

Role of Two Different Silane Coupling Agent on Wood Carbon / General Purpose Unsaturated Polyester Particulate Composites

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Abstract

The present investigation was to evaluate the effect of silane coupling agent on the spectral, thermal, morphological and hardness properties of four different carbon viz., rose, neem, ground nut, teak prepared from agricultural waste along with general purpose unsaturated polyester resin (GPR) particulate composites were made using casting technique. The incorporation of coupling agent into the carbon/polyester composites were clearly noticed using the FTIR spectroscopy. The properties of the composite with and without coupling has also been investigated and compared. A result of the studies implies that amino propyl trimethoxysilane treated composites are experiences excellent properties than vinyl triethoxy silane treated composites and untreated ones.

INTRODUCTION

A composite material is made by combining two or more materials to give a unique combination of properties. Composites based on a polymer matrix have become more common and are widely used in many industries due to the advantageous properties offered by the polymers. Filling polymers with mineral dispersion has long been a practice in the plastic industry as a way to reduce overall production costs and enhance certain properties.¹ generally; most mineral fillers used in thermoset and thermoplastic composites are ground into fine particles with relatively low aspect ratios. The low aspect ratios and relatively low price of the fillers are very attractive in a plastics market that grows more and more competitive.¹ Almost any powdered material can be used as filler, the common ones being obtained from natural deposits. Of the several hundred fillers used, those that find widespread use are various grades of calcium carbonate, quartz, mica,² silica flour, talc,³ and various clays.⁴ The utilization of as an additive component in polymer composites has received increased attention recently, particularly for price-driven/high-volume applications.⁵ Srivastava and Shembekar⁶ evaluated tensile and flexural properties of fly-ash-filled epoxy resin, and they reported that the loading of FA in epoxy-resin causes a decrease in the tensile and flexural properties of the composites. A wide variety of fillers have been incorporated in pure polypropylene (PP) to impart flow and mechanical properties and to reduce costs.⁷ Chand and Gautham⁸ developed composites of FA and glass

fiber with polyester resin and re-reported their abrasive behavior and wear loss. Coutinho et.al.⁹ prepared a composite of fiber/PP and found a decrease in mechanical properties. Many studies have been published concerning the processing conditions and properties of thermoplastics with fiber,¹⁰⁻¹³ glass fiber,^{14,15} mica,¹⁶ and calcium carbonate.¹⁷ Unfortunately, the better stiffness obtained through filling is often accompanied by drawbacks such as lower processibility and lower toughness.

Enormous amount of research work focuses on various fillers on unsaturated polyester composite were found to have deteriorated in overall properties of the composites. To our best of knowledge, no work has been reported on the carbon prepared from agricultural waste. This development has been brought about because the incorporation of carbon from renewable offers several advantages; because it is the best way to dispose the environmental waste carbon. It is a fine and powdery material. The fillers have been shown to increase the stiffness of the composites, but the strength, however, suffers a setback.¹⁸ To overcome these problems, a variety of methods have been adopted, including the choice of processing aid and modification of the filler surface. Based on the reasoning that a proper interlayer results in a balance between toughness and strength, the efforts has been noticed in the developing of new coupling agents (CAs) for the fillers during the past decade.¹⁹⁻²¹ The properties of a composite, such as strength and modulus, are important factors for producing high-quality composites. Many researchers have tried to improve the adhesion between filler and

matrix resin by chemical reaction with CAs. Silane CAs are generally considered to be adhesion promoters between mineral fillers and organic matrix resins and, as such, provide improved mechanical strength and chemical resistance to the composites.²² One of the authors, previous contribution reported that a 40% loading of FA caused minor strength reductions of filled polyester resin, whereas loading beyond 40% caused a drastic deterioration of properties. Based on the above discussions, authors aims to describe the various carbons viz., rose , neam , ground nut, teak carbons into the unsaturated polyester resin and the influence of two different silane-based CAs on the mechanical, thermal, morphological properties of carbon / polyester resin with maximum of 40% loading have been discussed.

EXPERIMENTAL

Materials

General purpose unsaturated polyester resin (GPR) is composed of maleic anhydride, iso-phthalic anhydride, aliphatic diol, styrene monomer, 1% solution of methyl ethyl ketone peroxide (catalyst), 1% solution of cobalt-naphthenate (accelerator), and

TABLE - I

CHARACTERISATION OF CARBON

Parameter	Concentration (Average)			
	C1	C2	C3	C4
Moisture content (%)	6.4587	6.9508	5.8537	7.2376
Ph	7.4000	7.200	7.6000	7.1000
Bulk density (g/cc)	0.8487	0.7437	0.8678	0.7982
Loss on ignition (%)	0.9566	0.8506	0.7543	0.8592
Sulfate content (%)	0.2023	0.2961	0.3333	0.1307
Chloride content (%)	0.3090	0.3292	0.4210	0.3828

