SCALING UP OF MANUFACTURING PROCESSES

OF RECYCLED CARPET BASED COMPOSITES

By

KRISHNAN LAKSHMINARAYANAN

Bachelor of Science in Chemical Engineering

University of Mumbai

Mumbai, India

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SCALING UP OF MANUFACTURING PROCESSES OF

RECYCLED CARPET BASED COMPOSITES

Thesis Approved:

Dr. Martin High
_____
Thesis Adviser

Dr. Ranji Vaidyanathan
_____

Dr.Tyler Ley
_____

Dr. Arland Johannes
_____

Dr. Mark E. Payton
_____
Dean of the Graduate College

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CHAPTER I

INTRODUCTION

1.1 OBJECTIVE

The objective of this work is to develop novel composite materials by recycling nylon based waste carpets. These novel composites will have improved mechanical and sound barrier properties to meet the needs of infrastructure in the transportation industry as sound barrier walls at the highway turnpike. This will be achieved by scaling up the Vacuum Assisted Resin Transfer Molding (VARTM) technique of manufacturing carpet composites.

The research hypothesis of this study is to investigate the impact of scaling up manufacturing processes on improvement of properties of recycled carpet based composites. This hypothesis can be more formally stated as the research question, research purpose, and research objectives:

I.   For this study, the **<u>research question</u>** was: how to recycle waste carpet lying in landfills into structural composite materials useful for infrastructure applications?

II.   The **<u>research purpose</u>** for this research was to develop a manufacturing process based on scale-up of VARTM to recycle discarded carpet into improved composite materials called carpet composites. This scale-up was achieved by improvisation in the fabrication process and the final composite product.

III.   The research objective was the scale-up of VARTM of waste nylon based carpets to produce novel carpet composites with superior mechanical and acoustic properties. The theme of this thesis was to present the progress made in advancing this technology product development as well as the feasibility of what it can do for solving two environmental problems, waste carpet and traffic noise, simultaneously.

1.2 MOTIVATION

The world's primary energy needs have increased by 66 percent in the last 30 years and today's energy path would mean rapidly increasing dependence on fossil fuels with alarming consequences for climate change and energy security [1]. Experts accurately predicted large and permanent increases in oil prices after the year 2000 due to increasing scarcity. A series of episodes including the oil reaching a record price of $120 a barrel in March 2008 has made this evident. The president of OPEC (Organization of Petroleum Exporting Countries) has warned of oil reaching $200 a barrel clearly indicating huge demand for oil. The rapid economic development of developing countries around the world (including India and China) has produced insatiable demand for oil and other energy sources [2]. However, apart from its demand-supply problem, there are even larger challenges in the energy industry, such as consumption of energy yielding to increase in greenhouse gas emissions that in turn results in increase of global temperature. Hence energy is crucial for sustainable development and World Energy Outlook 2009 report suggests that there is an urgent need to limit the global temperature rise to 2^0C [1].

For sustainable development, the materials recovery and recycling industry has to deliver marketable products which are based on cost effective technologies and have a positive life cycle environmental impact [3]. This served as a motivation to address a solution to the problem of recycling of waste carpet lying in the landfills. Land-filling is not an environmentally friendly solution because carpet fibers are not biodegradable [4]. In the United States, environmental

concerns and governmental regulations have started putting efforts in the direction of recycling all synthetic polymers, of which carpet and carpet fibers constitute a significant percentage [4]. Carpet is a petroleum-based product and it is estimated that carpet recycling can save more than 700,000 barrels of oil per year, conserving 4.4 trillion BTUs of energy [5].

In the United States alone, about 200 million tons of carpet waste is generated every year, and only 2 % of this amount is recycled [6]. Out of the 5 billion pounds of carpet sent to landfill only 1 % of old carpet has been recovered as per Carpet America Recovery Effort (CARE), an organization committed to carpet recycling in USA [6]. In every municipal solid-waste stream of USA, post - consumer carpets account for 1 wt% of the stream thereby indicating the high usage of carpet. Carpet offers compelling benefits like underfoot comfort, sound absorption, improved slip resistance and thermal comfort and has therefore been the reason for covering 60 percent of all floors in the United States [7]. The Carpet and Rug Institute sustainability report says that "carpet industry in USA produces more than 19 billion square feet of carpet each year" [7].

Carpet waste is both an environmental and economical problem because of the cost involved in disposal of waste carpet. The cost also involves discarding of valuable raw material in the form of high engineering value fibers like Nylon 6,6, polyester, polyvinyl chloride (PVC), polypropylene (PP), other olefins etc. going to landfills apart from the cost of transporting the waste to landfills. Thus post - consumer carpet represents a significant environment burden on the landfills, tax burden due to state sponsored subsidies, and a lost economic opportunity. Hence it is imperative to recycle post - consumer carpets for a sustainable society.

The chart in Fig. 1.1 has been adapted from the data provided by the Environment protection agency on Municipal Solid Waste (MSW). Waste carpet is an important constituent of the MSW and the chart below gives an idea about the steady trend in recovery of carpets over the decade. The rapid economic development throughout the world has increased the generation of

municipal solid waste. The imbalance between the amount of discarded waste and its minimal recovery indicates a deplorable outlook for the recycling industry. However the steady increase in awareness for recovery of municipal solid waste gives a hope for the waste recycling industry.
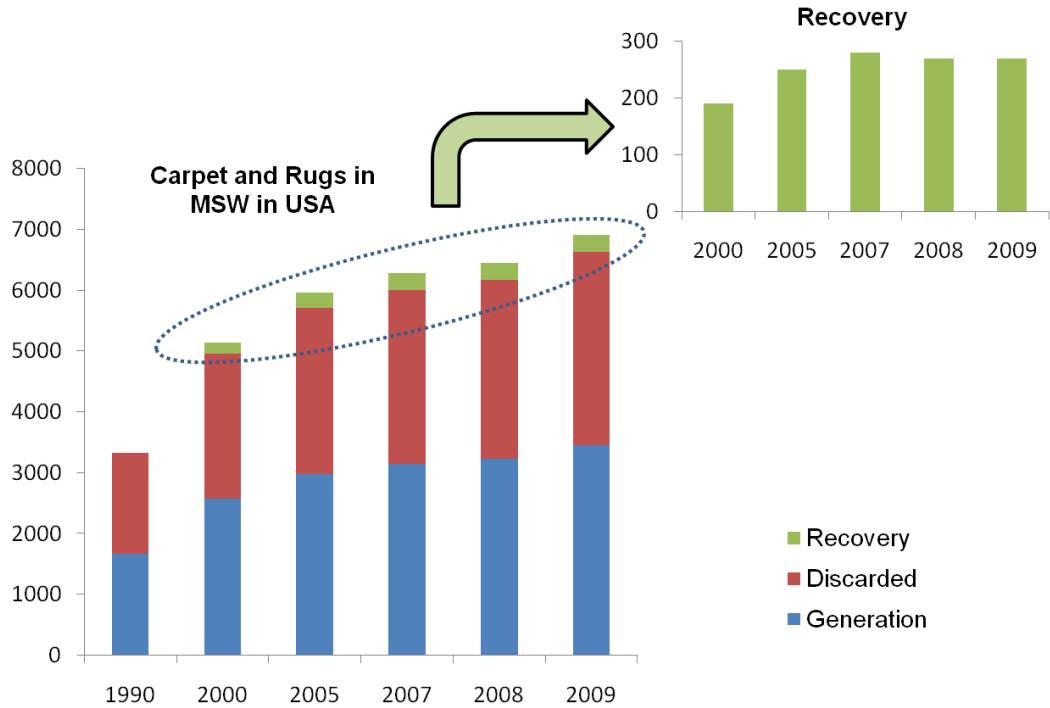
Fig. 1.1 A chart adapted from the data by EPA on characterization of municipal solid waste (MSW) by weight in Thousands of Tons [8].

In 2009, CARE reported that 311 million pounds of post - consumer carpet were diverted from landfills, of which 246 million pounds were diverted due to a direct result of reuse and recycling [9]. This indicates that there is an increasing trend in awareness of carpet recycling and the products which fall under this umbrella of recycled carpet would be well received.

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TABLE 1.1

A TABLE INDICATING THE NATIONAL DISCARD ESTIMATES PROVIDED BY
THE CARPET AND RUG INSTITUTE [10]

(in millions of pounds)	2002	2005	2008	2010	2012
Total Discards	4678	5038	5642	6020	6772
Reuse	0	25	113	211	203 - 339
Recycling	180	353	620	903	1354 - 1693
Waste to Energy (Maximum)	NA	50	56	60	68
Cement Kilns[*] (Maximum)	0	100	300	200	200
Landfill	NA	4510	4552	4646	4812
Recycling Rate	3.8%	7%	11%	15%	20-25%
Landfill Diversion Rate	3.8%	10%	19%	23%	27-34%

Note* - (1) Cement kilns use incineration of carpets as a fuel supplement in kilns (2) NA - Not available.

