Mechanical & Thermal Properties of Fly Ash Filled ABS

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***Abstract* - Fly ash is used as reinforcing filler in Acrylo Nitrile Butadiene Styrene (ABS) to develop lightweight composites. Acrylonitrile butadiene styrene (ABS), a terpolymer is widely used engineering thermoplastic, known for high performance product applications. The polymer has a good mechanical property together with chemical resistance, toughness, surface appearance, and process ability. Fly Ash is inert hollow silicate spheres, a naturally occurring by-product of the burning process at coal-fired thermal power plants. Fly Ash as filler is primarily used to reduce the weight of plastics, rubbers, resins, cements, etc. used extensively as filler lubricants in oil drilling operations under high heat and high stress conditions down the hole. Also used as oil well cementing, mud putty and similar applications. Fly Ash is widely used in a variety of products, including sports equipments, insulation, automobile bodies, marine craft bodies, paints, and fire and heat protection devices. Providing the advantages of reduces weight, increased filler loadings, better flow characteristics, less shrinkage and warping and reduces water absorption.**

In the present work, in order to improve the interaction between the inorganic filler and the organic matrix, the Fly Ash is preheated and Maliac Anhydrite is used as compatibilizer. The tensile and thermal properties of the composites are measured according to ASTM methods. The results reveal that, Fly Ash accompanied by compatibilization led to the slight decrease in Tensile strength, Flexural strength and impact strength but substantial improvement in Tensile modulus and Flexural modulus along with thermal stability of the composites. As Flyash is low cost filler by incorporating it in ABS reduces the cost of the product.

Keywords: ABS, Fly Ash, Mechanical and Thermal properties, Compatibilizer

1. INTRODUCTION

Fillers are used to improve the working properties of thermoplastics, such as the strength, rigidity, durability, and hardness [1]. Not only do they provide a significant cost reduction but certain fillers may improves various properties of the materials such as mechanical strength, modulus and heat deflection temperature, material processing and its optical properties. In general the mechanical properties of particulate filled polymer composites depend strongly size, shape and distribution of filler particles in the matrix polymer and good adhesion the filler—polymer interface [2]. Numerous inorganic fillers like fly ash, mica, talc, calcium carbonate, hollow glass bead etc. have been incorporated in polymer matrix with the advent of plastics and the wide range of fillers that are available have made modifications as precise as the tailored resins themselves [2]. Bentonite has been introduced as filler into polypropylene [3]. Use of Fly ash cenospheres is very attractive because it is inexpensive and its use can reduce the environmental pollution to a significant extent. It can be also used in reinforced concrete construction since the alkaline nature will not corrode steel. This not only solves the problems associated with the disposal of fly ash (like requirement of precious land, environmental pollution, etc.) but also helps in conserving the precious top soil required for growing food [4].

Fly ash is a fine ash byproduct commonly produced by the combustion of coal during the generation of electrical power. Coal is composed of combustible organic matter with a variable amount of inorganic mineral matter. During combustion, the minerals in coal become fluid at high temperature and are then cooled. In a pulverized coal fired boiler, the furnace operating temperatures are typically in excess of 1,400 °C (2,500 °F). At these temperatures, mineral matters within the coal may oxidize, decompose, fuse, disintegrate or agglomerate. Rapid cooling in the post combustion zone results in the formation of spherical, amorphous particles[4].

Flyash cenospheres are a waste by-product of coal combustion and, as such, are available at very low cost. These are hollow thin-walled spheres of sizes several tens of micron to 500 μm [4]. According to their chemical compositions, these materials belong to the Multi-component systems with SiO_2+ Al_2O_3+ Fe_2O_3 content of approximately 90 wt% [5].

Incorporation of fillers within ABS matrix could possibly overcome these drawbacks. Several workers have reported ABS filled with different inorganic fillers and fibres like $CaCO_3$, sawdust, manganese hydroxide sulfate hydrate whiskers, hollow glass bead, and textile fiber to improve its overall properties [6].

Methods of compatibilising PP and inorganic filler by modifying the filler surface using coupling agents such as silane, titanate, and also by grafting small molecules such as acrylic acid, maleic anhydride, and acrylic esters onto the polyolefin chain. Modified PP such as polypropylene grafted-maleic anhydride (PPMAH) is successfully used as a compatibilizer in PP based composite because it can efficiently improve the fiber matrix bonding due to the formation of covalent linkages and hydrogen bonds between the maleated anhydride and the hydroxyl groups of the fillers [6]. Other than PPMAH, much cheaper and nonreactive compatibilizer has also been successfully employed in polymer with lack of reactive groups particularly, PP and PE [7].

