SYNTHESIS, CHARACTERIZATION AND EVALUATION OF EPOXY / GUAR–GUM BASED POLYMER COMPOSITES

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FOR THE AWARD OF THE DEGREE OF

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BY

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UNDER THE SUPERVISION Of

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CERTIFICATE

This is to certify that the thesis entitled, **"SYNTHESIS, CHARACTERIZATION AND EVALUATION OF EPOXY / GUAR–GUM BASED POLYMER COMPOSITES".** Which is being submitted by **Mr Gopal Arora** for the award of the Degree of DOCTOR OF PHILOSOPHY to the Faculty of Technology, University of Delhi, Delhi, India is entirely based on the experimental work carried out by him under my supervision. The work reported in this thesis embodies the work of the candidate himself and is original one, has not been submitted to any other University or Institution for the award of any degree or diploma.

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ABSTRACT

Now a days polymer from renewable resources have been attracting increasing attention, primarily for two major reasons: environmental concerns and the realization that our petroleum resources are finite. A third reason for growing interest in polymers from renewable resources relates to adding value to agricultural products, which is economically important for many countries. Generally polymer from renewable resources can be classified into three groups:

1) Natural Polymer such as starch, Protein and cellulose, Guar Gum :

2) Synthetic Polymer from natural resources such as Poly (Lactic acid):

3) Polymer From Microbial Fermentation such as Poly (hydroxy butyrate). [1].

A major advantage of all these materials is that they are biodegradable and that their final productof degradation are environment friendly. As with numerous Petroleum based polymers many properties can be improved through appropriate blending and composite formulation. These new blends and composites are extending the utilization of polymers from renewable resources into wider applications.Guar gum or guaran is a non-ionic, branched polysaccharide extracted from endosperm of the seed of *"Cyamopsistetragonolobus"*, family leguminosae, which grows naturally in the arid regions of the Indian subcontinent and is now also commercially grown in North Africa and South America. Guar gum is a galactomannan, structurally consisting of 1,4 - β- D ~ mannopyranosebackbone with branch pointsrandomly distributed from their 6-positions linked to 1- α - D - galactopyranose units [4-6]. Galactomannans can often be used in different forms for human consumption.featuring different physicochemical properties, galactomannans are a versatile material used for many applications; they are excellent stiffeners and stablizers of emulsions, and the absence of toxicity allows their use in the textile, pharmaceutical, biomedical, cosmetics and food industries[50, 51], Recently new and alternative souces of galactomaannans have been characterized [52, 53], and some works showed the possibility of using galactomannan to the formation of films and coatings [54-57].However in a very few studies conducted investigating the use of these material as fillers in polymer composites. Guar gum and Hydroxy propyl guar gum were successfully used a reinforcing filler in epoxy based composites.

Native guar gum is usually not used as such industrially because of a variety of

reasons such as its susceptibility to enzyme hydrolysis and bacterial attack and the difficulty in controlling its solution viscosity so in order to overcome these this problem chemical modification of the parent polysaccharides is carried out. One such method is its reaction with allyl chloride in the presense of analkali [31].Which result in a derivative with reduced molecular weight allylated guar gum are more soluble in water, resulting in clearer solutions while the viscosity decreases to some extent. The degree of allylation greatly affects the properties of the polysaccharides. The degree of substitution of allyl guar gum were determined by titration analysis.

The Present work aims at preparing a polymer composites, which is cost effective, meeting the desired properties requirement and obtained from natural material.

Guar gum was etherified using a Williamson synthesis reaction using allyl chloride. The synthesized allyl guar gum with varying degree of substituition were characterized for their Chemical and thermal properties. The allyl guar gum has been characterized through FTIR, and ^{1}H NMR methods. The Morphology of the allyl guar gum were studied by Scanning Elecrtron Microscope.The addition of allyl guar gum with varying degree of substitution were incorporated as filler in an epoxy resin to study the effect of degree of allylation on the mechanical properties including Tensile Strength, % Elongation at Break and Flexural Strength of the composites were evaluated . In all these instances the optimum concentration of allyl guar gum was ascertained with respect to the mechanical and thermal properties (Thermogravimetric analysis and Dynamic Mechanical Analysis) of resultant composites. The morphological properties of the resultant composites were studied by Scanning Electron Microscopy. The storage modulus of the resultant composites were increased only at lower concentration. The Tg values obtained from Tan d initially increased and then decrease with concentration as well as the extent of allylation.

Guar gum are generally subjected to modification via grafting reactions using a number of initiators techniques including Peroxides, Persulphates, redox system and microwave radiation. In the Present work Allyl guar gum has been grafted with acrylic acid by using Ferrous ammonium sulphate and Hydrogen peroxide as redox pair. The synthesized Allyl guar gum-g-Polyacrylic acid with varying carboxyl value has been characterized for their chemical and thermal properties. The carboxyl value of allyl Guar gum –g- Poly Acrylic acid has been obtained through titrimetric analysis. The effect of addition of allyl guar gum–g-Polyacrylic acid in the epoxy matrix on the mechanical, chemical and thermal properties of the composites were

also investigated. The inclusion of allyl guar gum –g-polyacrylic acid (0.033, 0.019) into epoxy matrix resulted in an increase in Tensile , flexural strength of the composites , while the % elongation of the resultant composites increases as the carboxyl value of the composites gets increases , however the thermal stability of resultant composites gets decreases with the decrease in carboxyl value of the resultant composites .The storage modulus of the resultant composites increase with carboxyl value while the glass transition of the composites decreases with the carboxyl value .

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Place- Delhi (GOPAL ARORA)

Date- 05-08-2013 Candidate

This work is

Dedicated to

My mother

SmtRenuArora

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CHAPTER - 1
INTRODUCTION

1.1 NATURAL POLYMERS

Now a days polymer from renewable resources have been attracting increasing attention, primarily for two major reasons: environmental concerns and the realization that our petroleum resources are finite. A third reason for growing interestin polymers from renewable resources relates to adding value to agricultural products, which is economically important for many countries. Generally polymer from renewable resources can be classified into three groups:

1) Natural Polymer such as Starch, Protein and Cellulose, Guar Gum :

2) Synthetic Polymer from natural resources such as Poly (Lactic acid):

3) Polymer From Microbial Fermentation such as Poly (hydroxy butyrate). [1].

A major advantage of all these materials is that they are biodegradable and that their final product of degradation are environment friendly. As with numerous petroleum based polymers many properties can be improved through appropriate blending and composite formulation. These new blends and composites are extending the utilization of polymers from renewable resources into wider applications.

A gum can be defined as any polymeric material that can be dissolved in water to give a viscous solution or dispersion **[2].**Gums can be classified into three categories.

1. Natural gums: found in nature or extracted from natural sources most of these gums are polysaccharides.
2. Semi– Synthetic gums: This category consists of gums obtained by the chemical modification of natural gums.
3. Synthetic gums: These are non polysaccharides.

Thus natural gums may be defined as any water soluble polysaccharides that can be extracted from plants, algae, micro-organisms and that possessed the ability to contribute to the viscosity or gelling ability to their dispersionsor solutions [3]. some common gum extracted from plant endosperms include guar and locust bean gum, plant exudates, gum arabic and gum tragacanth and gums derived from seaweeds, which include agar, carageenan and algin.

Guar gum or guaran is a non-ionic, branched polysaccharide extracted from endosperm of the seed of *"Cyamopsis tetragonolobus",* family leguminosae, which grows naturally in the arid regions of the Indian subcontinent and is now also commercially grown in North Africa and South America. Guar gum is a galactomannan, structurally consisting of 1,4 - β- D ~ mannopyranose backbone with branch points randomly distributed from their 6-positions linked to 1- α - D - galactopyranose units [4-6].

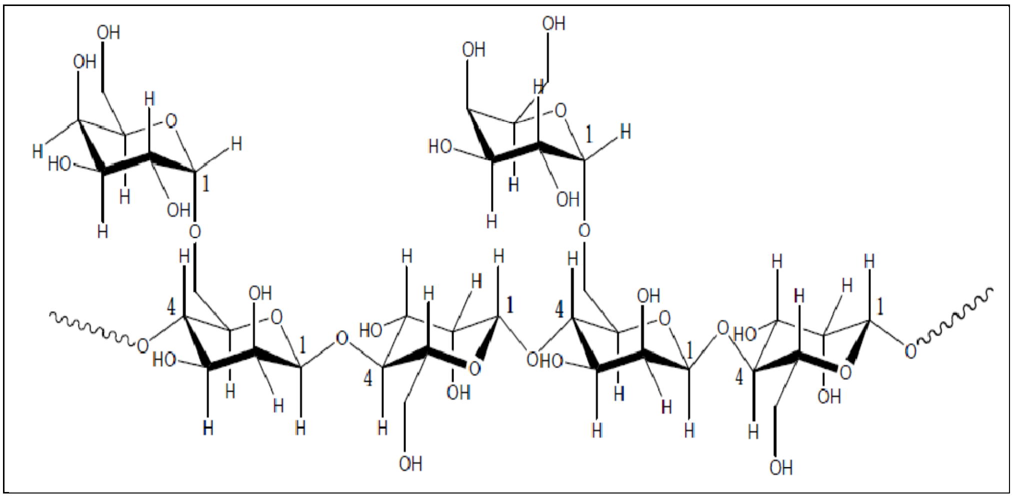


Fig -1.1 Structure of Guar gum

Overall the galactose to mannose ratio is roughly 1 :2. Guar gum when added to water results in a solution with a very high viscosity. Native guar gum is usually not used as such industrially because of a variety of reasons such as its susceptibility to enzyme hydrolysis and bacterial attack and the difficulty in controlling its solution viscosity. In order to overcome this problem chemical modification of the parent polysaccharide is carried out. One such method is its reaction with propylene oxide or ethylene oxide in the presence of alkali [7]. Which result in a derivative with reduced molecular weight. Propoxylated and ethoxylated guar gum are more soluble in water, resulting in clearer solution while the viscosity decreases to some extent. The degree of propoxylation greatly affects the properties of the polysaccharide. Guar gum and Hydroxypropyl guar gum both have the same number of hydroxyl groups per repeat unit and can thus be chemically modified using these hydroxyl groups.

1.2 ISOLATION AND PURIFICATION OF GALACTOMANNAN

On commmercial scale, the seeds of Guar gum are first treated to loosen the seed coat from endosperm either by soaking in sulphuric acid or water or roasting the seeds in furnace followed by milling[8,9] Figure 1.1 .

The endosperm generally sticks to the hull and must be re subjected to a milling process. High molecular weight polymers are sensitive to milling process. A careful control of the process is necessary to avoid their degradation of which it is preferable to carry out under humid conditions. The variables involved in the pulverization stage determines some gum powder properties such as viscosity which can be modified using different condition of humidity or temperature **[8]**Sieving or cyclonic separation is used to select endosperm particles of gum, commercial gum or crude gum which is applied in different industriesfor pharmaceutical purposes crude gum must be purified because crude gum contains a low fraction of soluble galactomannans(62-68%)and variable percentages impurities; pentosan, proteins and fibres. The purification process allows a material with 91-99% soluble galactomannans to be produced. The gum is dissolved in water and regenerated by precipitation with polar solvents for the purification [11] or can also be purified

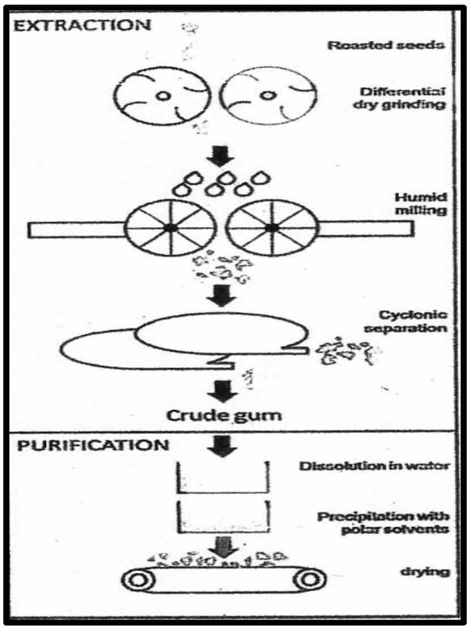


Fig 1.2 Extraction and Purification Process from Leguminous seed [10]

Fig 1.3 Shows the different forms of guar gum ranging from the pod, to the seed extracted dried guar gum powder

by complexation wit Cu^{2+} and Ba^{2+} salts. for futher purification dialysis and membrane filtration can be carried out **[12-13]**.

Galactomannan are reserve polysaccharides consisting mainly of the monosaccharides mannose and galactose units.The mannose units from a linear chain consisting of 1-4 – β–D mannopyranosyl residues with 1-6 α –D linked galactoyaronosyl residues as side chain at varying distances.

1.2.1 Chemical structure of guar gum

Guar gum is a galactomannan with 1-4 linked β D mannopyranose backbone with branch points from their 6 position linked to α- D galactose (i.e 1-6 linked α- D galactopyranose). There are between 1.5-2 mannose residues for every galactose residue. The chemical structure of guar gum was confirmed by methylation, fragmentation and periodate oxidation studies of native guar gum **[14]**. The structure of guar gum has been elucidated in figure 1.3. Guar gum is made up of non –ionic polydisperse rod shaped polymers consisting of molecules made up of about 10, 000 residues. Higher galactose substitution increases the stiffness (decreases the flexibility) but reduces the overall extensibility and radius of gyration of the isolated chains **[15].** The galactose residues prevent strong chain interactions as few unsubstituted clear areas have the minimum number required for the formation of junction zones of the different possible galactose substituition patterns, the extremes of block substituition and alternating substituition give rise to the stiffer, with greater radius of gyration and more flexible conformations respectively (random substituition being intermediate) **[15]**. If the galactose residues were perfectly randomized it is unlikely that molecules would have more than one such area capable of acting as a junction zone, so disallowing gel formation. A block substituition pattern for which there is some experimental evidence [**16**], would allow junction zone formation if the blocks were of sufficient length. Further evidence supporting the block substituition pattern is the formation of colloidal dispersions as the galactose rich areas would be the hydrophilic portion where as the galactose deficient areas would be hydrophobic **[4].**

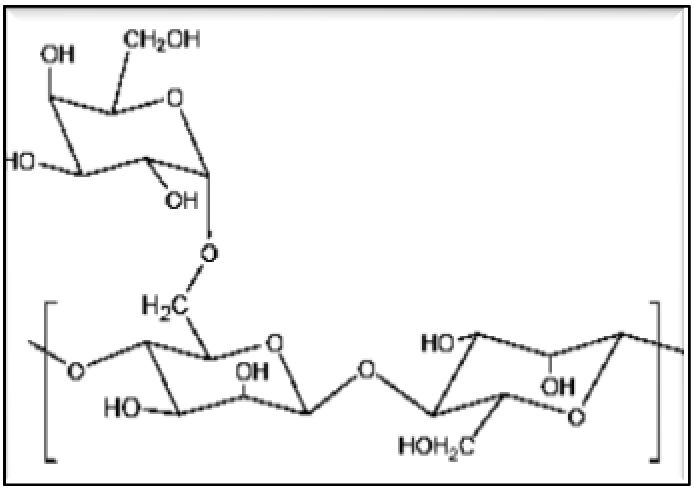


Fig1.4 – Chemical Structure of Guar Gum

Properties of Guar gum

Traditionally viscosity is the most important characterstics of Guar gumand leads to its use as a thickening agent. Guar gum and its derivatives result in solutions with high viscosity, even at 1 % w/ w concentrations. It is easily dissolved even in cold water. Aqueous solution of guar gum exhibit non Newtonian behavior, i.e shear thinning behaviour. Concetrated solution of guar gum, above its critical micelle concentration, also show a shear thining behavior, however it was observed that impurities in the guar gum, namely proteins effect the rheology of the solutions to a great extent [**17**]. The viscosity of guar gum solutions depend on avariety of parameters, such as time temperature, concentration, pH, ionic strength of solution, type and rate of agitation and particle size of guar gum.

In general, guar gum requires a certain amount of time to completely Hydrate and attain its stable solution viscosity, Once the solution is formed various anti – microbial agents are added to prevent microbial attack on guar gum and thus maintain its viscosity commonly used preservatives are formaldehyde and chlorinated phenolics. however,recent environment concerns have restricted the use of such agents, which preclude their use. Currently sodium benzoate and propionate and isothiazolinones are used.

The temperature at which hydration occurs also has a profound affect on the rate of hydration i.e the rate at which viscosity increases. The lower the temperature the lower the hydration rate.guar gum exhibits good thermal stability towards prolonged heating at 80 ^{o} C for up to 2 hours. The maximum viscosity of guar gum solution is achieved with temperatures ranging from 25 -40 ^{0} C.

Guar gum is non ionic in nature, which result in its almost constant viscosity at various pH ranges the optimum rate of hydration occurs between a pH range of 7.5-9. The nonionic nature also increases its compatibility with a variety of salts. however high concentrations of multivalent salts affect the rate of hydration and can results in gels.

In general the molecular weight of native guar gum ranges from 2, 20, 000 + 20, 000 From the fig – 1.2 we can see that the hydroxyl group attached to the pyranosyl ring are cis to each other. Whichreinforces each other in hydrogen bonding reactions as opposed to molecules where they are trans to each other, e.g cellulose. Galactomannan 1, 2 where an average each second mannose unit is blocked by galactose, show much steric hinderance and so little hydrogen bonding between the molecular chains that it hydrates instantly. polymannan is almost insoluble in cold water as well as hot water.

1.3 MODIFICATION OF GUAR GUM

Derivatisation is defined as the transformation of a chemical compound into another similar chemical compound by altering one or more of its functional group. Derivatisation is generally performed to alter reactivity or change a physical property such as solubility, boiling point, melting point, thermal stability etc. Derivatisation of guar gum includes the methylation, carboxymethylation ethylation phosphorylation, nitration, sulphonation etc. Guar -gum has per repeat unit of 2 mannose and 1 galactose sugar residues containing in total 9 hydroxyl groups, of which two are primary and the remaining secondry. these hydroxyl groups are capable, under appropriate condition of behaving as ordinary aliphatic alcohols. As mentioned earlier there are a large number of possible reactions that come under the category of "derivatisation" we will now deal with some of these reactions below.

1.3.1 Esterification

The esterification reaction of Guar gum is defined as the reaction of hydroxyl group of guar gum with an acid chloride a vigorous reaction at room temperature producing an ester and acid streams of hydrogen chloride. The esterification reactions of polysaccharides have been well documented, with the most number of reactions being carried out on starch and cellulose.

Given below are some esterification reactions involving starch Fatty acid esters of starch were prepared using starch and the relevant acid chloride in pyridine [18]. Use of the non- aqueous solvent media resulted in esterified starches with DS of 2.7. a succinic ester of starch was prepared by marcazzan etal[19] using a mixture of pyridine and Dimethyl sulphoxide as the reaction solvent system.

A change from the conventional solvents of the time was carried out by hylnianski who used a hybrid route for the esterification of starch by using both water and organic solvents [20]. The researchers first gelatinized starch in Hot water to fracture the granules and cause swelling, which result in the activation of the amylase and amylopectin making further reaction easier. To this solution of activated starch was added N, N dimethylacetamide at a rate slow enough to prevent deactivation of the starch through aggregation or precipitation. after this step the lower boiling water was distilled off resulting in an anhydrous dispersion of gelatinized starch in the organic solvent.

Other methods of activation of starch includes treatment with alkali, ammonia gas, formaldehyde pyridine, steam or boiling water after which the required reaction was carried out by using acetic acid vapours, [21] acetic anhydride [22] benzoyl and lauryl chloride [23] among other methods

A comparision can be drawn between starch and guar gum because they are both polysaccharides and a number of procedures that are used on starch can also succeed with guar gum. However they are not the same, The main differences arises due to their different solubilities in water. While guar gum is readly soluble even in cold water starch is only partially soluble in hot water. The correspondingly has an effect in the solvent solubility of guar gum as compared to starches. Another major difference between between the two is the fact that starch is not a single polysaccharide but in fact a mixture of two seperate polysaccharides i.e amylase and amylopectin. The following portion will focus on the preparation of guar gum esters.

Mohammed et al have reported the esterification of guar gum to result in a cross-linked guar gum, which was used as super –absorbent [24].the crosslinking agents specified in the patents are succinyl dichloride, pyromellitic dianhydride among other ether forming agents. The aim was to introduce crosslinking between the polymer chains leading to the formation of a three dimensional hydrophilic network.

Tranesterification of guar gum using methyl esters of fatty acids to result in partially esterified products, which were used a s fat substitute that ranged from waxes to oils was studied by white et al [25] These compounds were targeted for use in cooking as they had charaterstics similar to vegetable oils. A part from which, they also had a zero calorific value due to their low absorption and low degree of hydrolysis in the intestinal tract.

Guar gum formates were synthesized in this patent with a DS ranging from 0.1 to 3 [26] The application cited for the guar gum formates are as floccullating agents and as sizing agent in paper and textile industries. The method of synthesis was to bring into contact the guar gum with anhydrous concentrated sulfuric acid (97 %) though the reaction mixture could be diluted with water. It was found that DS was time dependent as well as being dependent on the concentration of formic acid.

In this study guar gum was benzoylated and the resultant compound used in the formulation of quaternized polysulphone blends [27].guar gum was dissolved in water an alkali added to the solution. To this solution benzoyl chloride was was added and the reaction allowed to proceed to completion. At the end of the reaction and the product was obtained as a precipitate and was soluble in dimethyl formamide with a Ds of 1.3.

The esterification of guar gum by the reaction of Guar gum with various anhydrides in acetic acid as the solvent was studiedfor the thermal stability of the ester products. [28]. The reaction mixture containing pyridine was refluxed at 120 ^{0} Celcius for 4 hrs to effect the esterification of guar gum using mixed anhydrides of acetic and butyric anhydride. Maleates and propionates were also prepared. It was observed that in the case of aliphatic anhydrides as the chain length of acid increases the reactivity towards the esterification of guar gum decreases. It was also observed that higher DS were obtained when dicarboxylic anhydrides were used as the reactants as compared to another anhydrides with the exception of maleated guar gum other esters resulted in derivatives with reduced thermal stability as well as increased thermal degradation rates.

1.3.2 Etherification

As opposed to esterification, etherification reactions involving guar gum are more common partially because of the large number of application in which the commercially established product, carboxy methyl guar gum was used. A part from carboxy methyl gaur gum alkoxylated guar gums are also extremely viable and have indeed been commercialized and are widely used. The following paragraph will further dwell on guar gum ethers

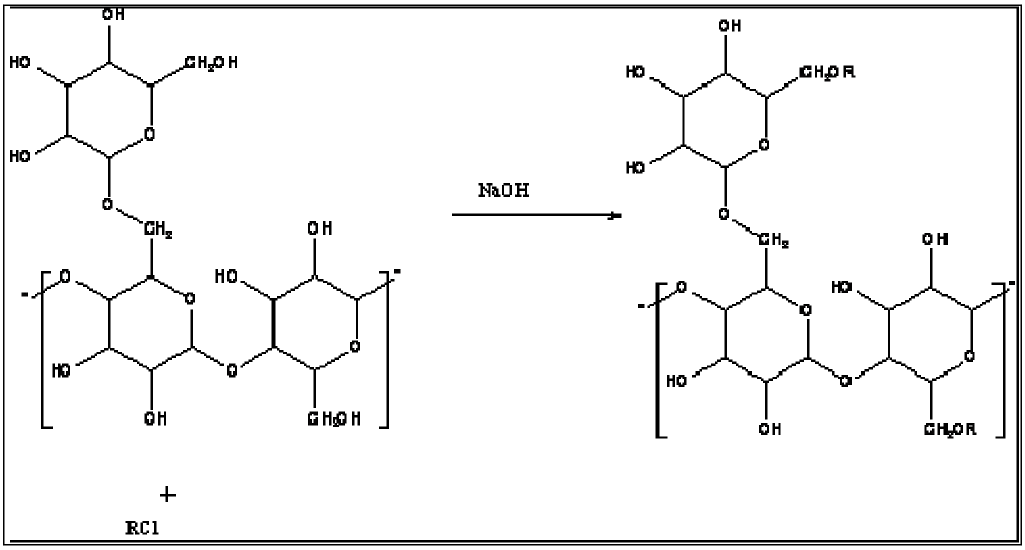


Fig 1.5 –Schematic representation of etherification of guar gum

In the preparation of an amphoteric guar gum derivative the guar gum was first reacted with epoxy ammonium salt in an isopropyl – water solvent system with sodium hydroxide as catalyst [29]. After the reaction between epoxy and guar gum was completed than the product was further reacted with monochloroacetic acid in the presense of sodium hydroxide to result in an amphoteic guar gum derivative. The study claims high DS substitutes were placed using this procedure.

Another cationic derivatives of guar gum were prepared by the reaction of guar gum with an epoxy ammonium chloride. [30] The difference between the procedure followed and the one discussed above is the reaction medium. In this case the reaction medium was a mixture of an alcohol viz isopropyl alcohol and water. The use of the alcohol suppresses the viscosity of the solution making the stirring of the reaction mixture easier. While at the same time allowing for hydration of the guar gum by water to allow for activation of all active reaction sites. The use of a combination of alcohol and water in the modification of guar gum has now become standard practice. This also make it easier to separate to products as well as reduces the drying of the separated products.

The etherification of guar gum by its reaction with an alkyl halide has also been well documented and patented[31]. The process involves the reaction of guar gum with allyl chloride in the presense of a water – isopropanol solvent mixture to effect etherification. Sodium hydroxide and quarternery ammonium salt, which act as a phase transfer catalyst. The end of the reaction the excess sodium hydroxide and the slurry separate and washed was neutralized with acetic acid and the slurryseperated and wased with a mixture isopropanol of water -isopropanol and finally with isopropanol. It was reported that the derivativised guar gum had increased stability to a wide range of pH which further

A patent filed by Gen Mills Inc. disclosed a procedure for the reaction of a quaternary ammonium compounds containing an epoxy group and guar gum resultingin quaternary ammonium ether of guar gum [32]. Thesecationic guar gum were sujjested for use in paper industry as water drainage aids as well as dry strength additives. They claimed a decrease in the drainage time of water from the paper slurry during its preparation as compared to conventionally used additives of the time. At the same time the additives were observed to increase the dry strength of paper.The reaction was carried out in a completely aqoueous medium in the presense of catalytic amount of alkali.

1.3.3 GRAFTING TECHNIQUES

Grafting Reactions

Grafting is a method where in monomers are covalently bonded (modified) onto the polymer chains.there are various techniques of graft copolymerization of different monomers on polymeric backbones. These Techniques include chemical radiation, photochemical plasma induced techniques and enzymatic grafting. The First part of the review discisses different techniques of grafting and ther primary factor which control the grafting grafting reaction is the addition of unsaturated compounds onto the guar gum molecule. The number of monomers, which can be grafted onto guar gum, make this a very useful reaction that leads to a variety of derivatised guar gum with varying properties.There are a number of parameters that influences the rate of reaction as well as the structure of grafted guar gums. Some of these parameters are the concentration of substrate, reactant, initiator, time of reaction and temperature. There are a number of initiators which are commonly used such as peroxides, persulphates and redox initiator pairs as well as more exotic initiation methods such as gamma radiation inducedgrafting and microwave mediated grafting reactions.

Chemical Modification of guar gum through graft copolymerization of vinyl monomer onto it is used for altering chemical and physical properties to give this natural polymer new application Vinyl graft copolymerization through chemical modification is an easier process than thermal Photochemical and other methods of initiation because activation energy for the redox initiation is comparatively low. Guar –grafted polymers have been prepared mostly by free radical initiated graft copolymerization

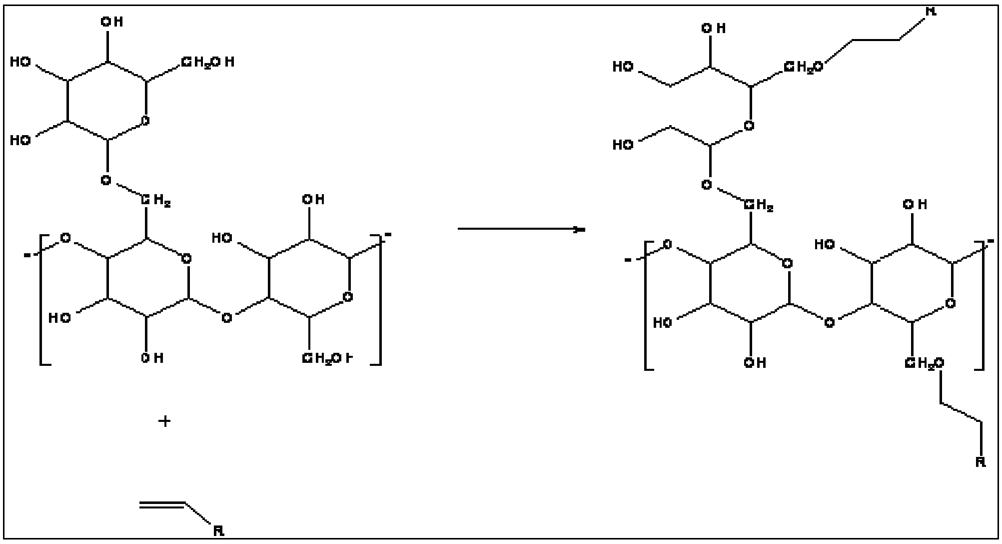


Fig 1.6 –Schematic representation of grafting of guar gum

1.3.4 Grafting initiated by chemical means

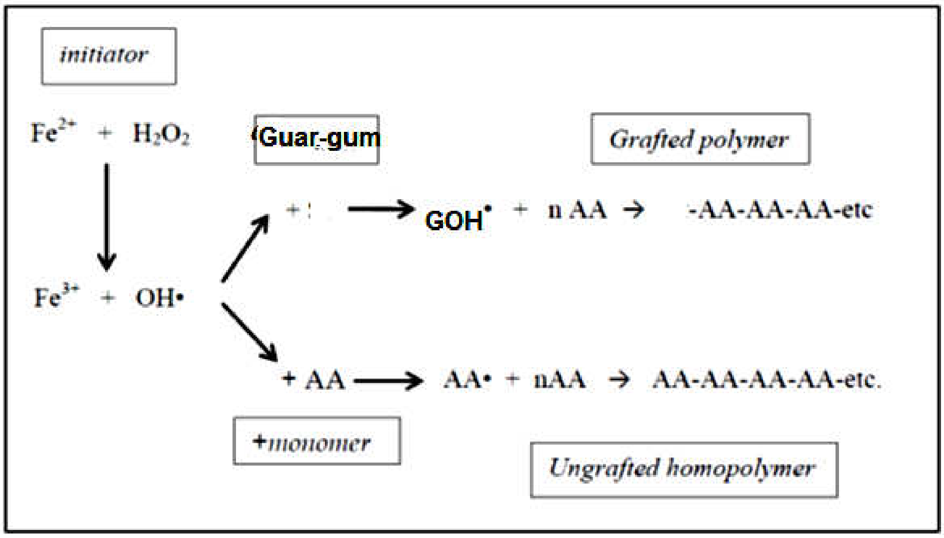
The chemical means of grafting includes two major paths first by free radical initiation and ionic method In the chemical process the role of initiator is very important as it determines the path of grafting process. In the chemical process free radical free radical are produced from the initiators and transferred to the substrates to react with monomers to form graft copolymers An example of free radical produced by indirect method is the production through redox reaction viz. M^{n+} / H_2O_2.persulphates.[32-37]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\cdot$$

$$Fe^{2+} + {}^-O_3S\text{-}OO\text{-}SO_3^- \rightarrow Fe^{3+}SO_4^{2-} + SO_4^{-\cdot}$$

It may be observed that the active species in the decomposition of H_2O_2 and Potassium persulphate induced by Fe^{2+} are $OH^{\cdot}$and $SO_4^{-\cdot}$ Some authors reported that initially formed SO4-. Initially reacts with water to form OH.subsequently producing free radicals on the polymer backbone :

$$SO_4^{-\cdot} + H_2O \rightarrow HSO_4^{-} + OH^{\cdot}$$



An alternate view is that SO_4^{-}. Reacts directly with the polymeric backbone eg (cellulose) to produce the requisite radicals

$$SO_4^{-\cdot} + R_{polymer}\text{-}OH \rightarrow HSO_4 + R_{polymer}\text{-}O^{\cdot}$$

However Mishra etal [38] established that during grafting of vinyl monomers onto wool/ cellulose OH. Is more reactive than SO4^{-}.similar electron transfer reaction may also occur when organic hydroperoxides, persulphates, Fe $^{3+}$, Cu $^{2+}$,are used in place of H_20_2 together with a reducing agent such as sodium bisulphite thiosulphate or Ag^{+}

$$\begin{aligned}
&S_2O_8^{=} + HSO_3^{-} \rightarrow SO_4^{=} + SO_4^{-\cdot} + HSO_3^{\cdot}\\
&\text{Polymer} + SO_4^{-\cdot} \rightarrow \text{Polymer}^{\cdot} + HSO_4^{-}\\
&SO_4^{-\cdot} + H_2O \rightarrow HSO_4^{-} + OH^{\cdot}\\
&HSO_3^{\cdot} + H_2O \rightarrow H_2SO_3 + OH^{\cdot}
\end{aligned}$$

Bajpei et al [39] reported peroxydisulphate –ascorbic acid initiated graft co-polymerization, In this case the reaction between peroxydisulphate –ascorbic acid initiated graft copolymerization. In this case the reaction between peroxydisulphate and ascorbic acid involves chain reaction catalyzed by Ag+, because of the production of sulphate ion radical, ahich are well known chain carriers.

$$\begin{array}{l}
AH^{\cdot} + S_2O_8^{--} \rightarrow A^{\cdot} + SO_4^{=} + SO_4^{-\cdot} + H^{+} \\
AH^{\cdot} + OH^{\cdot} \rightarrow A^{\cdot} + OH^{-} + H^{+} \rightarrow A^{\cdot} + H_2O \\
AH^{\cdot} + SO_4^{-\cdot} \rightarrow A^{\cdot} + SO_4^{=} + H^{+} \\
S_2O_8^{=} \rightarrow 2SO_4^{-\cdot} \\
S_2O_8^{=} + Ag^{+} \rightarrow SO_4^{=} + SO_4^{-\cdot} + Ag^{2+} \\
SO_4^{-\cdot} + H_2O \rightarrow SO_4^{=} + OH^{\cdot} + H^{+} \\
OH^{\cdot} + AH^{-} \rightarrow AH^{\cdot} + OH^{-}
\end{array}$$

Where AH refers to Ascorbic acid. It is apparent from the above that SO4-.or AH. may initiate graft copolymerization by Hydrogen Abstraction from a polymer chain, e.g from guar gum backbone. However for the latter, Bajpai [40] etal have proposed the generation of guar gum macroradical GO. By reaction a) below Since initiation of vinyl polymerization is faster than Hydrogen abstraction by primary radical:

$$\begin{array}{ll}
R^{\cdot} + M \rightarrow RM^{\cdot} & \\
RM^{\cdot} + M \rightarrow RMM^{\cdot} & \\
RM_{n-1}^{\cdot} + M \rightarrow RM_{n}^{\cdot} & \\
GOH + RM_{n}^{\cdot} \rightarrow GO^{\cdot} + R\text{-}M_{n}\text{-}H & \text{(a)} \\
GO^{\cdot} + M \rightarrow GOM^{\cdot} & \\
GOM^{\cdot} + nM \rightarrow GOM_{n}^{\cdot} & \\
GOM_{n}^{\cdot} + GOM_{n}^{\cdot} \rightarrow \text{graft co-polymer} &
\end{array}$$

Hydroperoxides and Fe^{2+} comprise another important redox system, with free radicals generated by the interaction between them via thermal decomoposition [41]. By analogy with Fentons reagent (Fe^{2+} - H_2O_2) the activity of tert butyl hydroperoxides TBHP and $Fe^{2+;}$

$$t\text{-BuOOH} + Fe^{2+} \rightarrow t\text{-BuO}^{\cdot} + OH^{-} + Fe^{3+}$$

The resulting t-BuO$^{\cdot}$May participate in hydrogen abstraction reaction to generate OH.and the macroradical on polymeric backbone by direct oxidation of the backbone by certain transition metal ions (e.g Ce $^{4+}$: Cr $^{6+}$, V $^{5+}$, Co 3+)The redox potential of the metal ions is the important parameter in determining the grafting efficiency. In general metal ions with low oxidation potential are preffred for better grafting efficiency . The proposed mechanism for such a process has been ascribed to the intermediate formation of a metal ion polymer chelate complex, viz ceric ion is known to form a complex with hydroxyl groups on a polymeric backbone.which can dissociate via one electron transfer to give free radicals.[42]

$$Ce^{4+} + R_{polym}OH \rightarrow \text{complex} \rightarrow R_{poly}O^{\cdot} + Ce^{3+} + H^{+}$$
$$R_{poly}O^{\cdot} + M \rightarrow R_{cell}OM^{\cdot} \rightarrow R_{poly}OMM^{\cdot}$$

Mno^{4-} dissolves in the acid medium to give rise to Mn^{3+} ion via Mn $^{4+}$. These Highly reactive Mn^{3+} ions are responsible for initiating graft – copolymerization and Homopolymerisation.

$$PH + Mn(III) \rightarrow PH\text{-}Mn(III)[COMPLEX]$$
$$PH + Mn(III) \rightarrow P^{\cdot} + Mn(II) + H^{+}$$
$$P^{\cdot} + M \rightarrow PM^{\cdot}$$
$$Mn(III) + M \rightarrow M^{\cdot} + Mn(II) + H^{+}$$
$$PM^{\cdot} + nM \rightarrow PM^{\cdot}_{n+1}$$
$$M^{\cdot} + nM \rightarrow M^{\cdot}_{n+1}$$
$$PM_{n+1} + Mn(III) \rightarrow PM_{n+1} + Mn(II) + H^{+}$$
$$P^{\cdot} + Mn(III) \rightarrow \text{oxidizedproduct} + Mn(II)$$

Where PH refers to polymer.

