Journal of Scientific & Industrial Research
Vol. 80, July 2021, pp. 612-616

Thermal Power Plant Flue Gas Desulfurization (FGD) Gypsum Waste Particulates Reinforced Injection Molded Flexible Composites

Payal Bakshi[1,2], Asokan Pappu[1,2]*, Manoj Kumar Gupta[1,2] and Avanish Kumar Srivastava[1,2]
[1]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201 002, India
[2]CSIR-Advanced Materials and Processes Research Institute,
Near Habibganj Naka, Hoshangabad Road, Bhopal, Madhya Pradesh 462 026, India

Received 04 June 2020; revised 16 June 2021; accepted 23 June 2021

Low density, thermally insulative and moisture resistant flexible polymer composites were developed using Flue Gas Desulfurization (FGD) gypsum waste particulates with Low Density Polyethylene (LDPE) under injection molding technique without any additive or filler modification. The moisture content, particle size, specific gravity, density, pH, electrical conductivity and Fourier-Transform Infrared Spectroscopy (FTIR) analysis of FGD gypsum waste particulates were evaluated together with mineralogical, morphological and elemental analysis by X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (FESEM-EDS) studies. Developed composites were tested for Density, Water absorption, thermal conductivity and mechanical strength. Density of FGD-LDPE composites varied from 0.91±0.01 to 1.33±0.01 g/cm^3 with different concentrations of FGD gypsum filler (10–70 weight %). The water absorption showed 0.69±0.04% for maximum (70 weight %) filler concentration and the corresponding thermal conductivity was found to be minimum (0.3964 W/m/K). The composites were very flexible and exhibited lower tensile strength (6.17±0.05 to 7.15±0.09 MPa), flexural strength (11.25±0.14 MPa) and impact strength (22.70±1.57 KJ/m^2) with 50% and 10% filler content. Findings of these results have showed a new path for making flexible composites potentially having applications in sports ground, staircase and instrumentation rooms as a thermal insulation flooring material using FGD waste particulates generated from thermal power plants.

Keywords: FGD gypsum waste particulates, Flexible materials, Injection molding, Mechanical properties, Thermal conductivity

Introduction

Burning of coal generates various residues, including bottom ash, fly ash, flue gas desulfurization (FGD) gypsum waste (also called scrubber sludge) and fluidized bed boiler waste.[1] To remove sulfur dioxide (SO_2) from gas pollutants from thermal power plants, flue gas desulfurization (FGD) process is carried out and the by-product obtained in this process is called as FGD gypsum. Lime-gypsum wet flue gas desulfurization (FGD) process is used as the desulfurization technology to control emissions of SO_2. In FGD gypsum (also called synthetic gypsum or chemical gypsum) the main constituent is calcium sulfate dihydrate ($CaSO_4.2H_2O$). About 8 million tons of FGD gypsum is produced from National Thermal Power Corporation (NTPC), India annually. For effective waste management, fundamental data and proper handling mechanism is required, which is mostly unavailable in many developing countries.[2]

In cement industries, FGD gypsum is used as a set regulator for Portland cement as a total or partial replacement of natural gypsum. Recently, gypsum-based compounds prepared with different additions of polymers[3–5], with fly ash and lime for making cementitous binder[6], plaster and cement manufacturing[7] are reported by various researchers. First time, attempts were made to use FGD gypsum waste particulates produced by coal-fired thermal power plant for making low density, moisture resistant and thermally insulating polymer composites without any chemical additive or filler modification which can be used for sports ground, staircase and instrumentation room as a thermal insulating flooring material. The findings of the results showed very interesting, opening an avenue for development of new materials and providing solution to address challenge on FGD gypsum waste management.

Materials and Methods

Materials

FGD gypsum waste was obtained from NTPC, Singrauli Super Thermal Power Station, U P, India. Granulated low density polyethylene (LDPE) was purchased from Three Star Plastics, Grade No. 16 MA

*Author for Correspondence
E-mail: asokanp3@yahoo.co.in

400 and used as binder. FGD gypsum was processed and removed moisture by heating at 175°C for 24 hours, then cooled in desiccators and sieved through BS 60 (250 µm) sieve.

Fabrication of FGD Gypsum based Composite

FGD gypsum waste particulates as filler was used in concentrations of 0, 10, 30, 50 and 70% by weight in LDPE system. Tensile, flexural and impact test specimens were fabricated using FGD gypsum waste particulates and LDPE as binder under injection molding machine Milacron, Nova Servo 150, USA at 110°C temperature and 70 bar pressure. For comparative studies, neat LDPE test specimens were also prepared at 110°C with 70 bar pressure.

