REVIEW ON UTILIZATION OFMODIFIED RED MUD BY ORGANIC MODIFIER IN COMPOSITE MATERIAL

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ABSTRACT

Red mud is a solid waste residue of the digestion of bauxite ores with caustic soda (NaOH) for alumina production (Bayer's process). It is compound form of metallic oxide-bearing impurities in solid form. For extraction of the aluminum, red mud is a major industrial disposal problem. It mainly contains elements components such as Fe_2O_3, Al_2O_3, SiO_2, CaO, Na_2O and TiO_2 etc. This review paper gives a summary on the comprehensive utilization on red mud globally. Extensive work has been done by a lot of researchers to develop various economics ways for the utilization of red mud for the past decades. Red mud has good reinforcing property as filler material, by using this red mud as the filler, particulate reinforced polyester composite have been develop. Red Mud can be used for manufacturing of composites material in polymer matrix such as PVA with excellent anti-aging property and cheap thermal stabilizer. By utilization of red mud in manufacturing composites, pilling of huge stock of red mud can be minimizing. It is recently developed important engineering material. It is expected that the present work will result in industrial as well as social benefits for the nation

Keywords -Composites, Polymer Matrix, Red Mud, Bayer's Process, Bauxite Ore

I INTRODUCTION

Red mud is a by-product of alumina production (Bayer's process).[1] It is a reddish-brown colored solid waste produced during the physical and chemical processing of bauxite ore. Bauxite(Al_2O_3 .xH_2O) is composed of Aluminum hydroxide minerals, including primarily Gibbsite [$Al(OH)_3$], Boehmite [γ-AlO(OH)] and Diaspore [α-AlO(OH)] and other compounds such as Hematite [Fe_2O_3], Goethite [FeO(OH)], Quartz [SiO_2], Rutile/Anatase [TiO_2] and Kaolinite Al2Si2$O_5(OH)_4$] [2]. The red mud can be divided into Bayer process red mud, sintering process red mud and combined process red mud. It was reported that 0.8~1.5 tons of red mud is produced by each 1 tons alumina production. Globally the total amount of red mud produced every year is between 60 and 120 million tons [3] More than 4 million tons of red mud is generated annually in India only. Presently it is stored or dumped on land or in the oceans near alumina refineries. Because of high alkalinity of red mud it is disposed or recycled satisfactorily [5]. The conventional method of disposal of red mud in ponds has adverse environmental impacts, during monsoon the waste may be carried by run-off to the surface water courses and as a result of leaching may cause contamination of ground water. Further disposal of large quantities of Red mud dumped increasing problems of storage occupying a lot of space[6].The Dike beach at the Ajkai Timfoldgyar Zrt alumina plant in Hungary [4] is warning us to pay enough attention to the comprehensive treatment of the red mud. The comprehensive utilization of red mud can be divided into the following aspects.

- Recovery of Fe, Al, Na and rare earth elements like Sc, Y, La, Ti, V in red mud.
- Reuse of red mud as cement production and other construction materials like brick, glass and aerated concrete block.
- Utilization of red mud as road base material and filling material in mining application of red mud to absorb heavy metal ions like Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and nonmetallic ions and molecules.
- Application of red mud can absorb heavy metal ions in the soil and SO_2 in the waste gas [6].

II. MATERIAL: RED MUD

There are different aluminum production processes for different bauxite ores that subsequently produce different types of red muds. Red mud is mainly composed of coarse sand and fine particles of mud. Its composition, property and phase vary with the origin of the bauxite and the alumina production process and will change over time when stocked. The amount of alkali in red mud fluid is about 2 to 3 g/L (calculated by Na_2O), which results in a pH value between 13 and 14. Chemical analysis shows that red mud contains Si, Al, Fe, Ca, Ti, Na as well as an array of minor elements namely K, Cr, V, Ba, Cu, Mn, Pb, Zn, P, F, S, As, and etc. Red mud can be used as a potential filler material in polymer matrix composites. It has marginal effects on the mechanical properties such as hardness and tensile strength of the composites. The compatibility of red mud particles with polymer resin is fairly good [11].