Guar gum possesses many advantages such as abundant sources low production costs and better biodegradability. Numerous experiments and industrial trials have demonstrated that chemical modification constitutes a powerfull means of improving guar gum servicibility. Increasing the grafting efficiency is an effective way of improving the properties of guar gum graft copolymer and reducing their preparation costs. However the graft copolymerization of guar gum with vinyl monomers is always accompanied by the homopolymerization of vinyl monomers as reactants. The Homopolymerisation is a side reaction of the copolymerization. It can be imagined that through the introduction of polymerisable double bond into guar gum molecule before graft copolymerization, the double bond can be incorporated into copolymeric chains when they meet propagating activated chain, . If a propagating activated chain that initiates homopolymerisation meet with the double bond, the original homopolymerisation will be converted into copolymerization[43]. Therefore some portion of homopolymer will become graft copolymers and the grafting efficiency can be enhanced correspondingly the grafting ratio will be correspondingly enhanced with the increase in the efficiency. It has been elucidated that hompolymers are inferior to the copolymers in servicibility [42]**.** As a result increasing the grafting efficiency enhances the serviceability of the products. On the other hand if the grafting ratio is similar, the enhancement of the grafting efficiency required the decreases the required amount of the monomers, and this reduces the production cost.

The grafting reaction of Vinyl monomer onto guar gum involves a number of steps. The first step in the sequence is the formation of hydroxyl radicals by reaction of Fe^{2+} with hydrogen peroxide This Hydroxyl radical reacts with guar gum to form a guar gum radical, subsequently reaction with acrylic acid results in the formation of acrylic grafts on the guar gum and allyl guar gum backbone, However the OH radical not only react guar gum but may serve as initiator for acrylic acid homopolymerization, Clearly conditions have to be selected in such a way to promote grafting of Guar gum and reduce the tendency for homopolymerisation clearly, conditions have to be selected in such a way to promote grafting on guar gum and reduce the tendency for homopolymerisation. This means that the GE and add on should be maximized.

Determination of the optimal reaction condition – In this section optimum condition can be determined based on the chemical reaction, desired product properties and economic considerations.In this study high graft efficiency shows that the reaction to generate the desired product has occurred while the formation of side product (homopolymer is suppressed. But if we focus on product proprerties related with their application, the amount of grafted polymer represented by add on is the most important response. The optimum condition here is determined based on the highest add on and GE that could be achieved with in the selected range of variables.

Grafting Parameters –

A. **Graft Efficiency (GE)** – In This equation grafted Poly Acrylic Acid is the amount of acrylic acid grafted onto guar gum and HP is the amount of Homopolymer of polyacrylic acid.graft efficiency expresses the selectivity of the main reaction with respect to the most important by Product homopolymer.

$$GraftingEfficiency = \frac{WtofgPAA}{WtofgPAA + WtofHP}$$

B. **Degree of graft copolymerization or add -on**

$$Addon = \frac{WtofgPAA}{WtofAGG - g - PAA} x\ 100\%$$

Where AGG –g-PAA is the amount of copolymer of starch grafted with acrylic acid. The parameter add on represents the yield of desired product. It is common to define it as the Fraction(%) total of desired product .

C. **Grafting Ratio (GR)** Grafted ratio is grafted polymer with respect to original amount of guar gum Since GR and add on are closely connected, it is better to use only

D. **Monomer Conversion**

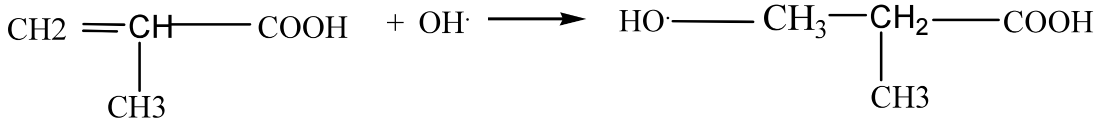
$$Conversion = \frac{wtofg - PAA + WtofHomopolymer}{WtofAAcharged} x\ 100\ \%$$

E. **Hompolymer (%H) = (100 - % E)**

Mechanism --

$Fe^{2+} + H_2O \longrightarrow OH^- + OH^{\cdot} + Fe^{3+}$

$XOH + OH^{\cdot} \longrightarrow XO^{\cdot} + H_2O$



$$CH_2=\underset{\displaystyle CH_3}{CH}-COOH + OH^{\cdot} \longrightarrow HO^{\cdot}-CH_3-\underset{\displaystyle CH_3}{CH_2}-COOH$$

Initiation

$XO^{\cdot} + M \longrightarrow XOM^{\cdot}$

$M + RM^{\cdot} \longrightarrow RM1^{\cdot}$

Propagation

$XOM_1{}^{\cdot} + M \longrightarrow XOM_2{}^{\cdot}$

$XOM_{n-1} + M \longrightarrow XOMn^{\cdot}$

$RM_1{}^{\cdot} + M \longrightarrow RM_2{}^{\cdot}$

$RM\,n\text{-}1^{\cdot} + M \longrightarrow RMn^{\cdot}$

Termination

$XOMn^{\cdot} + XOMn^{\cdot} \longrightarrow$ graft copolymer

$XOMn^{\cdot} + RMn^{\cdot} \longrightarrow$ graft copolymer

$RMn^{\cdot} + RMn. \longrightarrow$ Homopolymer

Scheme 1 & Scheme 2

Chemical Modification of guar gum through graft copolymerization of vinyl monomer onto it is used for altering chemical and physical properties to give this natural polymer new application Vinyl graft copolymerization through chemical modification is an easier process than thermal Photochemical and other methods of initiation because activation energy for the redox initiation is comparatively low. Guar –grafted polymers have been prepared mostly by free radical initiated graft copolymerization.

1.4 EPOXY- RESINS

Epoxy resins are another industrially important class of polymers characterized by the presence of more than one three membered heterocyclic ring known as the epoxy, epoxide, oxirane or ethoxyline group. There are compounds which contain only one epoxy group per molecule and these are not classified as epoxy resins athough they find application in epoxy resin chemistry as reactive diluents, viscosity modifier or adhesion promoters. Epoxies are one of the most versatile classes of polymers with diverse applications such as metal can coatings, automotive primer, printed circuit boards semiconductor encapsulants. Adhesiveand aerospace composites. Most cured epoxy resin provides amorphous thermosets with excellent mechanical strength and toughness; outstanding chemical, moisture and corrosion resistance ; good thermal adhesive and electrical properties ; no volatile emission and low shrinkage upon cure and dimensional stability – a unique combination of properties generally not found in any other plastic material. Commercial epoxy resins contain aliphatic, cycloaliphatic, or aromatic backbones and are available in a wide range of molecular weights from several Hundred to tens of Thousand. the most widely used epoxies are the glycidyl ether derivatives of bisphenolA. The capability of the highly strained epoxy to react with a wide variety of curing agents under diverse conditions and temperature imparts additional versatility to the epoxies.Themajor industrial utility of Epoxy resins is in thermosetting applications. The most common epoxy resins used industrially are liquid epoxy resin.Theyare low molecular weight resins. And Fig – illustrate the method of preparation of these epoxy resins.Epoxy resins essentially contain oxirane or epoxy ring (consisting of an oxygen atom bonded with two carbon atoms) in addition to pendent hydroxyl groups and other chemical moieties. Commercial epoxy resins contain aliphatic cycloaliphatic or aromatic backbones. A number of properties have led to rapid growth of epoxy resin and their use in wide range of industries. The most convenient product is bisphenol A used in all types of application due to excellent performance and relatively low price Its molecular weight can be controlled arbitrarily with in range of 350-10000. Generally the grades with molecular weights of less than 500 are available in solid form at room temperature. The solid form is often used as a solution product.

Considering the liquid resins, these are low viscosity liquids which readily convert to the thermoset phase upon the admixture of the proper curing agent. The liquid resins and their curing agent form low viscosity, easy to process systems There are other liquid resins, phenolics, polyesters acrylics, etc which cure in similar fashion but the epoxy resin possess rather a unique combination of properties. The major portion of these resins are derived from bisphenol –acetone and epichlorohydrin, The structure of Diglycidyl ether of bisphenol A (DGEBA, n-=o) is given in Fig -1.6

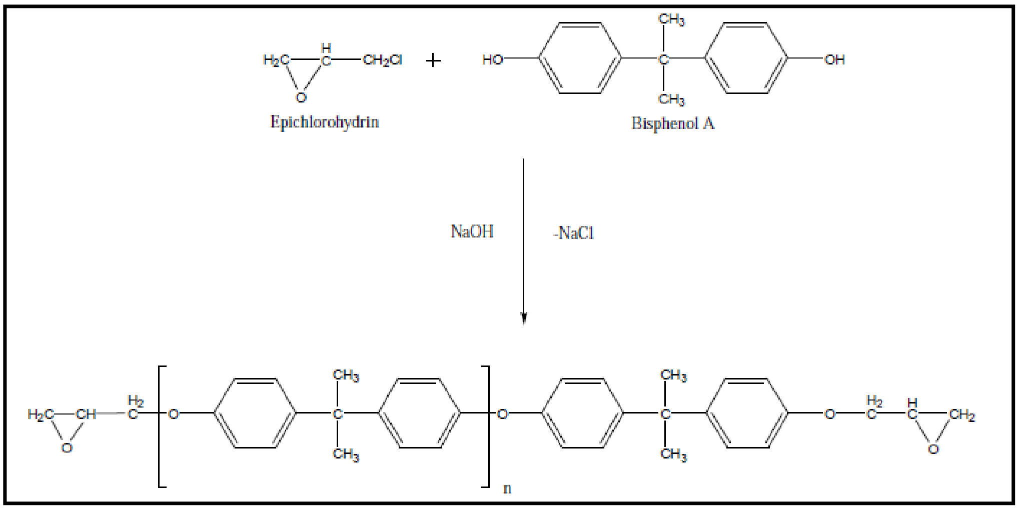


Fig 1.7 Schematic Represantation for Epoxy Synthesis

Bisphenol –A epichlorohydrin resins can be used for various applications and can be molded under various conditions, because their viscosity is low due to comparatively small molecular weight. Epoxy resin cure quickly and easily at practically any temperature from 5 to 150 ^{0} C depending on the selection of the curing agent. Epoxy resin show less curing shrinkage with better dimensional stability than condensation thermosetting resin such as phenolic resins, which evolve water reveal high shrinkage, as do the acrylic and polyester resins which must arrange and reorient considerably in the liquid and semi gelled phase. Epoxy resin react with very little arrangement and with no volatile by products being evolved presense of polar hydroxyls and ether groups, The epoxy resins are excellent adhesives. The resin cure with low shrinkage, so that the various surface contacts set up between the liquid epoxy resin formulations and adherants are not disturbed during cure. For the preparation of epoxy resins with different molecular weights and epoxy equivalent weights the ratio of epichlorohydrin to bisphenol A are varied the lower the ratio of epichlorohydrin to bisphenol A the higher is the molecular weight of the epoxy resin prepared as is shown in Table 1.1.There are a number of modifications which have been carried out on epoxy resins such as use of halogenated bisphenols, novolac based multi-functional epoxy resins are among a few.

Table 1.1 Effect of Epichlorohydrin –Bisphenol A Ratio on Resin properties of Taffy Solid Epoxy resin

Mole Ratio Epichlorohydrin :bisphenol	Epoxy equivalent weight	Softening Point ^{0} C
1.57:1	450-525	65-75
1.22:1	870-1025	95-105
1.15:1	1650-2050	125-135
1.10:1	2400-4000	145-155

Epoxy resins are cured through the reaction of the epoxy group, through high molecular weight epoxy resins also have a hydroxyl functionality that can be utilized in the cure process. The most important groups of co – reactive curing agents are those with active hydrogen atoms, eg primary and secondry amines, phenol, thiols and carboxylic acids. Lewis acids, eg, boron trihalides and lewis bases eg tertiary amines actsas curing catalysts. The choice of curing agent and the catalyst effects not only the cure kinetics which refer to the cure time, pot life,peak exotherm and other parameters but also greatly affect the properties of the cured polymer article. most epoxies are not used in the neat form. the addition of fillers, both organic and inorganic leads to the formation of epoxy composites, which result in changes in various mechanical, thermal electrical and chemical properties

1.4.1 Curing of epoxy resins

The most important groups of reactive curing agents are those with active hydrogen atoms. primary and secondry amines, phenol, thiols and carboxylic acids. Lewis acids, eg, boron trihalides and lewis bases eg tertiary amines act as curing catalysts. The choice of curing agent and the catalyst effects not only the cure kinetics which refer to the cure time, pot life,peak exotherm and other parameters but also greatly affect the properties of the cured polymer article. Primary and Secondry Amines. The number of amine hydrogen atoms present on the molecule determines the functionality of an amine. A primary amine group which has two hydrogens bound to it, will react with two epoxy groups While a Secondry amine will react with only one epoxy group. A Tertiary amine group which has no active Hydrogen will not react readily with epoxy group, but will act as a catalyst to accelerate epoxy reactions.

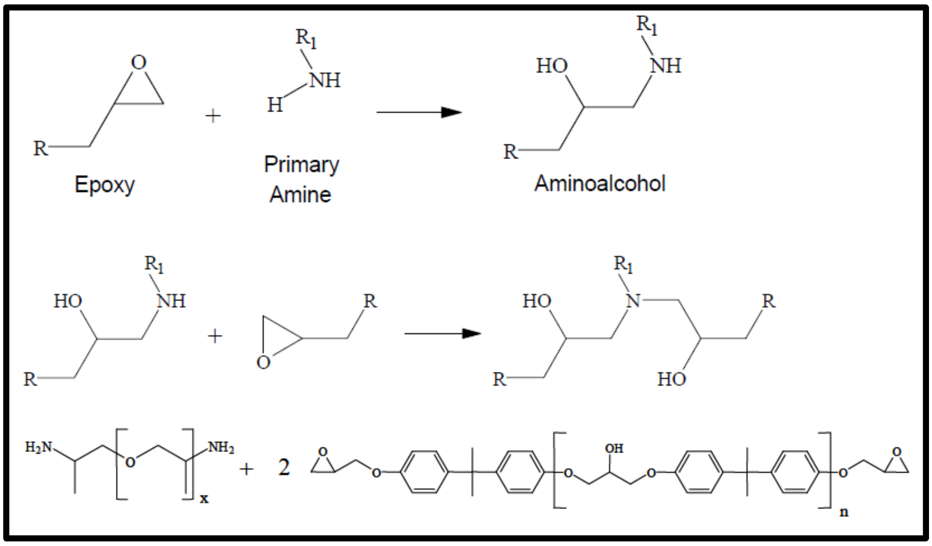


Fig -1.8 Schematic Representation of Curing reaction

1.4.2 Anhydride Hardening system

Numerous structurally different anhydrides can be used as epoxy curing agents Epoxy –anhydride systems exhibit low viscosity, long pot life, low exothermic heats of reaction and little shrinkage when cured at elevated temperatures. The cure system exhibits good mechanical and electrical properties and is used in filament wound epoxy pipe and electrical cadetting applications.anhydride cured formulations exhibit better thermal stabilities than similar amine cured systems. Anhydrides are the principal curing agent for cycloaliphatic and epoxidised olefin resins.Three types of anhydride may be recognized room temperature solids, room temperature liquids and chlorinated anhydrides e.g phthalic anhydrides, maleic anhydride and chlorendic anhydride. The anhydrides are usually used at ratio of 0.85:1.1 moles anhydride carboxyl group per epoxy equivalent [45], phthalic anhydride, tetra hydrophthalic anhydride and hexahydrophthalic anhydride are mostly used in resin polymerization. cycloaliphatic and epoxidised olefin resins react more rapidly with anhydrides than amines. but anhydride group does not react very readily with epoxide ring. thus in a simplified picture of non –catalyzed reaction, three steps can be distinguished as shown in fig – these steps are :

1) Opening of anhydride ring by hydroxyl group, yielding monocarboxylic ester

2) Reaction of carboxylic group of monocarboxylic ester with epoxide ring, formation of hydroxydiester

3) Reaction of hydroxyl group of hydroxydiester with anhydride ring, forming monocarboxylic ester and thus starts cascade of curing reactions.

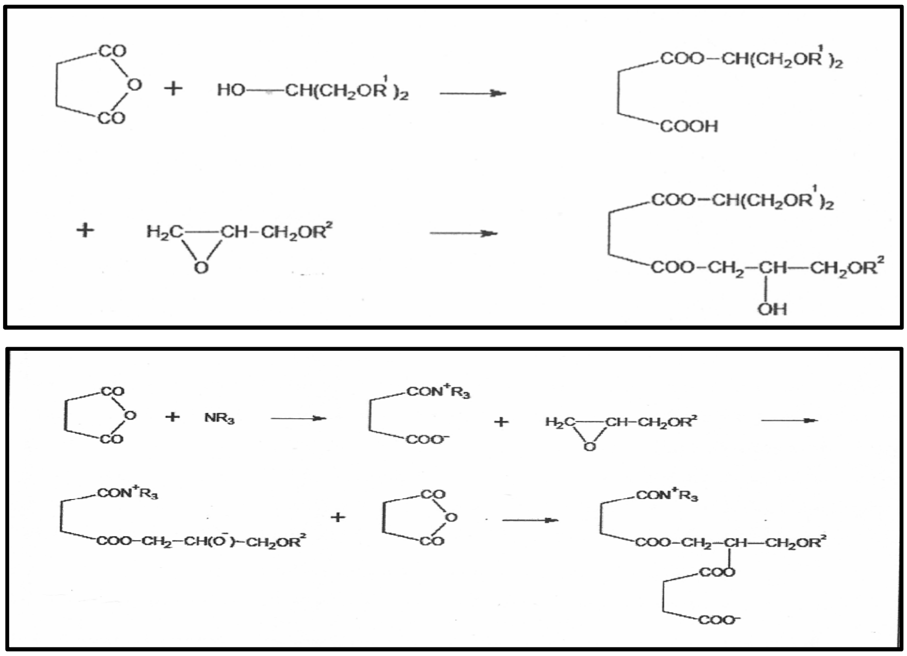


Fig – 1.9 Schematic reaction between anhydride and epoxy resin

1.5 TOUGHENING AGENTS AND FLEXIBLIZERS

Some cross-linked unmodified epoxy system exhibit brittleness,poor flexibility and low impact strength and fracture resistance. modifiers can be used to remedy these short comings. however, there usually will be some sacrifices of properties. In general there are two approaches used to modify epoxies to improve these features.

Flexiblization – Aliphatic diepoxide reactive diluents enhance the flexibility or elongation by providing chain segments with greater free rotation between crosslinks Polyaminoamide hardeners, based on aliphatic polyamines and dimerized fatty acids, perform similarly. liquid Polysulphide Polymers possessing terminal mercaptan functionality improve impact properties in conjuction with polyamine hardeners.

Flexible chain segments are incorporated in an epoxy resin by many means. One approach is the incorporation of oligomeric aliphatic polyesters containing carboxylic acid end –groups, forming an epoxy resin adduct . This is one of the reasons that epoxy –polyester powder coatings have become very popular. Flexiblization can enhance elongation of the system but is often accompanied by a reduction of glass – transition temperature, yield stress, and elastic modulus, other properties (eg thermal and chemical resistance, water absorption may also be affected. [46-48]

Toughening refers to the ability to increase resistance to failure under mechanical stress, Epoxies derive their modulus, chemical and thermal resistance properties from crosslink density and chain rigidity. Increasing crosslink density to meet higher thermal requirement (Tg) often comes at the expense of toughness

Elastomers such as carboxyl –terminated Poly(butadiene –co-acrylonitrile) (CTBN) have been popular toughener for epoxies. Toughening by elastomers can be attributed to the incorporation of a small amount of elastic material as a discrete phase of microscopic particles embedded in the continuous rigid resin matrix. The rubbery particle promote absorption of strain energy by interactions involving craze formation and shear deformation. Craze formation is promoted by 1-5 μM size and shear deformation by particles >0.5μm. System possessing both small and large particles i.e bimodal distribution, provide maximum toughness [48-50]. The rubber is incorporated in the epoxy resin in a ratio of 1:8 in the presense of an esterification catalyst. The Product is an epoxy ester capped with epoxy group. The adduct is then formulated with unmodified resin and cured with standard hardeners and accelerators. phase separation of the adduct occurs the curing process, resulting in the formation of segregated domains of elastomer –like particles covalently bound to the epoxy resin optimum particle size, and particle size distribution phase separation, phase separation and phase morphology are crucial for the development of desirable properties of the system. Other elastomer modified epoxies include epoxy terminated urethane prepolymers, epoxy terminated polysulphide, epoxy acrylated urethane and epoxidised polybutadiene. Preformed dispersions of epoxy –insoluble elastomers have been developed and reported to achieve toughening without tg reduction.

1.6 EPOXY –GUAR GUM COMPOSITES

Polyether amine was used as a curing agent because compared to other conventional curing agents, such as polyalkylene amine or aromatic amines, it would result in a more hydrophilic epoxy composites due to its ether linkages and thus offer greater compatibility to the filler, increasing the epoxy –filler interaction. The guar gum and its hydroxyl propyl derivatives were found to have varied particle shapes, ranging from irregular to fibrous [44]. It could be seen that the filler would behave as a reinforcing filler specially considering the fibrous component of the filler mixture These results indicate an increased compatibility i.e wetting of the HPG as compared to guar gum. In the present case the decrease in the crosslinking was probably caused by the increase in the viscosity of the composition. The substitution of GG resulted in an increase in the hydrophobic nature of the polysaccharide. This increase in the hydrophobic nature of the polysaccharide increased the compatibility or in other word the wetting of the polysaccharide surface by the epoxy polymer matrix. This translated to the increased tensile strengths of the HPG4 and HPG8 composites as compared to that of the epoxy-GG composites[44]. compared to GG which only showed a steady decrease. As in the case of the tensile properties the effect of HPG8 was more pronounced than that of HPG4, due to increased polymer matrix-filler interaction, both of which were greater than that of polymer matrix-GG interaction which was minimal resulting in the continual decrease of the flexural strength. Once again, as the concentration of the filler increased the properties decreased. The reasons for the decrease are the same as that for the trend observed in the tensile strength i.e. formation of agglomerates and a reduction in the crosslink density.

CHAPTER - 2

REVIEW OF LITERATURE

This Chapter Provides a Background about the work done on Guar gum, its method of modification and Epoxy based composites.

Adhikary P et al [51] have synthesized the graft copolymers of carboxymethylguargum and polyacrylamide using ceric ion induced / solution polymerization technique. The obtained graft copolymer charactrise through FTIR, NMR and intrinsic viscosity measurement, Scanning Electron Microscope, SLS, DTG, and Rheology. The Researcher observed that graft copolymer exhibit better flocculation performance than Carboxy methyl guar gum.

Alamri et al [52] have Prepared recycled cellulose fibre reinforced epoxy composites with fibre loading of 19, 28,,40 and 46 wt %. The effect of water absorption on mechanical & Physical Properties of RCF/ Epoxy composites was investigated. The value of max water uptake and Diffusion coefficient were found to increase with an in fibre content. The results showed that flexural strength, modulus and fracture toughness decreased as a result of moisture absorption. However the impact strength was found to increase slightly after water absorption.XRD, FTIR, and SEM studies were carried out to evaluate the composition and microstructure of RCF and RCF / Epoxy composites

A.M.Amreo et al [**53**]etal have investigated the effect of corrosive environment on glass /epoxy composites and its effect on material properties including flexural and impact strength of glass fibre epoxy composite after immersion in hydrochloric Acid and sodium hydroxide were analysed. This study reveals that alkaline solution promotes higher decrease of the flexural and impact properties than the acid solution

A.B Ben saleh et al [54] have premixed carbonyl terminated butadiene acrylonitrile copolymer (liquid rubber) and cured with a diamine curing agent (IPD) for one hour at 100 ^{0} C and postcured at 110 ^{0} C for two Hrs in an air oven. The compatibility, reactivity, thermal mechanical and morphological properties were determined. The gel time and cure time were increased with an increase of the CTBN content. The gel and cure temperature values for all of the CTBN modified epoxy samples are higher than those of the unmodified epoxy and a decrease with an increase in CTBN content. The gel and cure temperature values for all of the CTBN modified epoxy samples are higher than those of the unmodified epoxy and decrease with an increase in CTBN content, conversely an increase in thetensile strain with the incorporation of CTBN was observed. The results showed an improvent of fracture toughness of the epoxy with the presense of CTBN. The toughening effect become more apparent as the testing speed was increased from 1 to 500 mm min^{-1}. The fracture surface analysis by scanning electron microscopy (SEM) discovered the presense of a two phase morphology.

Abdel Halim E S et al [55] et al have prepared strong reducing and stabilizing agent for green synthesis of silver nanoparticles through grafting of acrylamide onto guar - gum. The gaur gum/ polyacrylamide graft copolymer have been prepared in the presenceof Potassium bromate / thiourea as initiation system. The researcher also collected U V Visible spectra of nanosilver prepared using polyacrylamide, guar gum and guar gum –g- PAM. It was observed that Guar gum –g- Polyacrylamide showed high improvement in absorption intensity at 45 min andpaek acquired ideal bell shape. It means that the reduction power got higher and no decrease in peak intensity was noticed after 60 min. which means that graft copolymer has better stabilization efficiency than each individual component alone.

Bajpai et al [57]reported the the graft copolymerization of polyacrylonitrile onto guar gum using potassium peersulphate / Ascorbic acid as the redox initiator in the presense of atmospheric oxygen at a temp of 35 ^{0} C. Who also relates the mechanism with the experimental results obtained. The researcher also studied the water and saline retention Properrties of the grafted guar gum and compared with the ungrafted guar gum.

Bajpai et al [56] have studied the grafting of polyacrylamide onto guar gum and the parameters influencing the reaction of potassium persulfate/ascorbic acid initiated grafting of polyacrylamide onto guar gum.A free radical is generated onto guar gum which react with the monomer to form a graft copolymer. Graft copolymerization can therefore be carried out at relatively low temp producing high yield of graft copolymer. At low temperature the possibility of side reaction is also negligible. Graft copolymer are usually characterized by three parameters,percent add on the (the amount of synthetic polymer in the graft copolymer, average mol weight of the grafted chain and grafting frequency . They have also studied the kinetics of the grafting, reaction of polyacrylamide onto guar gum initiated by potassium bromate–thiomalic acid **[58]** other studies involving the grafting of acrylamide on guar gum include those carried out by Bajpai etal using copper sulphate– sodium thiosulphate **[59].**The use of Potassium permagnate–oxalic acid as redox initiator system was also investigated **[60].**

B R Nayak and R P Singh et al [61] described the synthesis of Guar gum–g–Poly acrylamide and HPG–g-Polyacrylamide. The researcher also studied the flocculationcharacterstics of graft polymer in different suspension Kaoline, iron ore and silica suspension. The result shows that Guar gum exhibit better performance than HPG in all three suspension in case of base polymer and for the graft copolymer HPG–g–PAM shows better performance and it is also compared with various commercially available Flocculants.

Chowdary et al [62] reported the detailed study on the grafting of methylmethacrylate (MMA) onto guar gum. The researcher also studied the various factors affecting the grafting efficiency, including the concentration of MMA. CAS, Dextrose moiety and Guar gum, temperature and times. The obtained graft copolymer were characterized by FTIR and TGA. The biodegradability of the resulted copolymer were also studied.

B R Nayak et al [63] have reported the synthesis and characterization of ceric ammonium nitrate initiated graft copolymerization of polyacrylamide onto hydroxypropyl guar gum by solution polymerization technique The researcher optimized the product with different monomer and catalyst concentration. It was observred that the percentage of grafting increases with increasing catalyst concentration and decreases with monomer concentration

Duanmu et al [64] have synthesized Allyl glycidyl ether modified starch for use to prepare a new family of crosslinked composites. Allyl glycidyl ether derivative of starch with different degree of substituition under various reaction condition including different sodium hydroxide and AGE concentration reaction temperature and times.The degree of substituition of the modified starch was analysed by ^{1} NMR and FTIR. The premixes of allylglycidyl ether modified starch wood fibres and EGDA were cured in a hot press using 2% w/w of benzoyl peroxide at 150 °Cunder high pressure condition.The researcher reported that high degree of substituition exhibited good processibility and was easily processed for the highest fibre content. The gel content and the possible extractable reagents in the cured sample were performed by extraction with high boiling solvents in soxhlet apparatus

D J D melo et al [67] investigating the application of Guar gum and hydroxyl propyl guar gum as fillers in polymer composite. The inclusion of guar gum and hydroxypropyl guar gum resulted in an increase in the tensile, flexural and impact strength of the composites. while reducing the water acid and alkali resistance. The researcher also investigate that hydroxyl propyl guar gum resulted in an increase in properties as compared to guar gum.which was due to increased polymer filler interaction due to the increase in hydrophobic character brought about by propoxylation. The biodegradability of the composite was also studied and it was found that there was a marker increase in biodegradability on inclusion of the filler as compared to unfilled epoxy.

D J D Melo et al [66] have used guar gum and hydroxypropyl as a filler in Unsaturated polyester resins. This study shows that composite based on hydroxypropyl guar gum showed the best overall tensile tensile and flexural properties.This was attributed to the increase in hydrophobic nature of the filler resulting in an increase in polymer filler interaction.

D J D melo et al [65] have synthesized the acrylated guar gum and the reaction parameter were optimized with refrence to the effect of reaction time with degree of substituition.the derivatives were characterized for their physical chemical and thermal properties. the structure of the derivatives were elucidated by using FTIR and C^{13} NMR spectroscopy. The acrylated guar gum derivative were also incorporated in unsaturated polyester resin, where it was observed that the tensile strength, water and toluene resistance of the composite increases.However the elongation at break and impact strength of the composite were found to decrease with the increase in Degree of substituition. Thus the incorporation of acrylated guar gum in unsaturated polyester composites resulted in an overall increase in mechanical and chemical properties.

D J D Melo [68] The effect of acetylation of guar gum and hydroxypropyl guar gum on the filler properties in an unsaturated polyester composite was studied. It was observed that at high acetyl content the composite showed reduced mechanical and chemical performance. This was attributed to the reduction in cohesion of the particle themselves reduced the tensile and flexural properties of the composites as the acetyl content of the filler increased.

Dai et al [69] It was found that thermotropic hydroxyethyl cellulose acetate was completely soluble in uncured epoxy resin and it was found that the miscibility was uninfluenced by the degree of substituition of the hydroxyethyl cellulose acetate .The hydroxyethyl cellulose form a heterogenous composite on curing. The epoxy composites were found to have increased toughness and the impact strength greatly increased with those at 10 Phr cellulose derivative showing the maximum impact strength. when the epoxy resin was cured at the temperature where cellulose derivative existed in its liquid crystalline state it resulted in the toughest composites. The degree of substituition with refrence to the acetylation was found to greatly influence the toughness and the impact strength of the composites

GODI G et al [70] have synthesized and characterized carboxymethylated guar gum. The reaction condition including the concentration of sodium hydroxide, weight of chloroaceticacid and reaction temperature were optimized. The resulting product were characterizedby NMR FTIR spectroscopy and Thermogravimetric analysis. This carboxymethylated guar gum may provide an efficient alternative approach for the oral delivery of hydrophilic macromolecules

Gassan et al [71] The surface morphology of natural fibres was studied along with their interaction with epoxy resin jute fibres were corona treated and modified with an organic silane and were studied with dynamic contact angle, capillary rise, inverse gas chromatography and resin uptake. The corona treatment was observed to increase the polarity of the jute fibres also lead to increased interaction with the polymer matrix. These results provided a method for standardization of the dynamic contact angle and the cappilary rise methods which could than be used to evaluate other cellulose fibres for their interaction with epoxy resins.

Han et al [72] The synthesis and characterization of glycidyl methacrylate grafted sago starch for use as reactive component in epoxy resin was investigated. The grafting of glycidyl methacylate onto sago starch was carried out in aqueous medium using a ceric ion initiator system. It was observed that an increase in the glycidyl methacrylate concentration increased the degree of grafting. A core shell structure was proposed explain the hydrophobic nature of the grafted polymer. The grafting of glycidyl methacrylate onto the starch backbone was confirmed by FTIR spectroscopy. The grafted stach with its free epoxy group was than incorporated in a U-V radiation cure coating composition and and it was found that the inclusion of this component increased the flexibility of the resultant coating. It was further observed that an increase in the concentration of the grafted starch increased the hardness of coatings. The gel content of the coatings were seen to be unaffected by the addition of this reactive component and an increase in the photoinitiator concentration increased the hardness of the coatings at the expense of its flexibility. The bioegradibility of the composites was also studied.

Hag dorn et al [73] The reaction mixture containing pyridine was refluxed at 120 ^{0}C for 4 hrs to effect the esterification of guar gum using mixed anhydrides of acetic and butyric anhydride. Maleates and propionates were also prepared. It was observed that in the case of aliphatic anhydrides as the chain length of acid increases the reactivity towards the esterification of guar gum decreases. It was also observed that higher DS were obtained when dicarboxylic anhydrides were used as the reactants as compared to another anhydrides with the exception of maleated guar gum other esters resulted in derivatives with reduced thermal stability as well as increased thermal degradation rates

Huang et al [74] In this study guar gum was benzoylated and the resultant compound used in the formulation of quaternized polysulphone blends. Guar gum was dissolved in water an alkali added to the solution. To this solution benzoyl chloride was added and the reaction allowed to proceed to completion. At the end of the reaction and the product was obtained as a precipitate and was soluble in dimethyl formamide with a DS of 1.3.

H.Kumar et al [75] have reported the characterization of Polyurethane /polymethyl methacrylate Semi IPN prepared by insitu polymerization and filled with different (wt %) Guar gum. The composites were characterized for density, tensile strength and percent elongation at break, Positron annihilation life time measurement have been carried out to measure the free volume of these composites. The result obtained show good correlation between free volume content of the composites with the mechanical properties. These natural polymer- filled composites were subjected to biodegradation using a specific microorganisms, A Niger. This study shows a clear indication about the degradation of PU/PMMA system

Kokol et al [76] In this study guar gum was reacted with monocloroacetic acid to result in the formation of carboxymethyl guar gum, which was than used as thickening agent in printing pastes using reactive dyes. This study included the investigation of the of the interaction between the derivatised guar gum and the surfactant, an ethylene oxide condensate with varying length of side chainsas well the effect of the concentration of surfactant on the viscosity behavior of the printing paste. The effect of DS of the derivatised guar gum was also studied with reference to the rheological character of the paste as well as the printing efficiency.

Kumar Rajesh et al [77] have reported the graft copolymerization of methacrlic acid onto Xanthum gum by using Fenton's reagent as redox initiator. The reaseacher investigated the effect of reaction condition on grafting grafting parameter and on increasing the concentration of Ferrous ion and Hydrogen peroxide pair was investigated. The optimum Temperature and time duration of reaction for max percentage grafting were found to be 45 ^{0} C.and 150 min respectively. TGA results shows that Xanthan Guar gum is thermally more stable than pure guar gum.

Lokhande et al [78] have investigated the effect of the reaction conditions of gamma radiation induced grafting of acrylonitrile on guar gum. As in the case of microwave mediated grafting gamma radiation grafting too did not require the use of a free radical generating species or a redox initiation system

Lapasin et al [79] have studied the rheological properties of Hydroxyethyl guar gum. In the study the rheological behavior of hydroxyethyl guar gum in this study the rheological behavior of the guar gum derivative was investigated under oscillatory and continuousshear flow conditions. The cross type model was found to apply to the rheology data as obtained from both methods. The study focuses on the effect of concentration of hydroxyethyl guargum, temperature and molecular weight on the zero shear viscosity as well as the characteristictimes of the compositions

Lapasin et al [80] have studied flow properties of hydroxypropyl guar gum and their long chain hydrophobic derivatives. The study dealt with the solution behavior at continousshear flow condition. The hydroxypropyl guar gum was synthesized by the alkaline etherification of guar gum using propylene oxide.The preparation of the long chain fatty acid derivative were carried out by the reaction of the hydroxypropyl guar gum with the respective long chain fatty epoxides. The rheological behavior of the solutions was studied with respect to the effect of temperature and concentration.

Low et al [81] have studied the mechanical and fracture mechanics of cellulose fibre reinforced epoxy laminates. The reserarchers analysed the effect of cellulose fibre mats on the elastic modulus, hardness, flexural strength, fracture toughness indentation responses impact –fracture crack growth resistance and insitu fracture of the resultant epoxy laminates were evaluated. The reinforcement of the laminates by the inclusion of the cellulose fibre mats resulted in an increase in the strain at break, indentation creep, frature toughness and impact toughness. On the other hand there was only a moderate increase in the flexural strength and flexural modulus of the composites. The micro –mechanics of crack initiatiation were identified which lead to the design and application of new ecofriendly composites.

Liang Li et al [82] have analysed the water sorption behaviour of six epoxy system with different chemical structure of amine and epoxies at five temperature ranging from 35^{0}C to 75^{0}C by different techniques, including gravimetric measurements, positron anhilation life spectroscopy (PALS) and attenuated total reflection fourier transform infrared spectroscopy (ATR –IR).

Mottershead et al [83] The deformation micromechanics of cellulose – epoxy and cellulose polyester composites were studied. Two model theories were used in the study, namely droplet –fibre and thin flat film geometries were used to predict the properties of composites.each system consisted of single fibre traveling through a polymer matrix. The mechanical properties of the fibre in the polymer matrix were analysed and and used to predict their potential as reinforcing agents. Raman spectroscopy was used to map the stress generated at the fibre – polymer interface and thus characterized the composition by comparing results obtained with those predicted by the models it was found that the thin flat film fibre model was more reliable than the droplet fibre model

Naidoo et al [84] have investigated the grafting of polyacrylonitrile initiated by cerric ammonium nitrate at ambient temperature. The researcher also studied the various parameters affecting the rate of reaction as well as the grafting efficiency

Prabhanjan et al [85] have investigated the synthesis of hydroxyethyl, hydroxypropyl as well as carboxymethyl guar gum. The effect of variation of experimental condition on the DS as well as the molecular integrity of the substrate has been studied. The moisture regain, rate of hydration, solubility viscosity and rheology of these derivatives was also studied. It was found that the properties depended on the polysaccharide chain length as well as on the nature and degree of substituition.

Prabhanjan et al [**86**] have investigated the foaming properties of a hydroxypropyl guar gum as compared to that of unmodified guar gum. The study included the effect of DS on the foam stability as well as maximum foam height. It was observed that the foam was found to be most stable and the mostfoam formed when the DS of hydroxypropyl guar gum was the highest.This was explained due to the surfactant nature of the derivative due to the formation of derivatives with greater MS than the DS.

