Research Paper

Formulation of Geopolymer Building Blocks Using Locally Available Aluminosilicate Waste Material

P.K. Kairigo[1,*], P.G. Kareru[1], E.S. Madivoli[1] and F.K. Njonge[2]

[1] College of Pure and Applied Sciences, Jomo Kenyatta University of Agriculture and Technology, P.O. Box- 62000-00100, Nairobi, Kenya

[2] Department of Land Resource and Animal Sciences, Jomo Kenyatta University of Agriculture and Technology, P.O. Box- 62000-00100, Nairobi, Kenya

* Corresponding author, e-mail: (Kinoti.kairigo@gmail.com)

Abstract: *This paper presents research work done on the applicability and viability of geopolymer technology on the various types of soils present in Kenya. The main aim is to provide an alternative building material to the conventional materials available in Kenya. Stone Mining activities in Kenya have generated a lot of aluminosilicate waste that can be a good source of raw material for geopolymer synthesis. Geopolymers are amorphous aluminosilicate materials whose synthesis occurs in a fast chemical reaction. The proposed mechanism occurs in three stages, the dissolution of Al and Si present in the source material, the condensation of precursor ions into monomers and the polymerization of monomers into polymeric structures. For the reaction to result to a geopolymer the ratio of Si and Al is paramount. Structural characterization of the soil samples and the developed building blocks were done using Shimadzu FT 8000 FT-IR spectrophotometr, X-RF.*

Keywords: Geopolymers, allumino-silicate, FT-IR, X-RF, X-RD.

1. Introduction

With the ever increasing population worldwide, great pressure is put on availability of cheap housing. This in turn puts pressure on Portland manufacturing industries to produce more of the product at a lower cost. Housing projects are also in the increase especially in third world countries. It is estimated that the number of housing units, for instance in Kenya alone, would triple in the next decade so as to meet the growing demand of housing facilities that would be brought about by the

projected population increase. For instance there has been a boom in infrastructural development projects in Kenya, housing in particular, between 2002 – 2012 with the amount of capital invested on infrastructural developments estimated to be around 1billion USD in that period [15].In recent years, research work has been done to investigate the possibility of utilizing a broad range of materials as raw materials in the production of geopolymer cements. The use of geopolymer containing waste materials such as granulated blast-furnace slag and fly ash has been reported in many research works. Geopolymer cements are a group of alkali-activated materials exhibiting superior engineering properties compared to Portland cements. They have relatively high compressive strength, short to long setting times, relatively low pore volume, and resistance against aggressive media, compared to Portland cements. The role of alkalis is to activate raw materials such as blast-furnace slag and fly ash to take part in the geopolymerization reactions. These materials are activated by alkalis so that Si-O bonds in the silicates or aluminosilicates are broken and a number of reactions result in the formation of geopolymers[1].With the abundant availability of waste containing aluminosilicates in the country, little is still being done to exploit these resource that might ease the burden on our cement industry and in the process reduce the environmental impact and degradation caused by our Portland industry and in the process make the dream of cheap affordable housing facilities as envisioned in vision 2030, a reality.