Measurements and Characterizations

Moisture content of obtained FGD gypsum waste particulates was determined (IS: 2720(Part II)–1973 (Reaffirmed 1997)) by oven drying method**.** Specific gravity of FGD gypsum waste particulates (IS: 2720 (Part III/Sec 1)–1980 (Reaffirmed 2002)) and bulk density were determined with 50 mL density bottle. Particle size distribution of FGD gypsum waste was determined by Laser Scattering Particle Size Distribution Analyzer Partica LA-950. The pH of FGD gypsum was determined by LABMAN LMPH–12, pH meter (IS 12679:1989 (Reaffirmed 2000)). Electrical conductivity of FGD gypsum waste was determined by LABMAN LMCM–20, Conductivity meter. X – Ray diffraction pattern of FGD gypsum was obtained by Rigaku, MiniFlex II. The morphological and elemental analysis of FGD gypsum was done by NOVA NANOSEM 430, FEI, USA, FESEM-EDS. Attenuated Total Reflectance – Fourier Transform Infrared (ATR - FTIR) spectrum of FGD gypsum sample was studied using Thermo Scientific, iS50 FT-IR. A total of 64 scans were performed on sample in the range of 4000 – 400 cm^{-1}.

Density of composites was determined as prescribed in ASTM D 792-13. Samples were stored in an air and immersed in distilled water. Water absorption of composites was studied as per ASTM D 570-98 (Reapproved 2018) standard norms. Each sample was submerged in distilled water at 25 ± 2°C for 24 hours. After wiping the water from the specimen surface, the percentage water absorption was calculated from the weight of the composite specimens before and after immersion in distilled water. Thermal conductivity of FGD-LDPE composites were measured by a Box type probe PD-11N analyzer (KEM, Quick Thermal Conductivity Meter, QTM 710, Japan) at room temperature. Tensile strength of composites was tested (ASTM D 638-14) using Ametek, Lloyd Instruments, LRX plus, Universal testing machine, UK using a 5 KN load cell and a 50 mm gauge length with 5 mm/min cross-head speed. Flexural strength of composites was tested (ASTM D 790-17) using Ametek, Lloyd Instruments, LRX plus, Universal testing machine, UK using a 5 KN load cell with a span of 53 mm and a cross-head speed of 5 mm/min. For impact testing, notch is cut in the rectangular specimens using a Tinius Olsen, Impact specimen notcher for plastics, Model 899, USA. Izod impact test was performed (ASTM D 256-10 (Reapproved 2018)) using Tinius Olsen impact tester, Model Impact 104, USA with a pendulum weight of 0.459 Kg, pendulum radius of 334.96 mm, height of pendulum 612.23 mm and potential energy of 2.76 J at room temperature.

Result and Discussion

Mineralogical Analysis of FGD Gypsum Waste

The mineral phases were identified by matching all diffraction peaks with the JCPDS card numbers. Results from XRD showed that FGD gypsum waste particulates have crystal structure and brushite (CaH_5O_6P) is the primary mineral phase (JCPDS card no. 001-0395**).** It is evident from the XDR analysis, there is presence of calcium sulfate dihydrate gypsum (CaH_4O_6S or $CaSO_4.2H_2O$) mineral phase (JCPDS card no. 21-816) and coesite (SiO_2) phase (JCPDS card no. 13-0026) in the FGD gypsum waste particulates (Fig. 1a).

Fourier-Transform Infrared Spectroscopy (FTIR) Analysis of FGD Gypsum Waste

FTIR spectrum of FGD gypsum waste particulates was performed in the range of 4000–400 cm^{-1} and the recorded spectrum is depicted in Fig. 1b. The absorption peaks appeared around wave numbers of 3604, 3553 and 1617 cm^{-1} were assigned to the hydroxyl functional group (–OH), which could be present due to bonded crystalline water in the hydrated form in FGD gypsum waste.[8] The agglomeration of particles observed in SEM micrographs (Fig. 2a) may be because of the existence of this (–OH) functional group. The strong and broader peaks appeared at 1140, 1112, 1084 and 1006 cm^{-1} were attributed due to sulfate functional group (–SO_4). The peaks appeared at 658 and 595 cm^{-1} could also be attributed to sulfate functional group. The adsorption deformations around wave number 799 cm^{-1} confirmed the presence of silica (O-Si-O), which can also be observed in the XRD pattern.[9–11] Moreover, the adsorption peak at 459 cm^{-1} confirmed the presence of

Si-O with its bending vibration mode.[12] Presence of high hydroxyl group indicates that, FGD gypsum has tendency to absorb water because of its hygroscopic nature and poor compatibility with the hydrophobic LDPE.[13]