Patel et al [87] The esterification of guar gum by the reaction of Guar gum with various anhydrides in acetic acid as the solvent was studied for the thermal stability of the ester products. The reaction mixture containing pyridine was refluxed at 120 ^{0} C for 4 hrs to effect the esterification of guar gum using mixed anhydrides of acetic and butyric anhydride. Maleates and propionates were also prepared. It was observed that in the case of aliphatic anhydrides as the chain length of acid increases the reactivity towards the esterification of guar gum decreases. It was also observed that higher DS were obtained when dicarboxylic anhydrides were used as the reactants as compared to other anhydrides .with the exception of maleated guar gum other esters resulted in derivatives with reduced thermal stability as well as increased thermal degradation rates.

Raval et al and mehrotra et al [88] reported the graft co-polymerization of vinyl monomers like acrylonitrile, methyl methacrylate, acrylamide, styrene and acrylic acid using Hydrogen peroxide as the initiator.

Methacrylamide was grafted onto guar gum and the grafting parameters studied with refrence to the the grafting efficiency. The redox initiator pair in this case was potassium chromate – malonic acid. The researchers also investigated the efficiency of peroxy diphosphate – silver nitrate combination on the grafting of acylic acid onto guar gum. [58]

Singh et al [89] studied the microwave mediated grafting of polyacrylonitrile on guar gum in the in the absence of a free radical generating species or catalyst. The advantage cited in the use of microwave mediated grafting was the reduced reaction times.

Sharmaetal [90] have synthesized the graft copolymer of N vinyl -2-Pyrolidine onto guar gum.The reaction condition including nature and amount of solvent, change in concentration of monomer and, initiator, reaction time and temperature were optimized for grafting. The obtained graft copolymer were characterized by FTIR, SEM, XRD, Thermal analysis and swelling studies.

Srivastava Abhishek et al [91] reported the graft copolymerization of 4 vinyl pyridine onto guar gum using potassium peroxymonosulphate/Ascorbic acid as redox pair initiator in aqueous medium under nitrogen atmosphere. the reasearcher also investigated that reaction parameters including grafting ratio, grafting efficiency and add on were increased on increasing the concentration of Potassium peroxi ammonium sulphate from 5x10 $^{-4}$ to 10x 10 $^{-4}$ mol/L and ascorbic acid concentration from 0.4x10-3 to 2x 10^{-3} mol/L on increasing the hydrogen ion concentration from 2.5x 10^{-3} to 10x 10^{-3} mol/L.The researcher obtained max grafting when guar gum and monomer concentration were 1gm/L and 20x 10^{-2} ml/L respy. An increase in Temperature from 30 t0 35 ^{0} C increased the grafting ratio but conversion and homopolymer decreases. The graft copolymer were characterized by IR spectroscopy and thermogravimetric analysis.

Singh et al [92] have reported the synthesis of guar gum –g-Polystyrene with cerium (lV) ion in nitric acid medium. The researcher obtained different samples of guar gum –g – Polystyrene by varying the amount of styrene vinyl monomer. The rheological properties of guar gum –g – polystyrene copolymer have been studied by varying the degree of grafting, time, concentration, temperature, spindle number and shear rate. The obtained guar gum –g- Polystyrene samples were characterized by thermogravimetric analysis (TGA) and Fourier Transform infrared spectroscopy (FTIR).

Srivastava Aarti et al [93] have synthesised the graft copolymerization of N vinyl 2-Pyrolidone with guar gum by using potassium peroxymonosulfate (PMS) and glycolic acid (GA) as redox initiator. The researcher also studied the effect of PMS, GA, hydrogen ion, guar gum and N vinyl Pyrollidone (NVP) along with reaction time & temperature were studied by determining the grafting parameter, grafting ratio, efficiency, conversion, add on, homopolymer and rate of grafting. The max yield was optimised at a time of 120min anda temp of 45 ^{0} C at a guar gum concentration of 0.4 g/l. This study includes the calculation of activation energy for grafted and ungrafted gum.The obtained graft copolymer were characterized by Infrared spectroscopy and Thermal analysis.The swelling and metal ion sorption behavior of guar gum and guargum –g-N –vinyl 2 Pyrollidone were also studied.

Sharma et al [94] have carried out a method of Carbamoylethylation by reaction of acrylamide with guar gum in the presence of sodium hydroxide in water as the reaction medium. Afterthe reaction was completed the reaction mixture was neutralized with acetic acid and the product precipitated in ethanol. The optimization of the reaction time and condition was of paramount importance as the hydrolysis of the amide group by the alkali lead to the formation of a carboxyethyl guar gum. The researchers have characterized the various reaction parameters with referenceto the DS as well hydrolysis of the amide. This process has opened a new route to the formation of carbamoylethylation as well as carboxymethylated guar gum.

Singh et al [95] have studied the methylation of guar gum mediated by microwave using dimethyl sulphate. The reaction was carried out using dimethyl sulphate as the methylating agent in the presence of sodium hydroxide and was driven forward solely by microwave energy. The obtained methylated product were than hydrolysed by formic acid followed by sulphuric acid also under microwave power. These products were than separated, identified and characterized. The method outlined by the researchers have an advantage that the solvent used for both the substrate as well as the reagents is water and the reaction time is extremely low with high conversion rates of 60 % after 4 minutes of microwave irradiation.

Singh et al [96] have prepared cationic guar gum by using with (N (3 chloro -2 Hydroxy propyl trimethyl ammonium chloride (CHPTAC) and sodium Hydroxide in the presence of water at room temperature. The cationic guar gum has been characterized by elemental analysis, FTIR spectroscopy, intrinsic viscosity measurement Molecular weight determination, Thermal analysis and X-ray diffraction analysis. This modified naturally occurring polysaccharide can be developed, which used to be as High performance flocullating agent and viscosifier.

Shih etal [97] have synthesized the composites comprising bamboo husk fibres as the reinforcing agent and these composites were evaluated for their mechanical and thermal properties. The bamboo husk fibres were chemicall modified before incorporation in the epoxy matrix by the use of coupling agents. The use of bamboo fibres without the use of any coupling agent. The use of bamboo husk fibres without the use of any coupling agent was also carried out. The morphology mechanical and thermal properties of the composites were evaluated. The fibres were found to give similar properties as those of cellulose fibres. The morphology revealed that the fibre – matrix adhesion was increased with the use of coupling agent as compared to that of the unmodified fibres. The thermal properties of the composites were found to have increased with the addition of bamboo fibre husk.the improvement was due to the char formation on ignition which protected the polymer matrix from further thermal degradation to a certain extent, increasing its thermal properties. The glass transition of the epoxy matrix was also seen to be affected showing an increase by 8-18 ^{0} c by the addition of the fibres.

Stefan opera [98] have prepared multicrosslinked polyurethane composite films with different content of guar gum (1-10 wt %) were prepared through a solution casting method followed by a Thermal treatment or natural light crosslinking Procedure.The effect of guar gum content on the miscibility, morphology & physical properties of the blend films was investigated by fourier transform Infrared Spectroscopy, SEM, TGA, surface Properties & tensile tests. The result reveals that small guar gum content is well embedded in the crosslinked polyurethane network and form film with good mechanical properties, thermal behaviour and hydrophilic properties. These result prove guar gum to be ecofriendly filler for multicrosslinked polyurethane networks.

Seong Ok han [99] have synthesized a hydrophilic polymer matrices based on carboxylic functionalized glucose (glucose maleic acid ester vinyl resin) and epoxy resins and the effect of water absorption were studied as a function of curing temperature. The matrix cured at higher temperature shows compact crosslinks due to the higher concentration of ether bonds comparing to the matrix cured at the lower temperature. The polymer matrices cured at different temperature were immersed in water at room temperature for 1000 hrs and the Thermomechanical properties of the cured polymer were characterized using DMA &TGA. The researcher were identified two types of sorbed water. Type 1 sorbed water contributed mainly to increasing the weight and to the decrease in Tg due to plasticizer effect. Type I sorbed water was not removed after the polymer to 110 ^{0}C for an hour. Type II sorbed water cause changes in the mechanical properties of the polymers cured at different temperature depending on the crosslinks of the matrix. The cure matrix at the higher temperature has the comapritevily tight crosslinks in the network structure and the sorbed water disturbed the polymer network resulting in the degradation of the matrix such as microcracks.

T T Reddy et al [100] have studied the thermal and microwave mediated free radical degradation of guar gum. In this study the effect of free radical on the molecular stability of guar gum under the influence of thermal and microwave mediated using either potassium persulphate and hydrogen peroxide. The reaction medium for the degradation of the polymer was isopropanol and water. It was observed that the potassium persulphate degraded guar gum more efficiently than hydrogen peroxide and microwave irradiation was more efficient than thermal reaction. the infrared spectra reveals that there was no oxidative degradation and the molecular weight of the polymer was reduced with no change to its chemical make up than this method could be described as depolymerisation reaction.

Thiebaud et al [101] have prepared fatty acid esters of starch by using starch and the relevant acid chloride in pyridine. Use of non- aqueous solvent media resulted in esterified starches with DS of 2.7. Other methods of activation of starch includes treatment with alkali, ammonia gas, formaldehyde pyridine, steam or boiling water after which the required reaction was carried out by using acetic acid vapours, acetic anhydride benzoyl and lauryl chloride among other methods.

Trapasso et al [102] have synthesized Guar gum formates with a DS ranging from 0.1 to 3. The application cited for the guar gum formates are as floccullating agents and as sizing agent in paper and textile industries. The method of synthesis was to bring into contact the guar gum with anhydrous concentrated formic acid (97 %), though the reaction mixture could be diluted with water. It was found that DS was time dependent as well as being dependent on the concentration of formic acid.

Taunk Kavita et al [103] have reported the graft copolymerization of acrylic acid (AA) onto guar gum was carried out by Peroxydiphosphate (PDP) – Silver (I) system. The researcher Found that the grafting parameter including grafting ratio, efficiency add on and conversion increase upon increasing the concentration of PDP and Acrylic acid and decreases upon increasing the concentration of guar gum.The researcher also obserbed that on increasing the Temperature from 30 to 45 ^{0} C increases the grafting ratio but the conversion efficiency decreases. The optimum time period for graft copolymerization was found to be 2 Hrs. The graft copolymer were characterized by Infrared spectroscopy and thermogravimetric analysis.

Taunk and Bihari et al [104] have reported the synthesis of 4 Vinyl pyridine –g-guar gum and the grafting parameters studied with refrence to the grafting efficiency. [16] The redox initiator pair in this case was potassium monopersulphate and thioacetamide. The researcher also optimized time temp and the concentration of potassium monopersulphate and thioacetamide for highest grafting ratio and efficiency. The study included the thermal stability of guar gum and guar gum –g-4 vinyl pyridine.

Jaswani Tripathi et al [105] have reported the synthesis of partially carboxymethylated guar gum –g- 4 vinyl pyridine and the reaction condition were optimized using bromate and Thiourea redox pair under an inert atmosphere at 40 ^{0} C. The Researcher found that the grafting parameter increase on increasing the concentration (from 4 –vinyl Pyridine from 13 x10^{-2} to 25x 10 $^{-2}$ mol/dm^{-3} and Bro_3 from 4x 10^{-3} to 10x 10^{-3} mol/dm-3 and thiourea from 1.6x 10^{-3} to 4.8x 10^{-3} mol/dm^{-3} The optimum temperature and time for grafting of of 4 vinyl pyridine on partially carboxy methylated guar gum were found to be 40 ^{0} C and 120 min respectively. The metal ion uptake and flocculation behaviour shows that graft copolymer have better performance than substrate. The swelling behavior of graft copolymer has also been investigated.The graft copolymer were characterized by FTIR and thermal analysis.

Trivedi et al [106] have reported the graft copolymerization of Methyl Methacrylate (MMA) onto sodium salt of partially carboxy methyl guar-gum (DS=0.497) with ceeric ammonium Nitrate as initiator in an aqueous medium. The Researcher also optimized the reaction condition affording the max Percentage of grafting of MMA onto Na -PCMGG through the variation of the concentration of nitric acid, ceric ammonium nitrate, MMA and Na -PCMGG and the temperature and time. The effect of these parameters on grafting yield and the rate of polymersiation, graft copolymerization and homopolymerisation were studied. The graft copolymner sample was characterized by IR, TGA, DSC amd SEM.

Tripathi et al [107] have prepared a blend to increase the toughness of cycloaliphatic epoxy resin by using carboxyl terminated butadiene acrylonitrile copolymer (CTBN). The thermal and morphological properties were studied with Diffrential Scanning Calorimetry (DSC), Thermogravimetric analysis (TGA), Dynamic Mechanical analysis (DMA) and Scanning Electron Microscope (SEM) techniques. The resultant composites have lower storage modulus with increasing rubber concentration and its thermal stability as well as lower mass loss was observed with increasing rubber concentration.

Varma et al [108] have used starch, cellulose and their dialdehydes as fillers and accelerators in tertiary amine catalysed curing of epoxy resins were evaluated in this study **[109]**. The gel time of epoxy composition containing varying concentration of water cellulose starch and their aldehydes were estimated at 120 ^{0} c Using triethyl amine and hexamethylene tetaramine as catalyst. it was observed that moderately oxidized starches resulted in reduced gel times but on further oxidation the starches reduced the gel time of the epoxy resins. The gel time of the native starch epoxy composites showed the highest gel time. This incaed a short of synergism between the gel time and the oxidation of the starch at approximately 50 %. The difference between the curing times when triethyl amine and hexamethylene triamine on the curing was explained due to the degradation of the hexamethylene tetramine into formaldehyde and ammonia and ammonium derivative. These degradation products resulted in the formation of intermolecular and intermolecular acetals and hemiacetals, which affected the crystallinity and the availability of the hydroxyl group on the starches, which had an impact on the curing time of epoxy resins.

Varma et al [110] have studied the curing characterstics of cellulose periodate oxidised cellulose, chromic acid cellulose and ethylene glycol at 120 ^{0} C using hexamethylene tetramine. The gel time and the Brook field viscosities of these compositions were also evaluated. It was observed that the hydroxyl groups acted as accelerators for the catalyst system. A part from accelerating the curing reaction there was also evidence to show that these cellulose particles took part in the crosslinking reaction itself. The gel time of the filled systems were found to decrease with an increase in the filler concentration. Correlation were arrived at to equate the various gel times with the concentration levels of the cellulose and the oxidized cellulose. these differences were explained on the basis of the variation of the hydroxyl content of the cellulose and the oxidized cellulose on the acceleration of curing reaction. It was also concluded that the oxidized cellulose material showed a greater participation in the epoxy network formation reaction as compared to plain unoxidised cellulose.

Valeria D. Ramos et al [111] prepared composites by using Epoxy resin, Carboxyl terminated butadiene acrylonitrile copolymer (CTBN) and hydroxyl terminated polybutadiene (HTPB) in different proportions A chemical link between the epoxy resin and the HTPB was promoted employing tolylene diisocyanate (TDI). The reaction between elastomer and epoxy resin were followed by FTIR. The mechanical properties of the composites were evaluated and and the microstructure was investigated through scanning electron microscopy. The results showed that the impact resistance of CTBN modified epoxy resin was superior to that of pure Epoxy resin. For the composites with HTPB the impct resistance wer increased with elastomer concentration upto three parts per hundred parts of resin (phr). Highest concentration of HTPB resulted in larger particles and gave lower impact values.

Wembo wang et al [112] have synthesized superabsorbent composites. A series of novel guar gum –g- Poly (sodium acrylate –co styrene mucosvite superabsorbent composites were preapered by free radical grafting copolymerisation of natural guar gum.

J M. Raquez et al [113] have presented a review about the synthesis, properties and application of thermosetting material derived from renewable resources. The researcher also describes the potential oppurtunities and drawbacks concerning the use of renewable feedstock in the design of some commonly used networks such as phenolics, epoxy, polyester and polyurethane resins. The utilization of renewable resources were found as a novel and appropriate sustainable feed stock rather than as substitute for petroleum –based thermosetting materials.

Yadav Mithilesh et al [114] have reported the synthesis of partially hydrolysed graft copolymer (H-Cmg OH-g-MA) and the reaction condition were optimized by varying the concentration of methacrylic acid (from 8x 10^{-2} to 24x 10^{-2} mol/dm^{-3}) Potassium Peroxy monosulphate (from 0.4x10^{-2} to 2x10^{-2} mol/dm^{-3}), silver nitrate from (1.2 to

4.4x 10^{-3} mol/dm^{-3}) hydrogen ion from (1x10^{-3} to 9x 10^{-3} mol/dm^{-3}) and partially carboxy methylated guar gum (from 0.4 to 1.88gm/dm^{-3} along with N N Methylene bisacrylamide (3x10^{-3} to 7x 10^{-3} mol/dm^{-3}). The optimized temp and time of reaction were found to be 40^{0}C and 120 min respectively.The graft copolymer was charcterized by FTIRand Thermogravimetric analysis. The effect of Methacrylic acid and NN methylene bisacrylamide concentration on swelling ratio for partially hydrolysed graft copolymer was investigated in water.

Zhifenzhu et al [42] In another study graft copolymer of granular allyl starch with carboxyl containing vinyl monomers using H_20_2 / Fe^{2+} Initiator was studied for enhancing the grafting efficiency of the copolymerization.Variables such as molar ratio of Fe^{2+} to H_20_2, initiator concentration, monomer concentration, polymerization Temperature, and the time of graft copolymerization were also studied.it was found that allyl etherification enhanced the grafting efficiency and grafting ratio evidently .

Zhifeng zhu etal [41] have reported the allyl pretreatment of starch for use to enhance the grafting efficiency of the copolymerization of granular starch with acrylic acid and to improve the properties of starch –g-Poly acrylic acid use as warp sizing agent. The graft copolymerization was carried out in an aqueous dispersion with ferrous ammonium sulphate and hydrogen peroxide as initiators. This study included the relation of Degree of substituition of allyl starch with properties of film such as fibre adhesion and film behaviour. The results shows that after the introduction of allyl group into starch the grafting efficiency and properties of the copolymer were improved.

CHAPTER - 3
EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

3.1 Experimental Details

The present chapter presents a view point about the use of various chemicals and materials followed by an outlay for the Guar gum modification by derivatisation and grafting. Although a number of techniques have been reported in the literature for the Derivatisation and grafting but because of simpler experimental conditions and more pronounced and economic method in industrial view point.The reason for adopting only this method is the shorter reaction time and simplicity of the method. The samples were analysed by using following technique.

- Titrametry
- Fourier Transform Infrared (FTIR) spectroscopy
- Nuclear Magnetic Resonance Spectroscopy (NMR)
- Scanning Electron Microscopy (SEM)
- Thermogravimetric analysis (TGA)
- Dynamic Mechanical Analysis (DMA)
- X-ray Diffraction (X-RD)

3.1.1 Preperation of allyl guar gum

The Process involves the reaction of Guar gum by its reaction with allyl chloride in the presense of water –isopropanol solvent mixture to effect etherification for this the guar gum flour was dispersed to form a isopropyl alcohol solution in a three necked clean round bottom flask 1 litre maintained at 40 ^{0} C and purged with nitrogen after 1 hr predetermined amount of 50% (w/v)aq solution of sodium hydroxide and a quaternary ammonium salt (phase transfer agent) tetra methyl ammonium chloride was added to the slurry and the mixture was stirred and heated to a temperature of 50 ^{0} C.The reaction was heated to 8 hrs. The reaction mixture was cooled gradually dispersed in acetone and the excess of alkali is neutralized with glacial accetic acid bringing the pH to 7. The product than finally washed with acetone and than dried under vaccum and characterized by FTIR, TGA, XRD and SEM techniques.

Table -3.1 Properties of Allylated guar gum

Sample Name	**Volume(ml) (NaoH)**	**Wt (gms) (Allylchloride)**	**Temperature ^{0}C**	**Time (Hrs)**	**Degree of Substituition (DS)**
AGG	**7**	**6.846**	**50**	**4**	**0.0389**
AGG1			**50**	**8**	**0.0625**
AGG2			**50**	**12**	**0.0545**

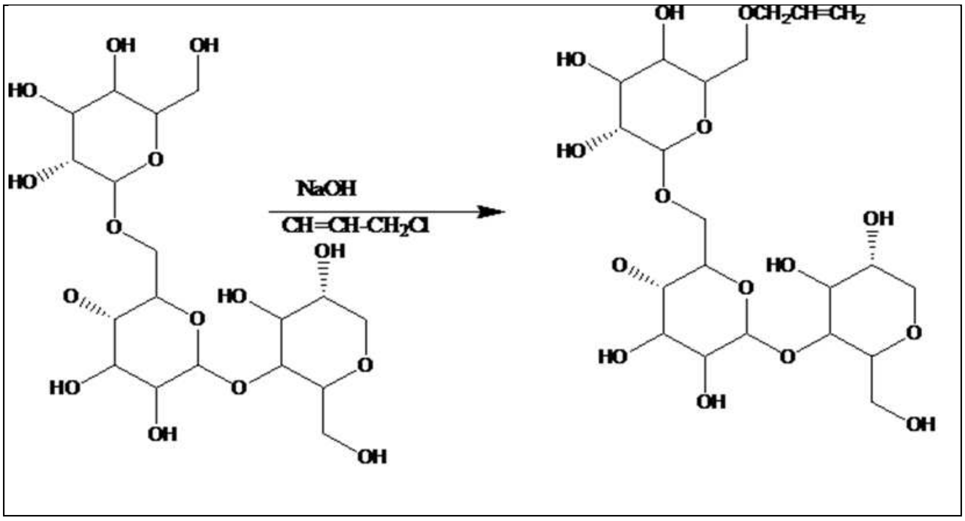


Fig-3.1 – Schematic reaction of Allyl Guar gum

3.1.2 Synthesis of Allyl guar gum –g-poly acrylic acid

Guar gum or allyl guar gum 10 gm is mixed with aqueous solution of isopropanol and the mixture was adjusted to Ph 3-4 with dilute sulphuric acid. A 1% solution of Ferrous ammonium sulphate solution and 1.6% solution Hydrogen peroxide solution were used as initiator solutions. The molar ratio [(H_2O_2/ $FeSO_4$ $(NH_4)_2$ SO_4 / Anhydroglucose unit of guar gum was 14/1/1000 after nitrogen gas was charged into the flask for 30 min. Acrylic acid and the initiator solution were added continuously so that uniform solution is obtained. The graft copolymerization was carried out under vigorous stirring and under the protection of nitrogen for 3 Hrs. The product was neutralised to Ph 6-7 filtered washed thoroughly with distilled water dried at 50 ^{0}C, Pulverized and sieved with 100 mesh size.

Table -3.2 Properties of Allyl Guar gum –g – Acrylic Acid

Polymer	**Degree of substitution of Allyl guar gum**	**Amount of FAS (mol) x 10^{-3}**	**Amount of H_2O_2 mol x 10^{-3}**	**% Conversion**	**% carboxyl value**
AGG-g-PAA 1	**0.0389**	**0.04**	**0.56**	**65**	**0.033**
AGG-g-PAA2	**0.0625**	**0.04**	**0.56**	**58**	**0.019**

Influence of the pretreatment on graft copolymerization when the weight ratio of monomer to allyl guar gum was 10 %, $H^+ = 2.5X10^{-3}$ mol/dm^{-3}, Polymerization time = 240 min, wt ratio monomer / allyl guar gum = 1:10 Polymerization temperature = 35 ^{0} C, Wt ratio of allyl guar gum / Liquor -4:6

3.1.3 Epoxy-Allyl guar gum Composites

The Epoxy composites were prepared by casting Technique. Once the fillers Allyl guar gum DS 0.0389, 0.0625 were dispersed in the epoxy resin. The filler were dispersed on phr basis i.e 0.5 phr would refer to 0.5 gm of filler present in 100gm of resin and stoichiometric amount of curing agent, polyetheramine D230, was added and the composition mixed thoroughly. The formulation was then de-aerated and poured into in a preheated metal mold at 60 ^{0} C. The cure cycle adopted for the preparation of the Epoxy composites was 60 ^{0} C / 4 Hrs. The composites had a thickness of 3mm +1%. The composites were cut into the respective shapes for testing and the edges were uniformly ground to remove imperfections, which could lead to errors in the test results. Prior to testing the samples were allowed to stabilize at 50 % humidity and at 30 ^{0} C for 7 days.

3.1.4 Epoxy – Allyl guar gum –g- poly acrylic acid composites

The Epoxy composites were prepared by casting technique. Once the fillers Allyl guar gum-g –poly acrylic acid 0.0675, 0.09843 were dispersed in the epoxy resin. The filler were dispersed on weight % basis i.e 0.5 wt % would refer to 0.5 gm of filler present in 100gm of resin and stoichiometric amount of curing agent, polyetheramine D230, was added and the composition mixed thoroughly. The formulation was then de-aerated and poured into in a preheated metal mold at 60 ^{0} C. The cure cycle adopted for the preparation of the Epoxy composites was 60 ^{0} C / 4 Hrs and post curing for 1Hr at 120 ^{0} C The composites had a thickness of 3mm +1%. The composites were cut into the respective shapes for testing and the edges were uniformly ground to remove imperfections, which could lead to errors in the test results.prior to testing the samples were allowed to stabilize at 50 % humidity and at 30 ^{0} C for 7 days.

3.2 RAW MATERIALS

The Following Raw Materials were used for the modification of guar gum as well as the analysis and testing of the products and composites

Guar Gum- Guar gum was obtained from M/s Dabur india Ltd, India it was used after washing with ethanol to remove any alcohol soluble impurities followed by acetone to remove moisture. After the washing with acetone the guar gum was kept in a dessicator prior to use.Allyl chloride –The allyl chloride was obtained from Merck chemicals, India and were used without purification. Acrylic acid - Acrylic acid was obtained from M/s CDH chemicals, India and were used without purification. Epoxy resin (DGEBA) (DER 331) The epoxy resin was diglycidyl ether of bisphenol (DGEBA) and was obtained from Dow chemicals. it was used without any further purification and had an epoxy equivalent of 180-190 mgKOH /gm of sample. Polyetheramine (D 230) – The Polyether amine was obtained from M/s BASF Ltd, India and was based on a propylene oxide adduct. the polyether amine had a molecular weight of 230 and an amine value of 470-480mg KOH/g.

Miscellaneous chemicals – Solvents such as acetone, methyl ethyl ketone, toluene was obtained from M/s Merck India Ltd and sodium hydroxide, ferrous ammonium sulpate and hydrogen peroxide were of Laboratory grade doubly distilled water was used for all experiments. Analytical reagents and indicator were obtained from Qualigens fine chemicals India.

3.3 CHARACTERIZATION TECHNIQUES

3.3.1 Titrimetry

Carboxyl value - The amount of Acrylic acid grafted onto guar gum molecules was measured by the titration of carboxyl in PAA branches. Sodium carboxyl in grafted branches was initially converted into carboxyl acid with a dilute HNO_3 solution. Then, an excessive sodium hydroxide standard solution was added to neutralize the carboxyl acid. Finally, the residual sodium hydroxide was titrated with a hydrochloric acid standard solution.

One gm dried acidified Guar gum sample is weighed precisely and added into a 250mL conical flask. Then 100mL water and 20mL sodium hydroxide standard solution (0.1mol/L) are added into the flask. The mixture is stirred and heated to boil for 15-30min. Thereafter, 0.05 mol/L of hydrochloric acid standard solution is used to titrate the excessive sodium hydroxide. The titration can not be stopped until the solution appears pink for 30s. Then the volume of the hydrochloric acid standard solution consumed is recorded and the blank experiment is carried out.The titration should be repeated at least 3 times in order to obtain the average value.[116-117]

$B=M*A$

$A=(V_1C_1-V_2C_2)/m$

B: The weight of PAA that 1g grafted guar gum contains (mg);

M: Molecular weight of AA (g/mol);

A: The mole number of sodium hydroxide consumed in neutralizing 1g acidified guar gum (mmol)

V_1: The volume of sodium hydroxide standard solution added (mL)

V_2: The volume of hydrochloric acid standard solution consumed for titrating the excessive sodium hydroxide standard solution (mL)

C_1: The concentration of sodium hydroxide standard solution (mol/L);

C_2: The concentration of hydrochloric acid standard solution (mol/L);

m: The weight of the acidified guar gum used for measurement (g)

Degree of substitution of Allyl guar gum-Where x% is the bromine Value, V1 (ml) and V2 (ml) are the volume of standard sodium hyposulphite solution consumed in blank and sample titration, respectively, C (mol/ L) is the concentration of the sodium hyposulfite solution, and W(gm) is the dry weight of the Guar- gum sample [41]

$$DS = \frac{162x}{79.9(2 - 0.5006x)}$$

$$X = \frac{(V1 - V2) \times C \times 0.079 \times 100}{W}$$

3.3.2 Spectroscopic studies

Fourier Transform Infrared (FTIR) Spectroscopy- Infrared red spectroscopy refers broadly to that part of electromagnetic spectrum between the visible and microwave regions. The absorption of Infra- red radiations (quantised) causes the various band in a molecule to stretch and bend with respect to one another.

The infrared spectrum of the electromagnetic spectrum extends from 2.5μ to 15 μ. The region from 0.8μ to 2.5 μ is called Near Infra-red and that from 15 μto 200 μ is called far infrared –red region. The region of most intrest for chemical analysis I 4000cm^{-1} to 666 cm^{-1} in which molecular vibration can be detected and measured in an Infrared spectrum.

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam. which changes in wavelength over time or by using a Fourier transform instrument to measure all wavelength at once.

The early –stage IR instrument is of the dispersive type in which the infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. The dispersive instrument is characterstic of a slow scanning. In Fourier transform infrared (FTIR) spectroscopy instead of recording the amount of energy absorbed when the frequency of the infra-red light is varied (monochromator) ; the IR light is guided through an interferometer fig. After passing through the sample, the measured signal is the interferogram. This measures all of infrared frequiencies simultaneously. Performing a fourier transform on this signal data results in a spectrum identical to that from conventional (dispersive) infrared Spectroscopy.

Fourier Transform infrared spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "Fingerprint". This refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. The FTIR spectra are usually presented as plots of intensity versus wavenumber (in Cm^{-1}) wavenumber is the reciprocal of the wavelength. The intensity can be plotted as the percentage of light transmittance or absorbance at each wavenumber. Consequently a Transmittance spectrum is obtained as follows.

$$\boxed{\%\ \textbf{Transmittance} = I/I0}$$

Where % T is transmittance; I is the intensity with a sample in the beam (from the sample single beam spectrum); Io is the intensity measured from the background spectrum. The absorbance spectrum can be calculated from the transmittance spectrum using the following equatioin.

$$\boxed{A = -\log_{10} T}$$

Where A is the absorbance For all the prepared samples, infrared spectra's has been recorded on FTIR spectrophotometer model NICOLET 380 between4000cm-^{1} to 400 cm^{-1}at 4 resolution with each scans. IR spectra were recorded by using KBr pellet technique. For all the prepared samples, infrared spectra's has been recorded on FTIR spectrophotometer model NICOLET 380 between 400 cm-^{1}4000 cm^{-1} at 4 resolution with each scans. IR spectra were recorded by using KBr pellet technique.

Fig 3.2 Fourier Transform Infrared Spectrometer (FTIR) (Nicolet 380)

Nuclear Magnetic resonance (NMR) Spectroscopy - Nuclear Magnetic resonance (NMR) Spectroscopy is a most effective and significant method for observing the structure and dynamics of polymer chains both in solution and in the solid state[119-125]. Undoutedly the widest application of NMR spectroscopy is in the field of structure determination.The identification of certain atom, or groups in a molecule as well as their position relative to each other can be obtained ny One Two and three-dimensional NMR. The time scale involved in NMR measurements make it possible to study certain rate processes, including chemical reaction rates other applications are isomerism, internal relaxation conformational analysis and tautomerism. NMR spectroscopy is the study of molecules by recording the interaction of radiofrequency (Rf) electromagnetic radiation with the nuclei of molecule placed in a strong magnetic field. which is governed by characterstics of the sample. it is a form of absorption spectroscopy and concerns radio frequency rf – induced transition between quantized energy state of nuclei that have been oriented by magnetic fields.Absorption is a fuction of certain nuclei in the molecules. A plot of frequencies of absorption peak versus peak intensities constitutes an NMR spectrum several non mathetical and mathematical introduction to NMR are recommended.

Like all other spectroscopic Techniques, NMR spectroscopy involves the interaction of the material being examined with electromagnetc radiation. The simplest example of electromagnetic is a ray of light.which occurs in the visible region of the electromagnetic spectrum and has wavelength of 380-780 nm. each ray of light can be thought of as a sine wave.However this wave can can actually be considerd to be made of two mutually perpendicular waves that are exactly in phase with each other i. e. they both pass through their maxima and minima at exactly the same point of time. One of these two perpendicular waves represents an oscillatory electric field (E) in one plane.while the second wave, oscillating in a plane perpendicular to the first wave represents an oscillating magnetic field B.

3.3.3 Thermal Properties

Diffrential Scanning Calorimetry– DSC is an ideal tool for use in polymer characterization such as parameters including melting point, glass transition temperature (Tg),Polymerization temperature, thermal degradation and oxidation reactions can be studied rapidly and conveniently The temperature below, which a polymer is hard and above which it is soft called glass transition temperature (Tg). Diffrential Scanning Calorimetry measures the diffrences in energy inputs into a substance and a referencematerial as they are subjected to a controlled temperatureprogram, because practically all physical and chemical process involves change in enthalpy or specific heat [126]. Fig 4 depicts the DSC instrument and its block diagram.

Sample Preparationfor DSC Measurement: 5 to 10 mg samples, encapsulated in Hermetically sealed aluminiumpan have been prepared for each sample. each run was performed under nitrogen atmosphere.

Parameters Analyzed:

- Rate of Change of enthalpy
- Melting Temperature, Tm is taken at maximum of endothermic peak from the second Heating cycle.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a technique to determine the weight loss of sample, while heating it at programmed heating rate. In the dynamic mode the weight loss or rate of weight loss is measured as a function of programmed rate of increase in temperature.Thermogram of DGEBA/Allyl Guar gum blends provide the information related to the degradation behavior of the material.

Onset Temperature or the temperature of inception or reaction corresponds to the first detectable temperature at which the degradation of material starts.Maximum decomposition temperature or inflection temperature corresponds to temperature at which the maximum weight loss is observed Final decomposition reaction or end temperature after which no weight loss or minor weight loss is observed. The onset Temperature generally represents the stability of the material It is also recognized that anhydrides are better curing agent than amines.

Dynamic Mechanical Analysis

In Dynamic Mechanical analysis (DMA) the sample is subjected to a periodically varying stress (usually sinusoidal of angular frequency w) The response of the sample to this treatment can provide information on the stiffness of the material (quantified by its elastic moduli) and its ability to dissipate energy (measured by its damping).For a viscoelastic material, the strain resulting from the periodic stress will also be periodic

Fig 3.3 Thermogravimetry (TGA) Instrument

but will be out of phase with the applied stress owing to energy dispersion as heat, or damping, in the sample. D is the phase angle between stress and strain. Viscoelastic polymers have the charactersics in between where some phase lag will occur during DMA tests. The equation derived are [127,128]

Stress:S = So sin ($\dot{\omega}$t+ δ)

Strain E= Eo sin ($\dot{\omega}$t)

Where $\dot{\omega}$ is the perod of strain oscillation, t is time, and d is phase lag between stress and strain. The Storage modulus measures the stored energy, representing the elastic portion, and the loss modulus measures the energy dissipated as heat, representing the viscous portion. The Tensile storage and loss moduli are defined as follows.

Storage Modulus E'= $\frac{\sigma 0}{\varepsilon}\cos\delta$

Loss Modulus E"=$\frac{\sigma 0}{\varepsilon}\sin\delta$

Phase angle, tan (δ)= E''/E'

The Storage modulus E' represents the stiffness of a viscoelastic material and is proportional to the energy stored during a loading cycle.

The loss modulus E'' is defined as being proportional to the energy dissipated during one loading cycle. it represents, for example energy lost as heat, and is a measure of vibrational energy that has been converted during vibration and that cannot be recoverd. Modulus values are expressed in MPa, but N/mm^2 is some times used. The phase angle is the difference between the dynamic stress and the dynamic strain in viscoelastic material subjected to a sinusoidal oscillation. The phase angle δ is expressed in radians.