TABLE - II

PARTICLE SIZE WOOD POWDER AND CARBON

NAME OF THE WOOD	PARTICLE SIZE OF WOOD POWDER (%) (BSS 40 - 425µm)	PARTICLE SIZE OF CARBON % (BSS 60 - 250µm)
Teak Wood	88.0859	70.5657
Groundnut	35.0112	57.3495
Neem Wood	64.5647	63.3031
Rose Wood	53.2606	69.6921

surface-modified calcium carbonate filler (120–150 m, bulk density 0.7289 g/cc) were obtained from Sakthi Fiber Glass Ltd., (Chennai, India). The carbon prepared from various renewable sources like Rose , Neem , Ground nut, Teak in a pre-dried powdered form were used as filler. CAs, Amino propyltrimethoxy silane (AMPS), and vinyltriethoxysilane (VES) were obtained from Sigma-Aldrich (St. Louis, MO). Methanol from Avra synthesis private Ltd. (Hyderabad, India) was also used in this investigation.

Characterization of carbon:

The carbon was characterized for the following properties: moisture content, loss on ignition, pH, and bulk density. The notations of various carbon and there composites are presented in **Table I**. The results are given in **Table II**. The particle size of the and their concern carbon were determined by sieving through a suitable sieve (standard test sieve BSS 40 to 425µm and 60 to 250 µm). The carbon with particle sizes in the range of 60-250 µm was used in this study.

Treatment of carbon with CAs:

A 5% solution of APMS and VMS in methanol was prepared. A 5% solution (11 mL) mixed with 40 wt % of dried carbon in a closed container was shaken for 20 min in a mechanical shaker and kept as such for 20 min. This surface-treated carbon contained 0.5% CA by weight. Similarly, 1.0 and 2.0% CA loaded carbon mixtures were prepared by taking 22 and 44 mL of CA solution with 40 wt % of dried carbon.

FTIR

The infra-red spectra were recorded on a Spectrum One (Perkin Elmer) in the range between 4000 - 400 cm^{-1} . The samples were analyzed as powders.

MORPHOLOGICAL STUDIES

Scanning Electron Microscopic (SEM) studies were carried out using VEGA3 TESCAN, CRANBERRY TWP, USA.

THERMAL STUDIES

TGA analyses were conducted using a TA Instruments SDT Q600 V20.9 Build 20 thermal analyzer, using constant heating rate (20 $^{\circ}$ C/min) from room temperature to 500 $^{\circ}$ C.

X-ray diffraction:-

X-ray diffraction patterns were obtained using a Bruker D8 advance diffractometer equipped with a Cu source (wavelength 1.54 nm) operating at 40 kV and 40 mA. Scanning rate was 0.02 $^{\circ}$ s $^{-1}$ from $2\theta = 2^{\circ}$ to 20° for various carbon samples and 2° to 40° for calcium carbonate samples to check for

alteration in the characteristic diffraction peaks of the material.

Hardness studies

The hardness was measured with a hardness tester (Kobunshi Keiki Co., LTD., Japan), as per ASTM D 2240-68 at CIPET – Chennai. It was determined by forcing a hard indenter into the surface of the material. The average of five hardness readings were consider for each samples calculation.

Results and discussion

Effect of CAs on the FT-IR of the composites

Figure (1 - 8) FT-IR spectrum of APMS and VES treated carbon shows the presence of absorption peaks at 1283 cm^{-1} and 1727 cm^{-1} , which may be assigned to asymmetric C-O and C=O stretching vibrations of ester bond. The peaks appearing at 2980 cm^{-1} , 2850 cm^{-1} and 1370 cm^{-1} also confirm the formation of $\text{SiOCH}_2\text{CH}_3$ and $\text{Si}(\text{CH}_2)_3$ stretching frequencies. Similar to our observation, Alagar et.al²³ was also observed for system. The peak at 3425 cm^{-1} which has been related to OH stretching frequency of Si-OH group present in the coupling agent AMPS. These peaks also overlap with amine peak from the coupling agent (REF). This suggests that a part of the silane was hydrolysed and reacted with carbon surface. A.E. Langroudi et.al²⁴ also observed similar to our observation on aminopropyl trimethoxy silane treated copper/epoxy composite system. Some of the peaks mentioned in the spectrum clearly indicated that the organic fractions (from coupling agent) have strongly been associated over the carbon surface in the coupling agent treated (C1, C2, C3, C4) / GPR composites.