1.1 Geopolymers

Geopolymers are inorganic polymeric materials with a chemical composition similar to zeolites but possessing an amorphous structure. They can be seen as man-made rocks that are produced by reacting solid aluminosilicates with highly concentrated aqueous alkali hydroxide or silicate solution [12]. The chief ingredients of geopolymers are alkaline solutions and source materials such as fly ash and kaolinite. Alkaline solutions frequently used are sodium hydroxide or potassium hydroxide in combination with sodium silicate [8]. Any material that contains mostly Silicon and Aluminum in amorphous form is a possible source material for the manufacture of geopolymer. These Metakaolin or calcined kaolin, low-calcium ASTM Class F fly ash, natural Al-Si minerals, combination of calcined mineral and non-calcined materials, combination of fly ash and metakaolin, and combination of granulated blast furnace slag and metakaolin have been studied as source materials. Due to the complexity of the reaction mechanisms involved, a quantitative prediction on the suitability of the specific mineral as the source material is not available but natural Al-Si minerals have the potential to be the source materials for geopolymerization [4].
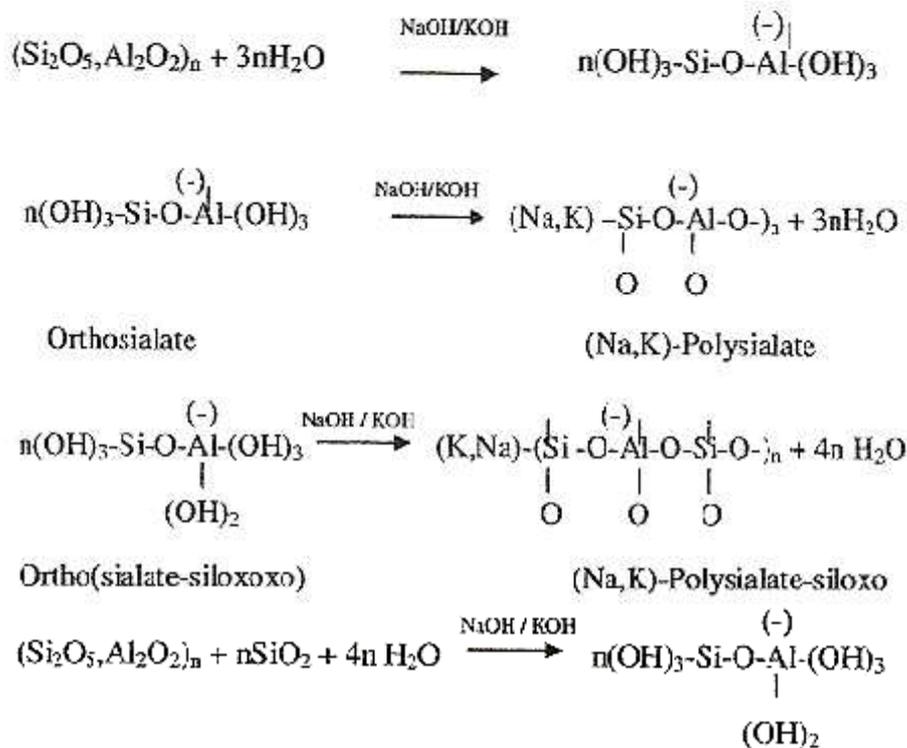
1.2 Geopolymer Chemistry and Reaction Mechanism

Conceptually, the formation of geopolymers follow the same route as that for most zeolites: dissolution, with formation of mobile precursors through the complexing action of hydroxide ions, partial orientation of mobile precursors as well as partial internal restructuring of the alkali polysilicates and reprecipitation where the whole system hardens into an inorganic polymeric structure. However, there are some marked differences between zeolite formation and geopolymerization and most of these are related to the composition of the initial mixture. Zeolites are usually formed in closed, hydrothermal systems; crystallize from fairly dilute aqueous solutions where the precursor species have the mobility and time to undergo proper orientation and alignment before bonding into a crystal structure. On the other hand, depending on the exact reaction conditions and absence of enough time for the formation of a proper crystalline structure, geopolymerization occurs fairly quickly thereby resulting in a microcrystalline, amorphous or semi-amorphous structure. There are certain compositional criteria that have to be met before geopolymerization may occur. First, the molar ratio of $SiO_2:M_2O$ must be between 4.0:1 and 6.6:1 in the aqueous soluble silicate solution where M is an alkali metal cation. Secondly, the alumino-silicate oxide must also contain Al which is readily soluble and finally the overall molar ration $Al_2O_3:SiO_2$ must be between 1:6.5. However, since it's very unlikely that all of the silica or alumina actually takes part in the synthesis

reaction, these ratios are not very critical when dealing with waste materials and for the most part they are only an indication of the approximate composition which are based on chemical analysis [7].

1.3 Chemical Structure

Geopolymeric structures consist of a poly (sialate) (-Si-) Al-O-) and a poly (sialate-siloxo) (Si-O-Al-O-Si-O-) with a general chemical formula of $Mn[-(SiO_2)z -AlO_2]n.wH_2O$, where M is an alkali cation, z is a number and n is the degree of polymerization [1].

$$(Si_2O_5,Al_2O_2)_n + 3nH_2O \xrightarrow{NaOH/KOH} n(OH)_3\text{-Si-O-Al-}(OH)_3$$

$$n(OH)_3\text{-Si-O-Al-}(OH)_3 \xrightarrow{NaOH/KOH} (Na,K) -Si\text{-O-Al-O-})_3 + 3nH_2O$$