Storage Modulus E'= $\frac{\sigma 0}{\varepsilon}\cos\delta$

Loss Modulus E"=$\frac{\sigma 0}{\varepsilon}\sin\delta$

Phase angle, tan (δ)= E''/E'

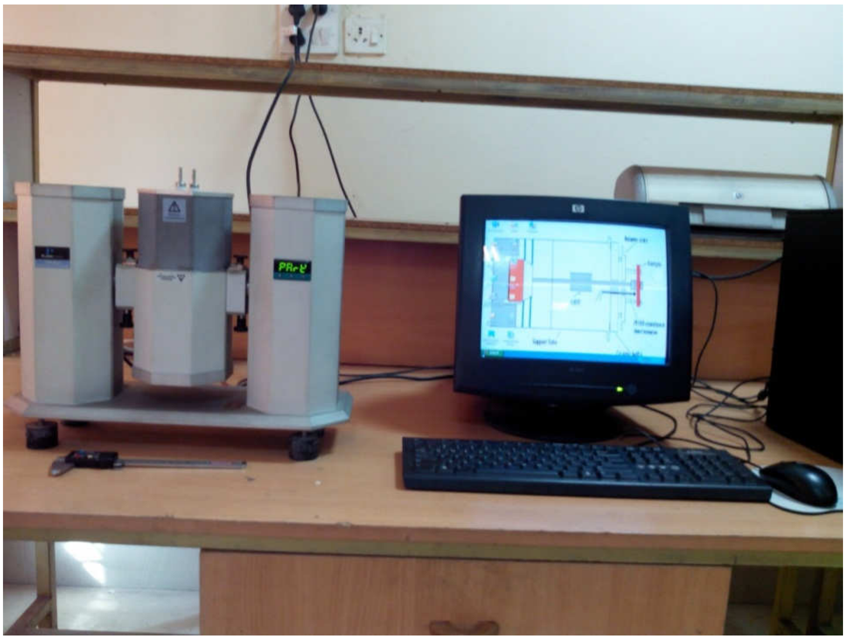


Fig 3.4 Dynamic Mechanical Analyzer (Perkin Almer), DMA 8000

The Storage modulus E' represents the stiffness of a viscoelastic material and is proportional to the energy stored during a loading cycle. The loss modulus E'' is defined as being proportional to the energy dissipated during one loading cycle. it represents, for example energy lost as heat, and is a measure of vibrational energy that has been converted during vibration and that cannot be recoverd. Modulus values are expressed in MPa,but N/mm^2 is some times used. The phase angle is the difference between the dynmamic stress and the dynamic strain in viscoelasticmaterial subjected to a sinusoidal oscillation. The phase angle δ is expressed in radians.The loss factor tan (δ) is the ratio of loss modulus to storage modulus. It is a measure of the energy lost, expressed in terms of recoverable energy, and represent mechanical damping or internal friction in a viscoelastic system. The loss factor **tan (δ)** is expressed as a dimensionless number. A high **tan (δ)** value is indicative of a material that has a high non elastic strain componenrt while a low value indicates one that is more elastic. As we move from a very low temperature, where the molecule is tightly compressed we first pass through the solid state transition as shown in fig – 3.4. as the material warms and expands the free volume increases so that localized bond movements (bending and stretching) and side chain movements can occur.This is the gamma transition, which may also involve associations with water.as the temperature and the free volume continue to increase, the whole side chains and localized groups of four to eight backbone atoms begin to have enough space to move and the material starts to develop some toughness. This transition called the beta transition (Tβ), is not always as clearly defined as we are describing here often it is the tg of a secondry component in a blend of a specific block in a block copolymer.

As heating continues, we reach the Tg or galss transition where the chains in the amorphous regions begin to coordinate large –scale motions one classical description of this region is that the amorphous regions have begun to melt. Since the Tg only occurs in amorphoius material, in a 100% crystalline material we would not see a Tg. Finally, we reach the melt where large –scale chain slippage occurs and the material flows. This is the melting temperature, Tm for a cured thermoset, nothing happens after the Tg until the sample begin to burn and degrade because the crosslinks prevent the chains from slipping past one another. This quick overview gives us an idea of how an idealized polymer responds.

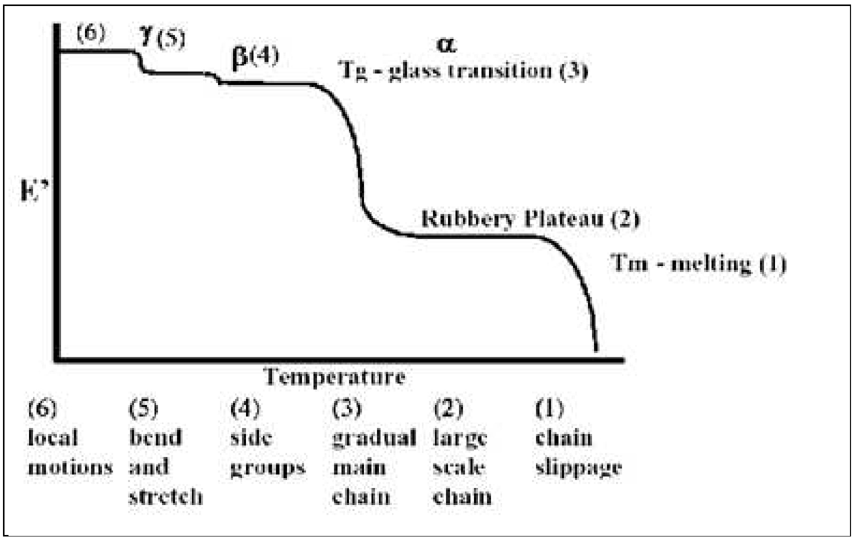


Fig 3.5 – Idealized multilevel DMA Scan

The DMA instrument used for the study of research samples is Perkin Elmer DMA 8000 shown in Fig 3.4 Heating rate used for all sample analysis : 20 ^{o} C to 150 ^{0} C at ramp of 3 ^{0} C / min Frequency used for analysis: 1Hz For multifrequency scans: 0.1, 1, 5 and 10 Hz Sample arrangement mode: Dual cantilever Sample Dimensions: From DMA we evaluate Tg, Storage Modulus and Crosslinking Density.

3.3.4 Mechanical Properties

Mechanical Properties include the study of tensile strength, flexural strength and impact strength along with the modulus.

Tensile Test (ASTM D638)

Among the many mechanical properties of plastic as well as composite materials, tensile properties are probably the most frequently considerd, evaluated and used through out the industry. Tensile properties were measured according to ASTM D - 638 on a Universal testing machine (Instron) at room temperature (i.e 25 ± 2^0C) Each dumbbell was gripped at its widened ends and mounted on the testing machine in axial arrangement with the direction of extension. The grip length was kept 126 mm and the guage length used was 90 mm. the specimens were analyzed at crosshead speed 5 mm /min. results of tensile properties are expressed as the means + SD for three –four determinations.

Fig 3.6 Universal Testing Machine (INSTRON)

$$\boldsymbol{TensileStrength = \frac{P}{A}}$$

The tensile strength of specimen was calculated from the load at break and the original area of the cross section by following formula:

Where

P= maximum load to cause the failure of the sample in K.N

A = Area of cross section in mm2

The elongation of the specimen at break was expressed as percentage of the original distance between the refrences lines marked at distance of 90mm i.e the change in length per unit of original length.

Where Lo= original length,L=stretched length

Flexural Strength- The flexural strength was determined in accordance to ASTM D-790 on a Univereal testing machine (Star Testing Machine). A three point loading system was utilized and the specimen were tested in flexure as a simple beam supported at two points and loaded at the mids points. The specimens were analysed at the rate of 2 mm/min cross head speed and the span length was 35mm. The flexural strength was calculated according to following equation by instrument software program.

$$\boldsymbol{Flexuralstrength(MPa) = {}^{3PL}/_{Bd}2}$$

Where P=Load L=span length B=width of the specimen d=thickness of the specimen

Izod Impact strength – (ASTM –D-256)

The impact strength was measured according to ASTM D-256 on unnotched izod specimen using impact tester. Model International Equipments at room Temperature 25+ 2 ^{o} C. The specimen was held at a vertical cantilever beam and was broken by a single swing of the pendulum. The izod impact strength is expressed in terms of the energy per unit width of the specimen. The testing was done on three four samples per composition to obtain reliable results.

Notched Izod Impact is a single point test that measures a material resistance to impact from a swinging Pendulum (Figure). Izod Impact is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. This test can be used as a quick and easy quality control check to determine if a material meets specific Properties or to compare material for general toughness.

Impact –Strength test were performed using an Izod impact tester (Make – Ceast) according to ASTM D256 with 453 gm Pendulum. Notch cutter with a Micrometer Screw guage, Vernier caliper of Accuracy 0.01mm. The Dimension of the Notched Izod impact specimens used were 63.5mm x12.7mmx3mm. A minimum of 5 specimens for each compositions were tested.

Fig 3.7 – Izod Impact Strength Tester

3.3.5 Morphological Properties

Scanning Electron microscope (SEM)- Scanning Elecron Microscopy (SEM) technique provides adequate information about the surface morphology, phase domains, pin holes defects and patterns and also about other topological features of blends. Scanning Electron microscopy reveals the indirect information about the particle size, about the nature of crosslinking between two polymers and also provides the information about the miuxing pattern of the two polymers and sonme information concerning the nature of the bonds between the fibres and the matrix.

Scanning electron microscope techniques show in fig 3.9 reports that an electron beam is focused into fine probe wich interacts with the sample in a vaccum 10 -4 torr to create signals. These signals to modulate the brightness of the cathode ray tube, scanning takes places in place synchronism with the electron beam as a result of which image is formed on the screen. This image is highly magnified and usually has the look of a traditional microscopy but a much greater depth of field. The contrast in the images is a result of diffrences in scattering from surface areas as a result of geometrical diffrences.

From the characterization of polymers composites, the impact featured samples were analysed by using HITACHI S3700N. Scanning Electron Microscopy and before running the samples, a fine gold coating was given by using the biorad fine gold coat ion sputtering –coating instrument under the vaccum of about 10 -3 torr.

3.3.6 X–ray Diffraction

The laboratory equipment employed with X-ray scattering generally involves an X-ray tube with CuKα (λ=0.154nm). Nickel foil is employed to filterout **Kβ** radiation. Scintillation detectors allow for the conversion of X-ray radiation into an electrical charge with a Photomultiplier. Wide angle X-ray Diffraction (10 to 50) can yield structure Determination less than several nanometers. X ray diffraction shows in Fig 3.11.

Fig3.8 – Scanning Electron Microscope

WAXD of crystalline parameters exhibit sharp concencentric rings indicating high degree of order. Amorphous polymers exhibit a Diffuse halo, indicating lack of order. It is also employed to study the miscibility in polymer mixes. Phase separated combinations result of molecular chain spacing Miscible combination exhibits a larger molecular chain inter chain spacing. Miscible combination exhibits a larger molecular interchain spacing. indicating a Unique amorphous structure developed from the components different than either of the constituents. It uses Braggs X –ray Diffraction Spectrometer.

Fig 3.9 – X –ray Diffraction Machine

CHAPTER- 4
STUDIES ON THE MODIFICATION OF GUAR GUM

Guar gum is one of the most abundant natural biopolymers, Guar gum is chemically or physically modified to obtain desired properties for different applications in food and non food industries.Allyl guar gum forms an important class of reactive guar gum due to the presence of highly reactive carbon –carbon double bond. These modified guar gum afford new possibilities for wider application from coating [136],textile [133,134] and for the preparation of laminated products or rigid plastics. In this chapter, the synthesis of allyl guar gum by synthetic route using allyl chloride and guar gum in an aqueous suspension under mild reaction condition is described.The isolated product were characterized by the determinationof the degree of substitution. X ray Diffraction and SEM were used to visualize the changes in the crystallinity and in granular morphology of Guar -gum and its derivative.

4.1 Preperation of Allyl Guar gum -

A general procedure for the synthesis of allyl guar gum is reported in literature [31] and it was modified as follows. Purified Guar gum were dispersed in aqueous solution of water and isopropyl alcohol in a 500ml round bottom flask, NaOH and a phase transfer agent (tetra methyl ammonium chloride) were added and the mixture was heated to 50 ^{0}C. The reaction was initiated by dropwise addition of allyl chloride over a period of 30 min The mixture was stirred vigorously for 8 Hrs at 50 ^{0} C . The suspension was then cooled in an ice water bath and neutralized to pH 7.0 with 2 mol HCl. After filteration the product was washed with water, ethanol, and acetone. After drying overnight in an oven at 50 ^{0} C. A white powder of allyl guar gum was obtained.

4.1.1 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

FTIR of Allyl guar gum was run in transmittance mode FTIR results for guar gum show characterstics peak at 3420 and 1650 cm^{-1} which was attributed to the hydration of Guar gum molecule and has been reported in other studies [95] . The allylation of guar gum was carried out in an aqueous environment and it was observed that allylated guar gum derivatives with the highest Degree of substituition (DS) were obtained at 3 Hrs and 6 Hrs after which the Degree of substituition (DS) decreased.This decrease was due to the hydrolysis of ether group as the time of reaction increased. Fig 4.2 shows the comparision of the FTIR spectra before and after reaction.It was observed that after allylation a peak at approximately 1638 cm^{-1} appeared which was attributed to the stretching vibrations of the introduced allyl group FTIR results for allyl guar gum shows characterstics peak at (-OH stretching), methyl absorption at (CH_2 and CH_3) at 2997 cm^{-1} and CH_2 bending at 1452 cm^{-1} increases.

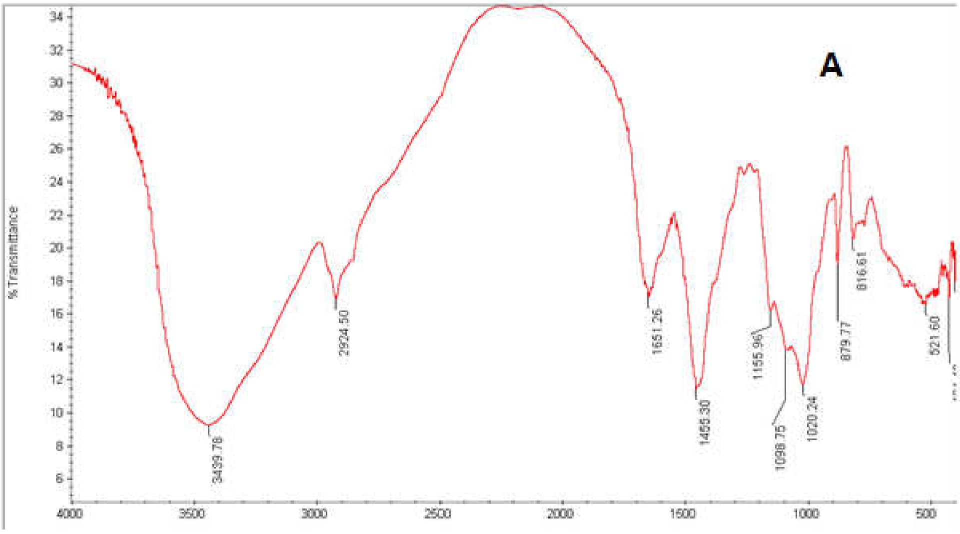


Fig4.1 -FTIR Spectra of Allyl guar gum (AGG1)

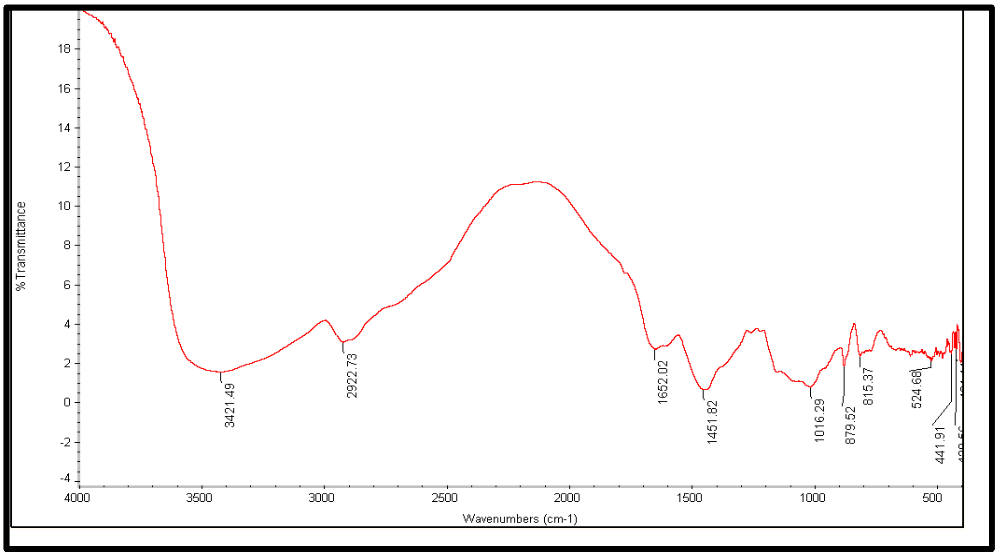


Fig 4.2 – FTIR spectra of Allyl guar gum (AGG2),

The emergence of this peak confirms the presence of allyl moiety, further it was observed that the peak intensity was maximum for the derivatives isolated after 4and 8Hrs reaction time after which the peak intensity decreased as the time of reaction was increased. It was observed that as the Degree of substituition of allyl guar gum increases the peak intensity at 1638 cm^{-1} and 1452 cm$^{\mathbf{-1}}$

Table4.1 - ^{1}H NMR analysis of AGG2

Peak (PPm)	Description
3.2 -4.2	Proton of Anhydroglucose unit of Guar gum
4.65	D_2O
4.93	Alpha anomeric Proton of Glucose residues
3.95	OCH2
5.21-5.24	CH=C**HH**
5.31-5.35	CH=CH**H**
5.88	**CH=C**HH

4.1.2 Nuclear Magnetic Resonance (NMR) Characterization of Allyl guar gum

Fig 4.3 Shows the ^{1}HNMR spectrum of Allyl guar gum. The peaks were assigned to the assumed structure of allyl Guar gum starting with the peak at 3.2 which belongs to the proton H 8(1H) and H 10 (2H) The peaks at 5.90 and 5.20 ppm were assigned to the ethylenic protons H9(1H) and H10 (2H).and the peak at 4.93 ppm was attributed to the alpha anomeric proton of glucose residues H-1 (1H) The characterstics peak for the H6 (2H) proton in Allyl guar gum substituted and unsubstituted glucose were identified at 3.2-4.2 ppm . Both spectrum exhibited the signal of 3.2-4.2 due to proton of Anhydroglucose unit of guar gum.The ^{1} NMR peak at 4.65 is due to D20. [121]

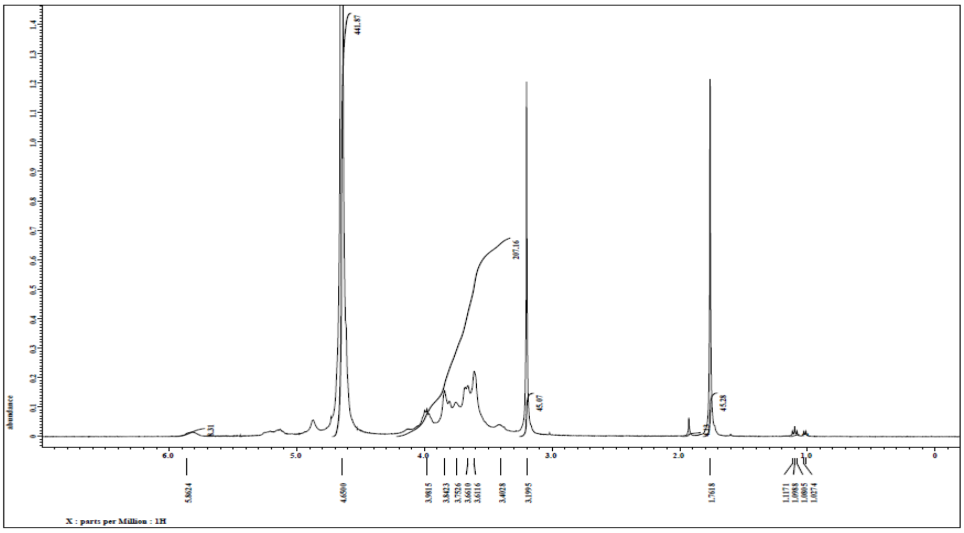


Fig 4.3 – Proton NMR Analysis Of AGG2

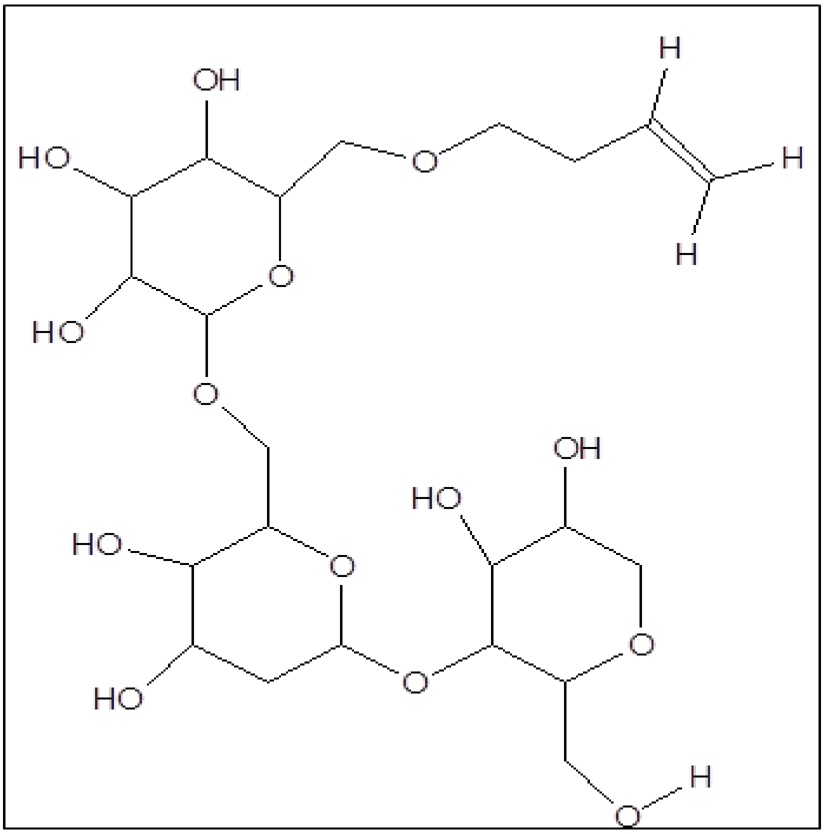


Fig -4.4 Schematic representation of allyl guar gum

4.1.3 X Ray –Diffraction (XRD)

The effect of substitution on guar gum crystallinity and type of Packing was investing using X –ray diffraction (XRD).It was observed that the crystalline nature of the AGG derivatives was affected by the change in their hydrophilic nature. This was indicated by the XRD patterns obtained and shown in Fig 4.5. The crystalline nature of the AGG derivatives were seen to increase with an increase in DS, which was attributed to a reduced interaction brought about hydrogen bonding in the sample. it was observed that there was narrowing of the peak obtained at approximately 2θvalue of $20^{0,}$ further there was the emergence of minor peaks at 2 θ value of 11.5^{0}, 14.6^{0} and 17.4^{0}, Which were prominently seen in the case of AGG1 and AGG but which disappeared or levelled off at higher reaction times . The effect of substituition on guar gum crystallinity and type of packing was investigated using X-ray Diffraction (XRD) because X - traces of AGG and GG showed similar pattern. An inspection of X RD spectra showed hardly any diffrences in the type of packing between native guar gum and their derivatives after the etherification

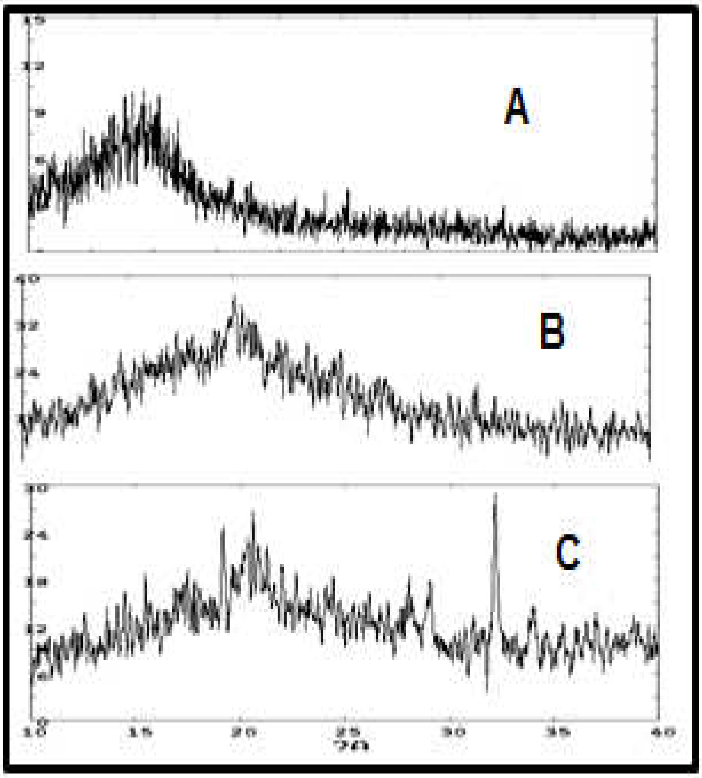


Fig -4.5 X-ray diffractogram of Guar gum and Allyl Guar gum, A=Gaur gum, B=AGG1, C=AGG2

4.1.4 Thermogravimetric Analysis

The Thermal stablity of the GG is partially due to the hydrogen bonding occurring in the sample. allylation reduces the hydrogen bonding thus could be the cause of the reduced thermal stability of the AGG derivatives.Thus it could be seen that allylation of GG resulted in AGG derivatives with various degree of substituition, which have a terminal unsaturation group into the chain.

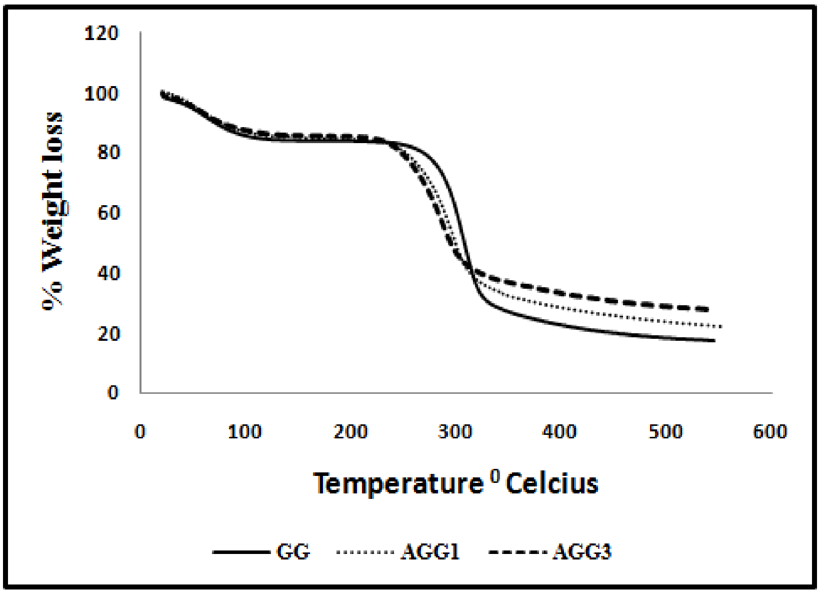


Fig -4.6 TGA curves for Guar gum and allyl Guar gum

Table 4.2 –Properties of Allyl Guar gum

Sample Name	**T i ^{0}C (onset)**	**Weight loss occurred between 200 ^{0}C to 400 ^{0}C**	**Residue at 600 ^{0} C**
GG	240 ^{0}C	75 %	16.5%
AGG1	228 ^{0} C	56.4%	21.12%
AGG2	209 ^{0} C	54%	26.4%

The initial weight loss is due to presence of small amount of moisture in the sample. The second zone i.e degradation zone is starts at 240 ^{o}C . where the polymer decomposition takes place the rate of weight loss is increased upon increasing the temperature upto 340 ^{0}C nearly 75 % guar gum degrades below 400 ^{0} celcius. A 16.2

% residue was obtained at 600 ^{0}C.In case of allyl guar gum(AGG1) the polymer degradation starts at 224 ^{0}C.The polymer decomposition temperature indicated that allyl guar gum AGG1 lowers the initial decomposition temperature about 56.4% weight loss occurred between 200 and 400 ^{o} C and 21.12% residue was obtained at 600 ^{0}C. In case of AGG2 and about 54 % weight loss occured between 200 and 400^{o}C in case of AGG2 26.4 % residue was obtained at 600 ^{0}C. As the degree of substituition is increased then % weight loss between between 200 and 400 ^{0}C is decreased and % residue is increased at 600 ^{0}C.

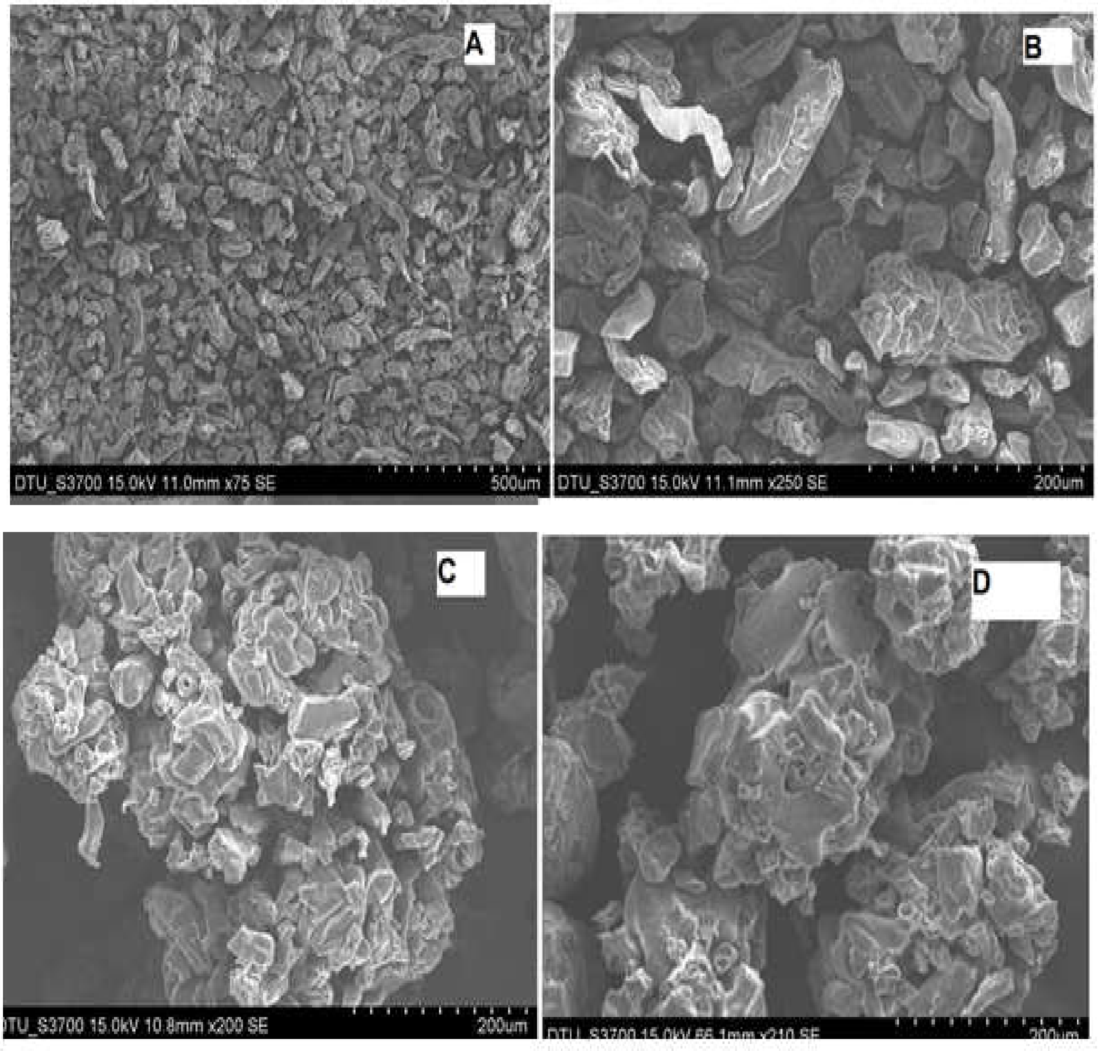


Fig 4.7 – Scanning electron Micrographs of Guar gum and allyl guar gum

4.1.5 Scanning Electron Microscope

The SEM micrographs of guar gum and allyl guar gum are presented in Fig (4.6) from (A to D), Fig 4.7 (A and B) shows the micrograph of Guar gum at X75 and X250 magnification. Fig C shows the micrograph of allyl guar gum (AGG1) and Fig D shows the micrograph of allyl guar gum (AGG2) .The particle appearance of the dry guar gum samples was investigated. The appearance of Guar gum was portrayed with distinct granules, having mixed shapes, with some almost spherical and some cubical shapes with irregular shapes with smooth surface. The size and appearance of the granules from allyl guar gum are rougher and more porous than that of Guar gum.In fig D the micrograph magnified at X 210 times and depict that after etherification the guar gum granules are being continuously destroyed with the higher reaction times. It sujjest that etherification of guar gum generates only minor surface modification upon reaction.

4.1.6 Diffrential Scanning Calorimetry (DSC)

Diffrential scanning calorimetry was employed to measure the degree of crystallinity of guar gum and allyl guar gum. Polymer melts over a temperature range due to difference in size and regularity of the individual crystallite. The melting point of a polymer is generally reported as a single temperature where the melting of polymer is complete. Crystallinity is a state of molecular structure referring to a long periodic geometric pattern of atomic spacing. guar gum is an amorphous polysaccharide material which upon the application of heat undergoes a process of melting where the crystalline character of polymer is destroyed. The analysis of crystalline thermogram was done in terms of various crystalline parameters such as melting temperature Tm, Heat of Enthalapy (Δ H), Degree of crystallinity, etc.

DSC was used for studying thermal transitions occurring in the course of heating under an inert atmosphere. typical DSC thermogram of Natural gum as well as allyl guar gum are representatively demonstrated in fig 4.8. The peak temperature for the various thermal effects as well as the associated enthalpy changes for all the polysaccharides studied are given in Table most of the DSC traces exhibited early endotherms peaking in the temperature range of 50 ^{0}C.

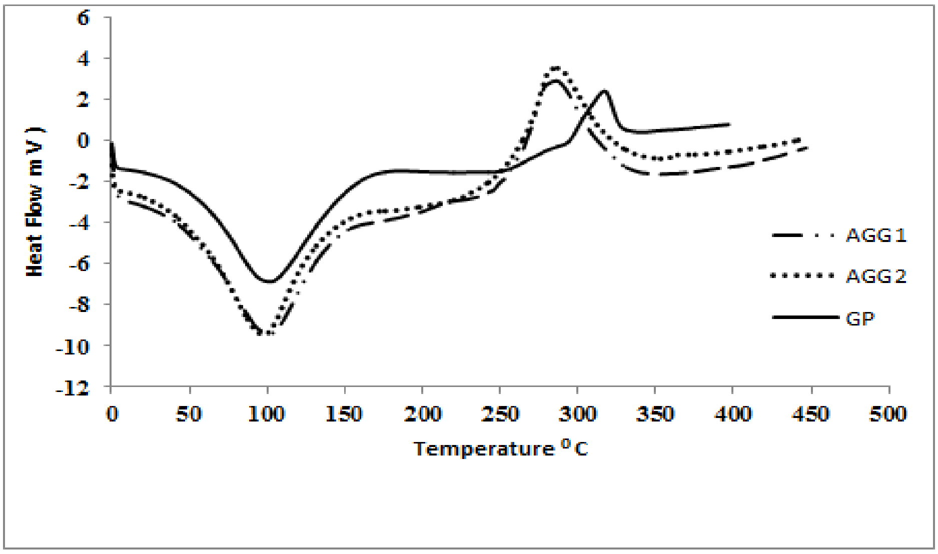


Fig 4.8 - DSC analysis of Guar gum and Allyl guar gum

Table 4.2 DSC analysis of Guar gum and Allyl guar gum

Sample	Endotherm Peak (^{o} C)	ΔH in J/g	Exotherm in (^{o} C)	ΔH in J/g
GG	50.44	339.5	316.44	54.12
AGG1	46.26	316.3	284.10	212.9
AGG2	28.69	257.6	283.59	184.5

4.1.7 Degree of substitution by Titration method

Degree of substitution is based on double bond titration method.This method is performed with standard solution.In this method DS value of allyl guar gum is actually the average number of the hydrogen atom replaced by allyl group. (R). The double bond of allyl group reacted with bromine and the residual bromine than reacted with iodine, the excessive iodine was titrated with sodium hyposulfite. The degree of substitution was calculated using follwing equations.

$$DS = \frac{162x}{79.9(2-0.5006x)}$$

Where x = $X = \frac{(V1-V2)\times C\times 0.079\times 100}{W}$

Where x% is the bromine Value, V1 (ml) and V2 (ml) are the volume of standard sodium hyposulphite solution consumed in blank and sample titration, respectively, C (mol/ L) is the concentration of the sodium hyposulfite solution, and W(gm) is the dry weight of the Guar- gum sample.With this method the Degree of substitution of 0.0389, 0.0625 were obtained for AGG1 and AGG2 respectively.

4.2 SYNTHESIS AND CHARACTERIZATION OF ALLYL GUAR GUM –g-POLY ACRYLIC ACID

Guar gum possesses many advantages, such as abundant sources, low production cost, and better biodegradibility, Numerous experiments and industrial trials have demonstrated that chemical modification constitutes a powerfull mean of improving guar gum servicability [41]. Increasing the grafting efficiency is an effective way of improving the properties of guar gum –g – copolymers and reducing their preperation costs . However the graft copolymerisation of Guar gum with vinyl monomers is always accompained by the homopolymerization of vinyl monomers as reactant. The homopolymerization is a side reaction of the copolymerization. It can be imagined that, through the introduction of polymerizable double bonds into guar gum molecules before graft copolymerization. The double bond can be incorporated into the copolymeric chains when they meet propagating activated chains. If a propagating activated chain that initiates homopolymerization meets with the double bond, the orignal homopolymerization will be converted to copolymerization.Therefore some portion of the hompolymers will become graft copolymer, and the grafting efficiency can be enhanced, consequently the grafting ratio, will be correspondingly enhanced with the increase in the efficiency. it has been elucidated the Homopolymers are inferior to the copolymers in serviceability.The enhancement of the grafting efficiency decreases the required amount of monomers and this reduces the production costs.Therefore by the introduction of polymerizable double bond onto guar gum through the preatreatment of allyl etherification the grafting efficiency and improve the properties of guar gum. The graft copolymerization of acrylic monomers onto natural polymers is almost exclusively performed by free radical add-on polymerization. There are two principally different methods to generate free radicals on the guar gum backbone, e.g.. The most common is chemical initiation, e.g.by the ceric ion system (Ce^{4+}/Ceric Ammonium Nitrate) [132-138] Ammonium or Potassium persulfate [148-149,160], Fentons reagent (Fe^{2+}/H_2O_2) [150], Manganese (Mn^{4+}) [151-153], etc. Less common is the creation of radical by irradiation of the starch with electron beams [154], UV- [155-158], γ-rays or microwaves [159]. Among the chemical initiators it is generally assumed that the ceric ion is the most selective initiator since it reacts directly with the starch backbones, creating radicals at the place where they can effectivelystart a graft polymer attachment. Such a method would suppress homopolymer formation. It is however an expensive reagent, so it would not be very suitable for industrial scale applications. The same argument holds for irradiation, apart from the technical and safety issues associated with radiation. Beside the cost aspect of the ceric ion system, who observed that for the use of ceric salt as initiator in the graft copolymerization onto starch. They also found that the monomer reactivity decreased in the following order: AN (acrylonitrile) > AAm (acrylamide) >AA (acrylic acid). From the results of earlier experiments in our laboratory, it was found that for AA, Fentons reagent (Fe^{2+}/H_2O_2) is the most suitable initiator, giving the highest graft selectivity among other initiators.