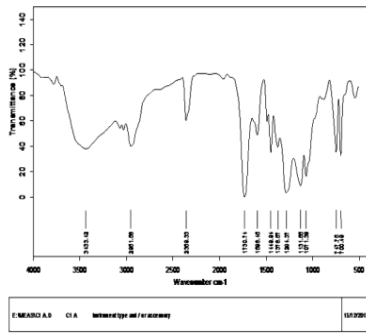


Fig 1 C1-APMS-GPR

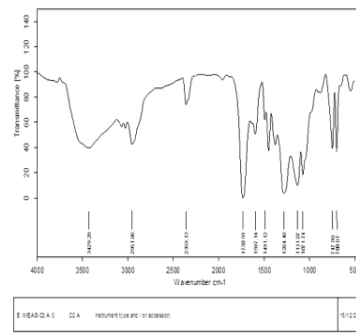


Fig 2 C2-APMS-GPR

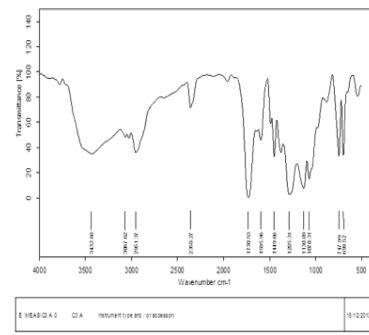


Fig 3 C3-APMS-GPR

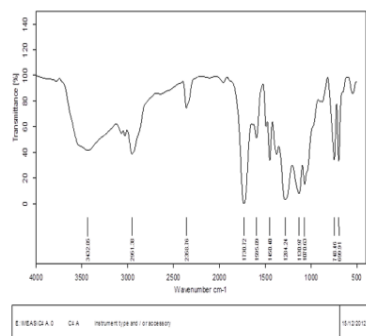


Fig 4 C4-APMS-GPR

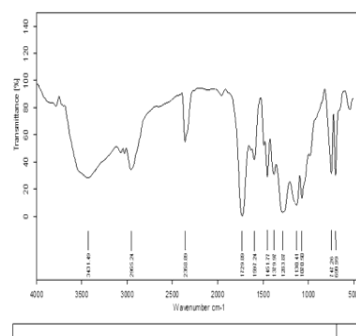


Fig 5 C1-VES-GPR

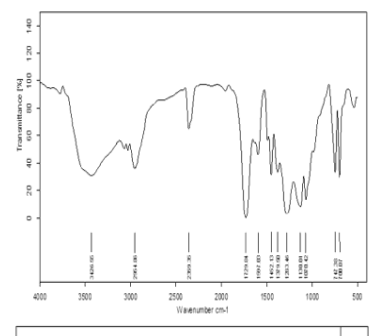


Fig 6 C2-VES-GPR

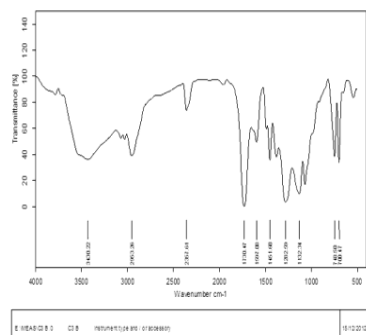


Fig 7 C3-VES-GPR

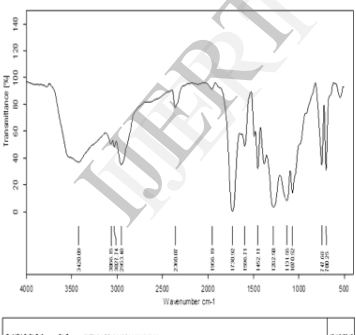


Fig 8 C1-VES-GPR

Effect of CAs on the SEM of the composites

In order to study the morphology of C1, C2, C3 and C4 with GPR composites examined by SEM studies were shown in Fig (9 - 20). These samples were subjected to Ag/Pd coating to render these conductive before examination. Polymer rich phase was shown in the top. SEM images of the so-obtained composites attested to have fine interfacial adhesion between renewable carbon and the polyester chains. Table (4a and 4b) Summaries the hardness of the carbon/GPR composite treated and untreated coupling agent. The microstructures of untreated composites show some aloofness of filler from matrix. This indicated the insufficient bonding between polyester and wood carbon as filler and less adhesion occurred between them. Hence, the results

of hardness clearly indicate that pure GPR has hardness value of 70.3, whereas the hardness value found to have 81.5 for C1, 78.3, 70.0 and 79.2 for C2, C3 and C4 in respect of untreated carbon. This may be clear that the incorporation of fillers enhances resistance towards penetration over GPR. This might be due to the proper intimate mixing of renewable carbon with the polyester resin were shown in figure (9 - 20). However, on further surface treated with two different coupling agents hardness was also increased. This might be due to the surface treated composites exhibits renewable carbon is better dispersed in the GPR. The presence of coupling agents less detachment and agglomeration of wood carbon in polyester matrix thus enhanced wet ability between renewable carbon and polyester. The effect of improve interfacial bonding between the filler and

the matrix. Our earlier observation, ²⁵ was also supported for increase of the hardness for untreated

to treated carbon/ GPR composites.