The 2010 Annual report by CARE pointed out that Nylon 6 and Nylon 6,6 represent 80 percent of all carpet diverted from landfills in 2009 [9]. The two predominant forces driving the waste nylon based carpet's reclamation are – 1) the opportunities for usage of recycled nylon fiber in various end markets and 2) the huge market share of nylon carpet sold in United States [9]. The carpets made of other face fiber materials like polyester, PVC and PP are therefore not economical to recycle with current technology because these face fiber materials are cheaper virgin materials and to recycle them is uneconomical [11]. Among the carpets sold in the United States, about 65 percent of them are nylon based because nylon is a more durable fiber and has excellent performance characteristics [12]. There has been extensive research on recycle of nylon based carpets due to the huge market for nylon fibers. Nylon 6 fibers are derived from

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caprolactum, which has a significant market value and are thereby recycled by chemical recycling methods. However the chemical recycling techniques for carpet fail to deliver in sustainable product development due to their characteristic requirement of high energy inputs.

Literature suggests that the energy consumed in manufacture of nylon fibers for polymerization, spinning and finishing is between 369 and 432 MJ/kg [13]. The calorific value of crude oil is between 38 and 46 MJ/kg and therefore it can be concluded that for 1 kg of fiber about 11 kg of crude oil is necessary [13]. Though thermal utilization is a lucrative option, the process of thermal utilization uses only the calorific value which is about the same or slightly lower compared to crude oil [13]. Hence it is imperative to evaluate a process to save the 11 kg of crude oil getting wasted for every 1 kg of nylon wasted in the carpet waste. Therefore carpet recycling becomes critical and to ensure sustainable development.

At Oklahoma State University (OSU), an innovative carpet recycling technology has been developed to recycle waste carpets from landfills into structural composites using VARTM. The main advantage of VARTM is that the carpets are recycled without any physical or chemical treatment which therefore results in process optimization and cost reduction. Fig. 1.2 includes a schematic of the VARTM process used to recycle carpet in this study.
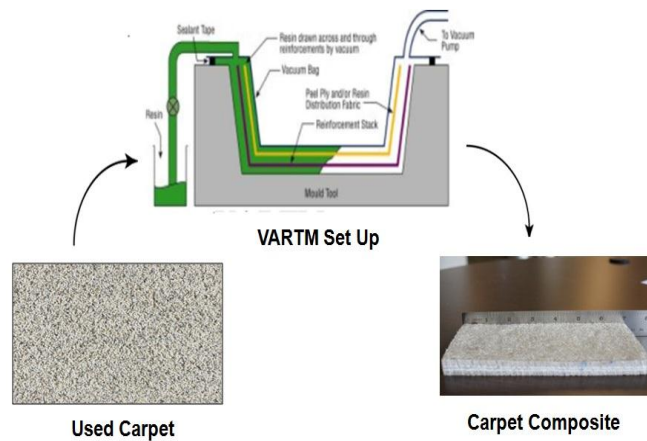
Fig.1.2 An illustrative diagram of VARTM process to make carpet composites.

The vitality of a globalized economy is directly linked to the productivity and efficiency of its surface transportation system among other factors. For instance the development of Interstate Highway System has stimulated the economy of the United States, but it also brings in increasing demands for safe, efficient and environmentally sound efficient transportation system with lower noise decibel levels. This indicates the feasibility for novel materials with better acoustic properties as highway noise barriers. In this study it has been proposed to use novel composite materials like carpet composites as sound barrier walls at turnpike.

1.3 OUTLINE OF THESIS

The thesis has been organized as per the following outline

- Chapter 2 includes a detailed background review of carpet, recycling methods of carpet and companies involved in carpet recycling. A brief background of highway noise barriers and the increasing trend in the research in product development for materials required for these barriers has been included.

- Chapter 3 presents the materials and methods used in the VARTM fabrication of carpets into composites. Scaling up of manufacturing of carpet composites using VARTM was achieved by incorporating the scaling up methods and materials. Incorporation of nanocomposite fillers in composite yielded clay based carpet composites with improved properties.

- Chapter 4 presents the results and discussion of the acoustic characterization test carried out on the carpet composite samples. The high noise absorption characteristics of carpet composites would make it good highway noise barriers.

- Chapter 5 consists of conclusions from this work and recommendations for future work.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 CARPET – A BRIEF REVIEW

2.1.1 Carpet Construction

A typical carpet has four main layers – face fibers, primary backing, binder and secondary backing. The arrangement of these four layers is as shown in Fig. 2.1.

Fig. 2.1 An illustrative diagram of carpet (cut- pile type) and its constituents – fibers, backing and binder [4].

The top layer consists of face fibers which are generally tufted through the primary backing, usually made of polypropylene (PP). Other fibers like polyesters, polyethylene and rayon are also used as backing materials [4]. Latex adhesive, usually made of a styrene butadiene rubber co-polymer (SBR) adhesive is applied under the primary backing to secure face fiber [4]. The SBR adhesive combined with inorganic filler materials like calcium carbonate or barium sulfate is then used as a binder to bond the secondary backing to the primary backing [4]. The secondary backing is usually made up of same material as material as primary backing [4]. The face fibers contain dyes, soil repellents, fire retardants, and other additives to improve the carpet quality [4].

The following table, Table 2.1 gives a detail account of the constituents of a typical carpet with PP/SBR construction, which accounts for 95 percent of all the residential and commercial carpets in the United States.

TABLE 2.1

A TABLE INDICATING THE COMPOSITION OF A TYPICAL CARPET WITH
PP/SBR CONSTRUCTION [4]

Sr. No.	Constituent	Composition (in oz. avg. wt.)	Composition (in percentage wt.)
1	Face Fiber (Nylon 6 / Nylon 6,6)	30	45.80
2	PP (Primary backing)	4	6.11
3	Latex Adhesive	29 (SBR – 6 oz., $CaCO_3$ – 23 oz.)	44.27
4	PP (Secondary backing)	2.5	3.82
5	**TOTAL**	65.5	100

Carpet recycling is a complicated issue mainly due to the multi-component construction, presence of backing material and presence of dyes and coatings.
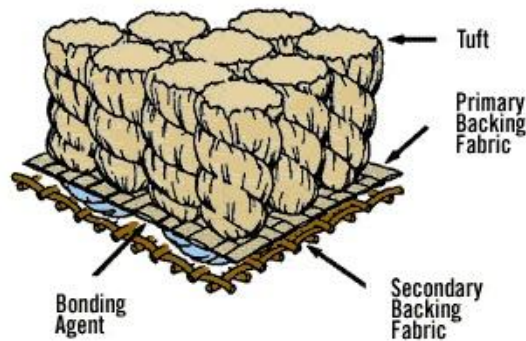
Fig. 2.2 An adapted figure illustrating the 3-D architecture of carpet [14].

Carpet padding is a cushioned material placed underneath carpet for longevity, comfort and noise absorption. It is mostly made with felt rubber and urethane. The cushion backed carpet

incorporates the padding as an integral part of backing while incorporating coal fly ash into polyurethane [14].

2.1.2 Carpet Classification

Carpets can be classified in three ways – (1) based on its consumption, (2) based on its construction and (3) based on the type of face fiber used.

Based on its consumption, carpets can be classified as virgin carpets, pre - consumer carpet waste and post - consumer carpet waste. A virgin carpet is an unused carpet and it is typically a carpet without any history of foot traffic. Virgin carpets are free of dirt, but they mainly consist of fibers, backing and a variety of chemical adhesives, fire retardants, dirt resistant, stain resistant dyes, color dyes and other materials. Pre-consumer carpet waste consists of the waste generated at the landfills largely due to the manufacturing process of carpet and the carpet fitting process. In the carpet manufacturing process, the edges of carpet need to be trimmed. These edge trims and off-cuts are disposed as pre - consumer carpet waste. The amount of carpet waste in the form of trimmings and waste is about 12% of the total carpet production [4]. In the automotive industry, a process called fitting process is used, where the carpets are cut into various irregular shapes and sizes. These cut edge trims and the waste carpet contribute to pre-consumer carpet waste in the landfill. Post-consumer carpet waste is defined as, "A used carpet generated at the landfills due to disposal of old carpets from residential and industrial areas." The average age of a carpet is 8 to 10 years. The weight of post-consumer carpet waste is 20 percent more than virgin carpet due to presence of dirt, dog hair, nails, metal fragments, food, bacteria and other microorganisms etc.

In this study the focus has been on the recycle of post consumer carpet. The recycling process suggested could also be applied to pre-consumer carpet but it would need further improvement in process modifications of the established scale-up process which is not desired.

Moreover the amount of pre-consumer carpet waste is low in comparison to post consumer carpet waste. Virgin carpets are not a part of the research to develop carpet composites in this study because this study aims at recycling the waste carpets in the landfills into highway noise barriers and it would defeat the objective of the study if virgin carpets are included in recycling of carpet composites.