Orthosialate   (Na,K)-Polysialate

$$n(OH)_3\text{-Si-O-Al-}(OH)_3 \xrightarrow{NaOH/KOH} (K,Na)\text{-}(Si\text{-O-Al-O-Si-O-})_n + 4n\ H_2O$$
$$(OH)_2$$

Ortho(sialate-siloxoxo)   (Na,K)-Polysialate-siloxo

$$(Si_2O_5,Al_2O_2)_n + nSiO_2 + 4n\ H_2O \xrightarrow{NaOH/KOH} n(OH)_3\text{-Si-O-Al-}(OH)_3$$
$$(OH)_2$$

The goepolymerization process [6].

The aluminosilicate network consists of SiO_4 and AlO_4 tetrahedral structural units connected to each other by sharing their oxygen atoms. The presence of cations such as Na^+, K^+, Li^+, Ca^{2+}, Ba^{2+}, NH_4^+, and H_3O^+ is necessary to balance the negative charge of aluminum. The molecular structure consists of an aluminosilicate network that is a product of the chemical reaction between aluminosilicate and alkali-polysialate in a relatively highly alkaline medium Any pozzolanic compound or source of silica and alumina that is readily dissolved in alkaline solutions will suffice as a source of geopolymer. Thus, the categories comprise of slag-based geopolymer cement, rock-based geopolymer cement, fly ash-based geopolymer cement, and ferro-sialate-based geopolymer cement.

1.4 Geopolymer Development

The major processes involved in geopolymer development are dissolution of the aluminosilicate species within a highly basic, alkaline environment, polymerization of the dissolved minerals into short-lived structural gel, precipitation of formed hydration products and final hardening of the matrix by excess water exclusion and the growth of crystalline structures.[6] Dissolution occurs immediately upon contact between the alkaline solution and the pozzolanic material and allows for ionic interface between species and the breaking of covalent bonds between silicon, aluminum and oxygen atoms. This process generates rapid and intense heat and is directly proportional to the pH level of the activating solution. The rate of dissolution is relevant to the amount and composition of the ashes and

the pH of the activating solution. Polymerization involves a substantially fast chemical reaction under alkaline conditions on Si-Al minerals, resulting in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds. The formed gel product contains alkaline cations which compensate for the deficit charges associated with the aluminum-for-silicon substitution. The slow growth of crystalline structures become evident during this process, as the nuclei of the polymerized gel reaches critical size. The matrix crystallinity is relative to the rate by which precipitation occurs: fast reactions between alkali and geopolymer raw materials do not allow time for growth of a well-structured crystalline environment [13]

2. Materials and Methods

2.1 Sampling

Soils with suspected high amounts of required minerals were collected from four selected areas in Kenya. The actual mineral content was assayed in the samples.

2.2 Determination of Sample Composition by X-RF

Samples collected were assayed and analyzed at the ministry of mines and geology to ascertain their alumino-silica content. The samples elemental content was analyzed according to ASTM standard D 4326 for mineral content. One gram of the powdered sample was weighed and mixed with 4g of anhydrous sodium carbonate (AR).

The entire bottle of flux was heated to the fused state, cooled, reground and stored in the desiccator. This was done to avoid volatile losses upon fusing. Results obtained were used to ascertain the viability of our samples as raw materials for the development of geopolymer binder material.

2.3 Preparation of Geopolymer Concrete Specimens

The geopolymers concrete specimens was prepared using an activator solution comprising of a blend of sodium silicate and 14M sodium hydroxide solution, which was mixed with the collected samples. 14 M Sodium hydroxide solution of was prepared by dissolving NaOH pellets in distilled water in a fume chamber. The sodium silicate solution used had a composition of 8.9 wt. % Na_2O, 28.7 wt. % SiO_2, and 62.5 wt. % H_2O. The aggregate was mixed until a highly viscous mixture was achieved. This was then set on moulds for setting and monitoring.

2.4 Determination of Compressive Strength of the Blocks

The compressive strength of the prepared specimen blocks was determined with varying drying times from 7days to 60 days. The compressive load was applied until the load indicator showed that the load was decreasing steadily. Some samples displayed a well-defined fracture pattern (ASTM C 39-04).The compressive strength will be calculated by dividing the maximum load carried by the specimen with the average cross sectional area.