The arguments in favour of this monomer are therefore only briefly summarized in the following paragraph below.There are several advantages of guar gum grafted with acrylic acid.. Since acrylic acid is completely water soluble, the reaction of this monomer with the initiator and allyl guar gum in water constitutes a more or less homogeneous system. This will be advantageous with respect to reaction rates and ease of operation. However, in the homogeneous system the formation of homopolymer can hardly be avoided.therefore optimization of graft selectivity will be an important issue all along the thesis.

4.2.1 Characterization of the grafted allyl guar gum

A purification process was applied to remove the homopolymers [(Poly acrylic acid) (PAA)] from the guar gum products. The samples were washed with distilled water to such an extent that no homopolymer existed in the filtrate. The effect of Guar gum etherification on the copolymerization –allyl etherification of guar gum shows evident effect on the graft copolymerization. The etherification is able to increase the grafting efficiency and ratio while conversion of monomer to polymer does not vary significantly**,** apparently when the graft copolymerization of allyl guar gum with acrylic acid occurs propagating chain radicals might collide with the double bond of allyl group on guar gum backbone. The double bond may be incorporated into the propagating chains, there by forming guar gum graft copolymer. Obviously the incorporation is capable of converting homopolymerisation into copolymerization. And the double bond on guar gum backbones can partly convert homopolymerization into copolymerization And the double bonds on guar gum backbones can partly convert homopolymerization into graft copolymerization. correspondingly part of homopolymers would be transformed to copolymers. Therefore both grafting efficiency and ratio are enhanced.

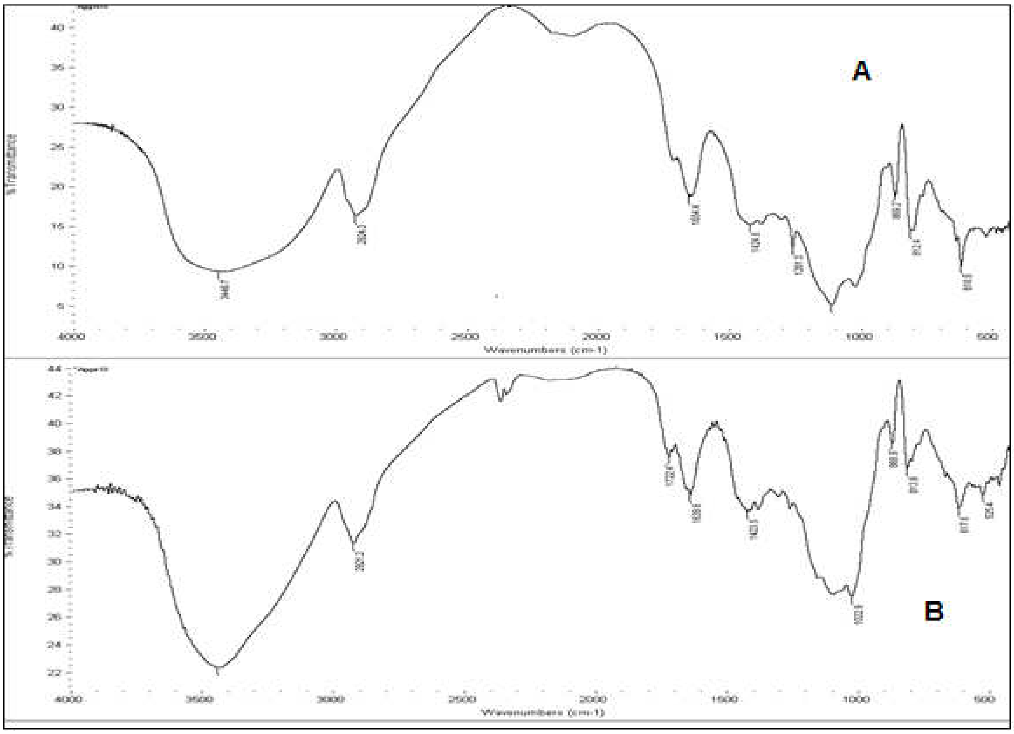


Fig 4.9 – FTIR analysis of Allyl Guar gum –g – Acrylic acid A – Allyl Guar gum- g-PAA1, B – Allyl Guar gum –g- PAA2,

Fig 4.9 shows that the IR spectra of both pure and grafted starch contain a broad band between 3750 -3300 cm$^{-1,}$ characterstics for the glucosidic ring of guar gum. diffrences in intensity may be caused by the presence of residual water. More interesting are the peaks at 1700cm^{-1} . These are present in both pure PAA and in the grafted guar gum but not in the native guar gum. The can be attributed to carbonyl groups (C=O). This is proof that polyacrylic acid is chemically grafted onto the guar gum backbones.[162]

4.2.2 Thermogravimetric Analysis

The initial weight loss is due to presense of small amount of moisture in the sample. The second zone i.e degradation zone is starts at 244 ^{0}C where the polymer decomposition takes place. The rate of weight loss is increased upon increasing the temperature upto 320 ^{0}Celcius . A 24% residue is obtained at 500 ^{0}C. In case of AGG-g-PAA2 the polymer degradation starts at 196 ^{0}C and this is a single step degradation process.The polymer decomposition temperature indicated that AGG –g-AA lowers the initial decomposition temperature about weight loss occurred between 200 and 400 degree celcius and 41.8% residue was obtained at 500 ^{0}celcius.

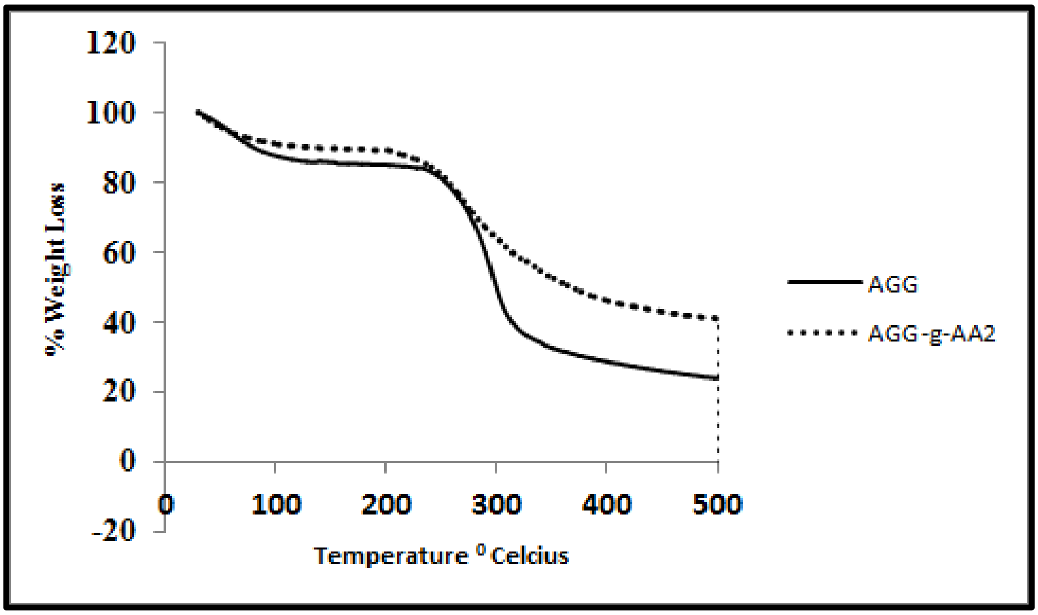


Fig 4.10 - TGA curves of allyl guar gum –g – polyacrylic acid (AGG-g-PAA2)

4.2.3 Scanning Electron Microscope

SEM pictures were recorded to gain insights in the morphology of the products of the graft polymerization and are not intended for quantitative analysis. The scanning electron micrograph of guar gum shows a granular structure. The SEM pictures of the grafting copolymerization show a variation in morphology, apparently dependent on the degree of grafting at a low level of addon, there are changes in the morphology, apparently dependent on the degree of grafting. at a low level of add on there are changes in the morphology but the picture does not reveal a definite structure, however, at higher add on a porous structure can be seen, such hollow structures may result from the agglomeration of smaller particles.

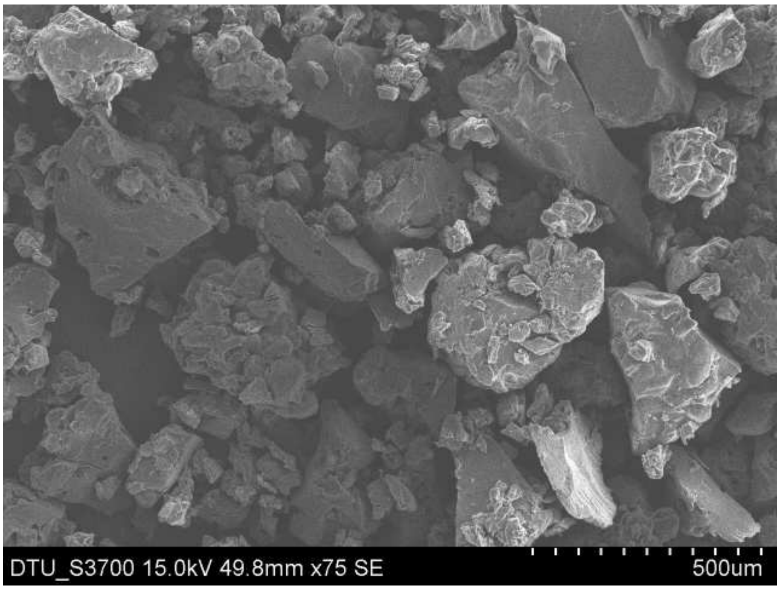


Fig -4.11 – Scanning Electron Micrograph of AGG-g-PAA1

The graft copolymerization was carried out in aqueous dispersion with ferrous ammonium sulphate and Hydrogen peroxide as initiator.The excessive increasing the modification extent of guargum allyl etherification lowers the properties of copolymers.Acrylic acid is an acceptor of guar gumresulting the initiation and thereafter themselves free radical donor to the neighbororing molecule leading to lowering termination. The decrement in the grafting parameters might be due to the formation of Homopolymer which decreases the viscosity of medium.due to which the movement of free radical restricted, therefore grafting parameter showed decreasing order.

CHAPTER - 5
PREPERATION OF EPOXY -ALLYL GUAR GUM COMPOSITES

The polyether amine is having ether linkages so it produces more hydrophilic epoxy composites and offer greater compatibility to the filler guar gum have found to be varied particle ranges from irregular to fibrous it would behave as reinforcing filler to the epoxy composites. After the addition of guar gum to the epoxy resin its viscosity of dispersion gets increases at higher concentration the workability of the epoxy – Guar gum slurry reduced drastically. In the present case the decrease in the crosslinking was probably caused by the increase in the viscosity of composition. The increase in the viscosity of the composition would result in a lower degree through a reduction in the rate of diffusion. The substitution of Guar gum resulted in an increase hydrophobic nature of the polysaccharide increase the compatibility or in other words the wetting of the polysaccharide surface by the epoxy polymer matrix

The increase in the filler concentration effectively reduces the polymer content in the composites and results in aggregation of the filler resulting in an increase in the overall particle size and reducing complete surface coverage of the filler by the polymer. This incomplete coverage of the aggregated filler causes them to be the weak point in the polymer matrix because the aggregates are held together.r by only weak bridging forces such as vander wall forces and hydrogen bonding further the crosslinking density of the composites was found to decrease as the filler concentration increased. This also contributed to the decrease in tensile strength of the composite with increase filler addition, small interacting particles which contribute to actual physical crosslinking of weak areas in the polymer matrix.where the tensile strength increased was caused by the reinforcing effect of the fillers.

The effect of addition of HydroxyPropyl guar gum were greater than that of Guar Gum this could again be explained on the basis of increased guar gum polymer interaction although guar gum had lower interaction with the polymer as compared to HPG it still had own increased impact property of the composites the excellent increase in impact property could be explained by the nature of the filler itself. [68]

The filler is not a compact filler like inorganic fillers this would allow for the dissipation of energy with in the filler matrix further the nature of guar gum was such that it has a large number of secondry bonds present in the particle namely hydrogen bonds these secondry bonds can be broken eaily by the application of energy which are then able to reform at a later time allowing for the dissipation of energy introduced into the matrix via the impact this dissipation of energy would be greater if the transfer of energy from the matrix to the filler matrix were more efficient which was again dependent on the extent of interaction of the filler with the polymer matrix.Considering that guar gum and its derivatives are extremely soluble in water the water absorption capacity of the composites become a paramount importance it was observed that irrespective of the filler used the increased concentration of filler resulted in an increase in water absorption by the composites.

The Unmodified epoxy resin exhibit brittleness and low elongation after cure.these polymers usually craze on their free surface and the crazed areas are converted into cracks, which propagate with brittle energy absorption resulting in fracture. The high glass transition temperature of epoxy thermosets are the result of crosslinked structure and this is achieved at the expense of reduced toughness and damage tolerance. Crazes contains voids and easily breakdown to form cracks crazing is frequently associated with brittle response.craze contain void and fibril.The focus of this study is to develop new toughened system for amorphous epoxy resin via physical and chemical modification of guar gum. A detailed account of the effect of allyl guar gum as a filler in epoxy resin by casting technique were presented. The incorporation of allyl guar gum into the glassy epoxy matrix resulting in particulate composites . The addition of allyl guar gum with different degree of substituition increases the overall ductility of the polymer over a wide range of temperature and also improves toughness and impact resistance .

The allyl modified guar gum with different degree of substituition (0.0389, 0.0625) has been used as a filler in epoxy resin to form a polymer composites. The mehanical, thermal and chemical properties of the prepared composites were determined. In case of low degree of substituition (0.039) shows higher storage modulus than the neat resin which indicates increased elastic behaviour the allyl guar gum particles absorb the energy of impact and prevent crack propagation. allyl guar gum composites showed a steady increase in flexural energy with the increase in Degree of substitution . The result prior to significant reduction in the stiffness of the blends which result from the introduction softer segment in the cured resin matrix. The decrease in the height of $\tan\delta$ for the system indicates significant plasticizing effect of AGG. Allyl guar gum gets dissolve to some extent in the epoxy resin and exerts some sort of a diluent effect. This is in fact a direct consequence of a simultaneous fall in both loss modulus and storage modulus.

The slight decrease in modulus is due to the increase in the dissolved allyl in the epoxy matrix. However the rate of increase of fracture energy with allyl content varies with test condition. TG- DTA analysis of the allyl toughned and neat epoxies showed that the percentage weight loss is slightly more for the allyl based composites.

Allyl guar gum that did not phase separate remains dissolved and could plasticize the epoxy matrix resulting in a lowering of Tg, glass transition temperature generally decreases with increasing allyl content and increases as the compatibility of allyl guar gum and epoxy decreases.

The essential requirement for toughness enhancement of thermosets matrices is that the additive showed be soluble in the uncured resin and phase separation must occur during curing cycle.If any additive remains after the cure cycle, the Tg of the resin is lowerd with deleterious effect on the ultimate performance of the composite.

Toughening mechanism in the laminate are characterized by two different process at the crack tip processes in operation are crazing, matrix microcracking plastic deformation fibre or particle debonding and phase transformation. The increase in toughness achieved by a specific mechanism is produced by the energy change in a volume element as crack propagate through the composites. The most successful method for epoxy toughening is the incorporation of a soluble phase into the glassy epoxy matrix resulting in phase separation. Toughening can be done by dispersing a small amount of allyl guar gum as discrete phase or by incorporation reactive liquid polymers.

This chapter deals with the preparation of Epoxy composites by the addition of allyl guar gum with different degree of substitution,The Thermal, mechanical properties and thermomechanical properties of the resultant composites were compared with those of the control resin.

5.1 MECHANICAL PROPERTIES

It includes the study of Impact strength, tensile and flexural properties of various systems. A series of tensile and flexural tests were carried out to study the the effect of allyl guar gum content on the mechanical properties of the composites .The results for Tensile and Flexural testing of the Modified systems are presented in Fig 5.1 to 5.3.

5.1.1 Tensile strength and %Elongation at Break

The tensile strength of the Epoxy composites were graphically depicted in Fig from which it it could be seen that the use of AGG1 resulted a moderate increase in the tensile strength at 0.5phr concentration. At the same concentration AGG2 based Epoxy composites showed only a slight increase in Tensile strength.The variation of the tensile strength of composites based on AGG1 derivatives was found to be lower that observed for AGG2 due to the increase in allylic content.An optimum concentration of 0.5 phr was observed in the case of AGG based composites after which the tensile strength was seen to decrease.This decrease a Higher filler concentration could be due to the much lower reactivity of Epoxy group and allyl group due to the presence of double bond. In general the tensile strength and the elongation at break are antagonistic in nature.The elongation at break increases on the addition of allyl guar gum to the composites From fig 5.2 it could be seen that At lower concentrations the reinforcing action of the fillers resulted in sharp decrease in the elongation at break values. There was a gradual, increase in elongation at break values as the concentration of filler increased

5.1.2 Flexural strength

The flexural strength showed a trend similar to that shown for the tensile strength of the composites and was depicted in Fig 5.3 The reason for the increase in the flexural strength are similar to those cited for the increase in the tensile strength. The flexural strength curves were found to be similar in nature to those of the tensile strength with an optimum value of 0.5Phr. Above this concentration the flexural strength decreaseswith the increase in allylic content.

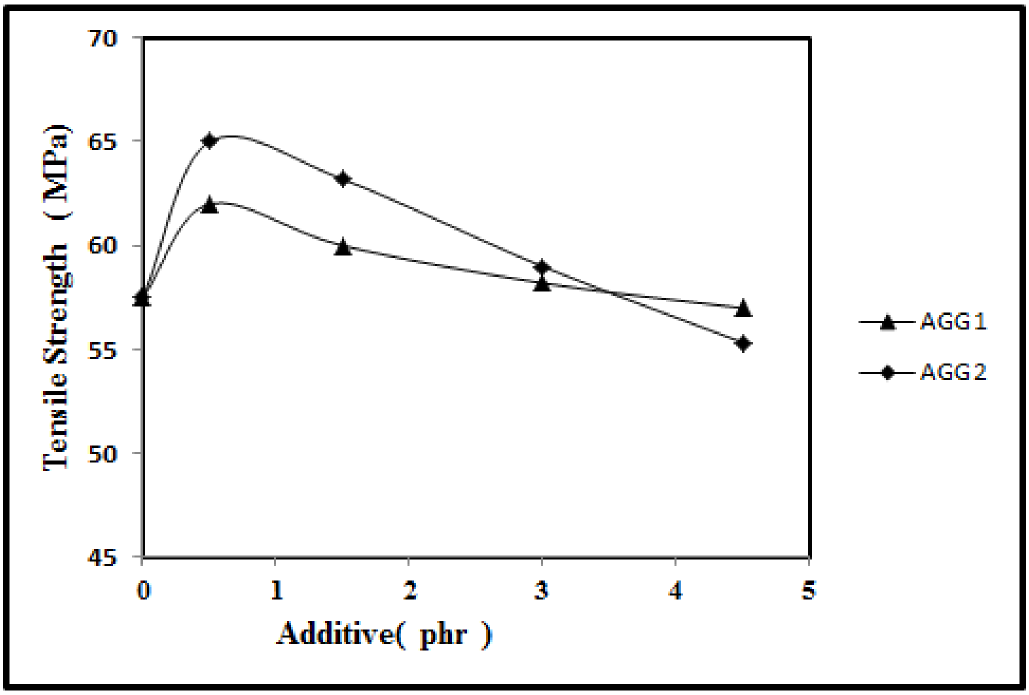


Fig 5.1 Tensile strength of Epoxy allyl Guar gum composites

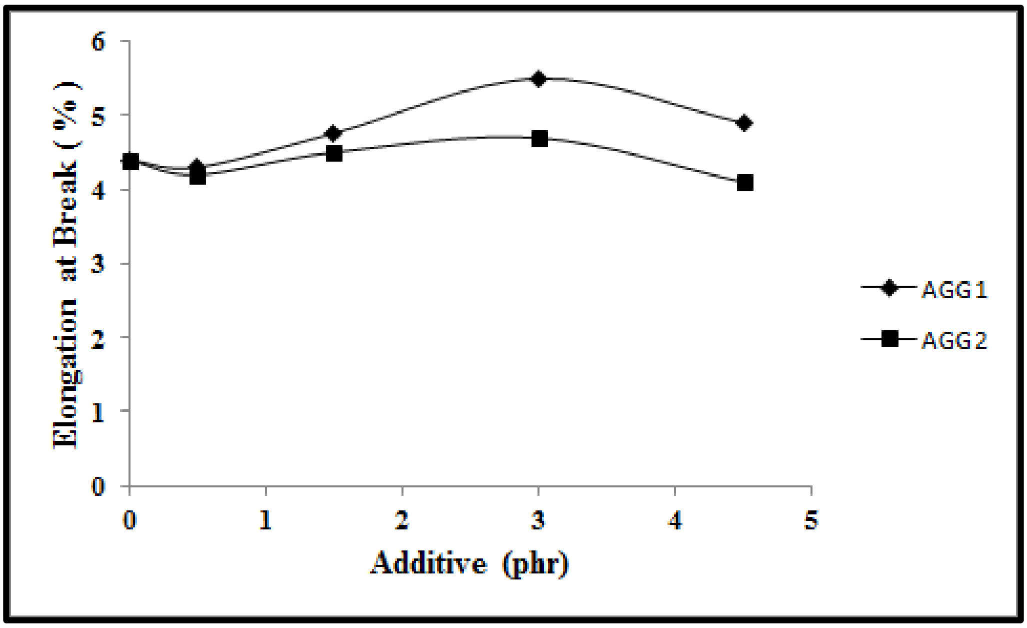


Fig 5.2 Variation of % Elongation at Break of Epoxy allyl Guar gum composites

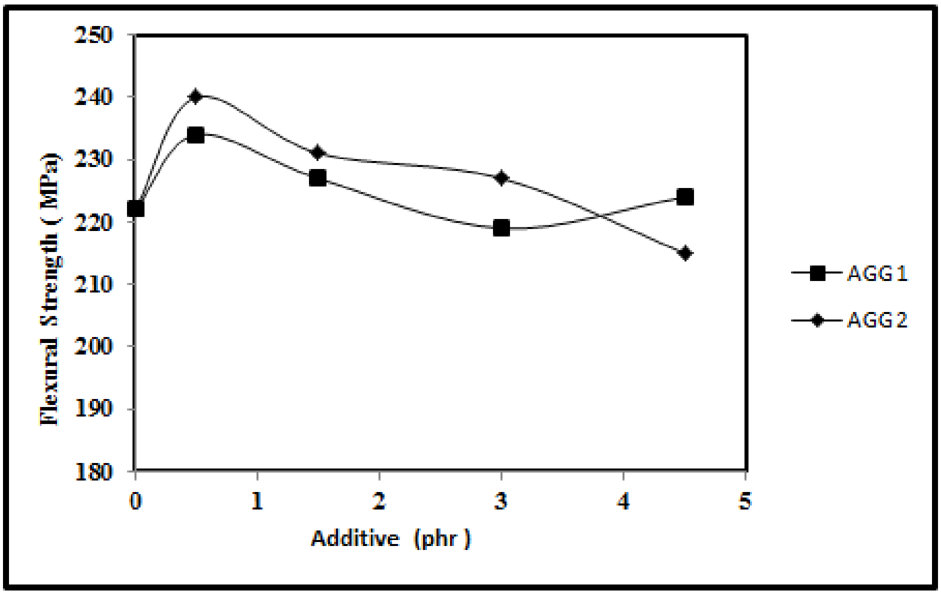


Fig 5.3 Flexural Strength of Epoxy – allyl guar gum composite

5.1.3 Izod Impact Strength

The impact Properties of the composites on addition of allyl guar gum could be seen in Fig5.4. The impact strength of the composites, as measured by the charpy impact test showed positive results at higher varying upto 3Phr of the fillers. The effect of addition of allyl guar gum (AGG1) were greater than that of allyl guar gum (AGG2) concentration.on the basis of increase interaction of Epoxy - allyl guar gum the impact property of a polymer composites can be explained by the nature of the filler itself AGG1 that have greater interaction would result in composites with greater impact strength.

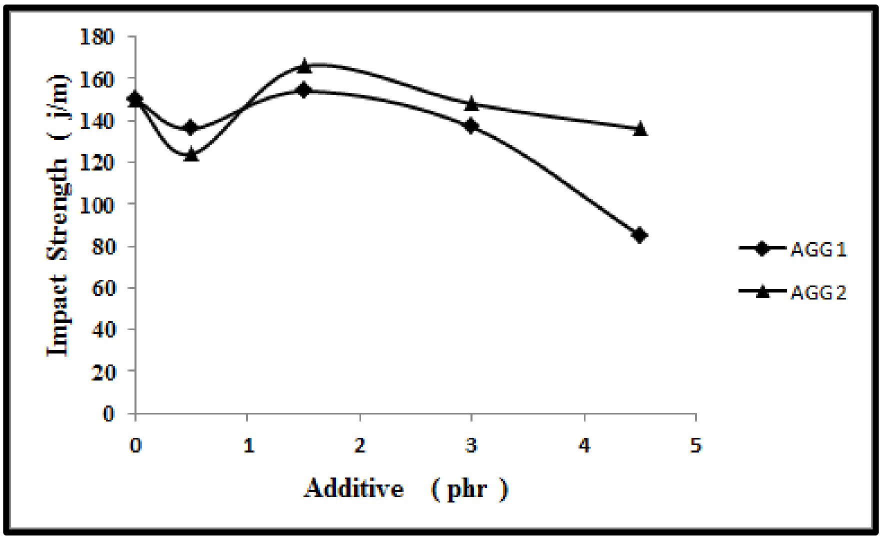


Fig 5.4 – variation of Impact strength of Epoxy allyl Guar gum composites

Table 5.1- Properties of Epoxy – Allyl guar gum Composites

Sample	Tensile Strength (MPa)	% Elongation at Break	Flexural Strength (MPa)	Impact Strength (j/m)
Epoxy	57.5	4.4	222	151
Epoxy +0.5phr AGG1	62	4.3	234	136
Epoxy + 1.5phr AGG1	60	4.76	227	154
Epoxy +3phr AGG1	58.2	5.5	219	137
Epoxy +4.5phr AGG1	57	4.9	224	85

Table 5.2- Properties of Epoxy – Allyl guar gum –g-PolyAcrylic Acid based Composites

Sample	Tensile Strength (MPa)	% Elongation at Break	Flexural Strength (MPa)	Impact Strength (j/m)
Epoxy	57.5	4.4	222	151
Epoxy +0.5phr AGG2	65	4.2	240	124
Epoxy + 1.5phr AGG2	63.2	4.5	232	166
Epoxy +3phr AGG3	59	4.7	227	148
Epoxy +4.5phr AGG4	55.34	4.1	215	136

5.2 DYNAMIC MECHANICAL ANALYSIS (DMA)

Dynamic mechanical analysis (DMA) is a method that measures the stiffness and mechanical damping of a cyclically deformed material as a function of temperature. The loss factor ($\tan\delta$) is a sensitive indicator of crosslinking and the glass transition temperature (Tg) value is assumed as the temperature corresponding the max of tan d versus temperature curve, therefore, the Tg of sample could indicate the crosslinking density of polymeric material.

5.2.1 Loss factor tan(d)

In this part we discussed the Epoxy/ allyl guar gum systems with different contents of Allyl guar gum, prepared by casting using polyether amine as hardner. Here allyl guar gum used as a filler for the epoxy composites. tan (δ) relates to the impact resistance of the material [163] as the damping peak occurs in the region where the material changes from a rigid to a more plastic state. It is associated with the movements of small groups and chains of molecules with in the polymer structure all of which are initially frozen in.

The variation of loss factor Tan δ for the allyl guar gum based composites as a function of temperature measured at a frequency of 1Hz showed in fig 5.6 and fig 5.7

Fig compared the tand curves of allyl guar gum based composites at different contents. In case of composites containing AGG1 the value of tand increases only upto 1.5 phr, after 1.5 Phr the value of tand decreaaes but higher than pure e poxy composites.

In case of composites containing AGG2 the tanδ value increases only upto 0.5 phr., Above this concentration the value of tanδ decreases but lower than pure Epoxy composites. The decrease in Tg with the increase degree of substitution of allyl guar gum may be due to low interfacial interaction between the filler and the polymer. from fig5.6 it could be see that composites peaks are shifted to lower temperature. In comparision to the pure epoxy composites, This may be due to the increase in flexibility of the epoxy chains caused by the incorporation of allyl guar gum.The low interfacial strength of allyl guar gum could permit the chains to move without much restriction at the contact with the allyl guar gum.The magnitude of Tanδ peak is indicative of the nature of the polymer system. Higher the tand peak value, greater is the degree of molecular mobility [107]. since in all composites the height of tan δ peak was larger than untreated ones. this indicates that all composites possess different damping capabilities.

5.2.2 Storage Modulus (E')

The plots consisting of the storage modulus (E'), loss modulus and loss tangent tan (δ) with different proportions of allyl guar gum as a function of temperature have been shown in Fig (5.5), respectively. The value of Storage modulus (E') decreased with increasing temperatures. Also,at any given temperature, the storage modulus decreased with increasing filler concentration which might be due to the lowering of the stiffnes of matrix .The storage modulus of the composites containing AGG1 initially increased and then decreased when compared with pure epoxy as seen from fig.This indicates a decrease in stiffness of the composites with increase in filler concentration.In case of AGG2 composites the storage modulus decreases with increasing filler concentration. This comparatively poor performance of AGG2 with respect to AGG1 was due to low interfacial interaction in the case of the AGG2 as the degree of substitution increased

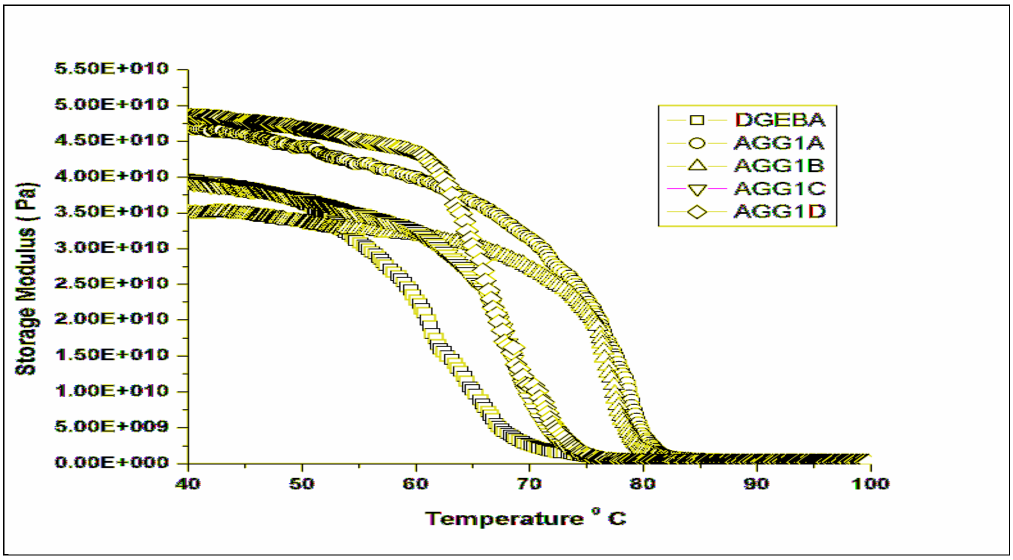


Figure 5.5Variation of Storage Modulus of Epoxy -ally guar gum (AGG1) composites

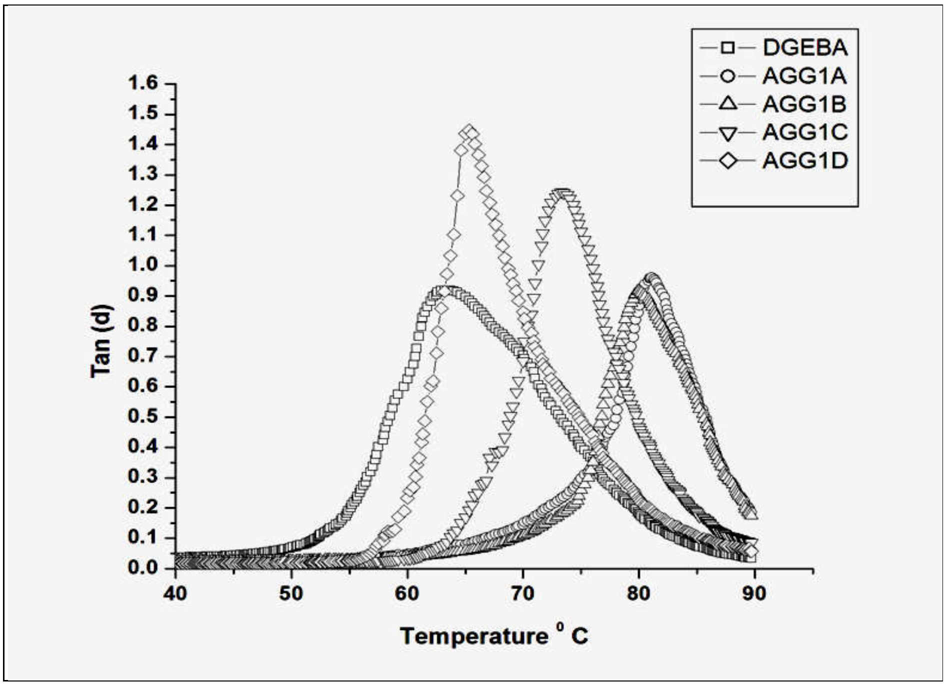


Fig 5.6Variation of Tan (δ) of Epoxy – allyl guar gum (AGG1) composites

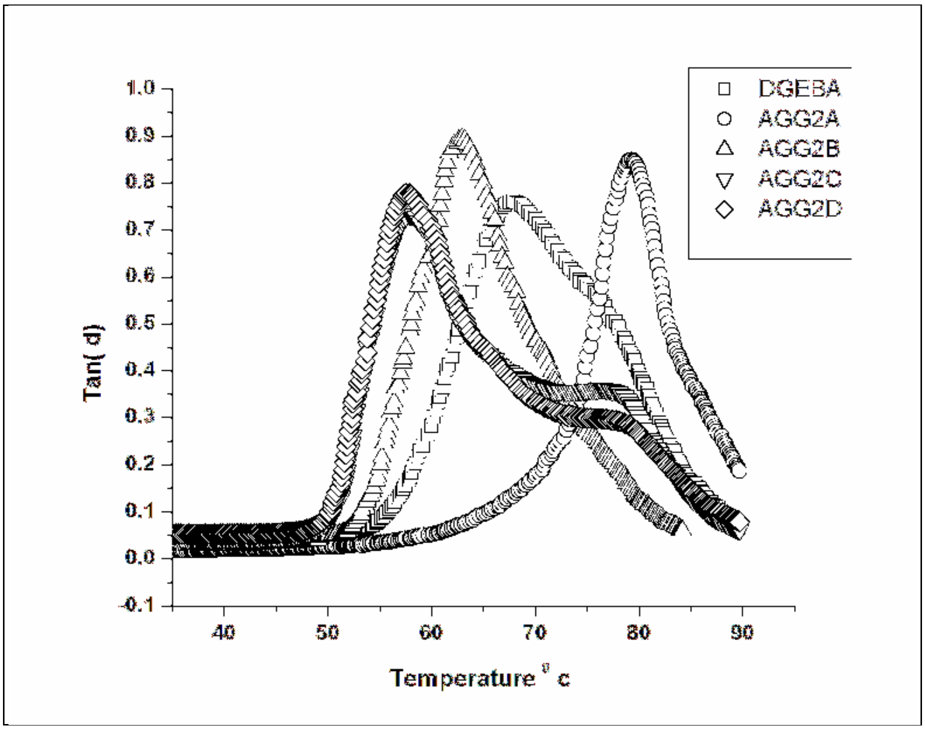


Fig 5.7Variation of Tan (δ) of Epoxy Allyl guar gum (E-AGG2) composites

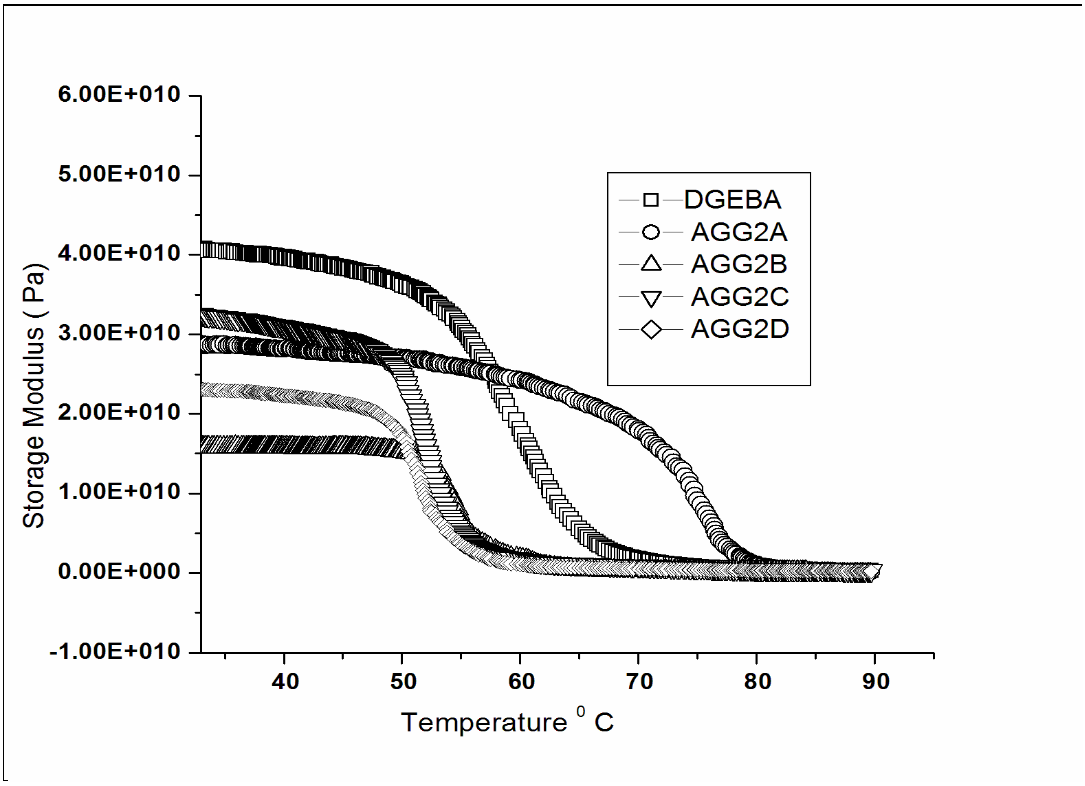


Fig 5.8-Variation of Storage Modulus of Epoxy Allyl Guar gum (AGG2) Composites

5.3 THERMOGRAVIMETRIC ANALYSIS

The effect of allyl guar gum were evaluated for thermal stability in nitrogen atmosphere by thermogravimetric analysis and the TG traces obtained for the blend sample is shown in Fig 5.9. The data on initial degradation temperature (T_I), The final decomposition Temperature Ts content on the thermal stability of the Epoxy system. The results are shown in Fig 5.9. TGA curves were characterized by thermal stability factors, including the initial decomposition temperature (IDT) and the temperature at T 50 wt % loss The results of IDT and T50 wt % for the epoxy system as a function of DGEBA content are shown in fig 5.3.From the figure it may be observed that AGG2 has higher initial degradation temperature than AGG1 and the % residue at 600 ^{0} C decreases due to the presence of double bond.when compared to unmodified system allyl modified epoxy system had lower char residue at 600 ^{0} C.The decrease in Thermal stability of the composites with increasing allylic content might be attributed to the fact that the thermal stability of allyl guar gum epoxy composite decreases with increasing temperature and resulted in decrease in thermal stability of Epoxy allyl guar gum composites.