Based on its construction, carpets can be classified as (1) cut-pile, (2) loop pile, (3) patterned loop and (4) cut & loop styles. These types of carpets can be manufactured by either weaving, tufting or by needle felt type of manufacturing process. Woven produces the highest grade of carpet in a loom by a process that is similar to woven cloth (cut pile type) [15]. Tufting is a widely followed industrialized process which involves sewing strands of yarn into the backing material and thereby creating thousands of yarn loops. In this study cut pile carpets were used for fabrication of carpet composites.
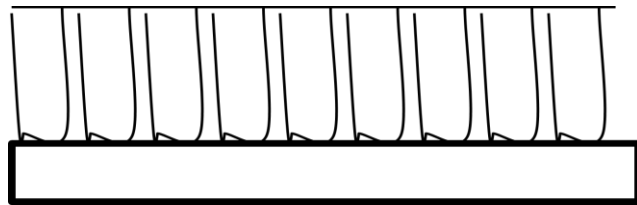
Fig. 2.3 An illustrative diagram of cut- pile type carpet (it is created by cutting the loops at the top) [16]

Fig 2.4 An illustrative diagram of loop - pile type carpet (when the loops are cut, you remain uncut) [16]

Fig. 2.5 An illustrative diagram of patterned loop type carpet (when the loops are uncut and have multiple heights) [16]
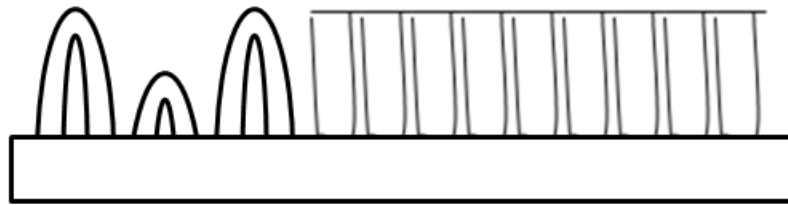
Fig. 2.6 An illustrative diagram of cut & loop type carpet (when the loops and cuts are combined to get a wide range of patterns) [16]

Based on the type of face-fiber material used, carpets can be classified into - Nylon (made of Nylon 6 or Nylon 6,6), Polyester, PP, Polyethylene Terephthalate (PET) and poly (vinyl chloride) (PVC), other olefins, jute, rayon, wool and cotton based carpets [4, 17]. Almost 97 percent of carpet manufactured in the United States is made from synthetic fibers because synthetic fibers are more resistant to stains while being less expensive [17]. However, as mentioned earlier nylon based carpets are used more significantly in the consumer world. About 90 percent of all residential carpets and 65 percent of all carpets are made of nylon fiber [17]. Nylon 6 and Nylon 6,6 account for 45 and 55 percent of the nylon carpet market [11]. In this study Nylon 6,6 based cut pile carpet was used for fabrication of carpet composites.

2.1.3 Nylon fibers

In the field of material science, there is a wealth of information about the invention of synthetic fibers for advancement in quality and availability of textiles. The discovery of Nylon 6,6 in 1931,

by the chemists at E. I. DuPont de Nemours and Company pioneered the revolution of textile industry and a huge impact of scientific world in the society [4]. Nylon 6,6 is a polyamide made from two monomers of 6 carbon atoms each, therefore the designation 6,6 [4]. Nylon 6,6 is formed by a polymerization reaction between its monomers hexamethylene diamine and adipic acid [4]. Currently, Nylon 6,6 is made by Dupont, Solutia and other manufacturers and is sold as fibers [11]. By around 1940, Paul Schlack of I.G. Farben Company in Germany obtained a different form of polyamide called Nylon 6 by using caprolactum as a monomer [4]. Currently, Nylon 6 is made by Honeywell, BASF and several other manufacturers and is extruded in to fibers by these companies or by the carpet manufacturers. The manufacturers of carpet procure the nylon material from these companies or have their own stand alone nylon production.

2.2 CARPET RECYCLING

Carpet recycling poses significant challenges due to the inhomogeneous and chemically diverse nature of the materials that constitute a carpet. However literature suggests that there is an increasing trend in research and development of carpet recycling methods. The carpet recycling methods can be broadly classified into four categories:

1) Primary recycling or depolymerization: It involves methods to breakdown the long polymer chains into their original monomers that can be repolymerized [4].

2) Secondary Recycling: It involves recovery of individual components of a polymeric mixture without breaking them into monomeric forms but by extraction and separation methods [4].

3) Tertiary Recycling: It consists of preparing a thermoplastic mixture by melt blending of carpet waste by reactive extrusion and compatibilization. Injection molding on this blend would yield products of lower quality [4].

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4) <u>Quaternary Recycling:</u> It involves energy recovery by incineration of carpet waste [4].

Research and development of carpet recycling has mostly been a part of one of the above four recycling techniques. However, there are companies like Polyamid 2000 that have processes to integrate all the above four recycling techniques into one recycling process. Polyamid 2000 has a plant at Premnitz (near Berlin, Germany) at operation since 2000 which uses a recycling process similar to the one illustrated in Fig. 2.7.
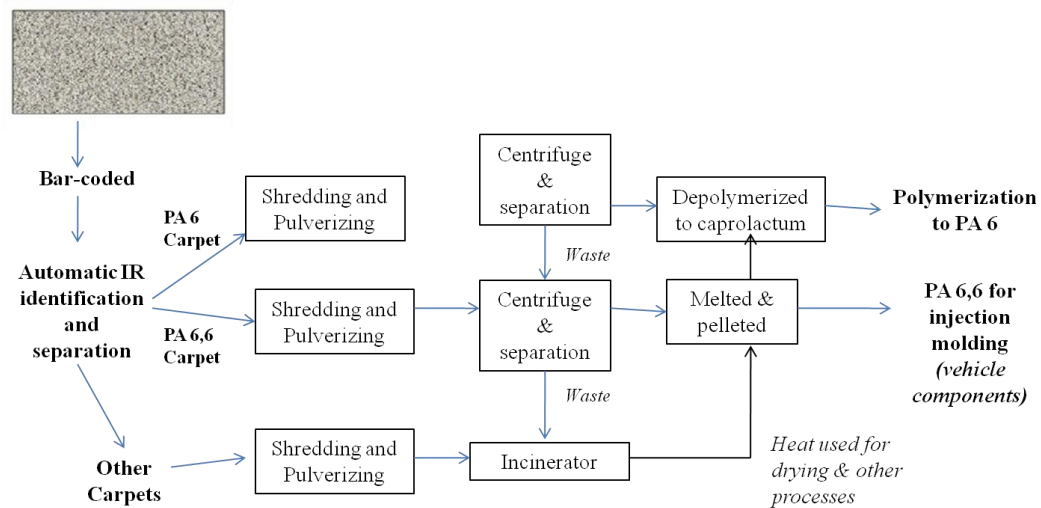
Fig. 2.7 An adapted block diagram of Nylon recycling process used by Polyamid 2000 [18]

The following sections cover a detailed technical literature review of the carpet recycling methods, covering patent and non-patent literature review.

2.2.1 Primary Recycling

Primary Recycling or Depolymerization is currently the most preferred route for the carpet recycling industry, since it allows recovery of monomers from carpet fibers (nylon 6 and/or nylon 6,6) which can be repolymerized into new nylon products of high quality [4]. In the non patent literature review, the paper by Mihut C et al. has provided valuable background information. Mihut C et al. mentioned the following depolymerization techniques of carpet in their paper [4] –

(a) Depolymerization with Ammonia (Ammonolysis)

(b) Acid/Base Catalyzed Depolymerization

(c) Depolymerization with water

(d) Pyrolysis

The depolymerization reaction of nylon 6 is a thermodynamically favored at low pressures and high temperatures, above the boiling point of caprolactum (around 267 $^{\circ}$C). At low pressures it becomes easier to separate the monomers from the melt. High temperature using superheated steam is maintained because the process is endothermic. For depolymerization of nylon 6,6 the key focus is the recovery of hexamethylene diamine and adipic acid. Some depolymerization processes include addition of catalyst for easier processing of polymeric melt by decreasing its viscosity [4]. The following Fig. 2.8 illustrates the companies involved in depolymerization process of nylon based carpet.

Fig. 2.8 An illustrative chart enlisting major companies in depolymerization of nylon carpets

Depolymerization of nylon 6 with superheated steam is a highly researched depolymerization technique. Patent literature review suggests that Sifniades et al. of Allied Signal Inc have several patents on the recovery of caprolactum from nylon 6. In their patent they developed a depolymerization technique using superheated steam [19]. In multicomponent mixtures or composites like waste carpets that contain nylon 6, the recovery of caprolactum is

complicated due to presence of other components [20]. Sifniades et al. August 1999, mention in their patent that, "In the absence of added catalyst, contacting the multi component waste material with superheated steam at a temperature of about 250 ^{o}C to about 400 ^{o}C and at a pressure within the range of about 1 atm to about 100 atm and substantially less than the saturated vapor pressure of water at the temperature wherein a caprolactum- containing vapor stream is formed. The formed caprolactum may then be used in the production of engineering resins and fibers" [20]. Mayer et al. of Allied Signal Inc. modified the depolymerization process by stating that "if the crude caprolactum from depolymerization of polyamide-containing carpet is subjected to a simple flashing operation, the condensed flashed material may be crystallized from the aqueous solution and good quality, washable crystals are obtained. The resulting caprolactum has purity greater than 99.9 weight percent (excluding water) and a permanganate number less than 3 and a color number less than 2 and thus, is world class caprolcatum." [21]. Hendrix et al. (1997), mention that depolymerization can take place at a pressure of between 0.5 and 5 atm in the presence of a nitrogen containing compound [22]. By this process, the carpet waste would undergo a depolymerization reaction to yield monomeric components and by - products. These by - products can be removed with a nitrogen containing compound via gas phase [22]. Allied Signal Inc. patented a process to remove caprolactum from hydrolyzable polymer like nylon based carpet waste by depolymerization with water [23]. The process by Jenczewski et al. (1997), uses "whole carpet," that is carpet that has not been subject to any mechanical separation, including cleansing of carpet [23]. The whole carpet is then fed to a continuous stirred tank reactor (CSTR) or a series of CSTR's via a gear pump, wherein it is mixed with water to form a multicomponent polymeric waste material [23]. This mixture is then subjected to heat and pressure to form a liquid aqueous solution and therefore dissolution of nylon 6 and partial depolymerization of nylon 6 is achieved [23]. Caprolactum is obtained by flash distillation while the water insoluble waste is sent to centrifuging to obtain solids which are combusted in a separate step to provide process heating and evaporation [23]. Frentzen et al. suggest their patent process for depolymerizing nylon 6 and