2.5 Determination of Density of the Blocks

The density of the prepared samples was calculated in accordance to the guidelines set out in ASTM C 39 as follows;

$$Density = \frac{W}{V}$$

Where,

W = mass of the specimen in Kg
V = volume of the specimen computed from the average diameter and average length

2.6 Determination of Water Absorption

The water absorbed was determined by immersing the prepared samples in water for 24hrs. The amount of water absorbed was calculated as follows;

$$M_w = \left(\frac{M_f - M_i}{M_f} \right) x\ 100$$

Where,

M_w = amount of water absorbed expressed as weight percentage
M_f = final weight of test specimen after 24hr immersion in water
M_i = initial weight of test specimen before immersion in water

3. Results and Discussion

3.1 Soil Moisture Content

The soil samples were tested for their moisture content by weighing the soils before and after drying. From table 1, it is clear that clay soil from muranga had the highest moisture content while sand soil from muranga had the lowest moisture content. The percentage water content was in the order Clay soil (Meru) > Clay soil (Muranga) > Quarry dust > Diatomite > Sand soil (Muranga). The moisture content of clay soil was higher in clay soils as compared to sandy soils.

Table 1: Percent moisture content of various soil samples

Sample	Wt_1(g)	Wt_2(g)	% water content
Quarry dust	20	17.87	10.65
Clay (murang'a)	20	17.6	12
Sand (murang'a)	20	18.61	6.95
Clay Soil (meru)	20	17.42	12.90
Diatomite (meru)	20	18.23	8.85

3.2 Optimization Results

The specimen blocks were made using different ratios of the , sodium hydroxide and sodium silicate blend ranging from 1:1:4 to 1:1:6 (Al_2O_3:M_2O:SIO_2) Table 2-4. All were monitored separately to ascertain the optimum point for each soils and the workability of different soils with varying mineral content. Compressive strength of the developed building blocks is largely influenced by three factors; the curing time, ratio of sodium hydroxide , sodium silicate and the type of soil used. From table 2, the comprehensive strength increases with a subsequent increase in curing time from 7 days to 60

days with no change after 60 days. With a ratio of 1:1:6 and a curing time of 60 days, quarry dust gave the highest compressive strength of 3.2 Mpa while clay soil (Muranga) gave the lowest comprehensive strength of 2.3 Mpa. Compressive strength was in the order quarry dust > diatomite > sand (Muranga) > Soil (Meru) > Clay (Muranga).
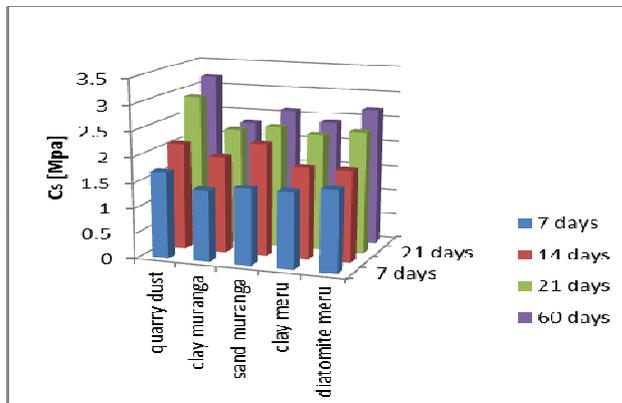