Table 5.3 IDT and T50 wt% values for Epoxy-allyl guar gum.

Epoxy / Allyl guar Gum	IDT (^{o}C)	T $_{50}$ wt%	% Residue at 600 ^{0} C
E-AGG1 B	296	371.2	9.38
E –AGG2 B	305	372.6	8.87

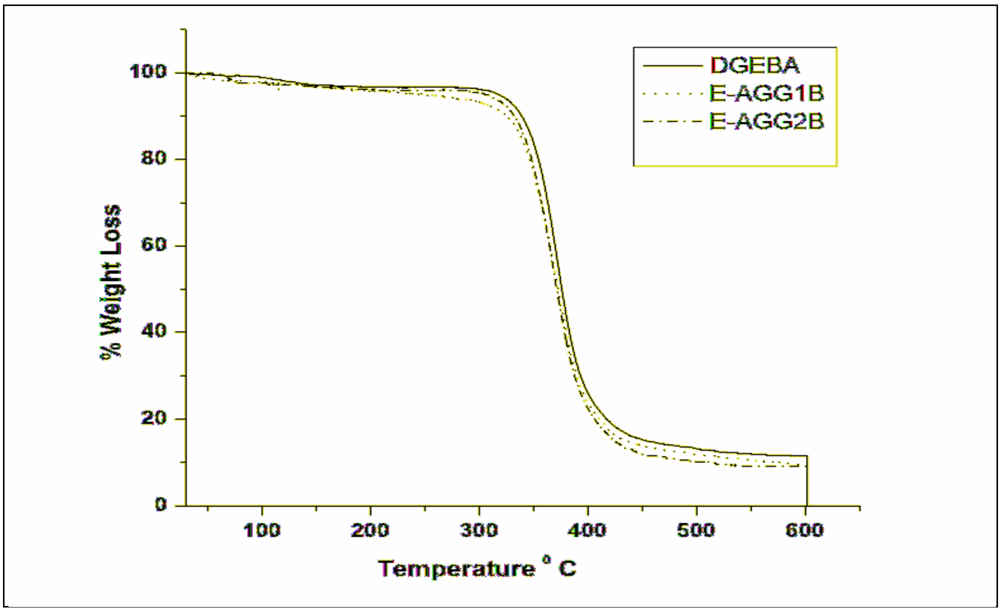


Fig 5.9 – TGA curves of Epoxy – allyl Guar –gum Composi

5.4 SCANNING ELECTRON MICROSCOPY

For polymer Composites, the morphology is one of the important factors that control theproperties of the modified systems. The morphologies of impact fractured surfaces of modified sytems were investigated by using scanning Electron Microscopy are shown in fig 5.10 to fig 5.15. The SEM micrograph in Fig shows the typical fracture surface of allyl guar gum epoxy composites loaded with contents of 0.5-4.5 phr, generally composite filled with low allyl guar gum show an increase in the matrix rich region compared to composite filled with high allyl guar gum. An increase in matrix rich regions means that the matrix is not restrained by enough fillers. In this case there is not sufficient filler to carry the mechanical properties compared to composites filled with higher filler content. moreover an increase in energy dissipation due to the increase in matrix deformation is observed for composite loaded with high filler content as shown in Fig.The fracture path of AGG1C shows fracture path with a large breadth and parallel fibril structure indicate the stretching prior to fracture.The fracture path of AGG2D is very narrow and continuous rapid crack propagation along the axis of crack growth. The micrograph of DGEBA is typical of brittle fracture with river marking and pulled out splinter.[166]

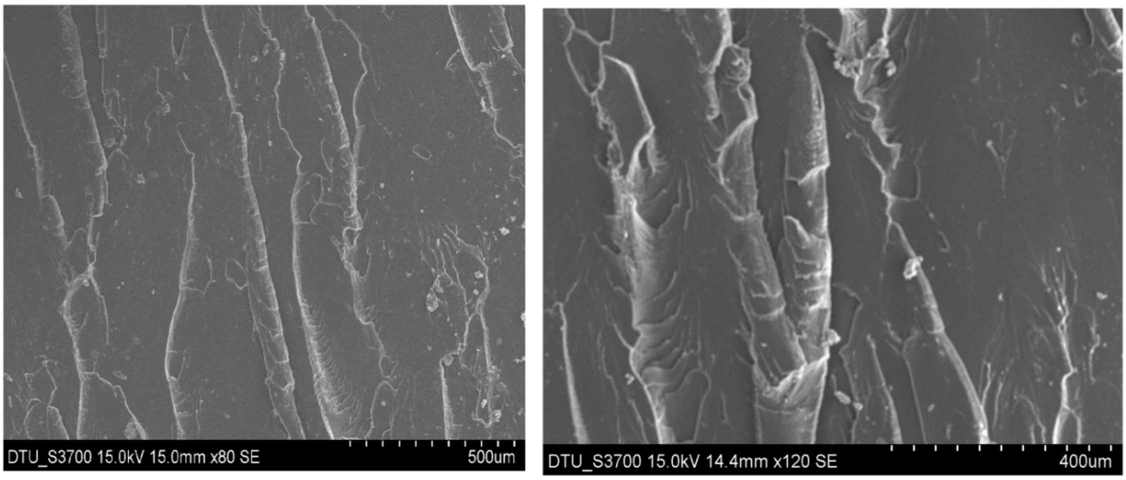


Fig 5.10 Fracture surface of Neat epoxy resin

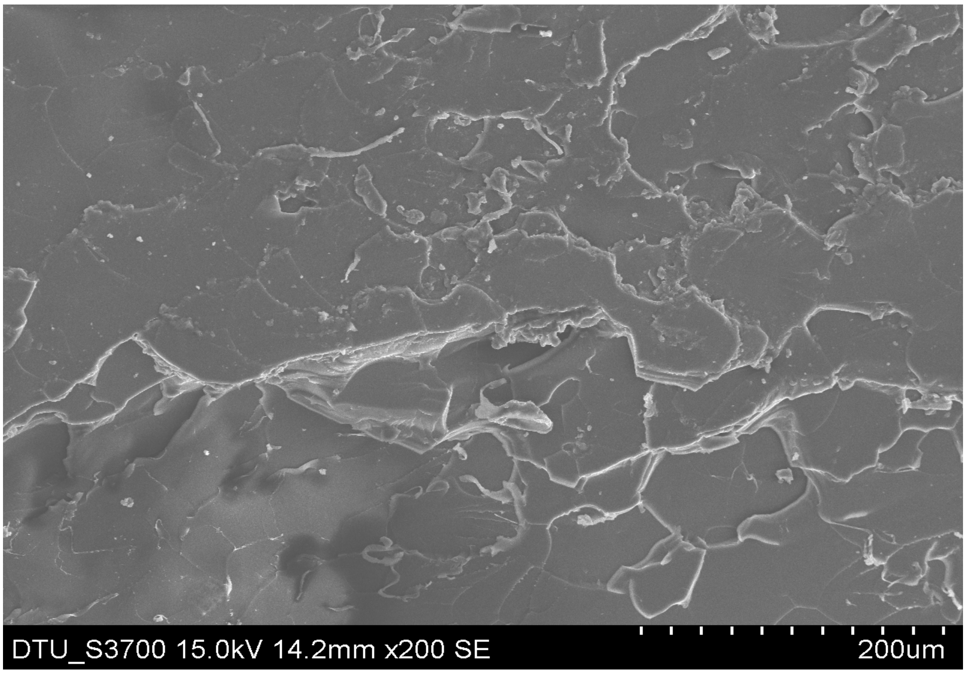


Fig 5.11 Fracture surface of AGG1B

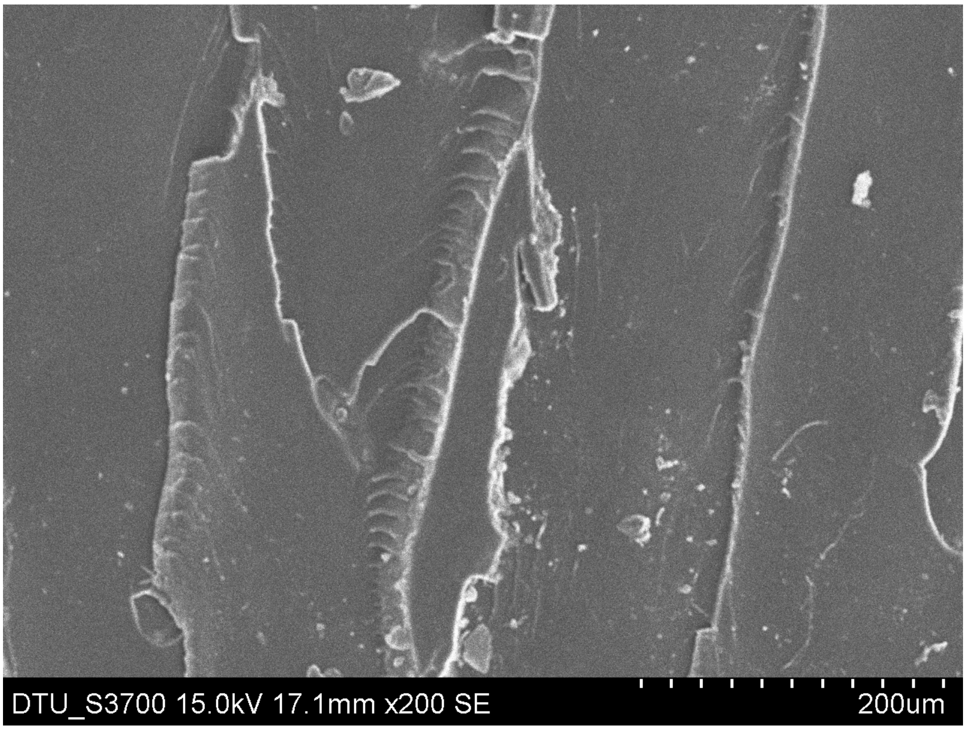


Fig 5.12 Fracture surface of AGG 1C

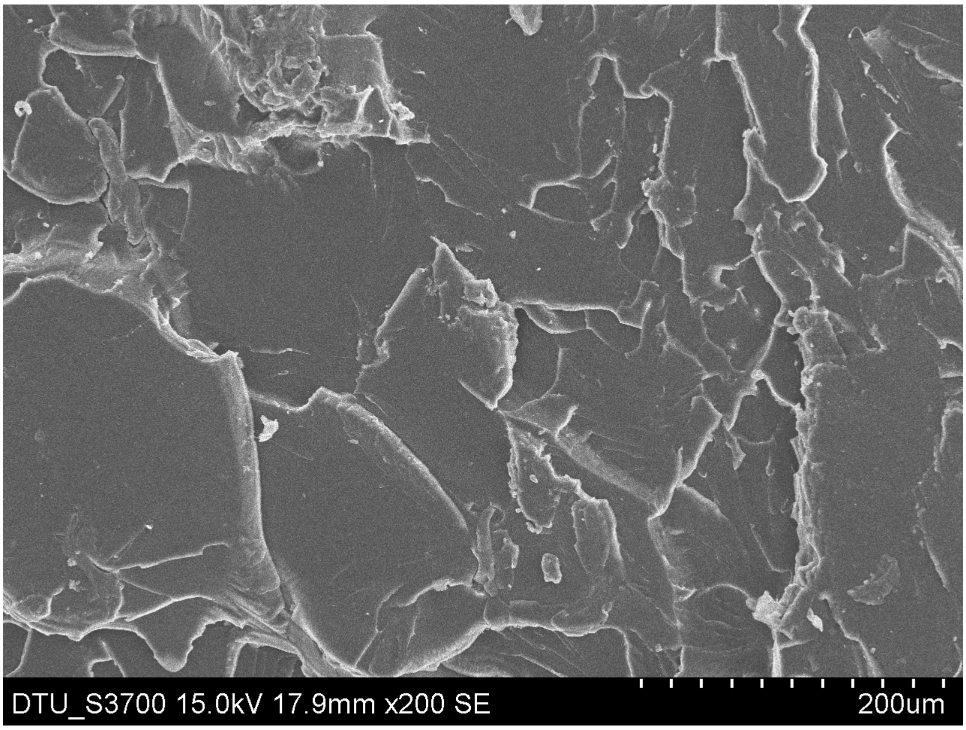


Fig -5.13 Fracture surface of AGG1D

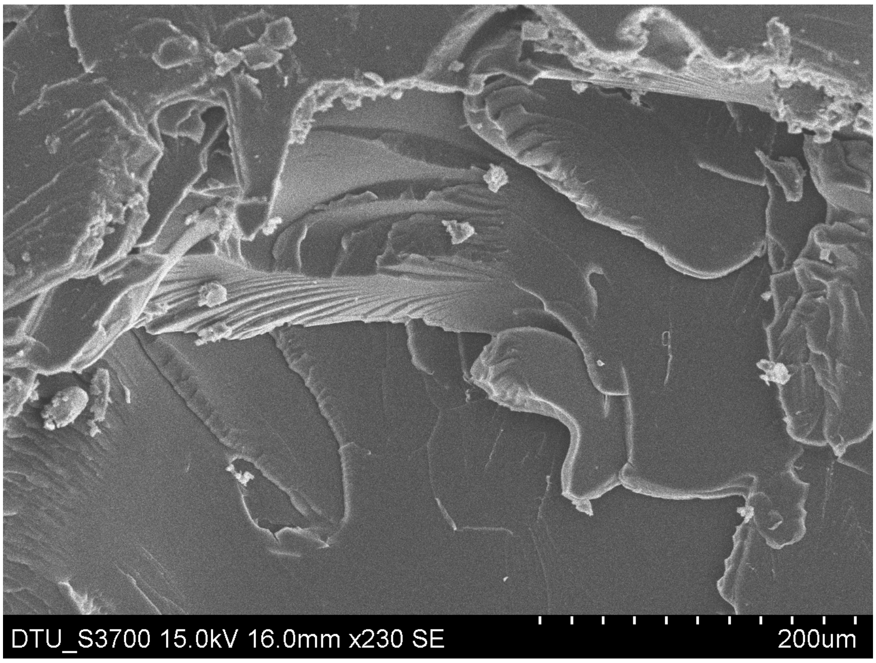


Fig 5.14 Fracture surface of AGG2C

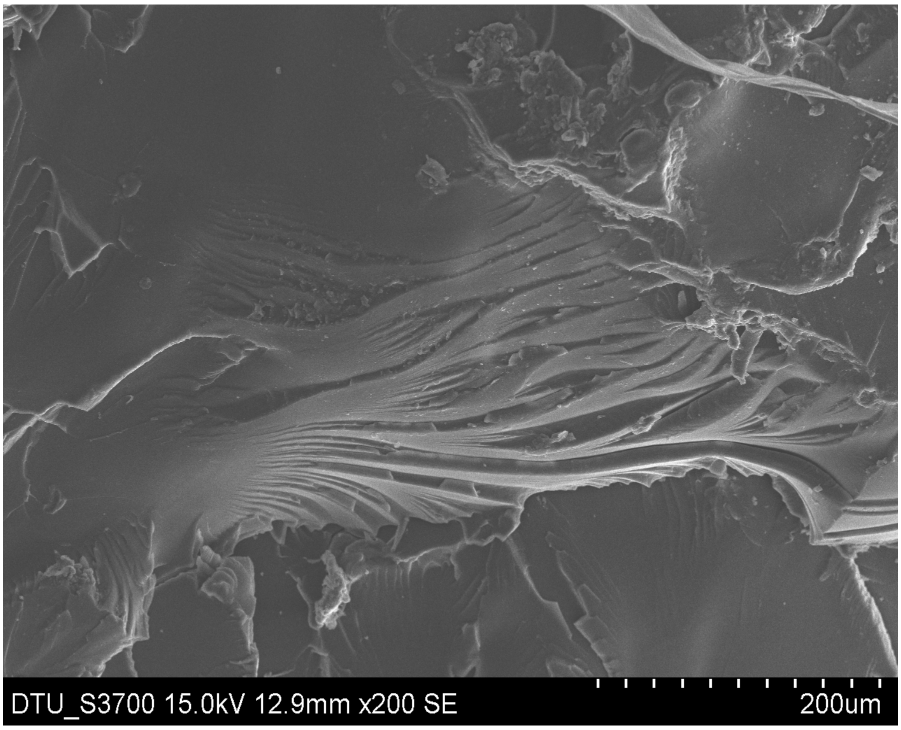


Fig 5.15 Fracture surface of AGG2 D

CHAPTER - 6

PREPERATION OF EPOXY- ALLYL GUAR GUM –g-POLY ACRYLIC ACID COMPOSITES

The polyether amine is having ether linkages so it produces more hydrophilic epoxy composites and offer greater compatibility to the filler guar gum have found to be varied particle ranges from irregular to fibrous it would behave as reinforcing filler to the epoxy composites. After the addition of guar gum to the epoxy resin its viscosity of dispersion gets increases at higher concentration the workability of the epoxy – Guar gum slurry reduced drastically. In the present case the decrease in the crosslinking was probably caused by the increase in the viscosity of composition. The increase in the viscosity of the composition would result in a lower degree through a reduction in the rate of diffusion. The substitution of Guar gum resulted in an increase hydrophobic nature of the polysaccharide increase the compatibility or in other words the wetting of the polysaccharide surface by the epoxy polymer matrix

The increase in the filler concentration effectively reduces the polymer content in the composites and results in aggregation of the filler resulting in an increase in the overall particle size and reducing complete surface coverage of the filler by the polymer. This incomplete coverage of the aggregated filler causes them to be the weak point in the polymer matrix because the aggregates are held together.r by only weak bridging forces such as vander wall forces and hydrogen bonding further the crosslinking density of the composites was found to decrease as the filler concentration increased. This also contributed to the decrease in tensile strength of the composite with increase filler addition, small interacting particles which contribute to actual physical crosslinking of weak areas in the polymer matrix. where the tensile strength increased was caused by the reinforcing effect of the fillers.

The filler is not a compact filler like inorganic fillers this would allow for the dissipation of energy with in the filler matrix further the nature of guar gum was such that it has a large number of secondry bonds present in the particle namely hydrogen bonds these secondry bonds can be broken eaily by the application of energy which are then able to reform at a later time allowing for the dissipation of energy introduced into the matrix via the impact this dissipation of energy would be greater if the transfer of energy from the matrix to the filler matrix were more efficient which was again dependent on the extent of interaction of the filler with the polymer matrix.Considering that guar gum and its derivatives are extremely soluble in water the water absorption capacity of the composites become a paramount importance it was observed that irrespective of the filler used the increased concentration of filler resulted in an increase in water absorption by the composites.

The Unmodified epoxy resin exhibit brittleness and low elongation after cure. these polymers usually craze on their free surface and the crazed areas are converted into cracks, which propagate with brittle energy absorption resulting in fracture. The high glass transition temperature of epoxy thermosets are the result of crosslinked structure and this is achieved at the expense of reduced toughness and damage tolerance. Crazes contains voids and easily breakdown to form cracks crazing is frequently associated with brittle response. craze contain void and fibril.The focus of this study is to develop new toughened system for amorphous epoxy resin via physical and chemical modification of guar gum. A detailed account of the effect of allyl guar gum as a filler in epoxy resin by casting technique were presented. The incorporation of allyl guar gum into the glassy epoxy matrix resulting in particulate composites . The addition of allyl guar gum with different degree of substituition increases the overall ductility of the polymer over a wide range of temperature and also improves toughness and impact resistance .

. This chapter deals with the preparation of Epoxy composites by the addition of allyl guar gum –g-Poly acrylic acid with different carboxyl value,The Thermal, mechanical properties and thermomechanical properties of the resultant composites were compared with those of the control resin.

6.1 DYNAMIC MECHANICAL ANALYSIS

Dynamic mechanical analysis (DMA) is a very useful thermal analysis technique used to measure changes in the viscoelastic response of a material as a function of Temperature., time, or deformation frequency. Generally, DMA can provide more information about a given polymer matrix than other mechanical tests since it can cover a wide range of temperatures and frequiencies which are not possible with others.[127-128]

Among all the techniques employed to characterize the composites, DMA is generally a good tool,because it provides a non –destructive direction. The damping property is denoted by tan d is an indication of all kinds of molecular movement existing in the materials. In a composite molecular motions at the interface contributes damping of the material.

A dynamic mechanical test measures the response of a material as it is deformed due to a sinusoidal or other periodic stress. The three important factors that can be obtained during a dynamic mechanical test are as follows.: (1) storage modulus Which is a measure of the maximum energy, stored in the material during one cycle of oscillation.. It also gives an idea of stiffness behavior and load bearing capability of composite material. (2) Loss modulus which is proportional to the amount of energy that has been dissipated as heat by the sample and (3) Mechanical damping term tan d, which is the ratio of the loss modulus to Storage modmodulus. It is related to the degree of molecular mobility in the polymer material The other useful quantities that that can be characterized by DMA are storage and loss compliance, dynamic and complex viscosity, creep compliance and the stress- relaxation modulus.

Dynamic test over a wide range of temperature and frequency are especially sensitive to all kinds of transitions and relaxation processes of matrix resin and also to the morphology of the composites. The dynamic mechanical properties of a composites material depend on the fibre -matrix interphase, fiber content and presense of the additives like filler, compatibilizer, fiber orientation and the mode of testing. a number of studies havev indicated thtb chemical modification of fibres has a profound effect on the dynamic mechanical properties of composites.

6.1.1 Loss factor Tan(d)

Tanδ relates to the impact resistance of the material [127]. As the damping peak occurs in the region of the glass transition region where the material changes from a rigid to a more plastic state. It is associated with the movement of small groups and chains of molecules within the polymer structure all of which are initially frozen in. In a composite system, tand is affected through the incorporation of fillers.

The glass transition temperature (Tg) can be defined as the maximum of the transition in the loss modulus curve or in the loss tangent curve. It is usually interpreted as the peak of the tand or loss modulus curve that is obtained during a dynamic mechanical test conducted at low frequency.

The variation of loss factor tand for the allyl guar gum –epoxy composites and Allylguar gum –g – Acrylic acid – Epoxy composites as a function of temperature measured at a frequency of 1 Hz showed in Fig 6.2 and Fig 6.3.

The variation of loss factor Tan d for the allyl guar gum-g-PAA based composites as a function of temperature measured at a frequency of 1Hz showed in fig6.5 and fig6.6 compared the tand curves of allyl guar gum based composites at different contents. In case of composites containing AGG-g-PAA1 the value of tand increases only upto 0.5 phr, after 0.5 Phr the value of tand decreaaes but higher than pure e poxy composites.In case of composites containing AGG-g-PAA2 the tand value increases only upto 0.5 phr.Above this concentration the value of tand decreases but lower than pure Epoxy composites. The decrease in Tg with the increase in concentration of allyl guar gum –g-PAA may be due to incomplete phase separation caused by the plasticization phenomena that has been noted in varied epoxy formulation from fig 6.2 and 6.3 it could be see that composites peaks are shifted to lower temperature. in comparision to the pure epoxy composites, This may be due to the increase in flexibility of the epoxy chains caused by the incorporation of allyl guar gum –g-PAA. The magnitude of $\tan\delta$ peak is indicative of the nature of the polymer system. Higher the tand peak value, greater is the degree of molecular mobility [164]. since in all composites the height of $\tan\delta$ peak was larger than untreated ones. this indicates that all composites possess different damping capabilities.

Table6.1 –Properties of Epoxy Allyl Guar gum –g poly acrylic acid

Sample	Tensile Strength (MPa)	Elongation at Break (wt%)	Flexural Strength (MPa)	Impact Strength (j/m)
Epoxy	57.5	4.4	222	151
Epoxy+0.5phr AGG-g-PAA1	64	4.7	236	170
Epoxy+1.5phr AGG-g-PAA1	62.7	4.9	212	161
Epoxy+3phr AGG-g-PAA1	57.7	4.76	209	157
Epoxy+4.5phr AGG-g-PAA1	52,36	4.12	202	140

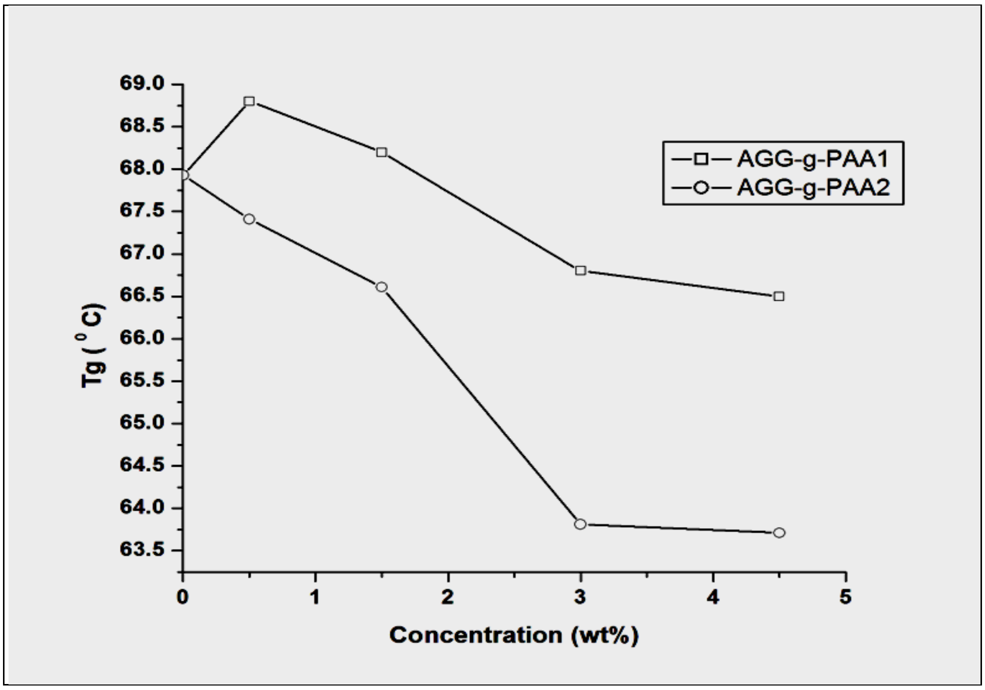


Fig -6.1 Variation of Tg of Epoxy composites

Table6.2- Properties of Epoxy – Allyl guar gum-g-PolyAcrylic acid Composites

Sample	Tensile Strength (MPa)	Elongation at Break (wt%)	Flexural Strength (MPa)	Impact Strength (j/m)
Epoxy	57.5	4.4	222	151
Epoxy +0.5phr AGG-g-PAA2	61.3	4.62	236	158
Epoxy+1.5phr AGG-g-PAA2	59.4	4.71	212	150
Epoxy+3phr AGG-g-PAA2	55	4.65	209	143
Epoxy +4.5phr AGG-g-PAA2	43	3.92	202	102

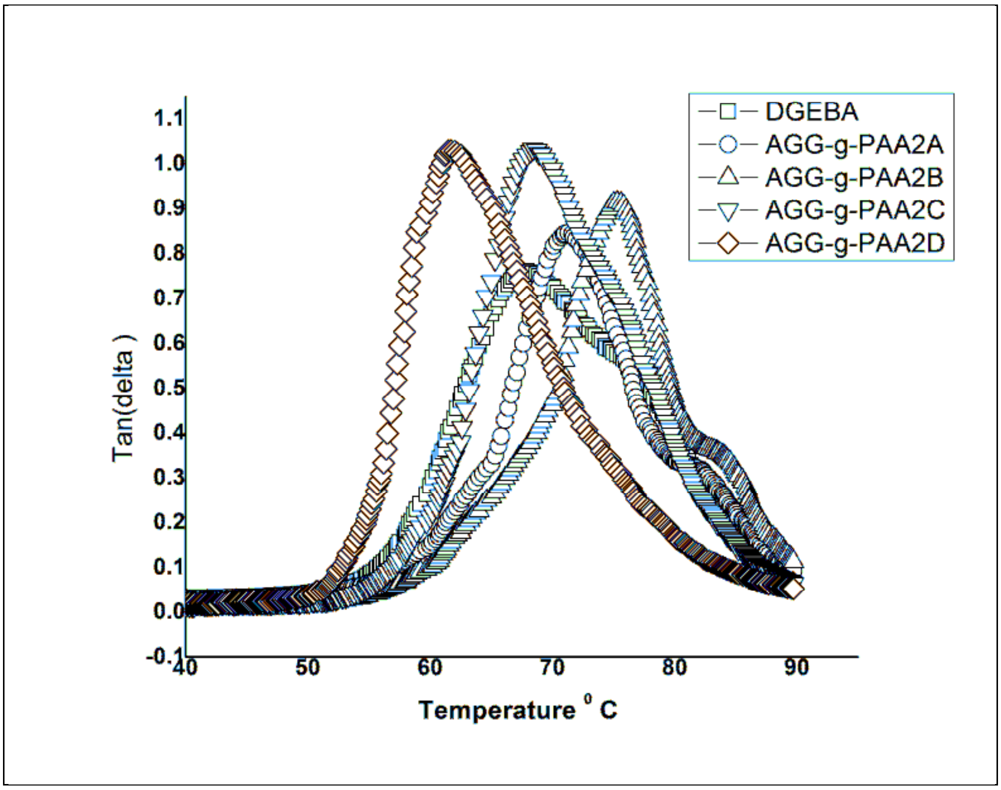


Fig 6.2 -Variation of tan(δ) of Epoxy – Allyl Guar gum-g-Poly Acrylic acid composites (AGG-g-PAA2)

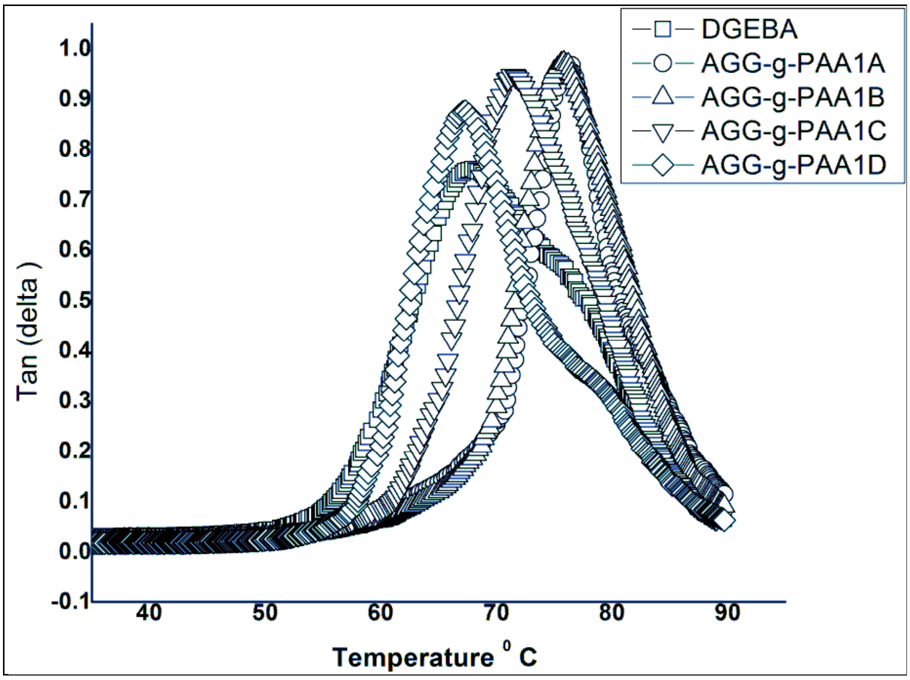


Fig-6.3 Variation tan δ of Epoxy – Allyl Guar gum-g-Poly Acrylic acid composite (AGG-g-PAA1)

6.1.2 Storage Modulus (E ‘)

The importance of the dynamic storage modulus in many structural applications is well known. The plots consisting of the storage modulus (E’), and loss tangent tan δ with different proportions of allyl guar gum-g-PAA 1 and allyl guar gum –g-PAA2 as a function of temperature have been shown in Fig (6.2 to fig 6.5) respectively. The value of Storage modulus (E’) decreased with increasing temperatures. Also,at any given temperature, In case of AGG-g-PAA1 the storage modulus value increased with increasing filler concentration upto 3phr when compared with pure epoxy resin from Fig6.4 which might be due to the lowering of the stiffnes of matrix [107].The storage modulus of the composites containing AGG-g- PAA2 initially increased and then decreased when compared with AGG-g-PAA1 as seen from fig.This indicates a decrease in stiffness of the composites with increase in filler concentration.The composite containing AGG-g-PAA1 is more flexible than composite containing AGG-g-PAA2. This comparatively poor performance of AGG-g-PAA1 with respect to AGG-g-PAA2 was due to low interfacial interaction in the case of the AGG-g-PAA2 as the carboxyl value is increased.

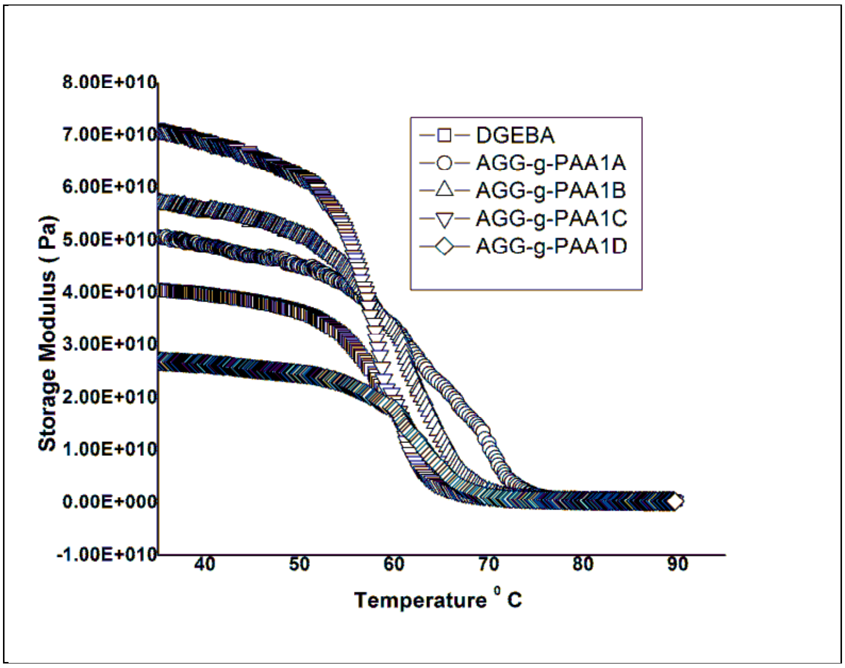


Fig 6.4 -Variation of Storage Modulus of Epoxy – Allyl guar gum –g- Poly Acrylic acid (AGG-g- PAA1)

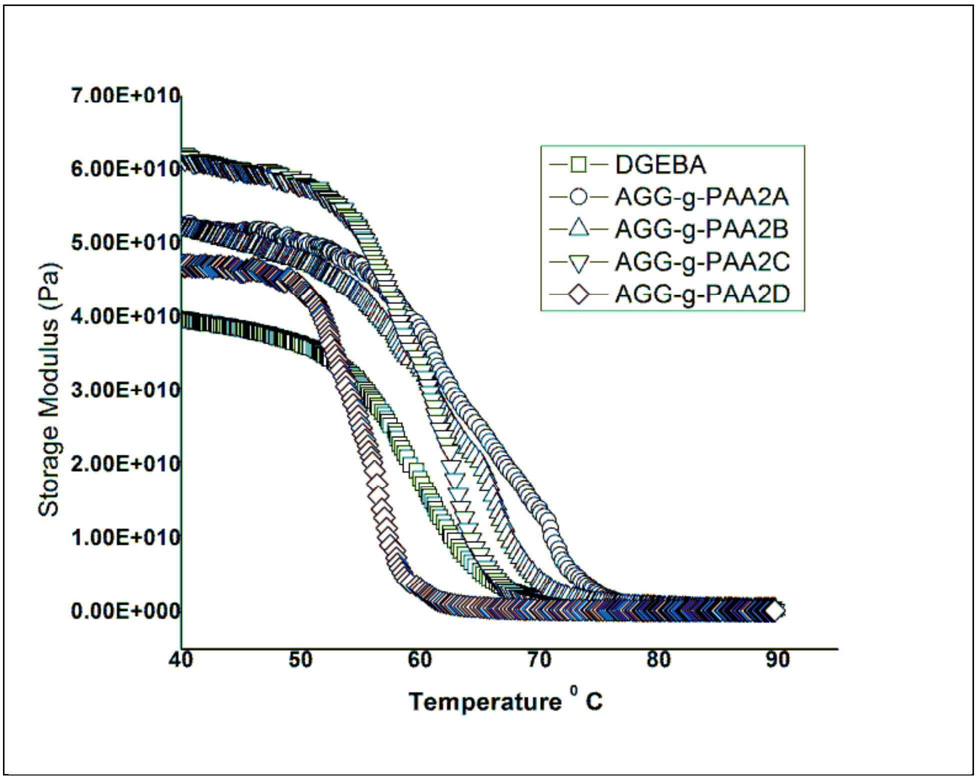


Fig6.5 Variation of Storage Modulus Epoxy – Allyl guar gum –g- Poly Acrylic acid (AGG-g- PAA2)

6.2 MECHANICAL PROPERTIES

Mechanical properties include the study of tensile strength and tensile modulus, flexural strength and flexural modulus and impact energy.