Palm oil is predominantly made up of triglycerides. Fatty acids obtained from palm oil processing waste consist of a mixture of myristic, palmitic, stearic, oleic, linoleic acid, etc.

Acrylonitrile butadiene styrene (ABS), a terpolymer is widely used engineering thermoplastic, known for high performance product application, has a good mechanical property together with chemical resistance, toughness, surface appearance, and process ability. However the polymer is having low thermal stability and poor flame retardancy. Incorporation of filler in ABS matrix could possibly overcome these drawbacks. Recently fly ash has been used as a feeler in polymer composites, saving the other commonly used mineral fillers used in polymers, also helps the environment.

In the present Investigation, ABS/FA composites are prepared by melt blending and investigation on Mechanical, Thermal and morphological properties of ABS/FA composites have been studied.

The aim of this work is to develop a composite that would ensure the continued successful application of Fly ash as filler in plastics i.e environmental friendly composites filled with fly Ash by incorporation of Maliac Anhydrite as compatibilizer to improve the interaction between the inorganic filler and the organic matrix, [8]. The tensile and thermal properties of the composites are measured according to ASTM methods. The results reveal that, Fly Ash accompanied by compatibilization led to the substantial improvement to mechanical properties and thermal stability of the composites [8].

2. EXPERIMENTAL PROGRAMME

2.1 Raw materials

ABS, having a density of 1.05 – 1.06 gm/cm^3 and MFI of 20-30 g /10 min (at 220°C and 2.16/5/10 kgf), were procured & Fly Ash was collected from the Khaparkheda Thermal Power Plant ,Nagpur.

2.2 Fly Ash

Fly Ash was collected from the Khaparkheda Thermal Power Plant .Nagpur. The physical and chemical properties of fly ash are as follows:

Table 1: Physical properties of the fly ash

S. No.	Properties		Values
1	Density(g/cm^3)		2.17
2	Bulk Density(g/cm^3)		1.26
3	Moisture content (%)		2
4	Particle Shape		Spherical/Irregular
5	Color	-	Grey

Table 2: General chemical composition fly ash [8],[9]

S. No.	Chemical Composition	Unit	Values
1	SiO_2	%	30 – 60
2	Al_2O_3	%	11 – 19
3	Fe_2O_3	%	4 – 11
4	MgO	%	5 – 6
5	CaO	%	2 – 45
6	Trace elements	-	Na, B, K, St, Ba,Mo, Li, Vd, Cr

2.3 Compatibilizer

Maleic anhydride (0.03%) is successfully used as a compatibilizer in ABS-based composite because it can efficiently improve the fiber matrix bonding due to the formation of covalent linkages and hydrogen bonds between the maleated anhydride and the hydroxyl groups of the fillers [9].

2.4 Blending and fabrication of blend

Blends of ABS is prepared containing different weight percentage of FA (0, 10, 20, 30, 40 wt %) using co-rotating twin-screw Extruder (SPECIFIQ), at screws speed of 50 rpm. Temperature was maintained at 170,180 &190ºC in zone 1,2 & 3 respectively .Prior to melt blending FA was dried at 80 ºC in a vacuum oven for at least 24 hours to remove moisture and ABS polymer was predried at 90ºC for 4 hours, Subsequently the melt mixed composite is brought to room temperatures and cut to prepare specimens [10]. Test specimens are prepared using injection moulding machine maintained at a temperature of 200 ºC with cycled time of 38 sec.

2.5 Specimen Preparation

The granules are then fed to injection molding machine (Boolani Engineering Corporation) of 150 kg/cm^2 capacity machine maintained at a temperature of 200ºC with cycled time of 38 sec .to prepare test specimens.The test specimens were prepared from the material by using a specimen mould as per ASTM-D 63, ASTM-D 790, and ASTM-D 256 .The samples of ABS composites prepared by injection molding are kept at room temperature for 48hrs prior to testing to promote relaxation of stress [11].