Chemical and Mineral Compositions of Red Mud

SR NO	RED MUD	COMPOSITION
1	Fe_2O_3	30-60%
2	Al_2O_3	10-20%
3	SiO_2	3-50%
4	Na_2O	2-10%
5	CaO	2-8%
6	TiO_2	Trace-25%

2.1 Engineering properties

Permeability test is carried out as per the IS: 2720 (Part XVII). The coefficient of permeability of the red mud specimen is found out using falling head method. Coefficient of permeability was found to be 5.786e-7cm/s.

Triaxial Compression test is best suited for clayey soil. The sample having size of 38mm dia. x 76mm height. After applying confining pressure (e.g. 0.5, 1.0 or 1.5 kg/cm2) deviator stress is applied till failure. Having minimum two readings Mohr's stress circles are plotted. A line tangent to the Mohr's circles is failure envelope and shear parameters: Cohesion and Angle of Internal Friction. Results are shown in the table 1

Strength and physical parameters of red mud

S.NO.	Tests	Values
1	Maximum dry Density (g/cc)	1.53
2	Optimum moisture Content (%)	33.5
3	Specific Gravity	3.04
4	Liquid Limit (%)	45.5
5	Plastic Limit (%	32.3

Unconfined Compressive strength: The samples of sizes 38 mm diameter and height of 76 mm were prepared by static compaction method to achieve maximum dry density at their optimum moisture contents. Unconfined compressive strength tests were conducted at a strain rate of 1.25 mm/min.

California bearing ratio test: The sample of nearly 4.5 to 5 kg was compacted in a mould of volume 2250cc with 5 layers and 56 blows were given for each layer. For soaked CBR value, the different sample of identical size is prepared and kept soaking for 4 days with the surcharge. This test was conducted as per IS: 2720 (Part XXXI).

2.2 Utilization of Red Mud

Among the uses standing out, are those reported on the utilization of red mud for building materials production such as cement, bricks, roofing tiles and glass-ceramics . The bulk production of building materials could eliminate the disposal problem. Red mud is considered as a raw material for production of these materials. [10].

2.3 Red mud as filler material

For PVC, red mud is not only filler that has a reinforcing effect, but is also an efficient and cheap thermal stabilizer, providing the filled PVC products with an excellent anti-aging property.

Its lifetime is 2 to 3 times that of ordinary PVC products. At the same time, the fluidity of red mud is better than other fillers, which makes it plastic with good processing properties

And the red mud PVC composite plastics have fire retardant property, and can be made into red mud plastic solar water heaters and plastic construction profile.

Comparison of Nano fillers to red mud

Nano Fillers	**Red Mud**
Low reinforcing property compare to red mud.	High reinforcing property compare to other nano fillers.
Low homogeneous dispersion	High homogeneous dispersion
Weak Chemical Bonding	Strong chemical bonding
High Cost	Low Cost

2.4 Importance of red mud in production of polymer based composites

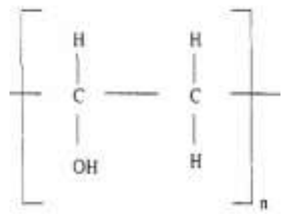
The use of layered inorganic fillers has been a common practice in the plastics industry to improve the properties of thermoplastics. The effects of filler on the material properties of composite materials depend strongly on its particle size, shape, aggregate size, surface characteristics, and degree of dispersion. Polymer composites prepared in combination with an organic component as a matrix and an inorganic component as filler on the nano scale [12] have additional advantages, such as the possibility of obtaining a material that has the advantages of both organic materials (e.g., light weight, flexibility, good moldability) and inorganic materials (e.g., high strength, heat stability)[13]. Low volume additions (≤5%) of nano particles of layered red mud provide property enhancements with respect to the neat resin that are comparable to those achieved by conventional loadings (15-40%) of traditional fillers. Red mud (nanofiller) is a major waste material obtained during the production of alumina from bauxite by the Bayer’s process. It comprises of silicates and oxides of iron, aluminum, sodium, calcium and titanium, along with some other minor constituents. Based on economics as well as environmental related issues, enormous efforts have been directed worldwide towards red mud management issues i.e. of utilization, storage and disposal. Different avenues of red mud utilization are more or less known but none of them have so far proved to be economically viable or commercially feasible.