Morphological and Elemental Analysis of FGD Gypsum Waste

Morphological study of FGD gypsum waste particulates was done by Field Emission Scanning Electron Microscopy (FESEM; Fig. 2a). The FESEM micrograph indicates cluster of micro sized particulates with irregular morphology and rhombic structure. The elemental composition of FGD gypsum waste is shown in Fig. 2b. EDS spectra shows the presence of oxygen, sulfur and calcium. It can be observed from the FESEM micrograph (Fig. 2a) that the particles are agglomerated, which may be due to the presence of moisture and also observed on the FTIR spectra in the form of the presence of hydroxyl (–OH) functional group. The particle size observed is in the range of 10–70 µm.

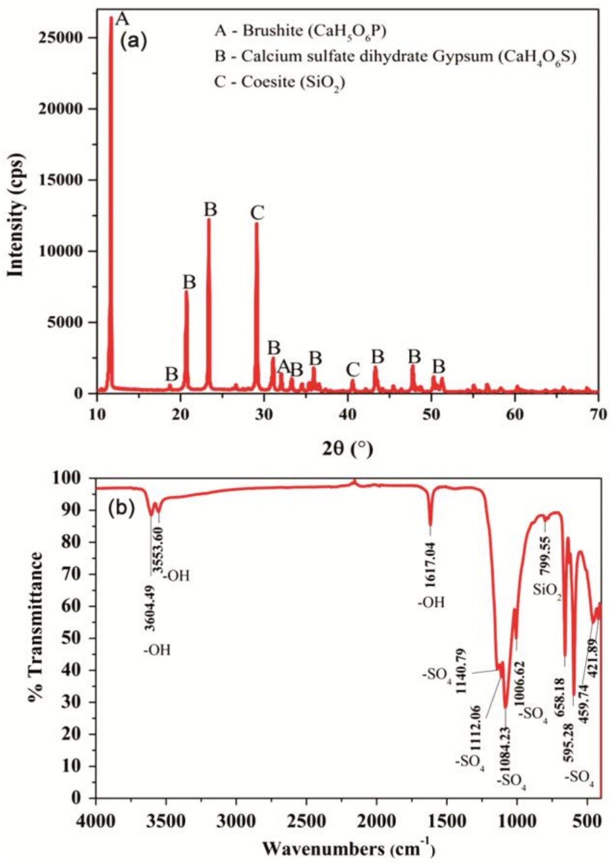

Fig. 1 — (a) XRD pattern and (b) FTIR spectrum of FGD gypsum waste

Physico-Chemical Analysis of FGD Gypsum Waste

Physico-chemical properties of FGD gypsum waste particulates were determined by taking three observations using standard methods. FGD gypsum waste showed silt texture and gray color. The moisture content, bulk density and specific gravity of FGD gypsum waste particulates were determined as 25.33±0.32%, 1.02±0.01 g/cm^3 and 2.36±0.01, respectively. The mean particle size of FGD gypsum was found to be 46.44±0.90 µm. pH of FGD gypsum waste was found to be 6.24±0.14 and electrical conductivity at room temperature was observed as 0.84±0.03 dS/m. Physico-chemical characterization of FGD gypsum showed it as potential raw material for making polymer composites.

Density and Water Absorption of FGD-LDPE Composites

To determine the density and water absorption of fabricated FGD-LDPE composites, the mean values of three observations were taken and are reported in Table 1. It is observed that the density and water absorption of the fabricated FGD-LDPE composites increased with increase in filler concentration (Table 1). It is worth to note that the fabricated

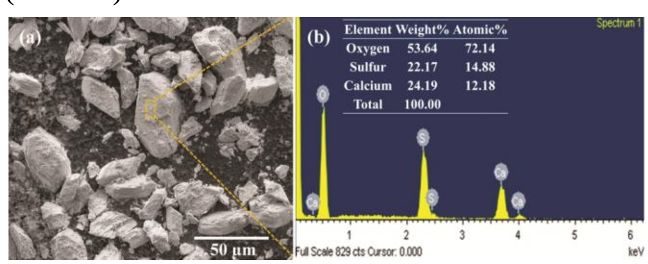

Fig. 2 — (a) FESEM micrograph and (b) elemental analysis of FGD gypsum waste by EDS

Table 1 — Properties of FGD-LDPE composites

Filler concentration (weight %)	Density (g/cm^3)	Water absorption (%)	TS (MPa)	TM (GPa)	FS (MPa)	FM (GPa)	IS (KJ/m^2)
0	0.87±0.01	0.05±0.02	8.09±0.12	0.058	5.40±0.07	0.140	27.88±1.40
10	0.91±0.01	0.30±0.04	7.15±0.09	0.061	6.19±0.20	0.146	22.70±1.57
30	1.14±0.02	0.35±0.02	6.17±0.05	0.130	8.76±0.36	0.230	6.49±1.12
50	1.31±0.03	0.61±0.06	6.78±0.14	0.191	11.25±0.14	0.459	4.70±1.23
70	1.33±0.01	0.69±0.04	6.34±0.09	0.162	10.07±0.25	0.294	3.28±0.25

composites showed very low water absorption (maximum 0.69%), which proved that LDPE acted as waterproofing for FGD gypsum in the composites.