Fig 1a: compressive strength of building blocks made using different soil samples with a geopolymer ratio of 1:1:4
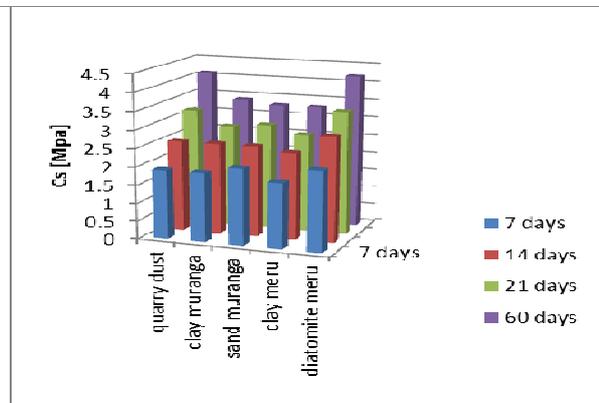
Fig 1b: compressive strength of building blocks made using different soil samples with a geopolymer ratio of 1:1:5
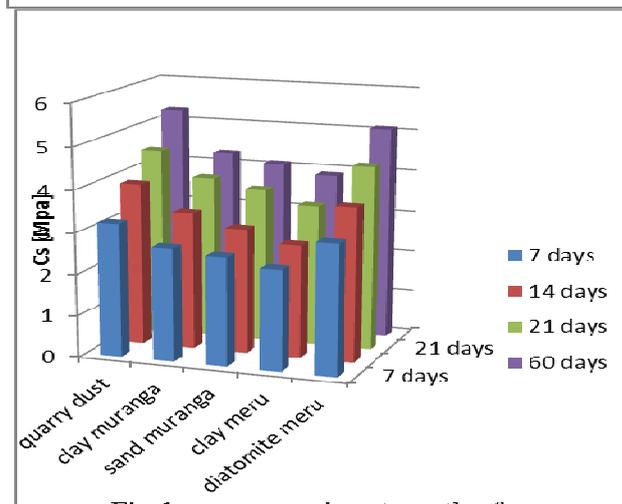
Fig 1c: compressive strength of building blocks made using different soil samples with a geopolymer ratio of 1:1:6

3.3 Density

Table 4 depicts the density of the building blocks made with different geopolymer ratio. From the results obtained building blocks with a high density were obtained when diatomite was used with the ratio of geopolymer being 1:1:6. From the results obtained the density of the building blocks is largely influenced by the amount of silicate added and the type of soil. As such it was found that with a ratio of 1:1:6 the density obtained were as high as 1.78Kg/m^3 when diatomite was used as the soil specimen. The density was in the order diatomite > sand > quarry dust > clay (Meru) > Clay (Murang'a).

Table 2: Density of building blocks made using different soil samples with a geopolymer ratio of 1:1:4, 1:1:5, 1:1:6

Soil Type	1:1:4 Kg/m^3	1:1:5 Kg/m^3	1:1:6 Kg/m^3
Quarry dust	1.17 ± 0.13	1.23 ± 0.09	1.42 ± 0.18
Clay murang'a	1.06 ± 0.07	1.1 ± 0.08	1.16 ± 0.08
Sand murang'a	1.33 ± 0.11	1.42 ± 0.09	1.51 ± 0.10
Clay meru	1.13 ± 0.13	1.2 ± 0.16	1.41 ± 0.09
Diatomite meru	1.44 ± 0.09	1.63 ± 0.12	1.78 ± 0.14

3.4 FTIR Analysis

FTIR analysis was carried out on all the soil samples and the blocks using a Shimadzu 8000 FT-IR Shimadzu corporation (Japan). The analysis was carried out in vibration range of 4000-400 cm^{-1} (Table 6). Thus the results of IR are quite helpful in the identification of various forms of minerals present in the soil. The coupled vibrations are appreciable due to the availability of various constituents. Nevertheless, observed bands (in the range, 4000–500 cm^{-1}) have been tentatively assigned. In the IR studies of clay, the Si–O stretching vibrations were observed at 790·9 cm^{-1}, 688·5 cm^{-1}, 545·8 cm^{-1} and 468·9 cm^{-1} showing the presence of quartz. The appearance of ν (Si–O–Si) and δ (Si–O) bands also support the presence of quartz, a strong band at 3696·7 cm^{-1}, 3622·5 cm^{-1} and 3450·4 cm^{-1} indicate the possibility of the hydroxyl linkage. However, a broad band at 3450·4 cm^{-1} and a band at 1633·4 cm–1 in the spectrum of clay suggest the possibility of water of hydration in the soil [10]. According to Nayak and Singh 2007, bands such as 3421·4 cm^{-1}, 1010.6 cm^{-1}, 914·5 cm^{-1}, 790·9 cm^{-1}, 693·4 cm^{-1}, 538·8 cm^{-1}, 468·9cm^{-1} show the presence of kaolinite.