Thermoplastics have a big potential for applications in the industry as well as in construction, electrical applications and food packaging. One of the few disadvantages associated with the use of nano fillers, is their high cost. The present research work has been undertaken with an objective to explore the use of red mud as a reinforcing material as a low cost option. This is due to the fact that red mud alone contains all these reinforcement elements and is plentifully available.

In mechanical reinforcement major issues are the homogeneous dispersion of nano fillers in the polymeric matrix and the developments of chemical bonding or strong interaction at the nanofiller-matrix interface. In this study we have used organically modified red mud for better homogeneous dispersion as well as enhanced material properties. The focus of this research was to experimentally characterize the two polymer nano composite systems and investigate the role of modification of filler in their behavior. Modified Red mud nano particles were dispersed in poly vinyl alcohol (PVA) and poly hydroxy ether of bisphenol-A (Ph) matrices.

• The conventional solvent casting technique was employed to generate polymer nanocomposites. Red mud was treated with boric acid and phosphomolybdic acid to develop the acidic functional groups or active oxygen, resulting in the better dispersion of the red mud into the polymer matrices. Red mud was also organically modified with the oligomers of aniline formaldehyde, for better interaction between the filler and the polymer matrices. The particle size of the modified red mud was determined by field emission scanning electron microscopy (FESEM). The as-synthesized composite films were typically characterized by FTIR spectroscopy and X-Ray Diffraction. The morphological image of the composite materials was studied by scanning electron microscopy (SEM) and the dispersion of the modified fillers within the matrix was studied by transmission electron microscopy (TEM).The thermal properties measured by thermo gravimetric analysis (TGA) showed enhanced thermal stability of a series of composite materials. The differential scanning calorimetric (DSC) showed increase in glass transition temperature and crystallization of the composite films. The physical topography of the composite materials was studied by Atomic Force Microscopy (AFM).

•Polyvinyl alcohol (PVA) is commercially available in dry granular or powdered form. It is a water-soluble and fully biodegrade [14].PVA is having planar zigzag structure like polyethylene [15].All PVA grades are readily soluble in water. As a hydrophilic polymer, PVA exhibits excellent water retention properties. Conditions for dissolution are governed primarily by degree of hydrolysis, but they are influenced by other factors such as molecular weight, particle size distribution and particle crystalline [16]. Optimum solubility occurs at 87-89% hydrolysis. The partially hydrolyzed grades in this range exhibit a high degree of cold-water solubility. For total dissolution, however, they require water temperatures of about 185°F (85°C) with a hold time of 30 minutes. It is, in fact, a refinement of PVA since the most common manufacturing process is to replace by hydrolysis (or alcoholysis) the acetate groups with hydroxyl groups. This is commonly achieved using the presence of catalytic quantities of alkali such as sodium hydroxide (which, since it acts only as a catalyst, should not in theory remain in the final product). The extent of hydrolysis will determine the amount of residual acetyl groups and this in turn apparently affect the viscosity characteristics.[Ray & Bousmina ,2005] PVA exists only as a polymer; a monomer has not yet been isolated, so the chemical structure is described in Fig.2



•The PVA concentration in an aqueous solution is determined by the type of application. However, at concentrations greater than 10 wt%, the viscosity of the aqueous solution at room temperature is such that pouring becomes difficult. In addition to its solubility, PVA is also appreciated for its good mechanical properties in the dry state, resistance to common solvents, barrier effect in dry atmospheres, possibility of food contact for suitable grades, biodegradability. Some of the physical properties of PVA are as presented in below table

Properties	Values
Appearance	White to cream granular powder
Density	1.23-1.30 g/cm3
Thermal stability	Gradual discoloration above 100 ^{o}C; darkens rapidly above 150 ^{o}C; rapid decomposition above 200 ^{o}C.
Coefficients of thermal expansion	7-8 x 10-5/ ^{o}C
Thermal conductivity	0.2 W/m.k
Yield Stress	40-50 MPa
Elongation at break	100-200%
Melting point	230 ^{o}C for fully hydrolysed grades 180-190 for partially hydrolysed grades
Glass transition temperature	75-85 ^{o}C