6.2.1Tensile Strength and % E longation at break

The tensile strength of the Epoxy composites were graphically depicted in Fig6.6 from which it it could be seen that the use of AGG-g-PAA1 resulted a moderate increase in the tensile strength upto 3 phr concentration. At the same concentration AGG—g-PAA1 based Epoxy composites showed the same trend .The variation of the tensile strength of composites containing AGG-g- PAA2 was found to be lower that observed for AGG-g-PAA1due to the decrease in carboxyl content.An optimum concentration of 3 phr was observed in the case of AGG-g-PAA based composites after which the tensile strength was seen to decrease.This decrease a higher filler concentration could be due to the agglomeration. In general the tensile strength and the elongation at break are antagonistic in nature.The elongation at break increases on the addition of filler to the composites From fig 6.7 it could be seen that At lower concentrations the reinforcing action of the fillers resulted in sharp decrease in the elongation at break values. There was a gradual, increase in elongation at break values as the concentration of filler increased.The improvement in tensile strength over that of the base resin at all percentages of allyl guar gum -g-Poly Acrylic Acid considerd is due to the high degree of compatibility and strong interaction of carboxyl group with the epoxy at higher post cure temperature (120 ^{0} C) The presence of amine hardner may also catalyse Epoxy –carboxyl interaction to some extent.

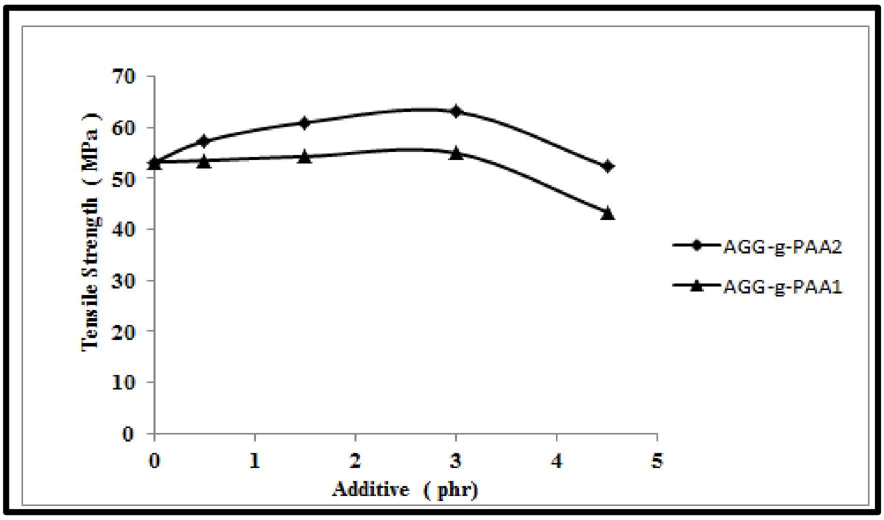


Fig 6.6 Variation of Tensile strength of Epoxy allyl guar gum –g- Poly Acrylic acid composites

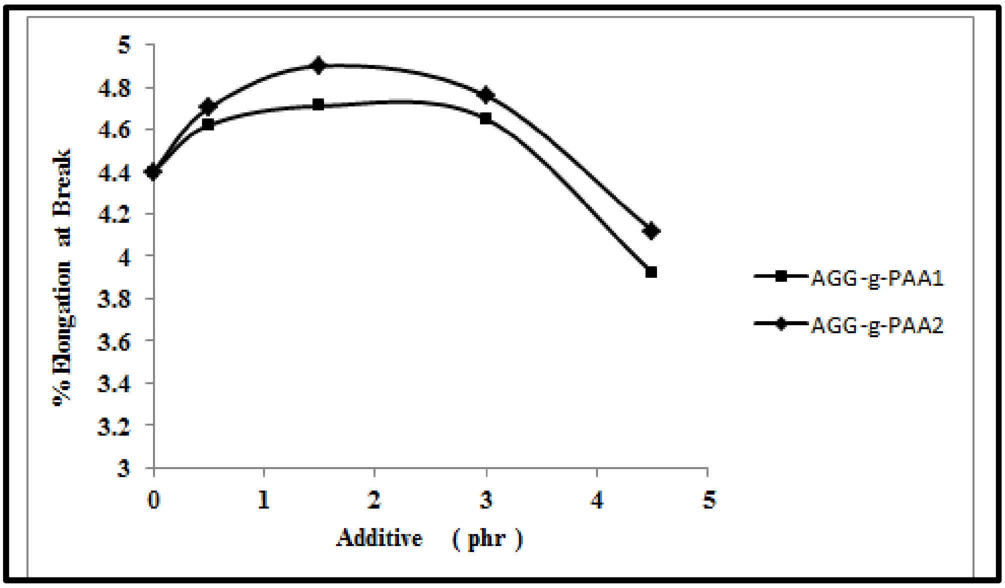


Fig 6.7 Variation of % Elongation at of Epoxy allyl guar gum-g – Poly acrylic acid composites

6.2.2 Flexural Strength

The flexural strength showed a trend similar to that shown for the tensile strength of the composites and was depicted in Fig 6.8 The reason for the increase in the flexural strength are similar to those cited for the increase in the tensile strength. The flexural strength curves were found to be similar in nature to those of the tensile strength with an optimum value of 3Phr. Above this concentration the flexural strength decreases with the increase in agglomeration.

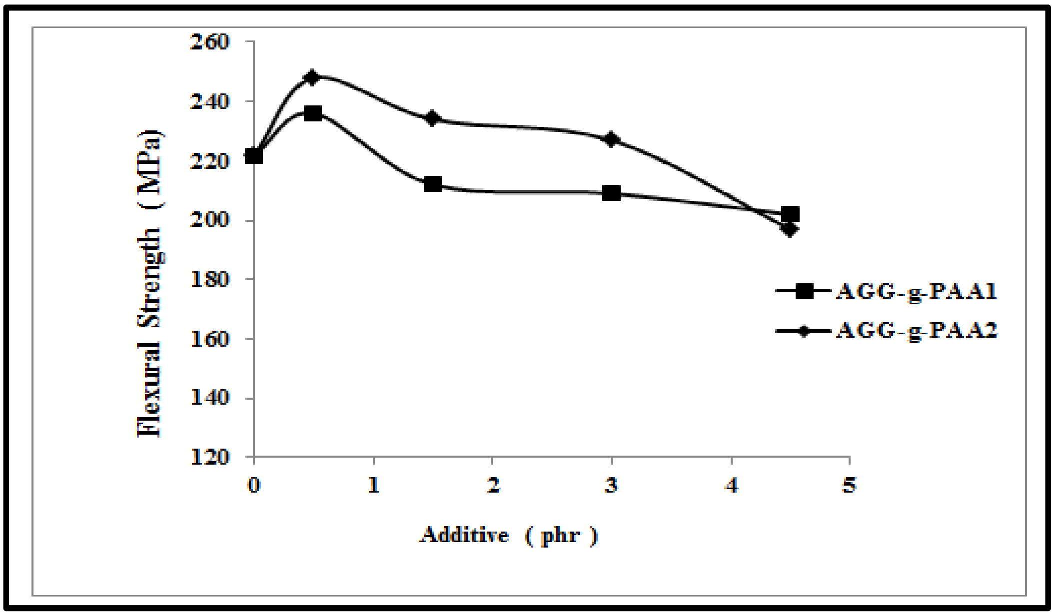


Fig 6.8 Variation of Flexural strength of Epoxy allyl guar gum –g _ Paa composites

6.2.3 Izod Impact Strength

The impact Properties of the composites on addition of allyl guar gum-g- PAA as filler could be seen in Fig 6.9. The impact strength of the composites, as measured by the charpy impact test showed positive results at higher varying upto 3Phr of the fillers. The effect of addition of allyl guar gum (AGG-g-PAA1 were greater than that of allyl guar gum AGG-g-PAA2 concentration.on the basis of increase interaction of Epoxy - allyl guar gum-g-PAA the impact property of a polymer composites can be explained by the nature of the filler itself AGG-g-PAA1 that have greater interaction would result in composites with greater impact strength.

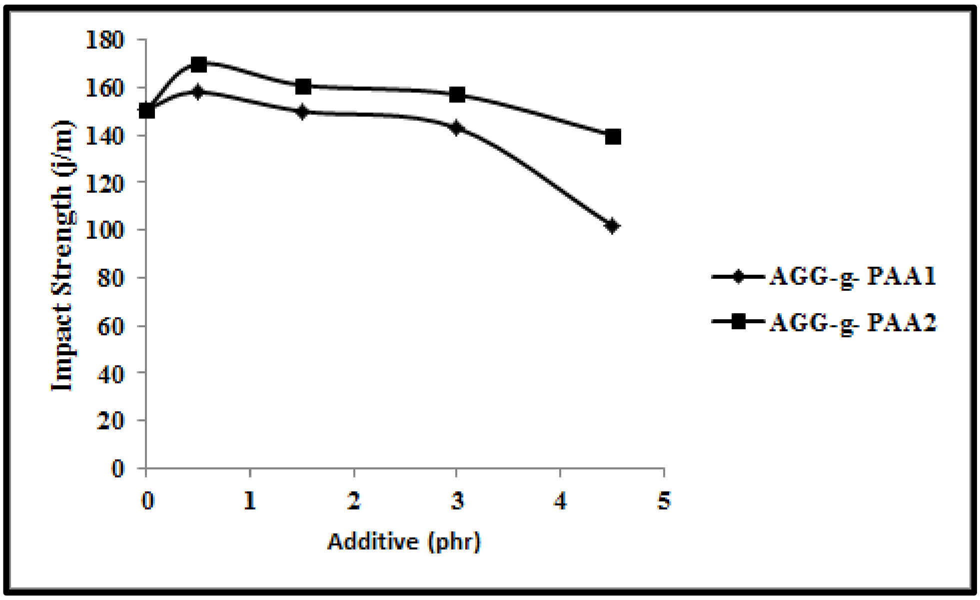


Fig 6.9 Variation of Impact strength of Epoxy allyl guar gum –g - PAA composites

6.3 DIFFRENTIAL SCANNING CALORIMETRY

The DSC thermograms are shown in Fig 6.10 to Fig 6.11, shows the effect of Allyl guar gum-g-PAA on epoxy based composites. A DSC scan of allyl guar gum –g – PAA based composites during heating from 0 to 450 ^{0} C. The exothermal peaks are observed in the regions of 230 -280 ^{0} C and 330 -380 ^{0} C. This exothermic Peak arises in the system due to incomple phase separation caused by the plasicization phenomena.

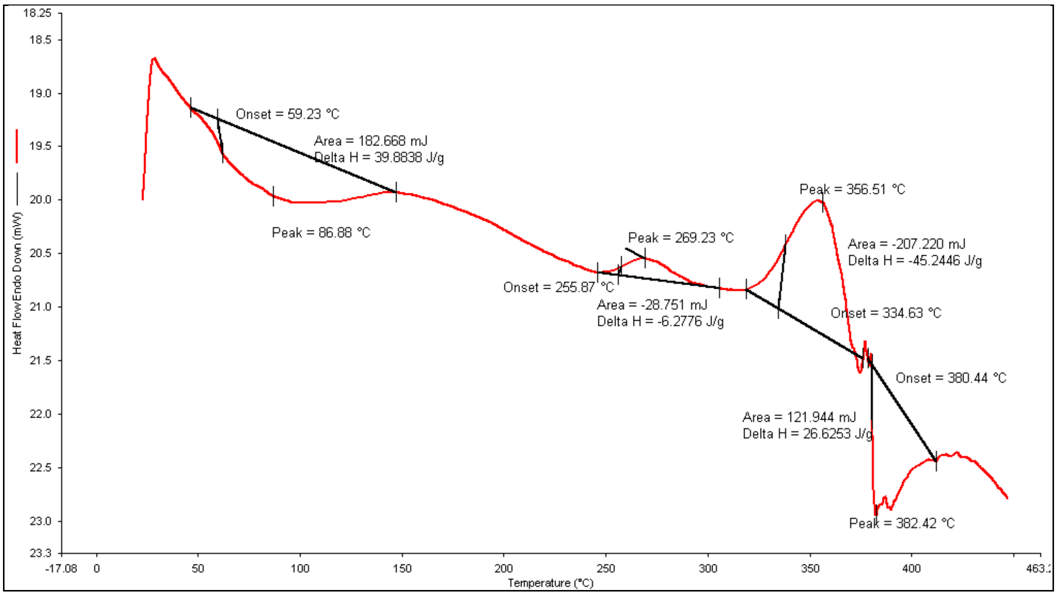


Fig 6.10– DSC Thermogram of Epoxy- AGG-g- PAA1B

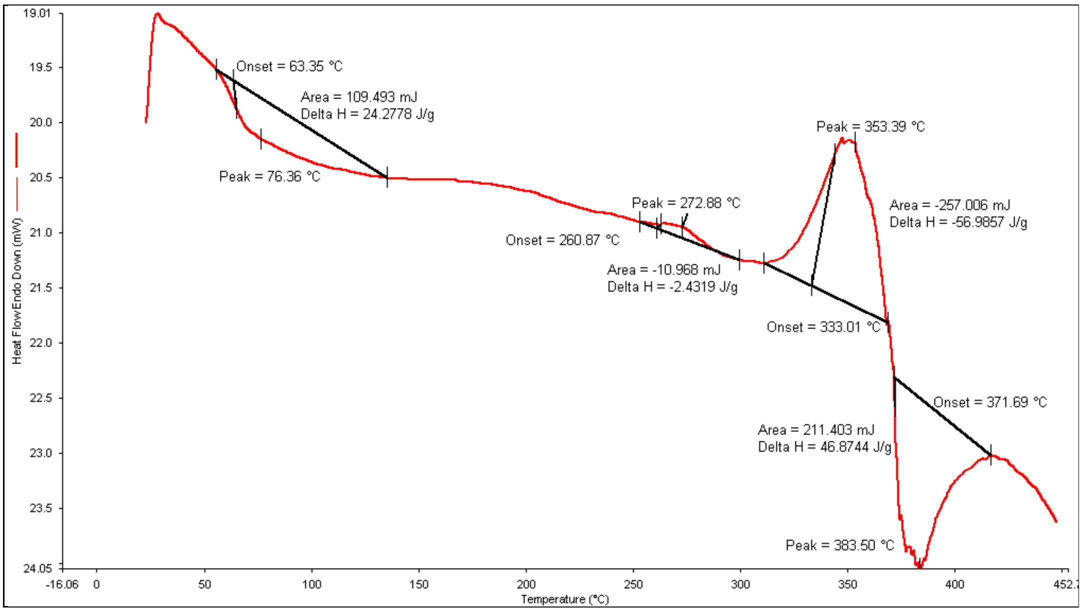


Fig6.11 DSC Thermogram of Epoxy- AGG-g-PAA 1D

6.4 SCANNING ELECTRON MICROSCOPY (SEM)

For polymer Composites, the morphology is one of the important factors that control theproperties of the modified systems. The morphologies of impact fractured surfaces of modified systems were investigated by using scanning Electron Microscopy are shown in fig 6.12 to fig 6.15. The SEM micrograph in Fig shows the typical fracture surface of allyl guar gum –g- PAA based epoxy composites loaded with contents of 0.5-4.5 phr. generally, composite filled with low allyl guar gum-g-PAA1 show an increase in the matrix rich region compared to composite filled with high allyl guar gum-g-PAA1. An increase in matrix rich regions means that the matrix is not restrained by enough fillers. In this case there is not sufficient filler to carry the mechanical properties compared to composites filled with higher filler content. moreover an increase in energy dissipation due to the increase in matrix deformation is observed for composite loaded with high filler content as shown in Fig.The fracture path of AGG-g-PAA2B shows a brittle fracture. The fracture surface shows a multilevel fracture paths with ridges and wavy crests indicate energy absorption. The fracture path of AGG-g-PAA2B shows a brittle fracture. The fractured surface shows river marking and are mostly straight. This multilevel fracture path with ridges indicate energy absorption on a large scale during failure continuous rapid crack propagation along the axis of crack growth. The micrograph of DGEBA is typical of brittle fracture with river marking and pulled out splinter. In case of allyl guar gum –g Acrylic acid based composites from fig 6.13 to fig 6.15 matrix was seen adhering to the fillers. Also more surface area are available for forming links with the Epoxy matrix. as a result a stronger bonding between filler and matrix will takes place. This is evident from the short broken filler ends projecting out of the matrix that can be seen in micrograph. In contrast to, allyl guar gum –g –AA showed the brittle texture with extensive filler tearing and less filler pullout. Thus scanning electron microscopic studies further supports the indication of better adhesion by chemical treatment. Fig correspond to the that of allyl guar gum –g-poly acrylic acid modified resin multilevel fracture paths with pulled up crests indicate energy absorption on a large scale during failure. There is distinct sign of stress whitening which is indicative of crazing.

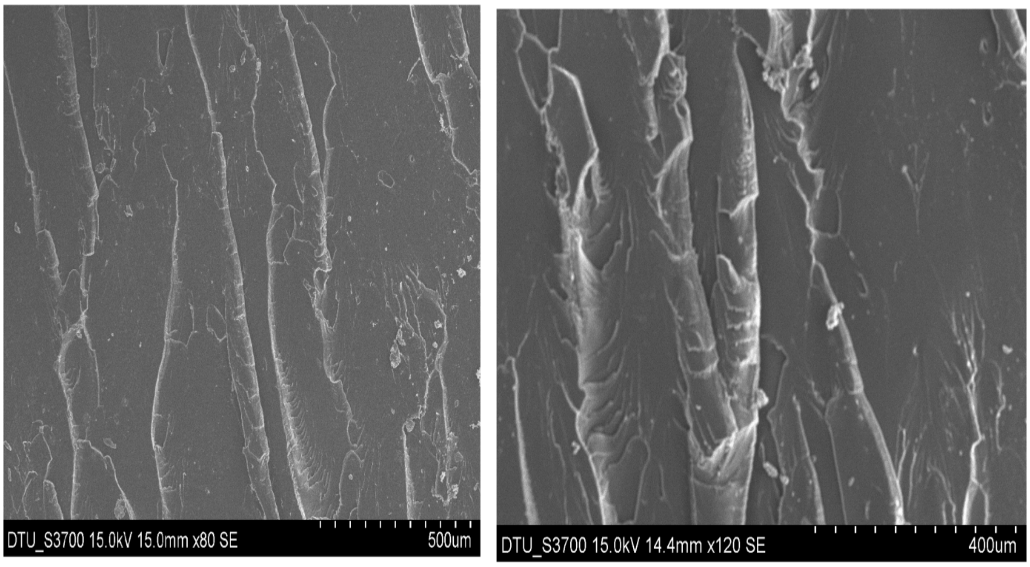


Fig 6.12 Fracture surface of neat Epoxy Resin

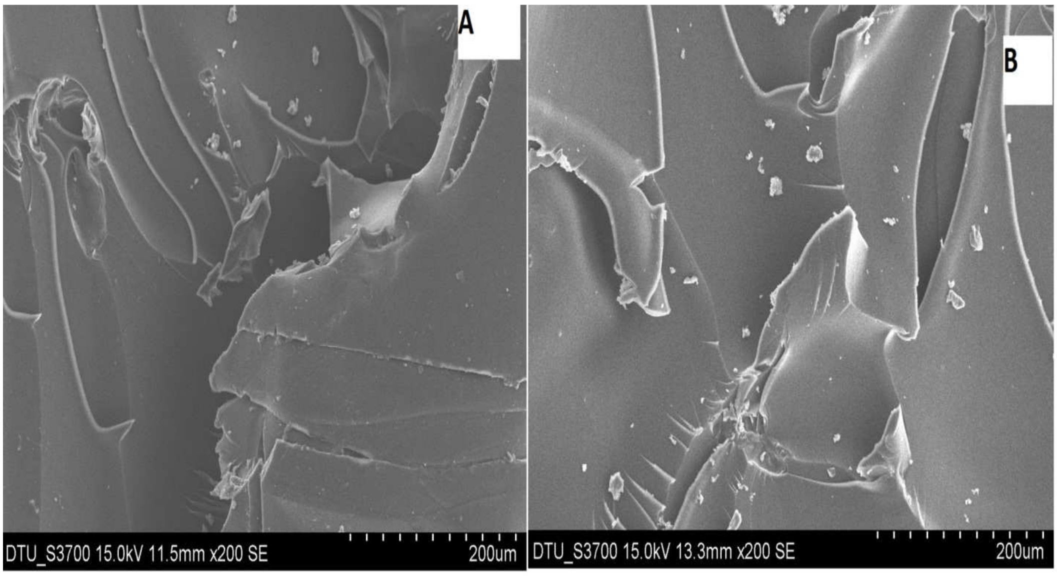


Fig6.13 – Fracture surface of Epoxy- AGG –g- PAA1C

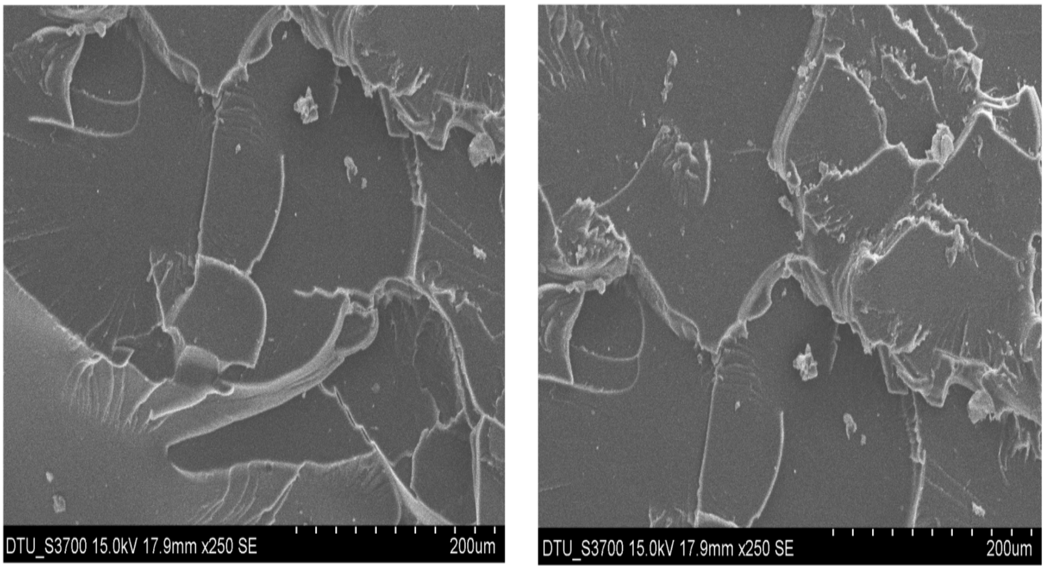


Fig6.14 - Fracture Surface of Epoxy- AGG-g-PAA2B

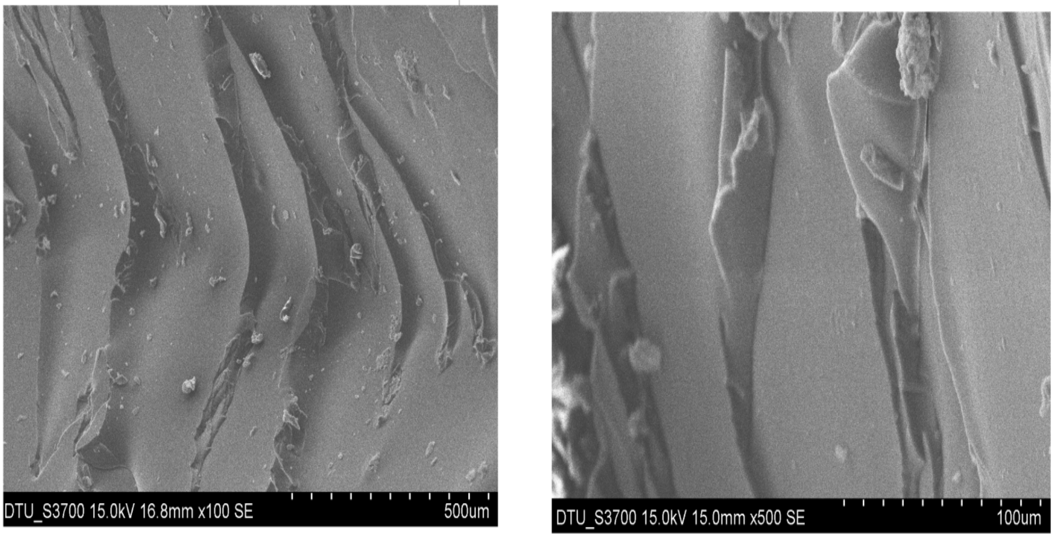


Fig 6.15– Fracture surface of Epoxy- AGG-g- PAA2 C

SUMMARY

Polymer from renewable resources have been attracting increasing attention, primarily for two major reasons : environmental concerns and the realization that our petroleum resources are finite. a third reason for growing intrest in polymers from renewable resources relates to adding value to agricultural products, which is economically important for many countries. Generally polymer from renewable resources can be classified into three groups : **1)** Natural Polymer such as starch, Protein and cellulose, Guar Gum **: 2)** Synthetic Polymer from natural resources such as Poly (Lactic acid): **3)** Polymer From Microbial Fermentation such as Poly(hydroxy butyrate).

A major advantage of all these materials is that they are biodegradable and that their final product of degradation are environment friendly. As with numerous Petroleum based polymers many properties can be improved through appropriate blending and composite formulation. These new blends and composites are extending the utilization of polymers from renewable resources into wider applications. Epoxy resins constitute a major class of Thermosetting resins and are extensively used as coatings, electronic materials, adhesives and in structural applications owing to their outstanding mechanical and electrical properties. adhesion, chemical resistance and minimal shrinkage after curing, However, some of the properties of the materials of epoxy resins are nonbeneficial such as the inherent brittleness due to the high crosslinking density formed in curing, which limits their many end use applications. A large number of studies have been conducted to improve the toughness of highly crosslinked Epoxy resins, Epoxy resins are usually toughened by modification with liquid elastomers, thermoplastics and inorganic particles.

Recently Biodegradable polymers have attracted considerable attention due to the increasing emphasis on environmental issues and Earth's limited Petroleum reserves. Biodegradable polymers from renewable resources such as biobased polymers including, Polysaccharides can be used as fillers in fabricating improved of Epoxy resins.The Biopolymer contain numerous hydroxyl groups. The numerous hydroxyl group present in such natural polymers allow them to properly disperse in synthetic polymers with high degree of polarity through forces such as hydrogen bonding and ionic interactioin .Studies investigating the use of particulate fillers of natural origin such as lignin saw dust or wood flour.starch, chitosan and a few on guar gum

are reported . GG, like these fillers are, is stiff in nature and would conceivably behave as a reinforcing filler. The most commonly used Biopolymers in plastics have been starches, which has been studied extensively for their interaction with polyolefins for the purpose of imparting Biodegradibility

Till date the use of Guar -Gum and hydroxylpropyl guar gum has been investigated extensively and the effect of Degree of propoxylation of the Guar gum on the properties of resultant composites . This study aims at further investigating the effect of guar gum and its derivative on an epoxy matrix.The effect of allyl Guar gum and the degree of aalylation of the guar gum on the properties of resultant composites have been studied.

Biopolymers have an advantage over silicate –based polymers such as Fly ash, clays, mica and silica in that they are renewable resources and are ecofriendly. materials such as Lignin, rice husks and wood flour are waste products and their incorporation in composites provide a commercial avenue for utilization of such materials which would otherwise be disposed off.

CHAPTER1. INTRODUCTION

This Chapter Presents an overview of recent developments in the chemistry of Guar gum and its Derivatives, Topics such as chemical nature, origin, abundance and Purification method and Properties are revealed**.**

Guar Gum

Guar gum is a natural polymer extracted from the endosperm of the“*cyamopsis tetragonolobus”* family leguminosaeand chemically is a galactomannan with galactose to mannose ratio of 1:2Guar crop has grown in India & Pakistan for centuries.Guar gum is a galactomannan with (1→4) linked β D mannopyranose backbone with branch points from their 6 position linked to α D galactoseie. (1→6) linked α D galactopyranose [2] .Guar gum is soluble in hot and cold water but insoluble in most organic solvents, strong hydrogen bonding properties, excellent thickening, emulsion, stabilizing and film forming properties. it's ability to hydrate rapidly in cold water to attain high viscosity at relatively low concentration this property has allowed this polymer to be commercialized in fields such as textiles,foods, cosmetics, pharmaceuticals, oil recovery.Guar gum is hydrophilic in nature & has poor mechanical properties so it can be modified by either grafting or by derivatisation.

Derivatisation

Guar gum has per repeat unit of 2 mannose a single unit of galactose is attached so Guar gum containing in total 9 hydroxyl groups of whichtwo are primary and the remaining secondry.These hydroxyl groups are capable under appropriate condition of behaving as ordinary aliphatic alcohols.

Etherification reaction

This reaction gives a large number of commercial product including hydroxypropyl guar gum, Carboxymethyl guar gum

Esterification

This reaction gives product including acryloylated Guar gum [3], methacryloylated guar gum [4]

Grafting

Grafting reaction includes the reaction of a compound containing an activated double bond with the hydroxyl groups, there are various reactant have been grafted onto guar gum such as acrylamide, acrylic acid, Methacrylic acid, acrylonitrile, vinylpyridineetc

Epoxy Resins

Epoxy resins are one of the most versatile classes of polymers with diverse applications. Epoxy resins provide amorphous thermosets with excellent mechanical strength and toughness and outstanding chemical,moisture and corrosion resistance.Commercial epoxy resins contain aliphatic, cycloaliphatic or aromatic backbones and are available in wide range of molecular weight from several hundred to tens of thousand the most widely used epoxies are the glycidylether derivatives of Bisphenol A. The curing agent of epoxy resin contain an active hydrogen atoms like primary and secondry amines, phenol, thiols, and carboxylic acid, lewis acids and lewis bases.

This introductory chapter explores with details of various possible modifications of guar gum including Derivatisationand Grafting reactions and mechanism of grafting and a little introduction about Epoxy resins .

CHAPTER 2 LITERATURE REVIEW

As Guar -gum have been used in Pharmaceuticals, Textile, Cosmetics coatings, oil recovery, Drilling but has had little use as a filler in thermosets including Epoxy resin and Polyester resin. This chapter reviewed about the literature on the successful use of Guar gum modification by Derivatisation, grafting and Miscellaneous reactions, their characterization and successful use of guar gum and its derivatives in preparing polymer composites was given.

This chapter meticulously delivers a comprehensive literature incorporating the significant and relevant research done by prominent scientist in this area

CHAPTER 3.

This chapter deals with raw material used, experimental part and processing techniques used for the synthesis of polymer samples.

3.1a) Synthesis of allyl guar-gum

It involves a reaction of guargum with an allyl chloride in the presense of sodium hydroxide and tetramethyl ammonium chloride (phase transfer agent) was added to the slurry and the mixture was stirred and heated to a temperature of 50 ^{0} C. The reaction mixture was cooled gradually dispersed in acetone and an excess of alkali is neutralized with acid the product than finally washed and dried under vaccum. A series of allyl guar gum has been prepared by varying the concentration of allyl chloride and sodium hydroxide at fixed temperature.

b) Synthesis of allyl guar gum –g –PolyAcrylic acid

Allyl guar gum has been mixed with an aqueous solution of isopropanol and ferrous ammonium sulphate and hydrogen peroxide were used as redox pair initator into the system.The graft copolymerization was carried out under vigorous stirring and under the protection of nitrogen atmosphere, The molar ratio (H_2O_2 / $FeSO_4$ ($NH_4)_2$ SO_4) was 14/1 and allyl guar gum and acrylic acid were mixed in 10 :1 ratio and initiator solution were added continuously so that uniform solution is obtained.The product was neutralized to pH 6-7 filterd and washed thoroughly with distilled water dried at 50 ^{0} C, pulverized and sieved with hundred mesh size.

3.2 Preparation of Epoxy composites

a) The allyl guar –gum(low and high degree of substituition) were dispersed in epoxy resin and a stoichiometric amount of curing agent polyetheramine D230, was added and the composition mixed thoroughly. The formulation was then deaerated and poured into a preheated mold at 60 ^{0} C. The cure cycle adopted for the preparation of epoxy composites was 60 ^{0} C /3Hrs. The composites had a thickness of 3mm**.**The samples were prepared by mixing 0,0.5,1.5, 3.0, 4.5 phr through casting technique.

b) The Epoxy composites were prepared by following a method similar method used above.Once the fillers (allyl guar gum –g – polyacrylic acid) were dispersed in the epoxy resin and a stoichiometric amount of curing agent, polyetheramine D230, was added and the composition mixed thoroughly. The formulation was then deareated and poured into a preaheated mold at 60 ^{0} C.The composites had a thickness of 3mm ±1%. samples were prepared and were allowed to stabilize at 50% humidity and at 30 ^{0} C for 7 days.

Finally the samples will be analyzed using various techniques in accordance with Standards

1. **Chemical Properties**
    a. Degree of substituition by titration method
    b. Carboxyl value by Titration method
2. **Mechanical properties**
    a. Tensile strength
    b. Percentage Elongation at break

c. Flexural strength

d. Impact strength

3. **Spectroscopic analysis**

a) FTIR spectra

b) ^{1}H NMR

c) X-ray diffraction

d) Scanning Electron Microscope

4. **Thermal analysis**.

a) Diffrential Scanning calorimetry

b) Thermogravimetric analysis

c) Dynamic Mechanical Thermal analysis

RESULTS AND DISCUSSION -

CHAPTER 4 – STUDIES ON THE MODIFICATION OF GUAR GUM

This chapter describes in details the spectroscopic, chemical, thermal, Morphology components and X ray diffraction studies about the allyl guar gum.

The samples have been characterized through the following techniques :

a) FTIR

b) NMR

c) Degree of Substitution

d) TGA

e) DSC

f) XRD

g) SEM

Degree of substituition is used to find the number of sites per anhydropyranose unit on which there are substituent group.The high end technologies like FTIR, SEM,XRD available have been used to relate with the degree of substituition.

The decomposition temperature of Guar gum and allyl guar gum was determined from TGA measurements. The TGA results of guar gum showed that the initial weight loss is due to the present of small amount of moisture, The second zone of degradation starts at 240 ^{0} C where the polymer decomposition takes place nearly 75% guar gum degrades below 400 ^{0} C.A 16.2% was residue was obtained at 600^0 C.In case of allyl guar gum The TGA results showed that increased degree of substituition lowers the initial degradation temperature of allyl guar gum and increases the % residues.

CHAPTER 5 - STUDIES ON ALLYL GUARGUM –g-POLYACRYLIC ACID

This chapter describes the chracterisation of allyl guar –gum g- polyacrylic acid, The reaction parameter including monomer and initiator concentration, reaction temperature and time has been optimized in order to obtain max grafting efficiency and grafting % and monomer conversion.

The samples obtained have been charcterized through the following Techniques

a) FTIR

b) TGA

FTIR results confirms the presense of carbonyl stretching vibration. The TGA results showed that the initial degradation temperature lowers with the increase in amount of carboxyl present in polyacrylic acid.The amount of carboxyl present in poly acrylic acid has been estimated by titration analysis.

CHAPTER 6-EPOXY –ALLYL GUAR GUM COMPOSITES

The effectiveness of using allyl guar gum (low and high degree of substituition) as particulate fillers in an epoxy matrix was evaluated.The polyether amine was used as a curing agent due to its ether linkages it offers greater compatibility to the filler as compared to other curing agent.

The resultant composites have been characterized through following Techniques

1. Mechanical properties including Tensile strength, % Elongation, Flexural strength and Impact strength.
2. Dynamic mechanical analysis
3. Thermogravimetric analysis
4. Scanning electron microscope

The inclusion of allyl guar gum(lower degree of substituition) resulted in an increase in tensile, flexural and impact strength of the composites upto lower concentration after which there is a rapid decrease in respective properties. The allyl guar gum with higher degree of substituition showed reduced mechanical and chemical performance.The obtained composites were also analysed for Thermomechanical analysis and Thermogravimetric analysis.

Epoxy –allylguargum-g-polyacrylic acid composites

The incorporation of allylguargum –g- polyacrylic acid as particulate fillers in an epoxy matrix was evaluated.The polyether amine was used as a curing agent due to its ether linkages it offers greater compatibility to the filler as compared to other curing agent.

The resultant composites have been characterized through following techniques

1. Mechanical properties including Tensile strength, % Elongation, Flexural strength and Impact strength.
2. Dynamic mechanical analysis
3. Scanning electron microscope

The inclusion of allyl guar gum –g-polyacrylic acid (low carboxy value) epoxy composites resulted in decrease in modulus with the filler addition,while in case of allyl guar gum –g-poly acrylic acid (high carboxyl value) epoxy composites resulted in an increase in Storage Modulus with the filler addition. The mechanical properties including Tensile strength and Flexural strength increase upto lower concentration and than decreases

Conclusions

This chapter summarizes results and describes relevant conclusion for study

- Allylation of guar gum resulted in a derivative with a Maximum Degree of substitution of 0.0625, The allylated guar gum were found to have reduced thermal stability and more porous in nature. This derivative have been charaterised through Fourier Transform Infrared Spectroscopy, thermogravimetric Analysis, X –ray Diffractometry, and morphological studies and ^{1}H NMR.