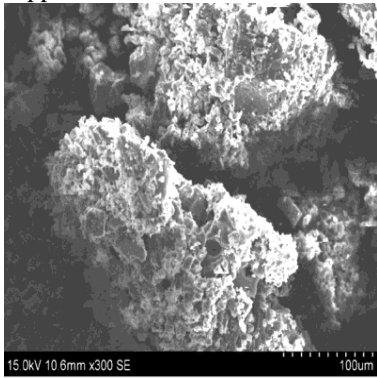


Fig 9 C1-GPR

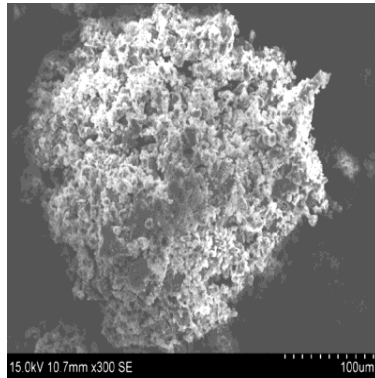


Fig 10 C2-GPR

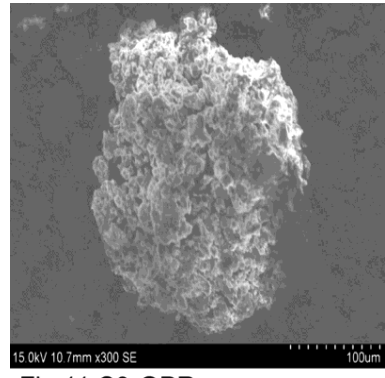


Fig 11 C3-GPR

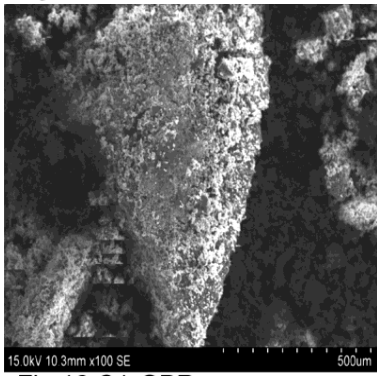


Fig 12 C1-GPR

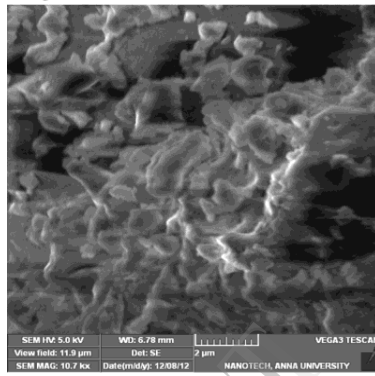


Fig 13 C1-APMS-GPR

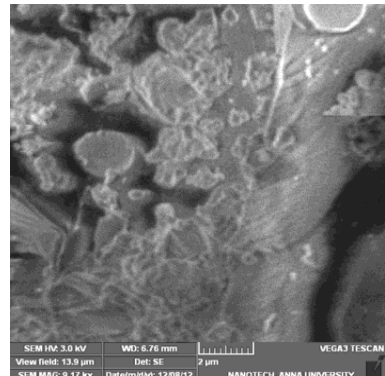


Fig 14 C2-APMS-GPR

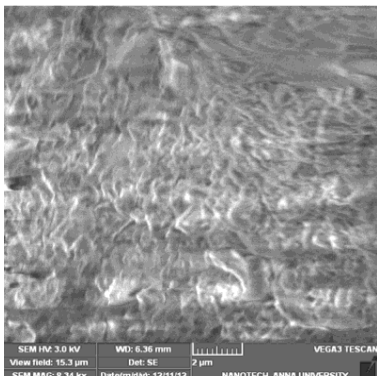


Fig 15 C3-APMS-GPR

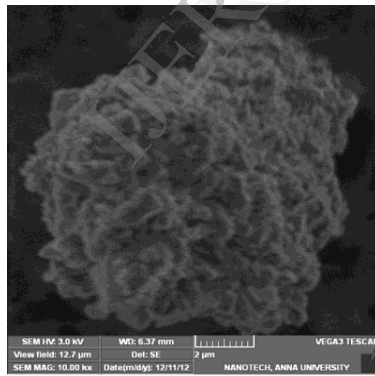


Fig 16 C4-APMS-GPR

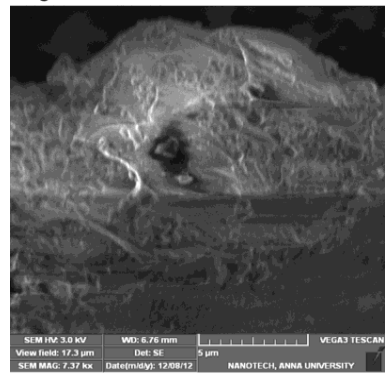


Fig 17 C1-VES-GPR

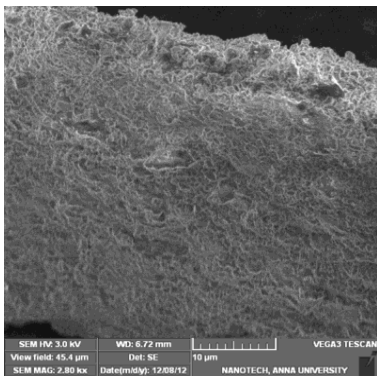


Fig 18 C2-VES-GPR

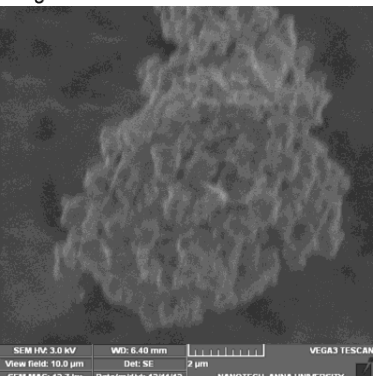


Fig 19 C3-VES-GPR

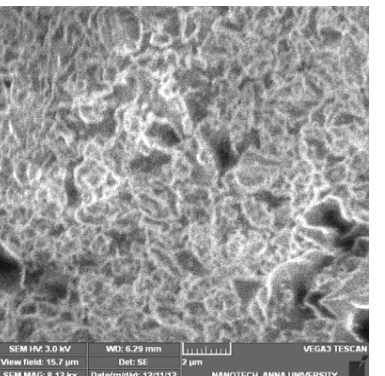


Fig 20 C4-VES-GPR

Effect of CAs on the Thermal studies of the composites

The thermal stability of the untreated carbon and APMS and VES based surface treated carbon GPR composites were presented in Fig. 21 – 32 which summarizes the TGA data on GPR, untreated carbon (C1-C4) followed by two different coupling agent (APMS and VES) treated carbon (C1-C4) composites. In general, all thermo grams shows two stages of decomposition were observed for all composites. The 10% weight loss was observed at 276°C for GPR, 210, 195, 210, and 210°C in respect of untreated C1, C2, C3 and C4 respectively. Almost

similar observation was observed for coupling agent treated C1-C4 viz., 210, 180, 200 and 200°C for APMS and 220,210,235 and 225°C for VES. The 50% weight loss was found to have around 464°C for GPR, nearly 14 and 21% lesser than the weight of GPR have been observed for untreated C1-C4 and surface treated C1-C4 correspondingly. In overall observation for all composite in respect of thermal studies is concern, GPR has thermally stable than untreated and surface treated carbon. Effect of surface treated over the carbon was found to be very minimal.