2.6 Mechanical Properties

The mechanical properties are often the most important sources to make a decision about product specifications. The material selection for a variety of end-use applications is mostly dependent on these properties, such as tensile strength, modulus, elongation and impact strength.

2.6.1Tensile Strength Test (ASTM D 638)

Tensile test was carried out in Universal Testing Machine (UTM, Instron 3382, UK). Tensile samples of dimension 63.5mm x 9.53mm x 3 mm (Type V dumbbells), were tested at a gauge length of 7.62 mm and crosshead speed of 50 mm/min as per ASTM D638. A minimum of five replicate samples were tested for each composition and the data reported were average of five specimens [12].

2.6.2 Impact Test (ASTM D 256)

In Izod type testing, the specimen is clamped vertically to a cantilever beam and broken by a single swing of the pendulum released from the fixed distance from the specimen clamp. Izod impact test a notch angle of 45°with a V notch depth of 2.54 mm was made with a notch cutter (M/s Tinus Olsen, USA) on specimens having dimension of 63.5 mm x 12.7 mm x 3.2 mm. Subsequently the measurements were carried out in an Izod Impact Tester (M/s.Tinus Olesen, USA) as per ASTM D256. The test specimen is clamped into position so that the notched end of the specimen is facing the striking edge of the pendulum [13].

2.6.3 Flexural Properties (ASTM D 790, ISO 178)

The fabricated specimens were tested using a 100 KN capacity UTM, with a cross head speed of 50 mm/min in accordance with standard ASTM D790 under ambient conditions. Load and elongation values are determined for the all samples. Utilizing the experimental values of load and elongation, flexural strength (fs), flexural modulus and elongation at break were determined. Reported values are the average of five samples in all measurements.

Method 1 is a three-point loading system utilizing center loading on a simple supported beam. A bar of rectangular cross section rests on two supports and is loaded by means of a loading nose midway between the supports. The maximum axial fiber stresses occur on a line under the loading nose. This method is especially useful in determining flexural properties for quality control and specification purposes.

The flexural modulus is represented by the slope of the initial straight-line portion of the stress–strain curve and is calculated by dividing the change in stress by the corresponding change in strain. The procedure to calculate flexural modulus is similar to the one described previously for tensile modulus calculations [14].

2.7 THERMAL PROPERTIES

2.7.1 Heat Deflection Temperature (HDT) (ASTM D 648, ISO 75-1 & 75-2)

The HDT of the virgin and ABS/FA composites were measured using HDT apparatus (M/s GOTECH, HV-2000-C3, Taiwan) according to the ASTM D648. Specimens of dimension 127mm x 13mm x 3 mm were tested at a temperature ramp rate of 120°C/ h and surface stress of 66 psi to determine the deflection temperature in the samples [15].

2.7.2 Vicat Softening Temperature (ASTM D 1525, ISO 306)

The VSP of the virgin, and ABS/FA composites was performed using the same HDT/VSP apparatus (M/s GOTECH, HV-2000-C3, Taiwan). As per ASTM D 1525 standard, specimen dimension of 10 x10 x 3 mm^3 were tested at a temperature range of 120 ^{0}C / h and loading of 50N for a standard penetration of 1 mm.

The test is carried out by first placing the test specimen on a specimen support and lowering the needle rod so that the needle rests on the surface of the specimen. The temperature of the bath is raised at the rate of 50°C/hr or 120°C/hr uniformly. The temperature at which the needle penetrates 1 mm is noted and reported at the Vicat softening temperature [16].

2.7.3 Differential Scanning Calorimeter (DSC) Analysis

Measurements of specific heat and enthalpies of transition can be carried out on quite small samples in a differential scanning calorimeter (DSC). In the present study, the samples were scanned from 30°C to 180°C at the rate of 20°C/min. Subsequently, the samples were held at 180°C for 5 min and then cooled to 30°C at a heating rate of 20°C/min and was again reheated from 30°C to 250°. Corresponding melting and crystallization temperatures of the samples were noted [16].

2.7.4 Thermogravimetric Analysis

Thermo gravimetric analysis or TGA involves heating a sample to some temperature and then monitoring its weight as a function of time. In the present investigation TGA have been carried out for the Fly Ash Filled ABS composites and matrix to assess the rates of decomposition, thermal stability of the samples respectively. The virgin matrix, FA composites were subjected to thermo gravimetric analysis using TGA (M/s TA instrument, Q50) equipment. Samples of a 10 mg approx were heated from 30 to 1000°C at a heating rate of 10°C per min in nitrogen atmosphere (60 mm/min). Corresponding TGA data, weight loss, and derivative weight loss were reported .