Table 3: FT-IR vibrational frequencies of various soil samples and their blocks

Assignment of peaks	Quarry dust	Muranga kaolin	Meru kaolin	Naivasha volcanic soil
Stretching of water OH	3436.9 cm^{-1}	3421.5 cm^{-1}	3421.5 cm^{-1}	3456.2 cm-1
Deformation of water OH	1645.2 cm^{-1}	1645.2 cm^{-1}	1645.2 cm-1	1647.1 cm-1
Si-O stretching	1010.6 cm^{-1}	1033.8 cm^{-1}	1031.8 cm^{-1}	1037.6 cm-1
Deformation of Al-Al-OH	916.1 cm^{-1}	918.1 cm^{-1}	914.2 cm^{-1}	914.2 cm-1
Si-O quartz and silica stretching	790.8 cm^{-1}	788.8 cm^{-1}	788.8 cm^{-1}	788.8 cm^{-1}
Si-O, perpendicular	688.5 cm^{-1}	688.5 cm^{-1}	686.6 cm^{-1}	686.6 cm^{-1}
Deformation of Al-O-Si	545.8 cm^{-1}	542.0 cm^{-1}	513.0 cm^{-1}	530.4 cm^{-1}

3.5 X-Ray Fluorescence Results

XRF tests were carried out on the representative soil samples and the results are indicated in the table below. It was performed to know the chemical compositions of the minerals that are present in the clay. The bar graph below shows that the aluminium silicon and oxide are present in major quantities, while other minerals are present in trace amounts. This confirms the chemical analysis of soils.
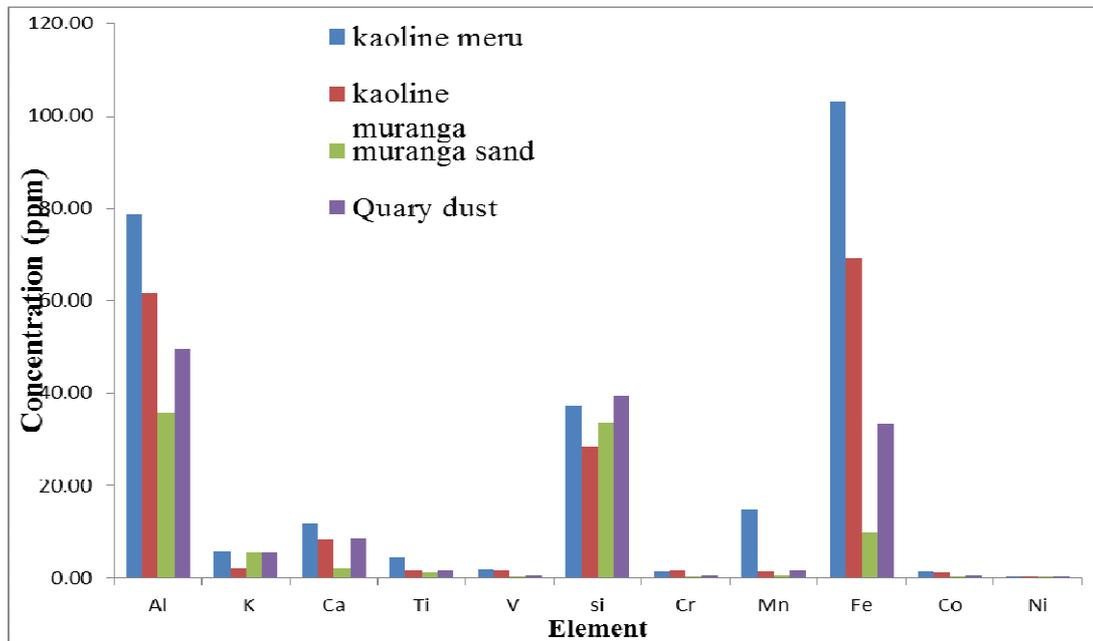

Fig 2: Concentration of various inorganic ions in various soil samples in mg/Kg

4. Conclusions

From the results obtained it can be concluded that the geopolymer blocks have desirable characteristics necessary for use in the local construction industry. Some of the characteristics are comparable to the convectional technology available, whereas in some, it exhibits superior engineering properties. The major scoring points for this type of block is the low cost of production, easy setting and fast drying, achieve considerable compression in short period of time and the applicability to different types of soils. Therefore the geopolymer technology is feasible for use.

I therefore recommend that further research be done on the applicability of other types of soils in Kenya not covered in this research. It would also be appropriate to research further on ways and mechanisms of improving the properties of the soil based geopolymer block, while maintaining the production cost at a minimum.

Acknowledgements

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