Thermal Conductivity of FGD-LDPE Composites

Thermal conductivity of the fabricated FGD-LDPE composites at room temperature was measured as a function of the filler (FGD gypsum) concentration by taking three observations and their mean is reported in Fig. 3. The thermal conductivity initially increases with the concentration of FGD gypsum and attained a value of 0.5032 W/m/K (~2 times) for 30% filler content then reduces up to 0.3964 W/m/K for 70% filler content (Fig. 3). The increment in the thermal conductivity was due to the heat conduction mechanism through lattice vibration.[14,15] Beyond 30% filler concentration thermal conductivity decreases, because of the strain generation and vacuum formation, create structural imperfection between the filler particles.

Mechanical Properties of FGD-LDPE Composites

The mechanical properties of FGD-LDPE injection molded composites with filler concentration of 0, 10, 30, 50 and 70 weight % were determined. Tensile strength (TS), flexural strength (FS) and impact strength (IS) of fabricated composites were determined as per the standard methods with tensile modulus (TM) and flexural modulus (FM). For determining mechanical properties of the fabricated composites, the mean value with standard deviation of five observations were taken and reported in Table 1. It is noteworthy that the tensile strength of fabricated composites decreased with increment in filler concentration, but is found very close to pure LDPE samples. Tensile strength of FGD-LDPE composite is maximum 7.15±0.09 MPa with 10 weight% filler concentration. The flexural strength of fabricated composites was found to be increased with increasing the filler concentration up to 50 weight% and was observed to be slightly decreased for 70 weight% filler concentration. The flexural strength of FGD-LDPE composites is maximum 11.25±0.14 MPa with 50 weight% filler content. Tensile and flexural modulus of FGD-LDPE samples are expressed in Table 1 for different filler concentrations. It is worth to note that the impact strength of FGD gypsum based polymer composites was maximum 22.70±1.57 KJ/m^2 for 10 weight% filler concentration and rapidly reduced with the increment in filler concentration (Table 1).

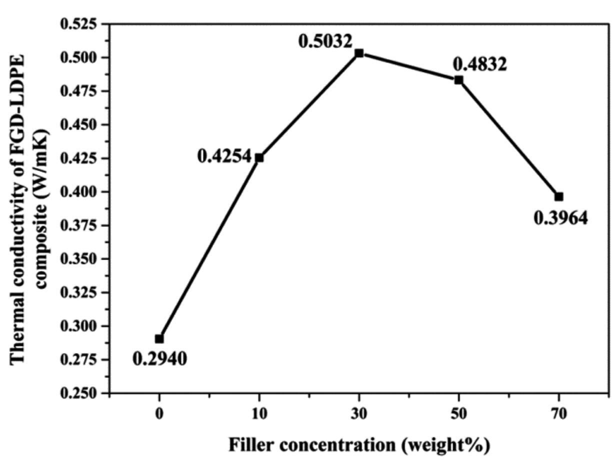

Fig. 3 — Room temperature thermal conductivity of FGD-LDPE composite

Reduction in the mechanical strength (tensile, flexural and impact) with increment in FGD gypsum concentration may be due to the agglomeration phenomenon of filler particulates creating massive clusters of FGD gypsum in the LDPE polymeric system. This resulted in the poor interfacial bonding between FGD gypsum and LDPE matrix, as well as the surface contact area between the filler particulates and the polymer matrix also decreased. To conquer this trouble, modification of FGD gypsum waste particulates can be done by appropriate non-reacting coupling agents and additives.[16, 17] As FGD gypsum has tendency to absorb water due to the presence of high hydroxyl group, the filler (FGD gypsum particulates) has hygroscopic nature as compared to hydrophobic LDPE. This difference in nature may cause the reduction on mechanical strength of fabricated composites.