recovering caprolactum from the depolymerized products by extraction with alkyl phenolic compounds [24]. Corbin et al. 1999, focused on the process improvement in depolymerization of nylon-6 carpet with water [25]. Corbin et al. invented the process in which the carpet is fed in a separator to prepare a scrap containing nylon -6 and auxiliary materials, from which, the scrap is fed to a depolymerizing reactor to produce a distillate rich in epsilon – caprolactum [25]. Here in the distillate epsilon - caprolactum is separated from other volatiles and the auxiliary materials are recovered and reused [25]. While most of the patents focused on recycling of nylon -6 to caprolactum by depolymerization with water, Dos Santos et al. 1999, focused on treatment of material comprising nylon 6,6 to recover adipic acid and other diacids [26].

A patent literature review revealed that depolymerization of nylon fibers into its monomers by pyrolysis is not as studied in comparison to other depolymerization techniques. However a few like Moens et al. (1999), invented a process to purify caprolactum from recycled nylon by pyrolysis [27]. Moens et al. (1999), used carbon dioxide to form a precipitate in a solvent dissolved pyrozylate containing caprolactum mixture [27]. The precipitate is removed from the solution and pure caprolactum is recovered from the solution [27].

The non-patent literature suggests that depolymerization of carpet fibers by acid/ base catalysis has been a highly reviewed and widely researched topic. Recovery of epsilon - caprolactum from waste polyamide 6 is competitive with traditional synthesis process and has a significant environmental impact [28]. The Zimmer AG process, which is applicable only for pure polyamide 6 materials, performs depolymerization using steam and a liquid catalyst like phosphoric acid [28]. The disadvantage of Zimmer process is the high yield of salts and traces of phosphoric acid in the recovered ε-caprolactum [28]. Generally, depolymerization of carpet using acid catalysis requires separation of fibers (beneficiation) from other components because $CaCO_3$ present in fillers can consume an equivalent amount of acid catalyst used [4]. Moran and McKinney have worked extensively on the subject of depolymerization using catalysts using acid

catalysts using aliphatic carboxylic acid like acetic acid and propionic acid to obtain caprolactum and adipic acid. According to the patent by Moran et al. for DuPont the following process for depolymerization of waste carpet was developed -

"Waste carpets can be entirely dissolved in the aliphatic acids used, at temperatures of about 110°C and atmospheric pressures. Carpet components, such as the primary and secondary backings and adhesive binder, which are insoluble in the acid solution, can be separated by hot filtration. The acid filtrate, containing the nylon fibers, can then be subjected to the depolymerization process" [4].

Bockhorn et al. investigated the use of two types of catalysts – basic catalysis by NaOH/KOH and acidic catalysis by H_3PO_4 (by Zimmer procedure), which remain liquid under degradation conditions [28]. Bockhorn et al. concluded that "The basic catalyzed degradation of polyamide 6 proceeds via an anionic chain mechanism, which explains high reaction rates in contrast to the non-catalyzed and acid catalyzed reaction. For these reasons, basic catalyzed degradation of polyamide 6 is the best suited for an application in a procedure for epsilon - caprolactum recovery from polyamide 6 wastes" [28]. Depolymerization with ammonia involves heating of a mixture of polyamide 6 and polyamide 6,6 in the presence of ammonia at high temperatures and pressures [4]. Lewis acid catalyst precursors makes the process highly efficient [4].
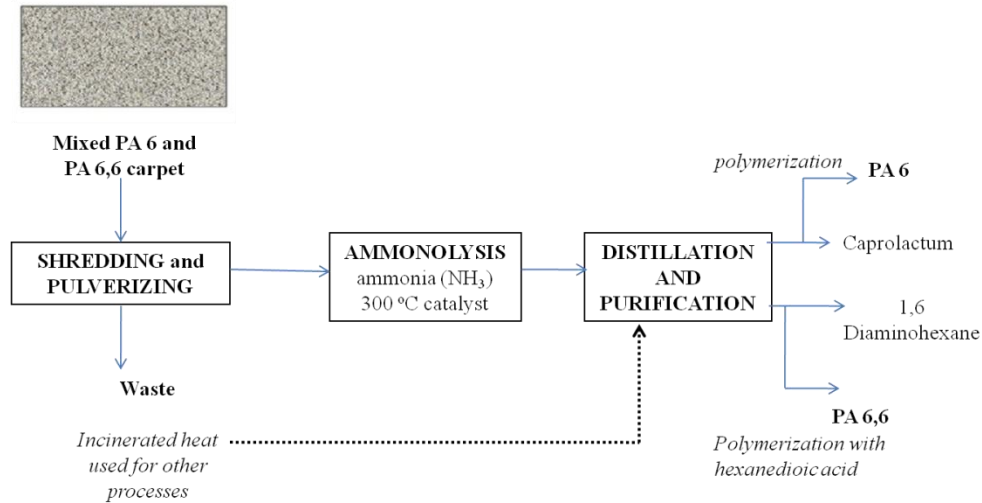
Fig. 2.9 An adapted block diagram of Dupont's Nylon recycling process [18]

2.2.2 Secondary Recycling

In the process of secondary recycling, the entire waste carpet is dissolved in a solvent at high temperature and nylon can be extracted from its fibers in its polymeric forms by extraction process. Although the final product can be used in various applications by further processing using injection molding, the problem associated with this process is the selection of a suitable solvent that selectively dissolves the nylon fibers and does not interact with or dissolve with any of the other carpet components [4].

A patent literature review of secondary recycling of carpet reveals that Roberts et al. in 1997 patented a process for recovering and recycling carpet waste by contacting the carpet waste with a solvent (like formic acid or phenol) which selectively dissolves nylon to form a polymer solution. The solvent and polymer solution is then contacted with an anti-solvent (like carbon dioxide) which causes the polymer to nucleate and precipitate from the solution [29]. The process is efficient in terms of safety and cost because it can be operated using low temperature solvents and anti-solvent like carbon dioxide for re-crystallization of nylon [29]. Costello et al. devised a method to remove the adhesive material from the waste carpet material feedstock to obtain a

mixture containing face fiber material which is passed with a liquid medium to a hydrocyclone for separation of solids on the basis of specific gravity for recovery [30].

2.2.3 Tertiary Recycling

Tertiary recycling of carpet materials consists of melting or extruding the waste carpet to form a blended mixture which is then used in production of injection molding and thermoplastics [4]. Although melt blending is cost effective compared to the expensive separation and depolymerization procedures it produces low quality melt blended plastics due to poor chemical compatibility of carpets [4].

Kotlair and Fountain developed a simple process to convert carpet waste to individual shreds, which on coating with structural adhesives gives fibrous composites like "synthetic wood" [4]. Young et al. focused on recycling of automotive carpet scrap by extruding the shredded and granulated carpet scraps [4]. The melt produced is then pelletized and used in injection molding applications [4]. This process for Lear Corporation included applications like flexible floor mats, automotive carpet backing with superior sound-insulating properties and rigid materials like door panels and truck liners [4]. David et al. developed an alternative method of melt blending for Monsanto in which, the carpet waste without excess dirt is fed into a twin screw extruder at a shear rate of 200 to 400 sec^{-1}, a temperature between $250^{o}C$ and $350^{o}C$ and a pressure of 350 to 450 psi [4]. Intense mixing converts the carpet into a flowing homogenous mixture containing all the components of carpet - face fiber, backing and SBR adhesive, which on cooling yields a resulting material exhibiting thermoplastic characteristics in the form of pellets or chips [4].

2.2.4 Quaternary Recycling

Incineration or quaternary recycling helps in partial recovery of the energy content of the waste materials like carpet waste. Two types of ash are produced by the incineration process: fly ash (fine particles entrained in the incinerator exhaust gases) and bottom ash (the large and heavy particles removed from the bed of the incinerator) [31]. Land filling these ash residues is not always acceptable because of the potential for groundwater and soil pollution due to leachate carrying heavy metals like lead and cadmium [31]. Even though there has been public resistance for incineration due to its emission of toxic fumes, there has been significant improvement in technology which makes incineration a robust recycling option [31]. Most of the municipal solid waste (MSW) combustion currently practiced in the United States involves recovery of an energy product (generally steam or electricity). The resulting energy reduces the amount needed from other sources, and the sale of the energy helps to offset the cost of operating the facility [8]. The USEPA report of 2009, in its chapter on Management of Municipal Solid Waste states that "Total U.S. MSW combustion with energy recovery, referred to as waste-to-energy (WTE) combustion, had a 2009 design capacity of 94,721 tons per day. There were 87 WTE facilities in 2009, down from 102 in 2000" [8].