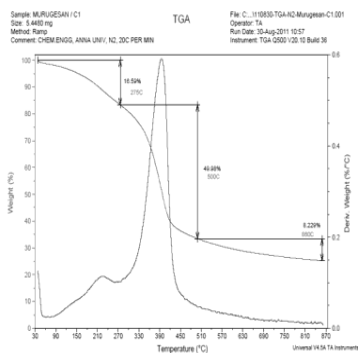


Fig 21 C1-GPR

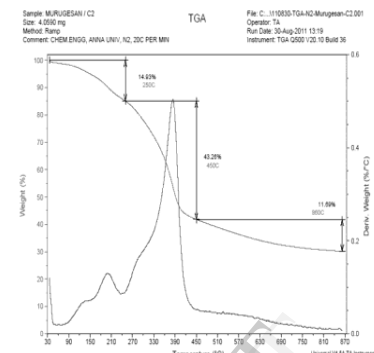


Fig 22 C2-GPR

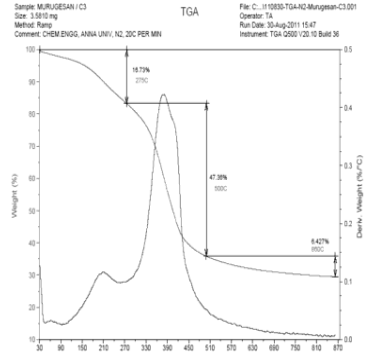


Fig 23 C3-GPR

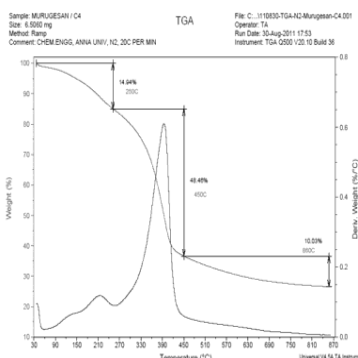


Fig 24 C4-GPR

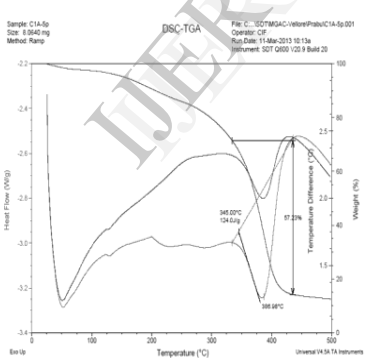


Fig 25 C1-APMS-GPR

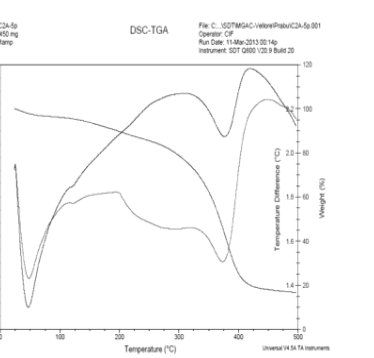


Fig 26 C2-APMS-GPR

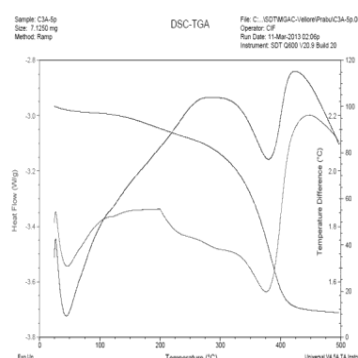


Fig 27 C3-APMS-GPR

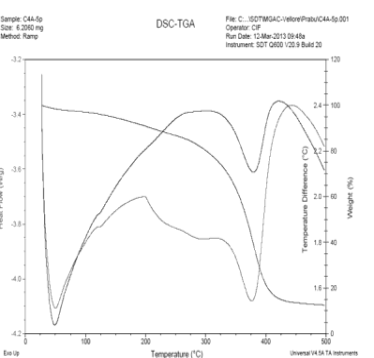


Fig 28 C4-APMS-GPR

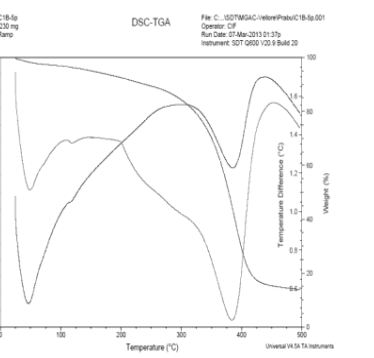


Fig 29 C1-VES-GPR

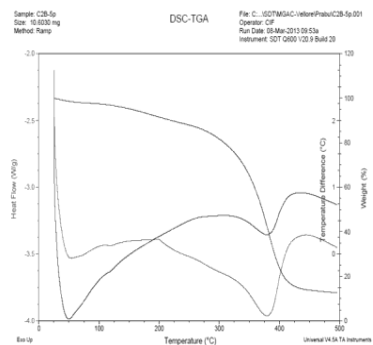


Fig 30 C2-VES-GPR

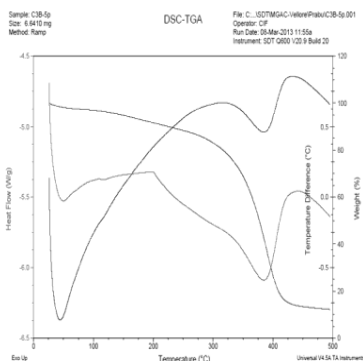


Fig 31 C3-VES-GPR

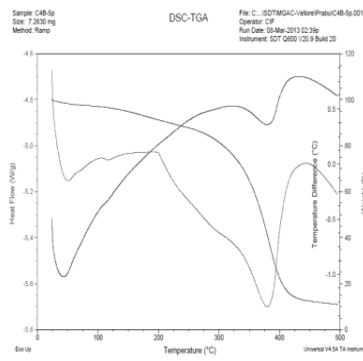


Fig 32 C4-VES-GPR

TABLE – III-a

TGA FOR C1, C2, C3 & C4-AMPS-GPR

% of Wight loss	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
GPR	276	374	392	406	464	538	620	-	-	-
C1-AMPS-GPR	210	295	345	360	370	385	390	410	-	-
C2-AMPS-GPR	-	25	280	290	330	350	370	380	390	420
C3-AMPS-GPR	-	25	200	290	330	360	365	380	390	405
C4-AMPS-GPR	-	25	200	295	337	355	370	380	387	415

TABLE – III-b

TGA FOR C1, C2, C3 & C4-VES-GPR

% of Wight loss	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
GPR	276	374	392	406	464	538	620	-	-	-
C1-VES-GPR	220	315	350	365	380	385	390	420	-	-
C2-VES-GPR	-	25	210	300	350	355	372	375	383	410
C3-VES-GPR	-	30	235	320	350	367	375	387	390	410
C4-VES-GPR	-	25	225	310	337	362	370	375	385	410

Effect of CAs on the X-ray Diffraction of the composites

Studies of amorphous materials represent a large and important emerging area of materials science. It is an area which is not amenable to the most of the conventional theoretical techniques of solid-state physics as there is no periodicity to simplify the mathematics. Due to the lack of periodicity, extraction of structural information from amorphous materials becomes very difficult. In this work we have used XRD technique to analyze the variations of the structural parameters of amorphous carbon due to irradiation. XRD is a very useful and simple technique to understand the structural details of the solid-state substances. Incident X-ray interacts with large volume of the material at a time and an average property of the material can be characterized rather than the local property. This makes XRD a powerful technique for studying the disordered materials which is inherently heterogeneous and

where the estimation of average property has got practical significance.