Conclusions

FGD gypsum waste particulates were found to be potential raw material for making low density, water resistant and low thermally conductive flexible polymer composite. The injection molded FGD gypsum waste particulates reinforced composite has resulted density as low as 0.91±0.01 g/cm^3 with lowest water absorption (0.30±0.04%). Thermal conductivity of composite found to be minimum (0.3964 W/m/K) with 70% filler concentration. Flexible composites prepared without any additive or filler modification having low tensile strength (6.78±0.14 MPa) and flexural strength (11.25±0.14 MPa) was achieved using 50% filler concentrations. The outcome of the studies has showed a new scope for development of composite materials with effective utilization of FGD gypsum waste particulates generated from Thermal

Power Plants. Developed composites may have possible use in multifunctional applications such as sports ground, staircase and instrumentation rooms as a thermal insulating flooring material.

Acknowledgement

The authors would like to thank Dr M Malik, NTPC-NETRA and Mr S K Saxena, General Manager, NTPC for providing FGD gypsum waste particulates.

References

1 Asokan P, Saxena M & Asolekar S R, Coal combustion residues—environmental implications and recycling potentials, *Resour Conserv Recycl*, **43(3)** (2005) 239–262.

2 Miezah K, Obiri-Danso K, Kádár Z, Fei-Baffoe B & Mensah M Y, Municipal solid waste characterization and quantification as a measure towards effective waste management in Ghana, *Waste Manage*, **46** (2015) 15–27.

3 Gomes C E M, Sousa A K D, Araujo M E D S O, Ferreira S B & Fontanini P, Mechanical and microstructural properties of redispersible polymer-gypsum composites, *Mater Res*, **22(3)** (2019) 1–9.

4 Yordan G, Denev G D D & Anton N P, Surface Modification of phosphogypsum used as reinforcing material in polyethylene composites, *J Elastom Plast*, **41** (2009) 119–132.

5 Essabir H, Nekhlaoui S, Bouhfid R, Bensalah M O & Aek Q, Phosphogypsum waste used as reinforcing fillers in polypropylene based composites: structural, mechanical and thermal properties, *J Polym Environ*, **25(3)** (2016) 658–666.

6 Degirmenci N, Utilization of phosphogypsum as raw and calcined material in manufacturing of building products, *Construction and Building Materials*, **22(8)** (2008) 1857–1862.

7 Asokan P, Saxena M & Asolekar S R, Solid wastes generation in India and their recycling potential in building materials, *Build Environ*, **42** (2007) 2311–2320.

8 Ibrahim S M, Hassan M R & Gad H M H, Isotherm and thermodynamic studies of the biosorption of humic acid from aquous solution by pine sawdust based activated charcoal, *J Sci Ind Res*, **80** (2021) 203–209.

9 Chernysh Y, Balintova M, Plyatsuk L, Holub M & Demcak S, The influence of phosphogypsum addition on phosphorus release in biochemical treatment of sewage sludge, *Int J Environ Res Public Health*, **15(1269)** (2018) 1–14.

10 Knittle E, Phillips W, Williams Q, An infrared and raman spectroscopic study of gypsum at high pressures, *Phys Chem Minerals*, **28(9)** (2001) 630–640.

11 Al Dabbas M, Eisa M Y & Kadhim W H, Estimation of gypsum-calcite percentages using a Fourier Transform Infrared Spectrophotometer (FTIR), in Alexandria Gypsiferous soil –Iraq, *Iraqi J Sci*, **55(4B)** (2014) 1916–1926.

12 Bharti D K, Gupta M K & Srivastava A K, Temperature dependent dielectric and electric properties of zinc silicate nanorods, *Nano-Structures & Nano-Objects*, **17** (2019) 123–128.

13 Adhikary K B, Pang S & Staiger M P, Dimensional stability and mechanical behaviour of wood–plastic composites based on recycled and virgin high-density polyethylene (HDPE), *Compos B Eng*, **39(5)** (2008) 807–815.

14 Tripathi D & Dey T K, Effect of particle size distribution on thermo-mechanical properties of NiO filled LDPE composites, *Bull Mater Sci, Indian Academy of Sciences*, **42(174)** (2019) 1–10.

15 Gu J, Zhang Q, Dang J, Zhang J & Yang Z, Thermal conductivity and mechanical properties of aluminum nitride filled linear low-density polyethylene composites, *Polym Eng Sci*, **49(5)** (2009) 1030–1034.

16 Pukánszky B, Influence of interface interaction on the ultimate tensile properties of polymer composites, *Composites*, **21(3)** (1990) 255–262.

17 Liu C, Zhao Q, Wang Y, Shi P & Jiang M, Surface modification of calcium sulfate whisker prepared from flue gas desulfurization gypsum, *Appl Surf Sci*, **360** (2016) 263–269.