2.8 MORPHOLOGY

2.8.1 Wide Angle X-ray Diffraction (WAXD)

The morphological structures of ABS/FLYASH composites were studied by wide angle X-ray diffraction. The XRD study was carried out using Philips X'Pert MPD (Japan) equipment using Cu Kα radiation ((wavelength λ) 0.154 nm) operated at 40 kV and 40 mA. The samples were scanned over the range 2θ = 2-15°. The basal spacing of the flyash was estimated from the d001 peak in the XRD pattern. To determine the structure of a crystal and thereby ascertain the position of its atoms in the lattice, a collimated beam of X-rays, electrons or neutron is directed at the crystal, and the angles at which the beam is diffracted are measured.

2.8.2 Scanning Electron Microscopy (SEM)

The morphology of impact fractured samples of Ultra thin specimens of 10µm thickness was studied employing scanning electron microscopy (SEM, EVA MA15, Cart Zeiss SMT,UK).The samples were sputter coated with Au-Pd to increase the surface conductivity and digitized images were recorded to study the interaction between the ABS matrix and FA particles .

3. RESULTS AND DISCUSSION

3.1 Testing and Characterization of ABS /Fly Ash Blend

The mechanical properties of ABS with Fly Ash are depicted in Table 3 and depicted in Figure 1 to 4. It is evident that ABS shows a tensile strength (TS) of 40.45 MPa with tensile modulus (TM) of 1200 MPa and impact strength (IS) of 109.89 J/m respectively. Incorporation of Fly Ash to the tune of 10 to 40 wt%, results in slight reduction in Tensile strength & Flexure strength but increase in Tensile Modulus & Flexure Modulus properties in the blends due to effective stress transfer from the matrix to the filler at the interface. This reveals miscibility between the two components resulting in the formation of two well differentiated phases indicating moderate adhesion at the interface. Hence application of a load causes deterioration in impact strength of the material, predominantly due to stress concentration effect of the impurity/ Fly ash as a consequence of the lack of the interaction among the interface.

From the test results reported in Table 3, it can be concluded that the addition of 10% fly ash shows improvement in Flexural strength ie 65.5 MPA .hence optimum concentration of Fly Ash allowed in the blend for successful recovery is 30 wt%, since at higher Flyash content, the inherent material property of ABS deteriorates. The weak adherence of dispersed Flyash phase within ABS phase has been discussed in the morphology studies employing SEM.

Table 3: Mechanical properties of FLYASH Filled ABS blend

Sample Designation (ABS/ FA)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexure Strength (MPa)	Flexure Modulus (MPa)	Impact Strength (J/m)
100/00	40.23	1200	65.0	2400	109.88
90/10	39.18	1255	65.5	2600	31.32
80/20	38.57	1440	63.5	3100	25.25
70/30	36.33	1671	62.5	3600	21.42
60/40	36.31	1912	56.5	4100	21.92