Fig (33 - 44) summarizes the XRD pattern of composites shows amorphous pattern for pure GPR, untreated carbon(s) viz., C1, C2, C3 and C4 as well as APMS and VES surface treated C1, C2, C3 and C4 composites. The untreated C1 has the d spacing at 4.268 with $A = 20.792^{\circ}$, whereas APMS and VES treated C1 has d spacing at 3.36148 and 1.54624, $A = 26.495^{\circ}$ & 59.759° and $d = 7.60613$, 3.4144, $A = 11.625^{\circ}$, 26.676° . This was clear that the additional d spacing may be due to the incorporation of organic moieties like AMPS and VES over C1. Similarly for C2, C3 and AMPS, VES treated d spacing values at 3.37, $A = 26.417^{\circ}$, 3.36148 and 1.54624, $A = 26.495^{\circ}$ & 59.759 , 7.60613, 26.676° , 3.38, $A = 26.681^{\circ}$, 7.58, 5.28, 4.29 & 1.547, $A = 11.661^{\circ}$, 16.768° , 20.684° , 59.701° , 7.615, 5.240, 4.297, 3.0742, $A = 11.61^{\circ}$, 16.906° , 20.652° , 29.022° , 3.4144, $A = 11.625^{\circ}$, 4.8526, 3.353, $A = 18.267^{\circ}$, 26.562° , 7.625, 4.282, $A = 11.596^{\circ}$, 20.725° respectively. The presence of peak was not observed

in diffractogram of composition C4-GPR composite which may indicate delamination of carbon added during polyester fabrication. Similarly to our observation Michal Kedzierski et-al,²⁶ was identified for the polyester/MMT nano composites preparation using intercalative copolyaddition reaction. However, APMS and VES surface treated C4 found to have the

d spacing at 1.326, $A = 71.031^{\circ}$, 7.623 , 4.303 , 1.826 , $A = 11.598^{\circ}$, 20.620° , 49.881° respectively. This might be due to surface treatment protected the delamination of carbon C4 during polyester fabrication. Further, the incorporation of coupling agents APMS and VES into various carbons (C1 to C4)