•PVA can be plasticized and processed by casting, dipping, injection and extrusion. (Biron, 2007). The main engineering applications, possibly in combination with other polymers, are:

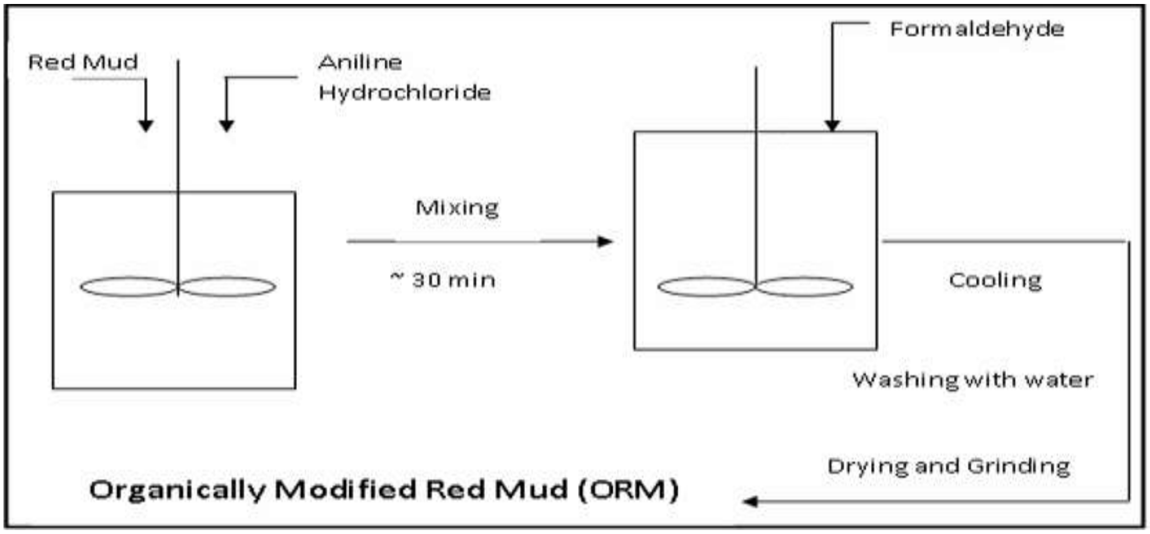
- Films for packing chemicals, fertilizers, herbicides, disinfectants, dyes, colorants, scalars, cosmetics etc.
- Release films for composite molding.
- Solvent resistant tubes and pipes.
- Membranes for pumps carrying petroleum or chemical products Trade names: Elvanol, Polyviol, Mowiol, Rhodoviol. The commercial name of poly (hydroxy ether) of bisphenol A is Phenoxy, and as a thermoplastic polymer it possesses many excellent properties such as (Zhang et al., 2002)
- Good chemical stability
- Excellent matrix material for producing polymer nanocomposites
- Thermal stability
- Tractability
- Transparency

•The poly (hydroxy ether of bisphenol A) (phenoxy (Ph)) has been revealed as a polymeric matrix able to intercalate in, and partially exfoliate a commercial organically modified montmorillonite. Dispersion was attributed to chemical interactions between the Ph and the inorganic clay (Fornes et al., 2004). Poly (hydroxy ether of bisphenol A) (Ph) based polymer nanocomposites (PN) reinforced with a layered red mud with acidic and organic modifications were prepared by conventional solvent casting technique. The best dispersion occurred in the PN where the interactions between the functional groups of the polymer matrix and those of the organic substitution of the red mud appeared to be the highest. The modulus increase is an indirect but quantitative measurement of the attained dispersion level.