There is also a trend in facilities seeking combustion of source separated MSW for use of rubber tires and used paper / wood products in boilers, cement kilns, pulp and paper mills, industrial boilers and dedicated scrap tire to energy facilities [8]. The use of tires have decreased the air emissions by 30 % for a plant at Atlanta, Georgia and has therefore helped the company to meet the stringent nitrogen oxides (NO_x) guidelines [32].It is estimated that about 3.1 million tons of MSW were combusted in this manner in 2009, with tires being the majority in this contribution [8]. However, the volume of these MSW is reduced by about 75% after incineration and the post-combustion ash needs to be treated separately and then land filled thereby owing to general public concerns [32]. The use of carpet waste in cement kilns is also an attractive option since the

relatively high fuel value of carpet polymers can reduce the need for fuels, and the calcium carbonate in carpet could become a raw material for cement [32].

2.3 WASTE CARPET RECYCLING

The following Fig. 2.10 shows the products obtained by recycling of carpet using the traditional methods of recycling.
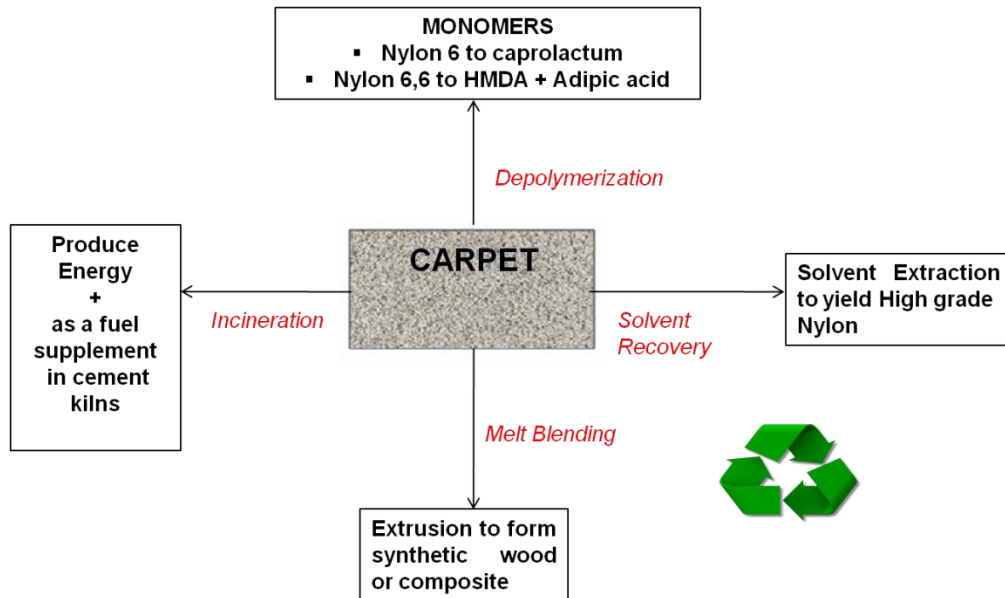
Fig. 2.10 A diagram of products obtained by traditional carpet recycling processes

The traditional methods of carpet recycling have many shortcomings of which the predominant drawbacks are - 1) being highly uneconomical and 2) excessive process time. This defies the aim of a sustainable development process for product recycling. Recycling is defined as a process to make products better in terms of properties and value than its current value. But the recycling process should be cheap and viable to make it lucrative. This helped us in choosing better products like - polymer composites which are cheaper in value and their manufacturing process for recycling waste carpets. Hence VARTM was used to recycle waste carpets into structural composites which can be used as highway noise barriers. The next section talks in

detail about the need for highway noise barriers and the requirements for a material to qualify as a highway noise barrier.

2.4 HIGHWAY NOISE BARRIERS

For vehicles in motion in highways, friction between the vehicle's body and the air touching the vehicle causes a change in the gradient of the air pressure field induced by the friction [33]. This friction renders aerodynamic effect called noise which can be heard at significant distances [33]. Noise is also created due to engine operations, exhaust systems and the contact of grooved tires on pavement surfaces [33]. This noise with a spectrum of multiple frequencies is called traffic noise [33]. A majority of this spectrum falls within the range of 250 Hz and 4000 Hz [33]. Human ear can easily hear a noise of this frequency and therefore traffic noise causes great discomfort to mankind. Noise barriers are built along highways to control the noise pollution because the barriers contain and absorb the noise within them and do not allow any propagation of noise to any significant distance [33]. As shown in the illustration below in Fig. 2.11 traffic noise is caused mainly due to traffic volume, speed of the traffic and volume of trucks.
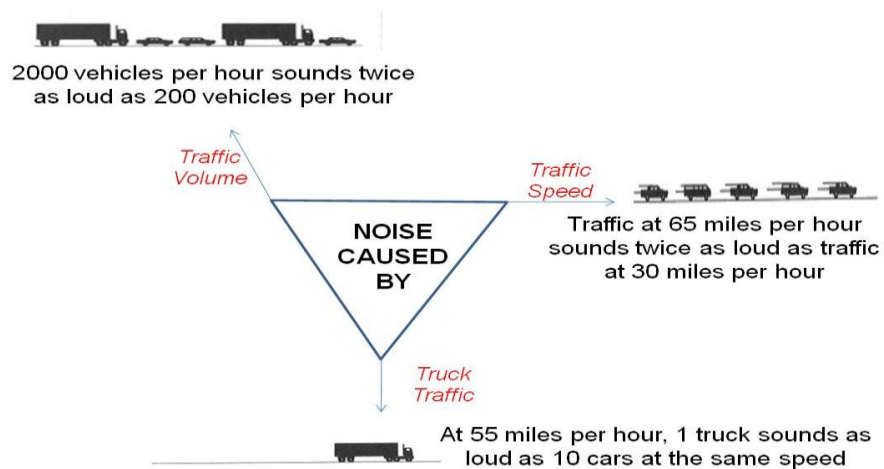
Fig. 2.11 An illustration to show the reasons for traffic noise on highways [34]

A formal definition is needed to define highway noise barriers as it one of the potential applications for our material - carpet composite. A highway noise barrier is defined as a barrier wall that attenuates noise by preventing the direct propagation of noise between the noise source and the listener by absorbing the sound energy incident upon the surface on the barrier [35]. Hence measurement of absorption of sound energy incident upon the surface of the barrier material is the most critical parameter for evaluation of the performance of the material as a barrier. This measurement can be achieved using acoustic characterization test based on the American Standard for Testing Materials, ASTM standard C 384 - 04. This characterization would enable a correct assessment of the structural material as a highway noise barrier. Barriers are generally applicable to the design of new highways and are an attractive means of providing noise relief to communities along existing highways [35]. There are four primary requirements for an acceptable highway noise barrier [35]:

1) It must function effectively as a noise reduction structure

2) The barrier must be a safe roadside structure

3) The total installation costs must be acceptable, and

4) The barrier must have an acceptable appearance.

Currently most highway noise barriers are built with precast concrete or concrete slabs, which have high acoustic reflectivity (95% and above) and low noise absorption for the frequency band of highway noise between 250 Hz and 4000 Hz [33]. There is a possibility for alternative highway noise barriers made up of materials with higher noise absorption coefficient or even the use of vegetation as a noise barrier. Vegetation can decrease highway traffic noise if it is high, wide and dense enough. A 200 ft width of dense vegetation can reduce noise by 10 dB, which cuts the traffic loudness into half, but is impractical to plant such scale of vegetation – at this era of rapid development [34].

| Concrete Noise Barrier | Wooden Noise Barrier | Earthberm Noise Barrier |
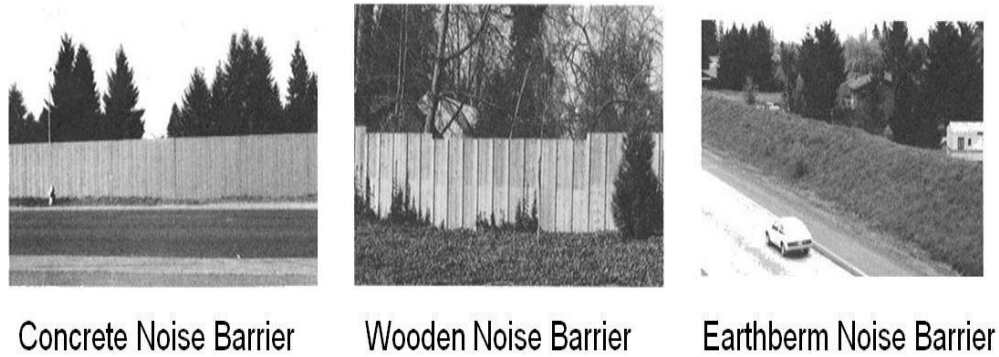
Fig. 2.12 Types of Highway Noise Barriers [34]

Due to exponential economic growth of the world economy in the past few decades, there has been a drastic increment in highway traffic and a need to develop new and better noise reduction barriers for highways and airports. This trend in increase of highway traffic is likely to continue in the near future and so has been an increase in dedicated research efforts to develop new noise barriers. Polycarbonate noise reduction panels made by a California based company, "Quitite International", have been used to build polycarbonate noise wall near Culver City park in Los Angeles, California in 1996 [33].Also a jet engine testing center was installed at Albany airport, Albany, New York in 1997 using polycarbonate noise barrier [33]. In both these cases the polycarbonate was made from Lexan plastic produced by GE Plastics [33]. Carsonite International of Early Branch, South Carolina developed hollow panels made planks of reinforced composite material crumbed rubber tires as nano-fillers [33].