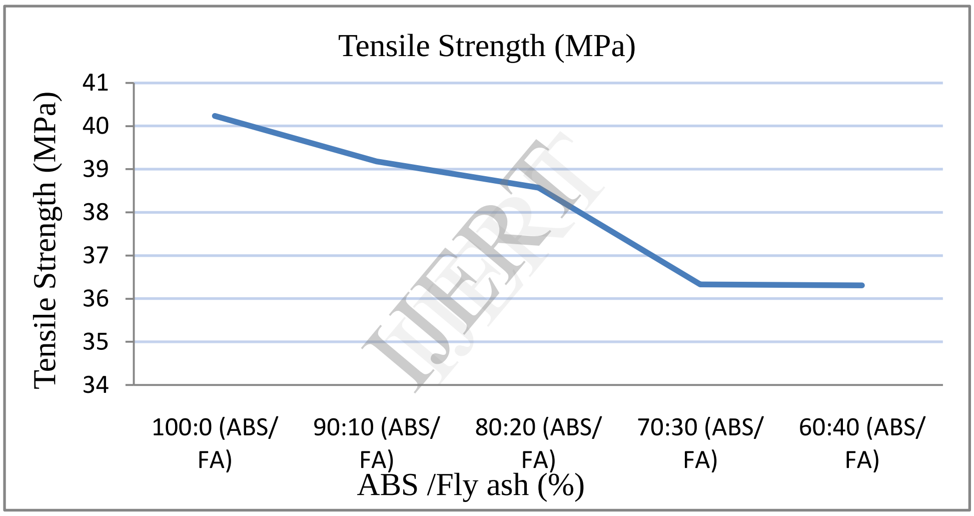

Fig 1: Effect of Filler loading on Tensile Strength of ABS

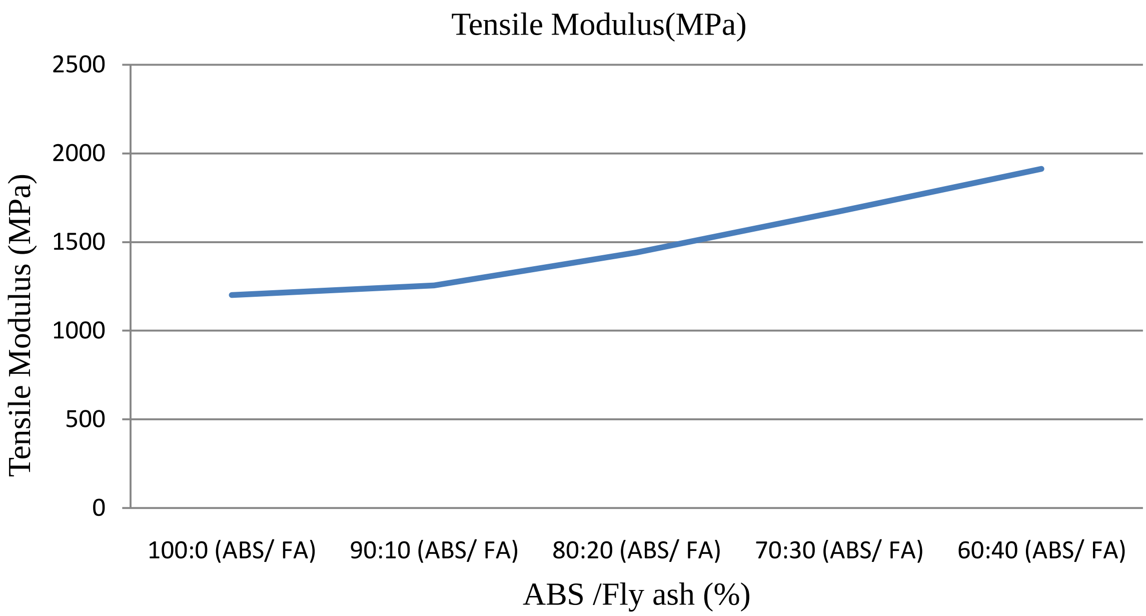

Fig 2: Effect of Filler loading on Tensile Modulus of ABS

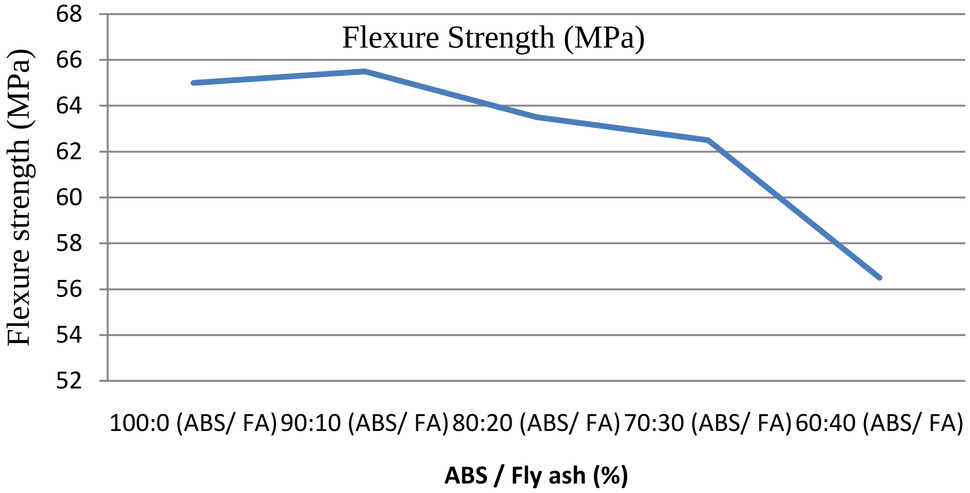

Fig 3 : Effect of Filler loading on Flexure Strength of ABS

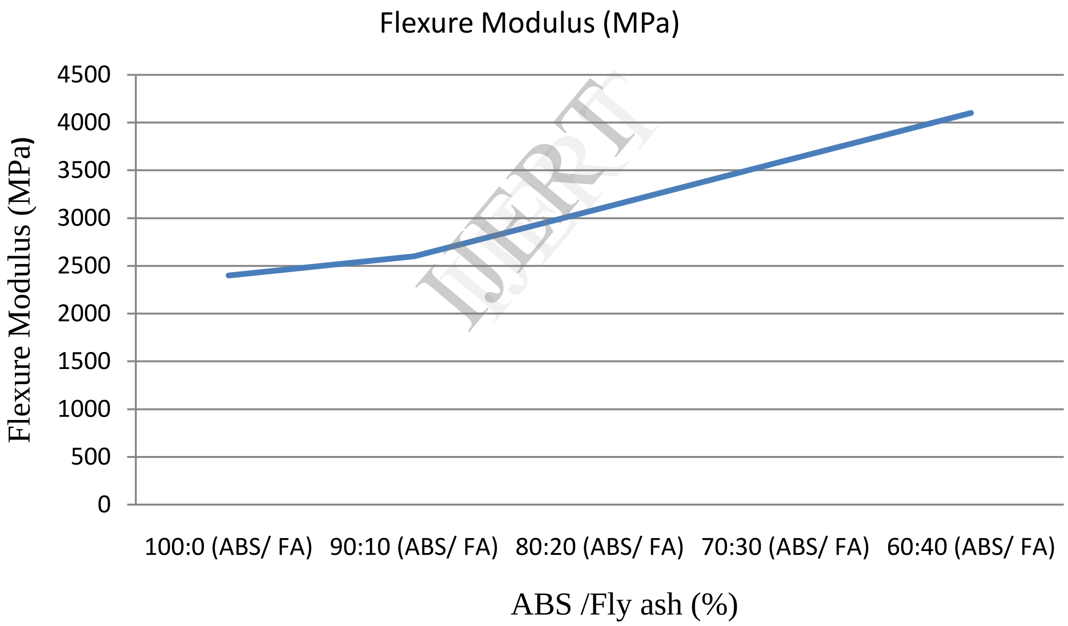

Fig 4: Effect of Filler loading on Flexure Modulus of ABS

3.2 THERMAL ANALYSIS

3.2.1 Heat Deflection Temperature (HDT) & Vicat Softening Point (VST)

Values of Heat deflection Temperature (HDT) and Vicat softening Temperature (VST) are shown in Table 4. It is observed that that the values of HDT & VSP increased by addition of filler content (Fly Ash) from 10-40 % in ABS. This indicates that the improvement in chain stiffness due to good bonding of filler with maliac Anhydrite and polymer matrix. Which also shows that by addition of Filler the service Temperature of ABS /Fly Ash composite continual increments.

Table 4: Thermal Properties (HDT/VSP) of ABS/ FLYASH blend

Sample Designation (ABS/ FA)	**VST**	**HDT**
100/00	93.4	88.40
90/10	96.4	87.30
80/20	96.9	88.20
70/30	97.5	89.30
60/40	98.5	89.40