2.5 Modification of red mud by organic modifier

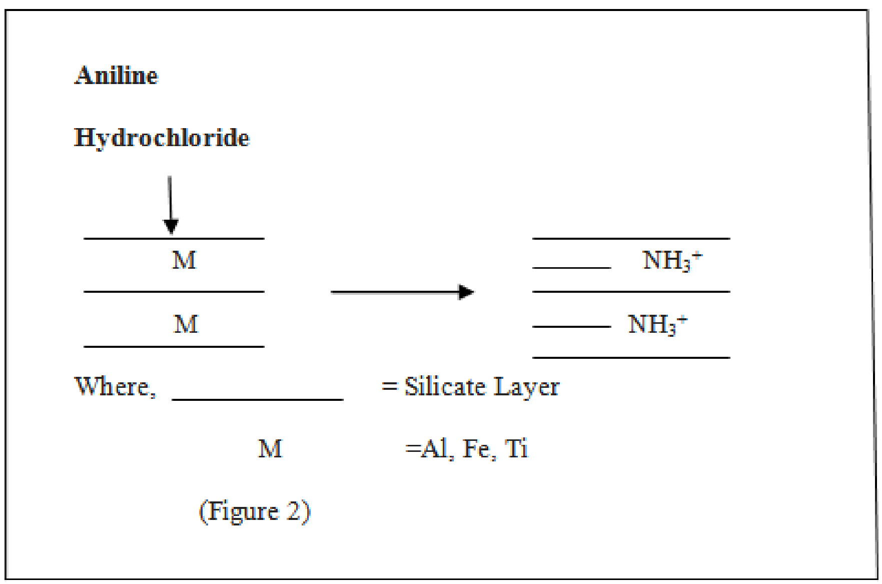
The organic modification of red mud was done by the following two steps:
1) Freshly prepared Aniline Hydrochloride is mixed with red mud with a magnetic stirrer.
2) Formaldehyde is then added drop by drop to the mixture with intense stirring action.

The addition of aniline hydrochloride to red mud replaces the cation present in the octahedral sites of the silicate with aniline occupying the same. The formaldehyde added would form a condensation oligomer as the product with the pendent group as formaldehyde which is compatible with the polymer. The ratio of Aniline to formaldehyde is kept 1:1 so as to stop any further condensation of the aniline and formaldehyde as this could lead to the polymer blend type nano composite, which could have the problems associated with miscibility of polymer blends and this filler would not be universal filler for the polymer matrix. The figure 1 depicts the experimental setup for the organic modification of red mud [16].



(Figure 1)

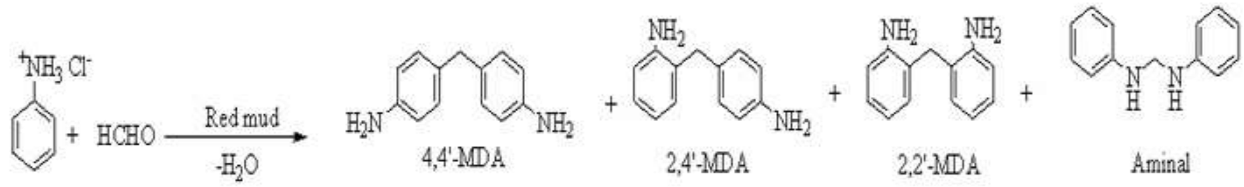
III MECHANISM



(Figure 2)

Figure 2 shows the mechanism and condensation reaction between substituted aniline and formaldehyde. After substitution of the metal cation, condensation reaction occurs between the substituted amine group with extra hydrogen and the formaldehyde molecule to form water as a byproduct. Thus the organic entity enters the space between the silicate layers thus providing a suitable site for binding the polymer. When this filler is mixed with the polymer, the polymer chains are attracted due to the presence of the organic species at the interlayer spaces, and thus get intercalated in between the layers, which have about nanometer size openings. The reaction mechanism can be best depicted by the following sequence Mechanism for organic modification of red mud.

Condensation reaction between substituted aniline and formaldehyde



(Figure 3)

Figure 3 Mechanism and Condensation reaction showing Organic Modification of Red Mud.

IV CONCLUSION

- As the compatibility of red mud particles with polyester resin is fairly good, an industrial waste can be used as a potential filler material to produce cost effective polyester matrix composites. The content of red mud in the composite determines the mechanical properties such as hardness, density and tensile strength of the composites.
- Although nano fillers are available but red mud is the developing best material as a filler with its good bonding strength and homogeneous dispersion and low cost.
- Environmental problems solution and stock piling is also reduced by red mud in adjacent product with low cost.

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