC composite purposes. Ceram. Int. **37**(7), 24052410 (2011). https://doi.org/10.1016/j.ceramint.2011.05.082
5. Malinowski, S., Jaroszyńska-Wolińska, J.: The physical and mechanical properties of magnesium oxychloride cement-based materials. Bud. I Archit. **14**(4), 089098 (2015). https://doi.org/10.35784/bud-arch.1539
6. Kandeel, A.M., El-Mahllawy, M.S., Hassan, H.A., Sufe, W.H., Zeedan, S.R.: Effect of type of mixing water and sand on the physicomechanical properties of magnesia cement masonry units. HBRC J. **8**(1), 813 (2012). https://doi.org/10.1016/j.hbrcj.2012.08.002
7. Ita-Nagy, D., et al.: Life cycle assessment of bagasse fiber-reinforced biocomposites. Sci. Total Environ. **720**, 137586 (2020). https://doi.org/10.1016/j.scitotenv.2020.137586
8. Sahu, P., Gupta, M.K.: Lowering in water absorption capacity and mechanical degradation of sisal/epoxy composite by sodium bicarbonate treatment and PLA coating. Polym. Compos. **41**(2), 668681 (2020). https://doi.org/10.1002/pc.25397
9. Gbadeyan, O.J., Adali, S., Bright, G., Sithole, B., Awogbemi, O.: Studies on the mechanical and absorption properties of achatina fulica snail and eggshells reinforced composite materials. Comp. Struct. **239**, 112043 (2020). https://doi.org/10.1016/j.compstruct.2020.112043

10. Uddin, M.A., Jameel, M., Sobuz, H.R., Hasan, N.M.S., Islam, M.S., Amanat, K.M.: The effect of curing time on compressive strength of composite cement concrete. Appl. Mech. Mater. **204208**(October), 41054109 (2012). https://doi.org/10.4028/www.scientific.net/AMM.204-208.4105
11. Pivák, A., et al.: Foam glass lightened sorel s cement composites doped with coal fly ash. Materials (Basel) **14**(5), 116 (2021). https://doi.org/10.3390/ma14051103
12. ASTM International. ASTM C1115/C1152M Standard test method for acid-soluble chloride in mortar and concrete, vol. i, pp. 700703 (2004)
13. Taffese, W.Z.: Low-cost eco-friendly building material: a case study in Ethiopia. Int. J. Civil Environ. Struct. Constr. Archit. Eng. **6**(2), 183187 (2012)
14. For, C.: (12) United States Patent Primary Examiner Paul Marcantoni, **2**(12) (2013)