- Allyl Guar gum has been grafted with acrylic acid by using Ferrous ammonium sulphate/ hydrogen peroxide redox initiator at room temperature in aqueous medium . This allyl guar gum grafted acrylic acid has been characterized through, Fourier Transform Infrared Spectroscopy, and thermogravimetric Analysis and Scanning electron microscope techniques. FTIR results showed a peak at 1722 cm^{-1} due to carbonyl stretching vibration. The excessive increasing the modification extent of guargum allyl etherification lowers the properties of copolymers. The allyl guar gum-g-polyacrylic acid were found to have reduce thermal stability and porous nature.

- The effective ness of using allyl guar gum with different degree of substitution (0.0389, 0.0625) as filler in an epoxy matrix resulted in an increase in the tensile flexural strength of the composites with the extent of allylation.,while decreasing the thermal stability of resultant polymer composites.while the % elongation and Impact Strength of the resultant composites were increased with the extent of allylation. The storage modulus of the resultant composites were increased only at lower concentration. The Tg values obtained from the Tand curves initially increased at lower concentration and then decrease with concentration as well as extent of allylation.

- The inclusion of allylguargum –g- polyacrylic acid (0.033,0.019)into epoxy matrix resulted in an increase in Tensile, Flexural strength of the composites.while the % elongation of the resultant composites increases as the carboxyl vaue of the composites gets increases. however the thermal stability of the resultant composites get decreases with the decrease in carboxyl value of resultant composites. The storage modulus of the resultant composites increase with carboxyl value while the glass transition of the composites decreases with the carboxyl value.

References – This chapter contains all the references used in the research work.

Suggestion for the future Work –

- Further work may be carried out by using different hardeners like anhydride, polyamides etc, Hardener ratios can be varied
- Effect of water acid and alkali on the mechanical, thermal properties of resultant composites
- Various copolymer can be grafted onto allyl guar gum and study its effect on the Properties of Epoxy resin
- Affect of fibers both natural and Synthetic may be undertaken.

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5. Preparation and Characterizaton ofGuar gum and Allyl guar gum grafted Acrylic acid by using Ferrous Ammonium sulphate redox pair, Designed Monomers & Polymers, Taylor & Francis Under Communication.

Research Publications and Proceedings

1. Research Paper entitled " Allyl Guar gum as a Filler in Unsaturated polyester resins "accepted on International Conference on Biodegradable and Biobased Polymers BIOPOL-2011, Strasbourg, France 29-31 Aug 2011.
2. Research paper entitled " Chemically Modified Galactomannan Derivatives Recent Developments 'accepted on National seminar on Frontiers In Polymer Science H.P University Shimla 18-19 Nov 2011.
3. Research Paper "Preperation Characterization of Crosslinked Guar Gum Based Films presented at International Conference GTGER Gurukul Kangri Visvidyalaya, 11-13 feb -2012.

4. Research paper entitled " Preperation and Properties of Guar Gum Based Films" A.P Gupta, GopalArora,, International Conference on Green Technology for green environment (GTGE 2010),Conference proceedings for poster presentation pp-92,27-30 Jan 2010,CCS University Campus Meerut.

5. Research paper entitled " Evaluation of PVA / Guar Gum based Films, A.P Gupta, GopalArora, Accepted to the European Polymer Symposium at Dresden Germany for PosterPresentation 7-10 March 2010.

6. Research paper entitled"Preparation, Characterization and Properties of Guar-Gum based Green Films, Gopalarora, A P Gupta, Paper Presented, National Conference in Advances in Polymer Sciences and Technology,(APST-2010) at NIT Hamirpur, 22-24 Oct 2010.

7. Research paper entitled " Guar Gum Alkyl ethers Synthesis and Characterization" GopalArora Presented on International Conference on Polymer Science & Engineering : Emerging Dimensions at Punjab University Chandigarh Nov 26-27 2010.

8. Research paper entitled " Biodegradable Polymers Recent Advances "presented on 3rdNational Seminar of recent trends in advancement of Mathematical and Physical sciences at D N College Meerut on 05th-06thfeb 2011

9. Best Oral Presentation award for Research Paper "Graft copolymerization of Guar-gum and Allyl guar gum With Acrylic acid by using Ferrous Ammonium Sulphate /Hydrogen Peroxide Redox pair "presented at National seminar on "RECENT ADVANCEMENTS IN CHEMISTRY",September 29-30,2012 C.C.S University Campus Meerut.

10." Evaluation of Epoxy -allyl Guar gum composites " accepted for Poster presentation on APM 2013 at CIPET Lucknow on March 01-03, 2013

REPRINTS OF RESEARCH PAPERS

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Preparation and Characterization of Guar-Gum/Polyvinylalcohol Blend Films

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Abstract: Guar gum is dispersible in cold or hot water to produce a colloidal dispersion of exceptionally high viscosity these properties make guar gum a highly valued gum in the food textile, cosmetics, pharmaceuticals, drilling and oil recovery industry, Guar gum is a natural polysaccharide which is capable of forming film by using the solution casting techniques. A series of blend films made of Guar Gum and PVA (GG-PVA), is to be prepared by solution casting. The effect of citric acid on the chemical structure and mechanical properties of GG-PVA were investigated. The miscibility and other properties of the GG-PVA films with varying concentration of Citric acid were studied by Fourier Transform infrared Spectroscopy FTIR, Tensile strength (TS) Elongation at break (%E). The FTIR results showed that no esterification have taken place between citric acid and Guar Gum during processing at 40℃. So the citric acid acted as an internal Plasticizer, the tensile strength of film decreases as the concentration of citric acid increases from (10%-50%) the % elongation at break of films increases as the CA percentage increased (from 10% to 20%)and then decreased (from 30% to 40%). The effect of borax on Guar Gum and GG-PVA blends with Citric acid as additive is also studied. The tensile strength of Guar Gum–Borax films increases while % Elongation at break decreases as the concentration of Borax is increased, it shows that borax act as a good cross linking agent where flexibility is not required. The nontoxic properties of citric acid prove worthy incorporation in GG-PVA films and such films would be showing potential application in food packaging industry and biomedical fields.

Key words: Biodegradable polymers, guar gum, PVA, solution casting.

1. Introduction

Plastics made from petroleum have been widely used throughout the world with increase application. The disposal of waste plastic has become a serious problem therefore development of novel plastic that could be degraded by Microorganism in soil and sea water has recently being attracted much attention [1] Therefore ,in the past two decades, biodegradable material has been paid attention as alternative to the petroleum–derived plastic [1-4].

A variety of natural biopolymers including Starch, Cellulose, and Chitosan were tested, alone or combined with synthetic polymers, for the possibility to form a fully or partially biodegradable film. GG is the endosperm polysaccharide of the seed of cyamopsis tetragonoloba, which belongs to the leguminosoe family. It is galactomannan consisting of backbone of α-1, 4-D-mannopyranosyl units with ever second unit bearing a β-1,6D-galactopyranosyl unit. It is easily available and cheap in India. India is the largest exporter of Guar Gum in the world [5].

Poly (vinyl alcohol) (PVA) is a Hydrophilic biodegradable polymer which is mainly composed of C-C bonds [6]. PVA possesses many useful properties such as excellent chemical resistance, optical and physical properties, good film forming capability, Water solubility and an excellent biocompatibility. The excellent chemical resistance and physical properties of PVA have resulted in its broad industrial use. Polyvinyl alcohol (PVA) is one of the hydrogels often used in biomedical applications [7]. It is a water-soluble

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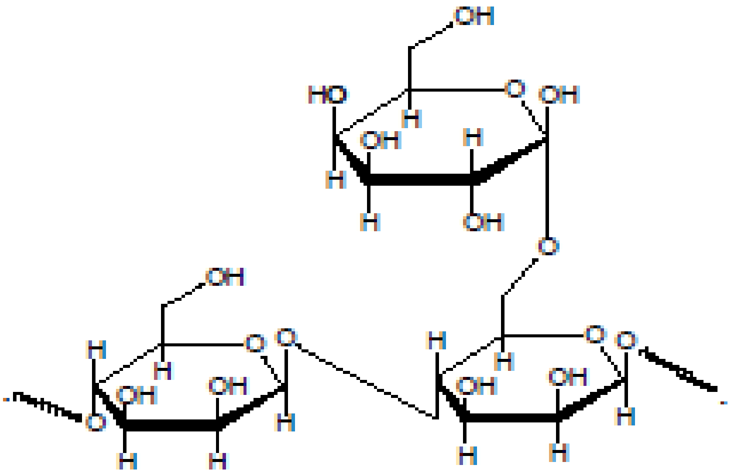

Fig. 1 Structure of guar gum (GG): guar gum has a linear backbone of β-1, 4-linked mannose units with ά-1,6-linked galactose units attached as side chains.

synthetic polymer with excellent film forming, emulsifying and adhesive properties. This polymer has outstanding resistance to oil, grease and solvents [8].

Citric Acid (CA) with one Hydroxyl and three carboxyl groups exist widely in citrus fruits and pineapples, where it is the main organic acid.CA was chosen as additive for the following reasons first of all as a result of its multi-carboxylic structure, esterification would take place between the between the carboxylic group on CA and Hydroxyl group on PVA or Guar Gum. CA may serve as a crosslinking agent due to the multicarboxylic structure the Cross-linking of a blend reinforces the intermolecular binding by introducing covalent bonds that supplement natural intermolecular Hydrogen bonding [9] so as to improve the mechanical properties and water resistibiliity. secondly the residual free CA may act as a plasticizer, Third point is CA is nutritionally harmless since it is a nontoxic metabolic product of the body. The aim of this study was to make biodegradable films based on Guar Gum (GG), Poly vinylalcohol (PVA), blends of CA as additive and the effect of citric acid and borax on the mechanical properties of these films.

2. Experimental Work

2.1 Materials

Guar gum was supplied as a sample by Dabur India Ltd having Viscosity is 5,000 cps (1% solution at 30^o celcius), Polyvinyl alcohol was obtained from CDH chemicals having viscosity is 35-50 cps (1%soln at 25 ^{o}C), citric acid was Obtained from Thomas Baker Chemical Ltd, Disodium tetraborate (Borax) was Obtained from Glaxo Chemical.

2.2 Preperation of GuarGum /PVA Blend Films

Solution blends were prepared using the required volumes of 1% GG, and PVA solutions. These blends were mixed thoroughly at 2,000 rpm to obtain a uniform homogeneous solution. The films were prepared by casting 100 ml of a 1% solution (w/w) onto a Teflon mold and evaporating the water at 40 ^{o}C in an air circulating oven.

2.3 GG-Borax Film Preparation

A similar method to that used for the preparation of blend films was used for the preparation of films containing GG and borax. A solution of the borax was prepared such that it had a concentration of 2.5 µmole/ml. Various aliquots of this solution was then added to prepared GG solutions making the total concentration of GG in the final composition 1% and containing therequisite amount of borax.

2.4 GG Blend Film with Citric Acid

GG/ PVA blend films were prepared using a casting method, Guar Gum and PVA are mixed in the weight fraction of 0.6 to 0.4 and the content of additives was expressed as mass percent ratio of additives to total GG and PVA. The mixture was blended to form homogenous gel like solution with a mechanical stirrer (1,000 rpm) at room temp for 50 minutes. The prepared solution was poured into the Teflon mold, water was evaporated from the mold in a ventilated air oven at 40 °C to the dried film. The mixing composition is shown in Table 1. Bubbles, by product of preparation, were removed by using an aspirator. The gel like solution thus prepared was poured on a teflon mold. The dried films were sealed in polyethylene bags and stored at 50% RH for one week prior to perform the test.

2.5 Characterization of Films

2.5.1 Fourier-Transform Infrared (FT-IR) Spectroscopy

The FTIR spectra were evaluated on Thermo-Nicollet Spectrophotometer using ATR assembly the spectra was taken of the respective films after being cast on a Teflon sheet, dried at 40 °C in an air circulating oven, from an aqueous solution. Films made of GG/PVA blends were evaluated in a similar manner.

2.5.2 Mechanical Testing

Tensile properties-The elongation at break and the tensile strength of the films were determined at 23 °C and 50% RH using a Universal testing machine. The initial grip distance was 50 mm and the rate of grip separation was 5 mm/minute. When continuous films were formed, at least two films of each type and six replicate specimens from each film were measured. The specimens were 10 mm wide and approximately 100 mm long. The thickness of the specimens was measured with a micrometer.

Table 1 Effect of borax addition on tensile strength and elongation at break of GG film.

Sample name	Guar gum (gm)	Borax (μmole/ ml)	Tensile strength (MPa)	% Elongation at break (%)
A	1	-	13.1	2.7
B	1	2.5	20.9	2.46
C	1	12.5	26.1	2.32
D	1	25	22.6	2.11

3. Results and Discussion

3.1 Effect of Citric Acid on Guar Gum Blends

Plasticizer is generally needed for the formation of flexible films, and in the present study, films prepared from native GG and PVA without added plasticizer were brittle and cracked during drying. Glycerol and Citric Acid are used commonly as plasticizers in biopolymer-based films. An increase in the amount of plasticizer generally increases the elongation at break and decreases the tensile strength of films [9]. When high plasticizer dosages are used, phase separation of the film-forming polymer and the plasticizer can occur, possibly resulting in the diffusion of the plasticizer from the film matrix to the surface. It is therefore sought to establish the appropriate amount of Citric acid for galactomannan-based films. Citric acid with one hydroxyl and three carboxyl group exist widely in citrus fruits and pineapples, citric acid was chosen as additive for the following reasons. As a result of its authentic carboxyl structure, citric acid is rated nutritionally harmless since it is non toxic metabolic product of the body (Krebs or citric acid cycle). It has been already approved by FDA for use in Humans. These non toxic properties of citric acid will benefit the incorporation of citric acid in GG-PVA films and such films would have potential application in food packaging industry and in the biomedical field. From the FTIR of GG-PVA film containing citric acid shown in Fig. 3, it was observed that the peak height at 3,340 cm^{-1} (stretching vibration of the hydroxyl groups) increased and shifted to higher wave number as the citric acid concentration increased. This is because the number of hydroxyl and carboxyl group increased as the citric acid concentration increased.

The effect of citric acid on the FTIR spectrum showed that as the % concentration of citric acid increased. The peak height at 1,709 cm^{-1} is also increases. The peak at 1,709 cm^{-1} is attributed to the C = O stretching vibration in carboxyl group [10]. It was observed from the FTIR that there is no esterification occurs when the citric acid was used as additive to prepare GG-PVA films at 40 °C. It was observed that esterification will not occur in the blending system under such a low temperature. The Mechanical Properties are not only related with the crosslinker but are also related with the plasticizer. Generally the tensile strength increases and the elongation at break decreases as the percentage of crosslinker increases. The results are opposite when plasticizer is increased. The Tensile strength and % Elongation at break as the function of citric acid are shown in Fig. 3.

3.2 Effect of Borax on the Mechanical Properties of GG Films

The addition of borax to GG solutions has been known to result in a gel. This gel formation was due to the reaction between the GG and borax. The borax moiety is tetra-functional and results in highly crosslinked mass on addition to a GG solution.

Table 1 and Table 2 show the formulation of the prepared film along with their mechanical properties.

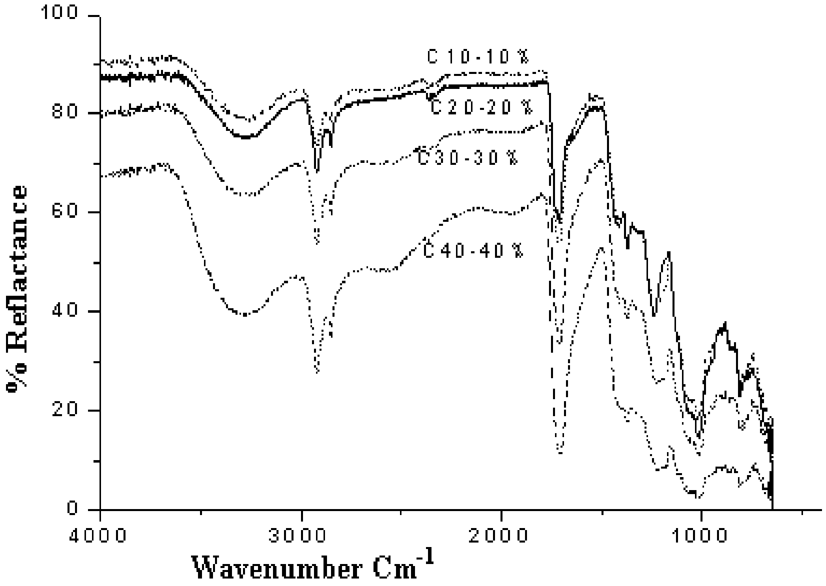

Fig. 2 FTIR Spectra of GG-PVA blends with varying concentration of citric acid C10-10%, C20-20% C30-30%, C40-40%.

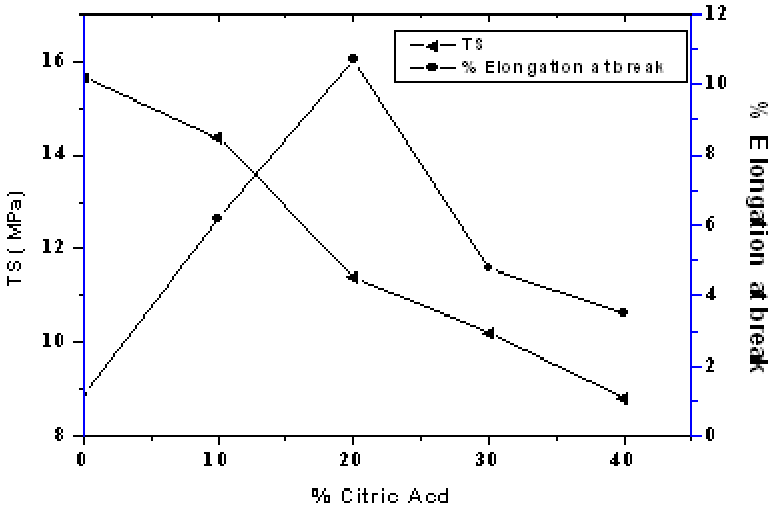

Fig. 3 Effect of citric acid on tensile strength and % elongation at break of GG –PVA blend film.

Table 2 Effect of borax and citric acid on gg-pva composition.

Sample name	GG-PVA (Wt fraction)	Citric acid (Wt%)	Borax (μmole)	Tensile strength (MPa)	% Elongation at break (%)
A	1-0			13.1	2.7
B	0.6-0.4	-	-	15.64	5.65
C	0.6-0.4	20	-	11.43	10.7
D	0.6-0.4	20	2.5	19.71	2.3
E	0.6-0.4	20	12.5	22.3	1.7
F	0.6-0.4	20	25	20.5	1.5

It could be seen that on addition of borax to the Guar Gum and on the composition the resultant films showed an increase in their tensile strengths. This was due to the increase in the crosslinking of the films, which has been approved to have such an effect on the tensile strength of films and coatings. On the other hand the addition of increased concentrations of borax resulted in films with reduced tensile strength, this was due to the fact that an excessive increase in the crosslinking agent in the formulation would result in improper film formation. The effect of addition of borax on the elongation at break of films formed from the resultant formulations indicate that as an increase in crosslinking lead to a more rigid and brittle films as expected. The increase in rigidity and brittleness in the films were reflected by the decrease in the elongation at break. It was observed that elongation at break continued to decrease with borax addition. Initially, at those concentrations where there was a corresponding increase in the tensile strength the increase in the crosslinking density was responsible for the observed trend in the elongation at break values. However when the tensile strength decreased, due to film defects brought about by excessive crosslinking the same reason was responsible for the decrease in elongation at break. Thus, this method clearly indicated that when required, the tensile strength of films of GG and similar polymers could be increased by the addition of crosslinking agents like borax. This provides for an easy method to increase the mechanical strength of such coatings where flexibility is not a requirement.

4. Conclusions

The GG-PVA films were prepared by solution casting and the GG-PVA films shows better properties than their individual polymers like GG and PVA, due to better interaction between GG and PVA. A Series of blend films made of GG –PVA were prepared and the FTIR result shows that the best interaction occurs in GG-PVA blends having PVA wt fraction of 0.6 to 0.4. These films are very brittle in nature, so when the study of the effect of citric acid onto the GG-PVA solution and the solution were cast at 40 °C, the FTIR spectrum showed that no esterification occurred into the system. When the citric acid was treated with GG–PVA solution at 40 °C, the citric acid acts as plasticizer into the system and the mechanical properties of films like tensile strength of a system get decreased, as the concentration of citric acid is increased (from 10% to 40%) and % elongation at break is increases as the Citric acid % increases from 10% to 20%, and on treating the guar gum with borax its tensile strength gets improved upto a certain concentration and then decrease and % elongation gets reduced. Hence it is observed that borax is a good cross linking agent and it can be used where flexibility is not required.

Acknowledgment

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Preperation and Characterization of Cross-linked Guar-Gum Poly(vinylalcohol) Green Films

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ABSTRACT

Guar –gum/ Polyvinyl alcohol (GG/ PVA) blend films were prepared by using Guar –gum , polyvinyl alcohol (PVA) and Citric acid (CA) as additive and gluteraldehyde as crosslinking agent for the mixing process . The additives , drying temperature , and the influence of crosslinker of films on the properties of the films were investigated . The mechanical properties tensile strength , elongation at break (% E) and thermal properties includes thermogravemetric analysis , degree of swelling (DS) of GG / PVA films were examined by using CA as additives .when the film was dried at low temperature , physical properties of the films were clearly improved because the hydrogen bonding was activated at low temperature ..

Key Words: Guar- Gum, Polyvinyl alcohol , Citric Acid, Gluteraldehyde crosslinking

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INTRODUCTION

There has been a growing intrest in the use of biodegradable polymers in order to reduce the environmental pollution caused by plastic waste. The disposal of waste plastic has become a serious problem therefore development of novel plastic that could be degraded by microorganism in soil and sea water has recently been attracted much attention . Among the several candidates including natural polymers and their derivatives, guar gum is very cheap , produced in abundance , and easily available from many renewable sources guar gum (GG) is a natural polymer extracted from the endosperm of the plant cyamopsis tetragonalobus .and chemically is a galactomannans with a galactose to mannose ratio of 1:2 [1], which consist of a (1-4) linked β D mannopyranosyl backbone partially substituted at O-6 with α- D- galactopyranosyl side groups In recent years , modified guar gum has been found numerous application in water based paints (2) , food (3) ,textiles (4,5), cosmetics (6),pharmaceuticals (7) and oil recovery and drilling [8,9] . Guar gum is a natural polysaccharide which is capable of forming films by using the solution casting technique. In the case of guar gum the solvent used is most commonly water. Guar gum is known to give brittle films with extremely poor flexibility and high moisture sensitivity [12] . To overcome these drawbacks guar gum is modified or blended with other materials (13-17) . Poly vinyl alcohol (PVA)which is biodegradable and water processable synthetic biodegradable polymers is blended with guar gum to modify their properties . It would seem , therefore that further investigations are needed in order to reduce water sensitivity and increase mechanical properties of the films. among many chemically modified methods chemical crosslinking is a convenient and feasible method to modify the structure of natural polymers and

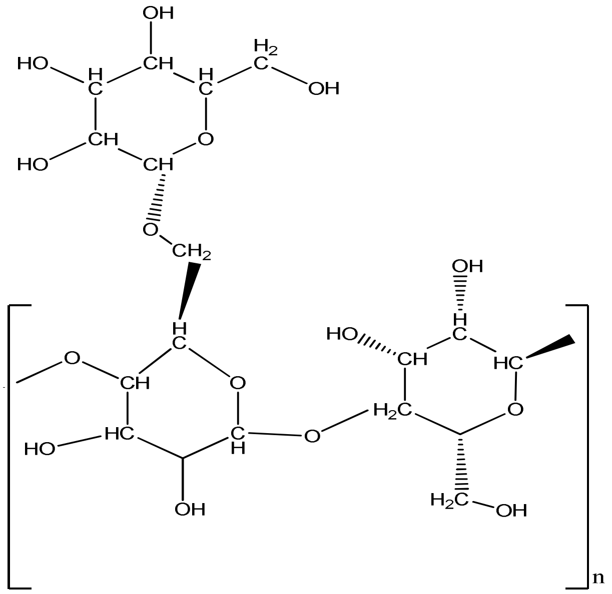


Fig-1 structure of Guar –gum

thus make them attractive biomaterial for further application(18,19). In Previous papers through Crosslinking with gluteraldehyde , phosphate , urea formaldehyde and borax , modified guar gum was applied in various field , such as controlled drug release (7), liquid pesticide (10) , However, the high water sensitivity and and bad form-film ability of guar gum and its derivatives limit their application as useful film material there are several ways to overcome these problems , one of them is mixture of synthetic polymers with natural polymers ;another option is the synthesis of polymer with use of products from natural resources (11) .The aim of this study was to make biodegradable films based on Guar gum (GG) , Polyvinylalcohol(PVA) blends by using citric acid as additive and gluteraldehyde as a crosslinking agent to determine the mechanical properties , degree of swelling , and its characterization by FTIR , TGA , and SEM of these films .

2.3 -Characteristics of Films

2.3.1 Fourier -Transform Infrared (FT-IR) Spectroscopy -

The FTIR spectra were recorded on Thermo- Nicollet Spectrophotometer using ATR assembly the spectra were taken of the respective films after being cast on a Poly propylene sheet, dried at room temperature , from an aqueous solution. Films made of GG/PVA blends were recorded in a similar manner.The spectra were obtained at a resolution of 4 cm $^{-1}$ in the 4000cm^{-1} to -400 cm^{-1}

2.3.2 Mechanical Testing

Tensile properties --The % elongation at break and the tensile strength of the films were determined at 23^{o} c and 50% RH using an Universal testing machine . The initial grip distance was 50 mm and the rate of grip separation was 5mm/minute .When continuous films were formed, at least two films of each type and six replicate specimens from each film were measured. The specimens were 10 mm wide and approximately 100mm long. The thickness of the specimens was measured with a micrometer.

2.3.3 Thermogravimetric (TG)analysis-Thermogravimetry analyses were carried out by Instrument TA About 10mg sample was positioned in silica pans and the samples were heated at 10^{o} Celcius / Minute from ambient Temp to 600^{0} celcius . Thermal analysis was performed under the nitrogen flow .

2.3.5 SEM Study .-The surface Morphology of the Film samples were investigated with HITACHI S 3700N using a Voltage of 15KV by Coating with Au.

2.3.6 Swelling analysis: The swelling analysis of dried specimen films were carried in distilled water the film samples were conditioned at 50 ^{0} Celsius for 24 Hrs in an oven , and the conditioned samples were weighed on a digital balance with a precision of 0.0001 gm . The specimen were than immersed in Distilled water .

$$\frac{Ww-Wd}{Wd} X100$$

Ww and Wd are the weight of wet and air dried samples

MATERIALS AND METHODS

2.1 Materials

Guar gum was supplied as a sample by Dabur India Ltd having Viscosity 5000cps (1% solution at 30^o celcius) , Polyvinyl alcohol was Purchased from CDH chemicals with an average Molecular Weight of 1,25000 , Citric acid was Purchased from Thomas Baker Chemical Ltd . Gluteraldehyde 25% w/v was Purchased E Merck India .The water used to prepare Guar Gum / PVA blend films was redistilled after deionization .

Preperation of Guar-gum/PVA blend Films

Guar gum and Polyvinylalcohol solution were prepared by dissolving them separately in water .Guar gum and Polyvinylalcohol solution are intermixed in required wt fraction and add citric acid and cross-linking agent (Guar gum and PVA dried weight basis) .The above solution were blended to form a homogenous gel like solution with a mechanical stirrer for 4 Hrs The gel like solution were casted on a polypropylene disc and allowed to dry at 40 ^{0} celcius .

Table1 .Composition of Guargum – PVA blend films

Sample Name	GG-PVA (Wt Fraction)	Citric Acid Wt % (Dried basis)	Gluteraldehyde wt% (Dried Basis)
GP	0.6-0.4	-	_
GPC	0.6-0.4	20	_
GPC3	0.6-0.4	30	_
GPC4	0.6-0.4	40	_
GPC GLU1	0.6-0.4	20	0.3%
GPCGLU2	0.6-0.4	20	0.6%
GPCGLU3	0.6-0.4	20	0.9%
GPCGLU4	0.6-0.4	20	1.2%

RESULTS AND DISCUSSION

Guar Gum and polyvinylalcohol molecules , having a large number of hydroxyl in their structures , remain associated with one another by inter- and intramolecular hydrogen bonding in the blend , The plasticizer molecule enter between the guar gum and the polyvinylalchol molecules , reduce the intermolecular force of attraction and also take part in hydrogen bonding with them . The crosslinking agents react with the –OH groups present in guar gum and polyvinylalchol and make ether linkages with the available hydroxyl groups . this help in increasing the mechanical properties of the films

3.1 Mechanical properties of Guar Gum / PVA blend Films Table 2. Showed TS and % E of film using GG and PVA with varying concentration of Citric Acid from 10% to 40% (% wt of dried GG and PVA) and gluteraldehyde 0.2 to 0.6% (% wt of dried GG and PVA). The tensile strength and % elongation at break as the function of CA concentration are shown in Table 2. The citric acid reacts with hydroxyl group of Guar Gum and the hydroxyl group of PVA .The free carboxyl group attached could increase the solubility of GG and prevent Crystallization , CA reacted with GG can be considerd as the internal plasticizer while the residual CA in the blend plays the role of external Plasticizer. The tensile strength of film were increased and % E were decreased and gluteraldehyde react with the hydroxyl group present in Guar Gum , PVA and Citric acid and it crosslinks the polymer films .

Table -2 Effect of citric acid and Gluteraldehyde on the Mechanical Properties of GG/ PVA Blends

Sample Name	Tensile Strength (MPa)	% Elongation at Break
GP	18.5	0.9
GPC1	23.2	1.5
GPC	21.4	1.9
GPC3	17.8	2.2
GPC4	11.4	2.7
GPCGLU 1	14.8	1.31
GPCGLU 2	16.35	1.04
GPCGLU 3	17.76	0.78
GPCGLU4	21	0.571

3.2 FTIR Analysis –The FTIR spectra of noncrosslinked are shown in Fig -2 . From the fig2 it may be observed that peak intensity at 1709 cm^{-1} increases as the content of citric increases into the system , which is attributed to C=O stretching vibration in carboxyl groups has only found in the spectra of pure citric acid . thus the result from the FTIR sujjest that the esterification not occurred during blending when the films were cast at 40 ^{0} Celcius after the addition of gluteraldehyde no any change in FTIR spectrum occurs .The peak intensity at 1709 cm^{-1} was increased as the concentration of gluteraldehyde was increased .

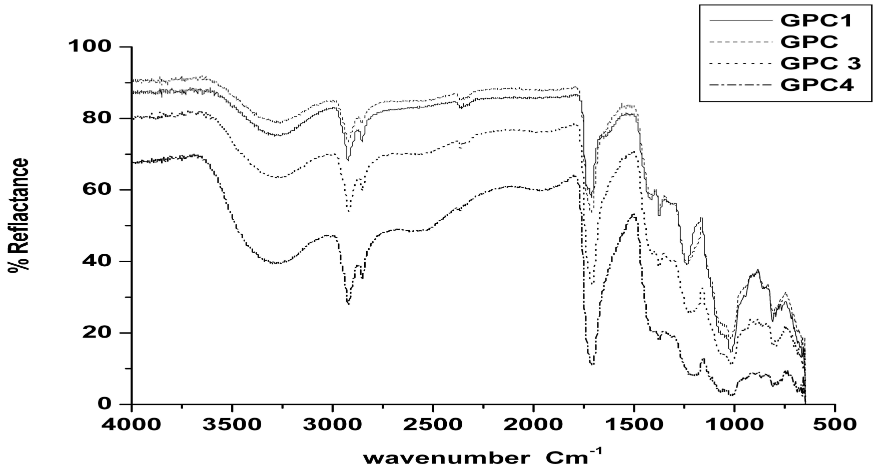
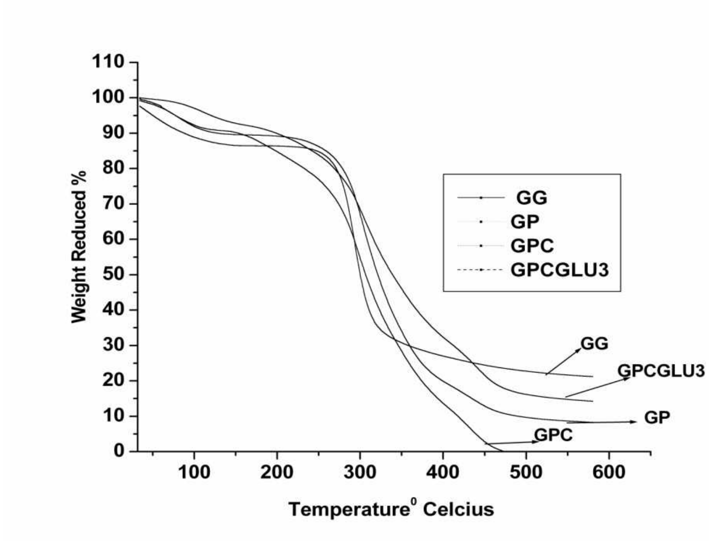


Fig 2 : FTIR of Guar gum –PVA Fims treated with Citric Acid GPC, GPC3, GPC4

3.3Thermogravimetric Analysis :

The thermal degradation behavior of individual components such as Guar Gum , and PVA of GPC non-crosss-linked, as well as crosslinked with gluteraldehyde , GPCGLU3 are shown in Figure 3. There was a remarkable difference in the thermal degradation of the crosslinked film compared to that of non crosslinked films . The TGA graph exhibited that the Cross-linked Guar-Gum films have about 14% lower Weight loss than noncross -linked films after heating the films to 600° celcius indicating much improved resistance to thermal degradation . The effect of Citric acid on TGA graph of GG/PVA were found that the addition of Citric acid increases the wt loss and decreases the residue % . It means that citric alone not crossslink the film at low temperature .The effect of gluteraldehyde in GPC2 films were found that the addition of gluteraldehyde lowers the wt loss , and increase the residue % , due to the crosslinking of film at low temperature ,



Fig(3) TGA Thermogram of non -cross-linked GG.GP .GPC.and crosslinked GPCGLU3

Table 3-Effect of Citric acid and gluteraldehyde on theral stability of GG/ PVA film samples

Sample Name	Weight Loss %					Residue at 550 ^{0}C
	100	200	300	400	500	
GG	12	14	50	73	77	21.9
GP	9	11	14	61	90	8.27
GPC	8	16	46	63	100	-
GPCGLU3	3	11	33	69	84	14.23

Swelling analysis : -The water absorbency of the film was decreased. A higher concentration of crosslinker produces a larger degree of polymer chains branching and generates an additional network. thereby, with the crosslinker content increasing, the crosslinking density increases the network space gets diminished, and less water enters the films .

Table 4 – Degree of swelling of crosslinked films

Sample Name	Swelling % after 2 Hrs	Swelling % after 4Hrs	Swelling % after 6Hrs
GPCGLU1	780	866	--
GPCGLU2	611	700	804
GPCGLU3	552	567	556
GPCGLU4	410	434	455

3.4 Morphological Structure – From the SEM micrographs , the porosity of uncrosslinked GP and GPC is reduced as gluteraldehyde concentration increases . The most of the porosities are eliminated by increasing gluteraldehyde concentration .It confirms the film strength and decreasing the swelling percentage of the guar gum films on increasing gluteraldehyde concentration .

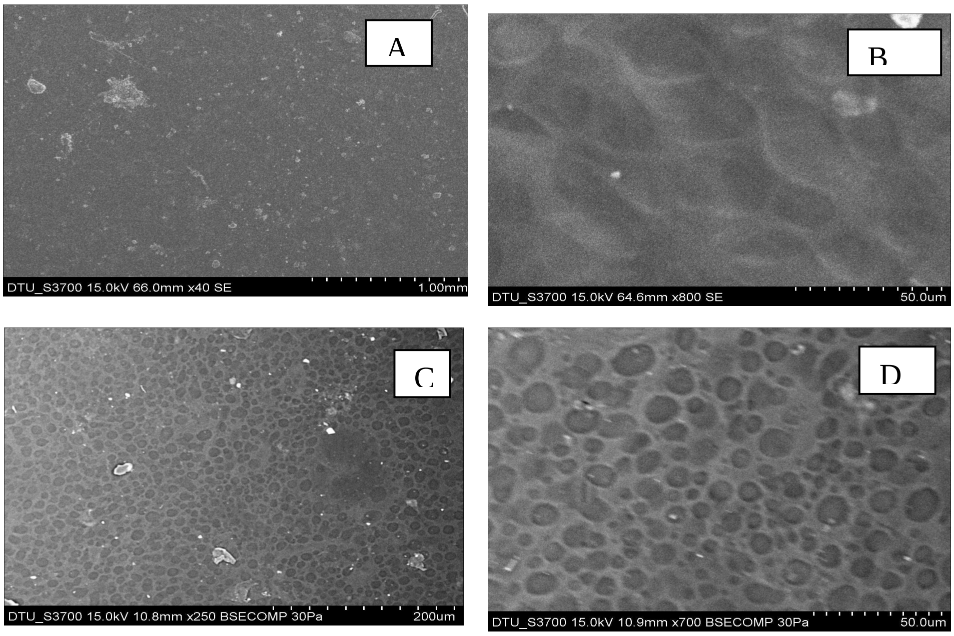


Fig 5- SEM images, Magnified 40 x (A) and 800 x(B)for sample GP, 55 x (C) and 250x(D) for sample GPCGLU3

CONCLUSION

Guar gum – PVA blends were crosslinked with gluteradehyde in the presense of citric acid with different wt % gluteraldehyde . These films were analyzed by FTIR , TGA and SEM and the mechanical properties including Tensile strength and % Elongation were also evaluated .The results showed that as the content of gluteraldehyde increases , the tensile strength increases and % Elongation and degree of swelling decreases , the addition of gluteraldehyde decreases the wt loss % and increases the % residue , and reduces porosity than the noncrosslinked films .This study demonstrate that gluteraldehyde is an effective crosslinker in the presence of citric acid into the Guar –gum –polyvinylalcohol films .

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