3.2.2 Differential Scanning Calorimetry (DSC)

DSC thermograms of Fly Ash Filled ABS Blend in different Wt % with corresponding Glass Transition temperature (Tg), melting temperature (Tm), heat of fusion (ΔH), represented in Table 5. It is observed that the ABS shows melting temperature of 130.6°C. Incorporation of Fly Ash results in marginal decrease in Tm to 128.2°C which further increases to 130.0°C in presence of 30% Fly Ash and further reduced to 126.8 at 40 % fly ash in ABS. This confirms compatibilization efficiency of Maliac Anhydrite which increases the interfacial area and improves the stress transfer in the system. The DSC thermograms of Fly Ash Filled ABS blend composite system also exhibited constant melting

Table 5: DSC analysis of FLYASH Filled ABS blend

Sample Designation (ABS/ FA)	**Glass Transition Temperature Tg (°C)**	**Melting Temperature Tm (°C)**	**ΔH (J/g)**
100/00	109.7	130.6	0.1534
90/10	108.2	129.4	0.4483
80/20	108.4	128.2	0.4056
70/30	108.8	130.0	0.2856
60/40	108.0	126.8	0.1534

3.2.3 Thermogravimetric Analysis (TGA)

The TGA Analysis results are depicted in Table 6 which shows Degradation temperature (°C) and percentage of residues of ABS/Fly ash blend.