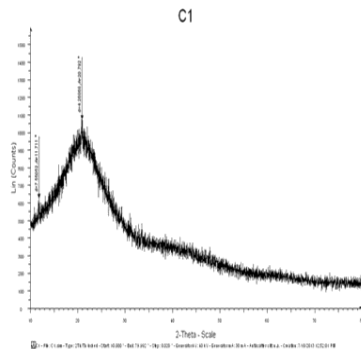


Fig 33 C1-GPR

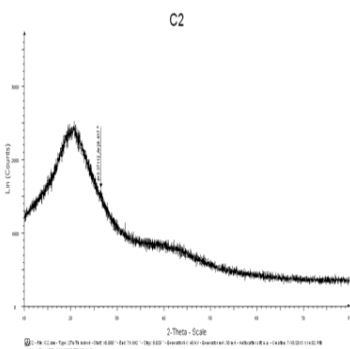


Fig 34 C2-GPR

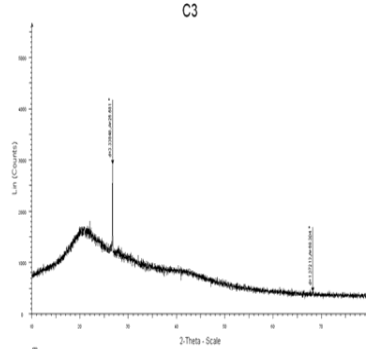


Fig 35 C3-GPR

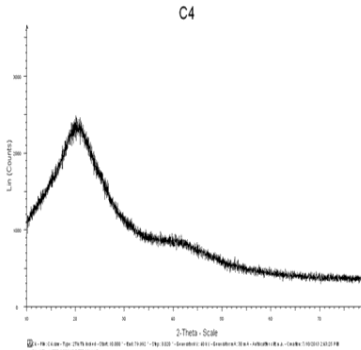


Fig 36 C4-GPR

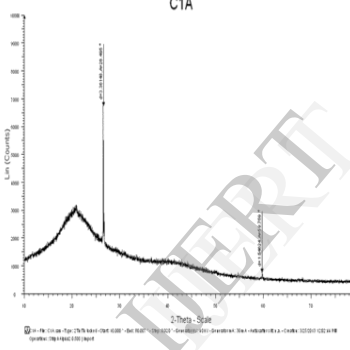


Fig 37 C1-APMS-GPR

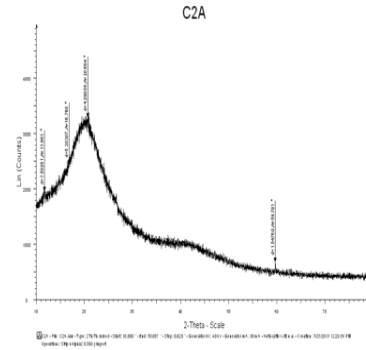


Fig 38 C2-APMS-GPR

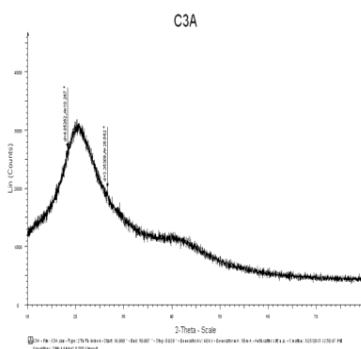


Fig 39 C3-APMS-GPR

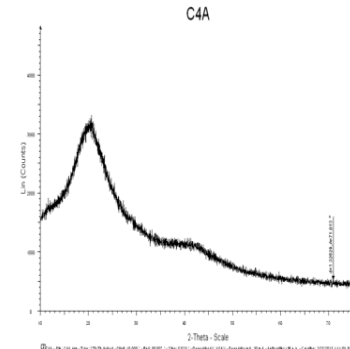


Fig 40 C4-APMS-GPR

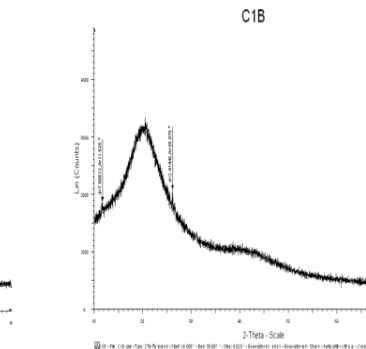


Fig 41 C1-VES-GPR

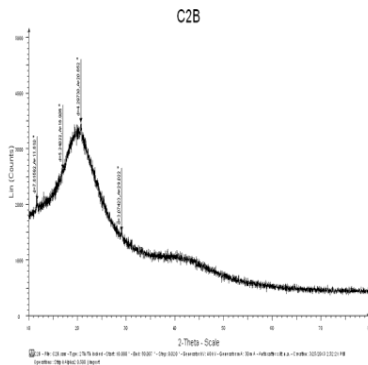


Fig 42 C2-VES-GPR

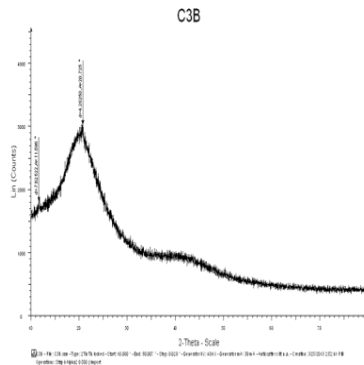


Fig 43 C3-VES-GPR

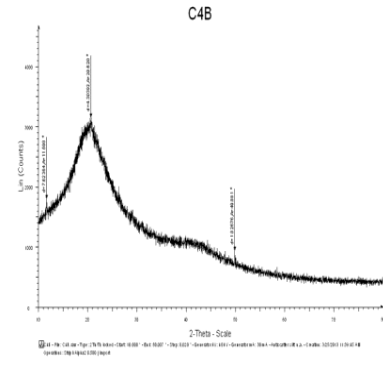


Fig 44 C4-VES-GPR

Effect of CAs on the hardness of the composites

The durometer hardness values of the various composites made in this study are given in Table.4. From the Table 4, it was clear that 15%, 12 %, almost level, and 12 % for C1, C2, C3 and C4 respectively. The values indicate that the mineral-filled composites were harder than the unfilled composites. The surface modification further

TABLE – 4- A

HARDNESS FOR CARBON – APMS – GPR:

HARDNESS TEST	GPR	C1-APMS-GPR	C2-APMS-GPR	C3-APMS-GPR	C4-APMS-GPR
10%	70.2	76.8	77.6	75.6	74.9
20%	70.5	82.1	84.5	78.5	77.8
30%	70.6	84.0	86.0	81.2	78.6
40%	70.3	86.5	87.8	83.0	80.3

TABLE – 4 – B

HARDNESS FOR CARBON – VES – GPR:

HARDNESS TEST	GPR	C1-VES-GPR	C2-VES-GPR	C3-VES-GPR	C4-VES-GPR
10%	70.2	74.2	75.7	77.5	79.9
20%	70.5	81.0	82.4	80.0	82.8
30%	70.6	82.4	83.8	81.9	84.6
40%	70.3	84.8	85.1	84.0	85.8

CONCLUSIONS

Based on the carefully analysis of the date the following conclusions were made.

- Wood carbon composites were fabricated with and without treated incorporation of coupling agents into wood carbon polyester were noticed using FT-IR Spectroscopy.
- The results of SEM images of untreated and surface treated wood carbon polyester was reveals that

increased the hardness. This observation is in agreement with the fact that the hardness is a measure of resistance to penetration. This resistance to the penetration of GPR increased when filled with the mineral carbon, and still more resistance was offered by the material when the surface of the filler was modified with CAs for improved compatibility between the filler and the matrix.

the perfect wetting and less detachments was observed for surface treated wood carbon perhaps, there was aloofness was noticed for untreated carbon.

- The result of the thermal studies shows GPR has thermally stable than the untreated and surface treated carbon. The effect of surface treated and the carbon found to be very minimal.

- The XRD pattern of all treated and untreated wood carbon composites shows amorphous in nature.
- The improved hardness was observed coupling agents modified wood carbon than untreated wood carbon composites in overall observation APMS treated composites has better influence than VES treated composites in all properties.

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