The literature review indicates that Wolfe et al. investigated the usage of cement wood composite as highway noise barriers while Watts et al. studied the effects on roadside noise levels by applying sound absorptive materials to the traffic face of noise barriers [36, 37]. Watts et al. also used the boundary element method to study the combined effects of porous asphalt surfacing and noise barriers on traffic noise [37]. Yamaguchi et al. studied the sound absorption mechanisms, void ratio and acoustic properties of porous asphalt surface by comparison with other porous materials like mineral wool and synthetic wool [38]. Meiarashi et al. and Oshino et

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al. studied the sound absorption mechanism of porous asphalt pavement and proposed a model for predicting vehicle noise propagation on asphalt pavement [39] [40]. Shukla et al. investigated the effect of addition of cenospheres on the acoustic properties of cement matrix and asphalt concrete [41]. Hence this shows clear evidence that replacement of concrete noise barriers with better acoustic composite materials is feasible.

The factors that influence the structural design of barriers are both acoustic and non-acoustic. Non acoustic factors include wind loads, fire-retardancy, and the weather and aging effects (which cause warping and corrosion) [42].

2.5 RESEARCH FOCUS

The main focus of this study is to fabricate large scale carpet composites as highway noise barriers. Considering the problems faced in recycling of nylon based carpets and the ubiquitous trend in advancement of research in polymer composites, it was decided that nylon based carpets would be recycled as carpet composites.

VARTM of waste carpet into recycled carpet composites is the most significant way of recycling waste carpet into valuable products in a cost - effective way. VARTM produces carpet composites which are better in quality, mechanical and physical properties than melt blending of waste carpet to yield composites. VARTM is better than other traditional methods of recycling like solvent recovery to yield high grade nylon; depolymerization to yield monomers like caprolactum, HMDA and adipic acid and incineration of waste carpet to produce energy. All these traditional processes are more expensive in comparison to VARTM.

The carpet composites produced have a huge scope for their use in structural applications like highway noise barriers. Highway noise barriers should have good acoustic properties and should be able to bear higher wind loads. For better acoustic properties, it is desired to have a material with good acoustic properties. However, the material should have good mechanical

properties to bear the strength of the wind loads, greater fracture toughness and higher impact strength. The remainder of this thesis has put forth a manner to address a solution to this problem of achieving superior mechanical properties with equally good porosity. The VARTM process is scaled up to inculcate porosity in the composites which results in a material with excellent acoustic properties.

CHAPTER III

CARPET COMPOSITES

Material science has always looked up to nature for its incredible inventions and its admirable job of innovations in design and manufacturing. Wood is a natural composite material consisting of one species of polymer as reinforcement - cellulose fibers with good strength and stiffness - in a resinous matrix of another polymer, the polysaccharide lignin [43]. Bone, teeth and mollusk shells are other natural composites [43].

Polymeric composites consist of reinforcements in a polymer matrix. The reinforcements are generally glass, aramid, carbon fiber or any fibrous material and the matrix is a thermoplastic or a thermoset polymer [44]. Polymer matrix is of two types: Thermoplastic and thermoset polymer. Thermoplastic polymer like polyether ether ketone (PEEK) and polyphenylene sulfide can be heat softened, melted and post-formed – an infinite number of times. On the other hand thermoset polymers like epoxy, polyester and vinyl ester, after being fully cured, cannot be melted and reshaped despite applying required heat and pressure [45].

The structural applications of polymer matrix composites have been ubiquitous in the fields of aerospace, automotive and marine industries because it offers lower specific gravity, higher strength to weight ratio, better corrosion resistance, and increased durability in comparison to conventional materials [45]. There a number of manufacturing techniques for fabrication of polymer matrix composites and in Fig. 3.1 presents a classification of some of these manufacturing processes.
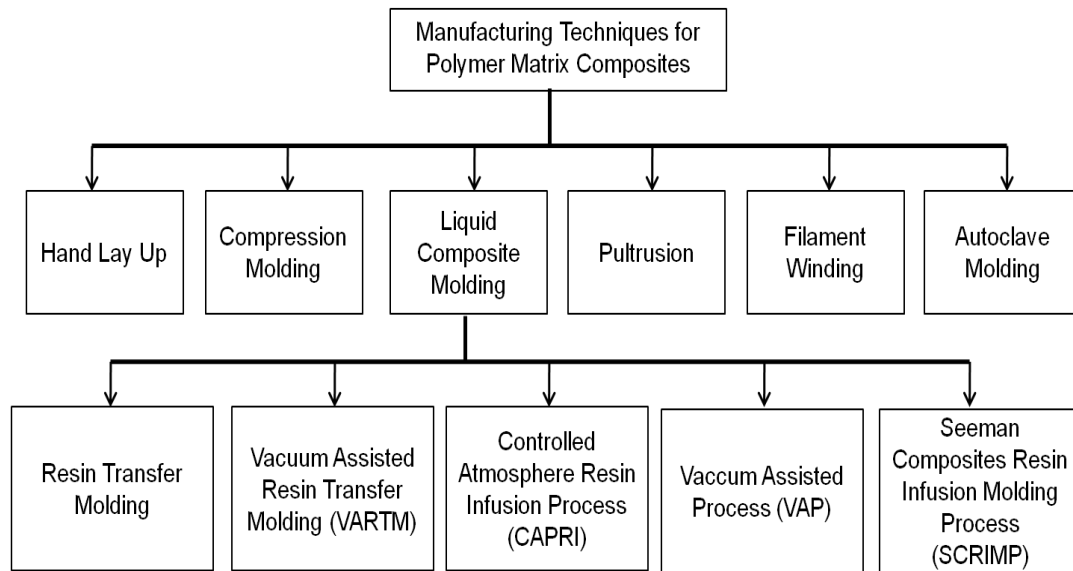
Fig. 3.1 Types of manufacturing techniques for polymer matrix composites

3.1 OBJECTIVE

One objective of this research is to recycle waste carpet into carpet composites of various sizes and shapes by using a scaled up vacuum assisted resin transfer molding (VARTM) technique.

3.2 BACKGROUND

Liquid composite molding refers to a number of processes that use liquid resin to impregnate a stack of stationary fibrous materials called preform. Resin Transfer molding (RTM) and Vacuum assisted Resin Transfer Molding (VARTM) are the two main variants of liquid composite molding used in the composites industry. This section includes a brief discussion about these two variants of liquid composite molding.

In RTM, the reinforcement fabric called preform is placed in the mold cavity, the mold is closed and resin is injected into the cavity under pressure [44]. Once the resin is cured, this once stationary preform turns into a composite which can be de-molded from the rigid mold walls. This technique is well known and has been traditionally applied to moderately large parts in

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composite applications whereas, in VARTM, the preform is sandwiched between a solid mold or a solid surface on one side and a vacuum bag on the other side [46]. Vacuum applied serves the following two purposes [46]:

1) The vacuum reduces the pressure within the mold, thereby causing the atmospheric pressure to compress the preform. This helps in achieving high performance composites with high volume fraction and yield a high fiber volume preform which is required for high performance composites.

2) The vacuum draws catalyzed thermosetting resin from strategically placed inlet ports, into the mold and through the preform.

Later, this resin saturated preform undergoes a cure temperature cycle which hardens the fiber resin mixture to create the final composite part. The process is completed by demolding which means removal of composite product from mold or surface [46]. VARTM offers numerous cost advantages over RTM process due to lower tooling costs, potential for room temperature processing and scalability for large structures [47]. In VARTM, the compaction of the reinforcement and pressure gradient needed for the resin flow is provided by applying a vacuum on the opposite side of the preform. Fig. 3.2 offers a comparison of the RTM and VARTM processes.
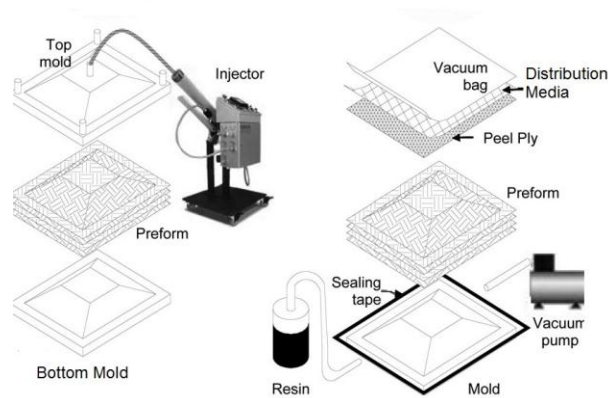
Fig. 3.2 An adapted figure [44] indicating the differences between RTM (on left) and VARTM (on right)

In general, the VARTM process can be divided into three main processing steps [47] –

1) Material and tooling preparation,

    a. Resin Mixing and Degassing

    b. Material Layup and Drying

    c. Preform Debulking

    d. Leak-free bagging and tooling

2) Infusion

    a. Optimum infusion setup

    b. Minimize thickness gradient

    c. Micro-void reduction

    d. Automation

3) Post – infusion

    a. Optimum resin bleeding

    b. Cure control

3.2.1 Material and Tooling Preparation

The fibers, preform and other reinforcing materials are placed in the mold as the first step in VARTM. In case if these reinforcing materials would have taken up moisture and depending on the resin selection and final part quality requirements, the material is dried under vacuum prior to infusion [47]. Pre - infusion debulking or Debulking is defined as a process of repeated compression and relaxation of the preform under vacuum pressure [47]. Debulking of fabric ensures an increase in nesting of fibers. Resin mixing and degassing ensures blending of various components and low content of entrapped gases. Leak rates can be monitored and minimized leak rates can be ensured by using tooling designed for VARTM applications and with properly installed bags.