Table 6: Degradation temperature (°C) and percentage of residues of ABS/Fly ash blend % residue

Sample Designation (ABS/ FA)	**$T_{0.1}$ (°C)**	**$T_{0.5}$ (°C)**	**T_f(°C)**	**% residue**
100/00	410	450	680.1	0.29
90/10	405	430	900.0	7.15
80/20	400	420	730.0	18.13
70/30	400	410	720.0	29.06
60/40	390	410	730.0	37.18

3.2.4 Scanning Electron Micrograph (SEM)

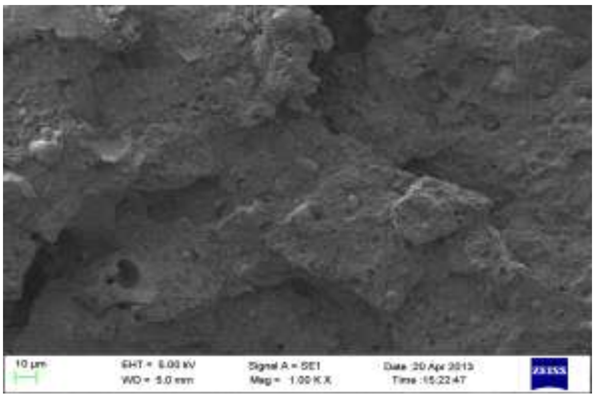

Fig 5: SEM ANALYSIS OF ABS/FA (90/10)

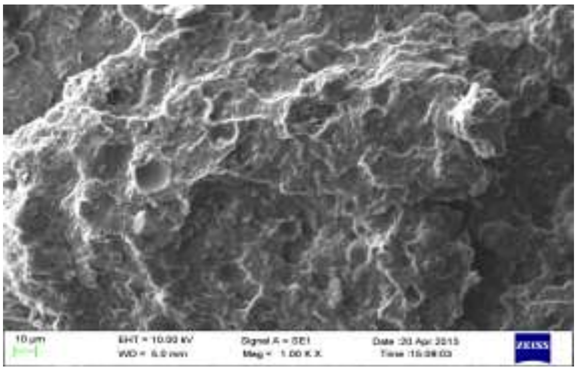

Fig 6: SEM ANALYSIS OF ABS/FA (70/30)

4. CONCLUSIONS

- The present investigation reports the compatibilization efficiency of Maliac Anhydrite in Fly ash filled ABS composites by varying wt % by 10 to 40 % . Following conclusions were derived from our experimental findings:
- Morphological studies confirmed the evidence of efficient interaction of Maliac Anhydrite and Fly Ash at the interface of ABS blend.
- ABS/FlyAsh (90:10) blend compatibilised with 0.03 wt % of Maliac Anhydrite improves the Tensile & Flexure properties. By further loading of fly Ash in ABS from (80:20) to (60:40), Tensile Modulus & Flexure Modulus gradually increased but Tensile Strength and Flexure strength decreased considerably. Decrease of 70% in impact strength has been observed with addition of Fly Ash with (10 Wt %) can be attributed to immobilization of the macromolecular chains by the filler which limits their ability to deform freely and makes the materials less ductile.
- DSC studies showed an increase in crystallinity of ABS in blend from 20.03 to 23.38 %. TGA studies confirmed an increase in T_f from 680 °C to 900 °C which shows good thermal stability of ABS polymer in ABS/FA composite.
- An excessive tri-block co-polymer concentration brings observable changes in the property. The compatibilizer and dispersed phase concentration plays a key role in developing multiphase polymers with well-balanced properties.
- Hence Fly Ash Filled ABS blend and its composites can be fabricated for value added products with desired attributes

REFERENCES

[1]. C DeArmitt "Functional fillers for Plastics" "Applied Minerals Inc, 110 Greene St, Suite 1101, New York, NY 10012, USA." (2011).
[2]. N.S.Pandian "Fly ash characterization with reference to geotechnical applications." *Journal of Indian Institute of Science* 84.6 (2004): 189-216.
[3]. N.othmen , H. Ismail "Effect of compatibiliser on Mechanical and Thermal properties of bentonite filled Polypropylene composites" Polymer Degradation and Stability 91 (2006).1761e1774 Elsevier Ltd.
[4]. O Meincke, D. Kemper, H. Weickmann, C. Friedrich,M. Vathauer, H. Warth "Mechanical properties and electrical conductivity of carbon-nanotube filled polyamide-6 and its blends with crylonitrile/butadiene/styrene. Polymer 45 (2004),739-748 science direct,
[5]. S. Bonda, S. Mohanty, S.K.. Nayak "Viscoelastic, Mechanical, and Thermal Characterization of Fly Ash-Filled ABS Composites and Comparison of Fly Ash Surface Treatments". Wiley Online Library.(wileyonlinelibrary.com).VVC 2011 Society of Plastics Engineers, POLYMER COMPOSITES—-2012, 22-34.
[6]. J. Gummadi, G.V. Kumar, G. Rajesh "Evaluation of Flexural Properties of Fly Ash Filled Polypropylene Composites" International Journal of Modern Engineering Research (IJMER) Vol.2, Issue.4, July-Aug 2012 pp-2584-2590 ISSN: 2249-6645.
[7]. J. V. Rutkowski and B. C. Levint "Acrylonitrile-Butadiene-Styrene polymers (ABS):Pyrolysis and Combustion Products and their Toxicity-A Review of the Literature. FIRE AND MATERIALS, VOL. 10,93-105 (1986)
[8]. Muller, H., R. Gachter, and H. Muller. "Plastics Additives Handbook." Hanser, Munich (1990).
[9]. I. Ahmad, P. A. Mahanwar "Mechanical properties of fly ash filled high density polyethylene." Journal of Minerals & Materials Characterization & Engineering 9.3 (2010): 183-198.
[10]. M.V,Deepthi , et al. "Mechanical and thermal characteristics of high density polyethylene–fly ash Cenospheres composites." *Materials & Design* 31.4 (2010): 2051-2060.
[11]. Shah V., 'Handbook of Plastic Testing Technology', 2nd Edition, Wiley-Interscience Publication, (1998).
[12]. 'Annual Book of ASTM Standards', Vol.08.01, American Society for Testing and Materials, Philadelphia, USA (1993). ASTM D 638-08 "Standard Test Method for Tensile Properties of Plastics"
[13]. Annual Book of ASTM Standards', Vol.08.01, American Society for Testing and Materials, Philadelphia, USA (1993),D 256 -08 'Standard Test Methods for Determining the Izod Pendulum Impact resistance of Plastics".
[14]. 'Annual Book of ASTM Standards', Vol.08.01, American Society for Testing and Materials ASTM D790-07, Philadelphia, USA (1993) 'Standard Test Methods for Flexural Properties of Plastics"
[15]. 'Annual Book of ASTM Standards', Vol.08.01, American Society for Testing and Materials ASTM D 648-07, Philadelphia, USA (1993), 'Standard Test Methods for Heat Deflection Temperature"
[16]. 'Annual Book of ASTM Standards', Vol.08.01, American Society for Testing and Materials ASTM D 1525-07, Philadelphia, USA (1993), 'Standard Test Methods for Vicat Softening Temperature of Plastics"
[17]. H.J Kwo**n,** P Y B Jar and Z Xia "Residual toughness of poly (acrylonitrile-butadiene-styrene)(ABS) after fatigue loading—effect of uniaxial fatigue loading."*Journal of materials science* 39.15 (2004): 4821-4828.
[18]. R. A. Kruger, M. Hovy, D. Wardle "The use of fly ash fillers in rubber." International Ash Utilization Symposium, Centre for Applied Energy Research, University of Kentucky. 1999. paper 72
[19]. B Ben Difallah, et al. "Mechanical and tribological response of ABS polymer matrix filled with graphite powder." *Materials & Design* 34 (2012): 782-787.
[20]. A. Das, B. K..Satapathy "Structural, thermal, mechanical and dynamic mechanical properties of cenosphere filled polypropylene composites."*Materials & Design* 32.3 (2011): 1477-1484.