3.2.2 Infusion Step

Infusion is a critical step in the VARTM process because of the fundamental challenge in this step to achieve adequate fiber wet-out by eliminating the occurrence of dry spots and voids in the final composite part. During infusion, resin flow follows Darcy's law, which states that the flow velocity is related to the local pressure gradient, fluid viscosity and permeability of the porous medium (permeability is a measure of resistance to the flow provided by the preform) [46]. During infusion, the vacuum pressure would compact the preform and pull the resin through the preform. The resin flow in any fabric can be approximately modeled by Darcy's law. Darcy's law in 1-D describes the average velocity, $\bar{u}$ (m/s) as shown in equation 3.1.

$$\bar{u} = \frac{K}{\mu} \times \frac{dp}{dx} \tag{3.1}$$

Where,

K = permeability parameter, (m^2)

p = pressure (Pa)

μ = viscosity of the resin injected (centipoise)

x = flow direction, (m)

Darcy's law indicates that the resin impregnation of the preform and the average fluid velocities depend on the permeability of the fabric [48].

For industrial grade VARTM processes it is preferred to have automation of the VARTM process to increase repeatability and reduce human error.

In the post infusion step, the resin has significantly low viscosity and the setup is designed to allow bleeding of excess resin into a vacuum trap. The resin bleeding takes out excess

resin from the area of low vacuum pressure and moves it toward the vent [47]. The volume loss reduces the thickness of the part and improves the fiber volume fraction [47]. Thus post infusion step is an important step in the VARTM process where the fast curing resins gel prior to reach uniform thickness while the excessive resin bleeding leads to dry spots and high void content. It is critical to understand VARTM because it involves the use of many parameters and all these parameters are significant. The change of a parameter or variation in parameters results in variants in type of VARTM.

In the composite fabrication industry SCRIMP, VAP and CAPRI processes are the most commonly used improvisations of VARTM which address variations in the critical step of resin infusion.

The Seeman Composites Resin Infusion Molding Process (SCRIMP) is a patented VARTM variation in which a highly permeable resin distribution medium is incorporated as a surface layer on the preform [49]. In the SCRIMP process, the resin infusion time increases exponentially with injection length during the VARTM process and therefore leading to premature curing of resin during infusion for fabrication of large scale composites. The use of sequential injection of resin with multiple injection ports is the preferred route for fabrication of large composites by the SCRIMP process.

The Vacuum - Assisted Process (VAP) was developed and patented by EADS Deutschland in which a gas permeable membrane is used to attain uniform vacuum distribution and continuous degassing of the infused resin [50]. The membrane is designed in such a way that it is permeable to gas/air and is impermeable to resin. The high air permeability ensures continuous surface venting during the VAP process. The VAP process is an improvised version of VARTM process which minimizes dry spot formation, lowers void content and improves dimensional tolerances [47].

The Controlled Atmospheric Pressure Resin Infusion (CAPRI), patented by Boeing Corporation, was developed mainly to improve the thickness/fiber volume variability in infused composites [51]. The characteristic of CAPRI is the application of partial vacuum to the resin reservoir during infusion thereby lowering the pressure gradient from inlet to vent location. The application of partial pressure gradient results in a smaller thickness gradient but it increases the infusion time significantly. Hence the CAPRI process changes the compaction and permeability behavior during the debulking process prior to infusion.

A detailed understanding of the VARTM fabrication processes was necessary since it helps in understanding the scale up of manufacturing. The learning curve in VARTM developed gradually after fabrication of many carpet composites of different configurations. The main reason for the slow learning curve was because the VARTM process has many parameters to be controlled simultaneously and it becomes challenging to maintain repeatability in results. To analyze this involved detailed investigation of the parameters and their significance. This was learnt by changing one parameter at a time and in fact, there were some changes which resulted in failures. However these failures have significantly improved the working knowledge about VARTM process and the material parameters involved.

3.3 RESEARCH THRUST

The VARTM process for recycling carpet has several advantages compared to traditional carpet recycling techniques like depolymerization and melt blending which require high energy. Singh et al. (2009) [6] made a detailed analysis of recycling waste carpet into carpet composites by VARTM with various thermoset resins. Singh et al. (2009) [6] used hot pressing for high temperature post curing step to achieve carpet composites as a final product. The use of hot press limits the fabrication of composites of different shapes and sizes primarily because hot press is designed for flat composite panels of a fixed size. Jain (2010) [52] extended the work performed

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on feasibility of carpet composites by studying the effect of carpet fiber treatment with Lewis acid / base chemicals on resulting carpet composites by VARTM. Jain (2010) [52] makes use of hot pressing as a post curing step to make carpet composites

However the challenge remains on scale-up of manufacture of carpet composites to make large scale composites of larger dimensions and different shapes. Hence a scaled - up process of fabricating large scale carpet composites is required. The following process of scaling up of VARTM was followed -

Samples were fabricated using a simple, vacuum assisted resin transfer molding fabrication technique with different combinations of layers. In the scaled up VARTM fabrication process caul plates and green mesh cloth (similar to SCRIMP process) are used. Initially, the glass plate is cleaned with acetone. Three layers of mold release wax and one layer of PVA release film coat are applied over the surface to ensure an easy removal of composite after completion of resin curing period.

Nylon bagging material (procured from Airtech International Inc.), tacky tape and connecting tubes (procured from Fiberlay Inc.) are cut to the required size. The tacky tape is laid to a size slightly greater than the size of effective material (e.g., the infusion area over the glass plate) and the carpet is placed between the tapes. The scaled-up VARTM fabrication process involves use of a thin release sheet placed over the carpet for minimum resin use. Thin pores on the sheet allow excess resin to flow out of the pores, which is then carried to the next level of green mesh (SCRIMP model) which adds local stress points inside the bag so that resin runs through carpet sample to reach the vacuum end of the set-up. A polyester release cloth is placed over the green mesh cloth to ensure that the resin does not stick to the vacuum bag and the bag can be attempted to be made reusable. Breather cloth is placed over the release cloth to ensure distribution of air (if any) in the vacuum bag. The breather cloth distributes the air evenly in the

setup if in case of air pocket. In the conventional VARTM nylon bag is used to enclose the entire

set up from end to end over the tacky tape with attention paid to avoiding air pockets at any end.

In the scaled up VARTM process, the same procedure is used but over an aluminum sheet placed

over the breather cloth layer (thereby sandwiching the entire carpet sample assembly). This sheet

of aluminum is a caul plate which saves in the cost and simplifies VARTM by avoiding the hot

press. The caul plates used are of the same dimensions as the sample of carpet cut.

The remainder of this chapter is focused on scale – up of VARTM process and the

materials and methods required in this process.

3.4 MATERIALS

Fig. 3.3 (a) and Fig. 3.3 (b) show a schematic of the setup of scaled up VARTM process

used for fabrication of carpet composites.
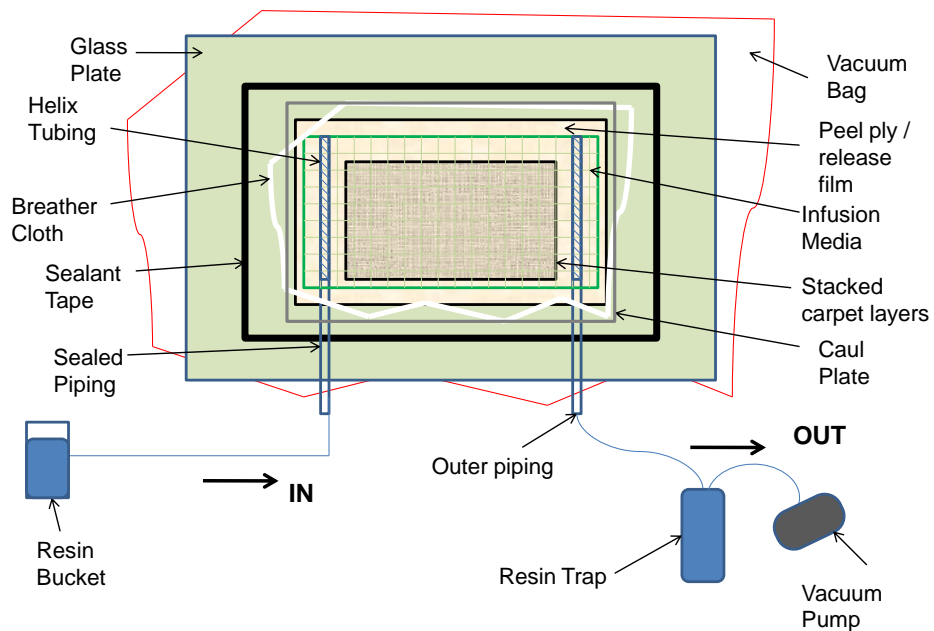
Fig. 3.3 (a) An illustrative schematic of the scaled up VARTM process (Plan View).
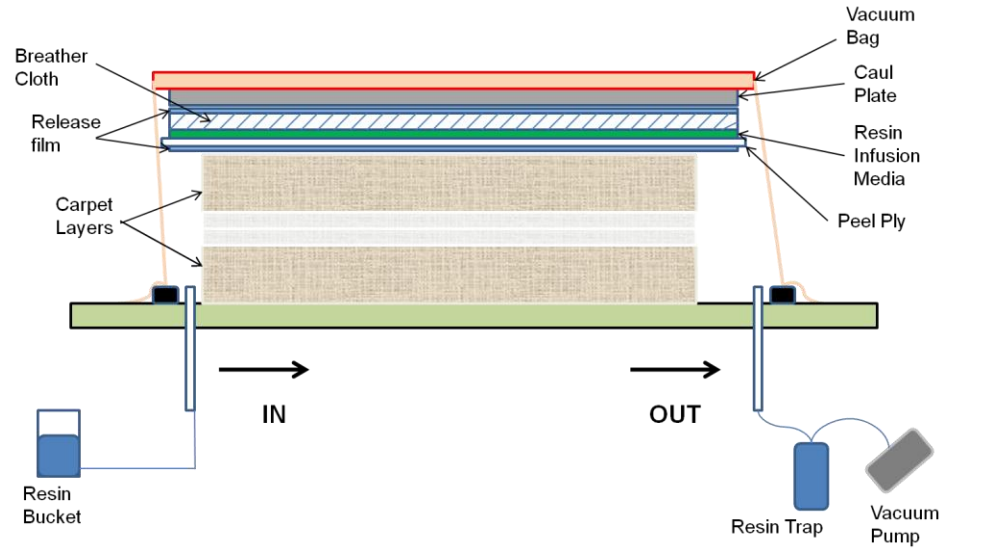
Fig. 3.3 (b) An illustrative schematic of the scaled up VARTM process (Elevation View).

The scaled up VARTM set-up constitutes laying the preform fabric (that is nylon based carpet) on a smooth surface tool or glass plate or a flat table. A release material like wax is applied to the mold so that after the cure of the part it is easy to demold the composite from the mold or glass plate. The resin inlet and the vacuum outlet piping are placed at both ends of the laid fabric. A release film, peel ply, low permeability resin distribution media, and breather cloth, in that order, are placed on the top of the fabric. Finally a vacuum bag is placed on top of this set up and is sealed with the help of a sealing tape. Finally, vacuum is drawn using a vacuum pump. After the setup of this process, the resin is infused (pulled by the vacuuming force of the pump) through the carpet. Thereafter the inlet manifold is clamped so that the resin feed can be stopped. The impregnated carpet fabric is allowed to cure. The curing time is decided by the type of resin and hardener combination used for resin impregnation.

3.4.1 Mold/Glass Plate

The mold is defined as a rigid material which does not change its shape during the VARTM process and acts as a stable base. In this study a stiff glass plate with fine finish was chosen as a mold. The glass plate gave a smooth finish for one side of a flat panel. However in

case of VARTM for larger samples, of the size 0.61 m x 1.22 m (2 ft. x 4 ft.) the surface of the work bench was used as a mold and sometimes, the floor was used as the flat end mold surface. Although the resulting panels had a smooth finish, the surface of workbench and floor as a mold gave other operational problems like cleaning the spillage of excessive resin and change in flow pattern of resin.

In case of curved shaped panels, a thin aluminum plate was curved to the shape of an arch and used as a mold.

3.4.2 Release agent

One of the preliminary steps of VARTM is the application of mold release wax to the mold surface before placing the fabric. A coat of wax was applied to the mold surface, set to dry and the wiped off with a clean cloth or paper towel. Three simultaneous coats of wax were applied using a paint brush to ensure good finish to the mold and making it so smooth that the impregnated preform would not stick to it once it cures and it could be taken off easily. One coat of poly vinyl alcohol (PVA) release film was applied over the tooling surface after the drying of the three coats of wax. The PVA release film gives a green tinge and a clear boundary for the areas applied with wax. A clear boundary free from wax is important because the sealant tape applied over the mold, does not stick well on the areas of the mold with a wax coating. Hence the PVA release film serves as a marker to indicate the areas for application of the adhesive sealant tape.

There are many commercial mold release agents like PTFE Mold release agent for VARTM applications. These release agents are just as effective as a combination of wax and PVA release film but are more expensive. These are not suited for scaled up VARTM process to make large composite structures as they may end up increasing cost.

3.4.3 Reinforcing Fabric - Carpet

Reinforcing fibers are the backbone of any composite material. In this study Nylon, cut loop type of carpet of the commercial name ESSENTL TWTGO, color Sandstone by Shaw Industries was chosen.

These carpets of size 3.66 m x 1.22 m (12 ft. x 4 ft.) were bought from M/s Georgia Carpet Industries Inc., Atlanta, Georgia, and then pieces of sizes 0.15 m x 0.15 m (0.5 ft. x 0.5 ft.), 0.15 m x 0.24 m (0.5 ft. x 0.8 ft.), 0.24 m x 0.24 m (0.8 ft. x 0.8 ft.), 0.30 m x 0.30 m (1 ft. x 1 ft.), 0.61 m x 0.61 m (2 ft. x 2 ft.) and 1.22 m x 0.61 m (4 ft. x 2 ft.) were cut in the sample preparation process for fabrication of composites.

The carpet was laid up in three different configurations - TBBT, BTTB and TBBTTBBT (4 layer carpet).
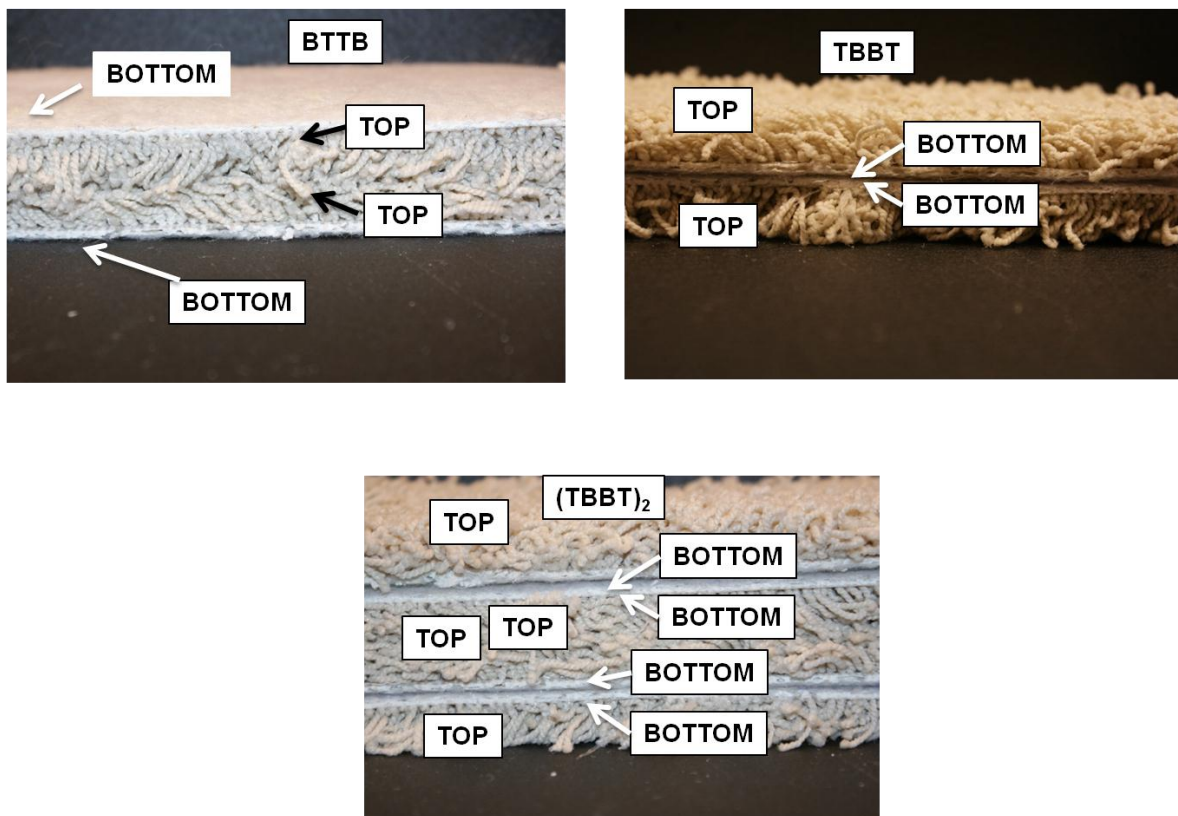
Fig. 3.4 Images of carpet configurations used for VARTM

The sole purpose of the use of thermoset resin is to impregnate the carpet layers and act as a matrix for the resulting carpet composite. The characteristics of the resin which directly affect the VARTM process are viscosity, gel time and the type of resin. Less viscous resins might infuse quickly, resulting in deformed parts. This deformation is due to uneven wetting of the fabric making some portions resin rich and others full of voids with dry - spots, while faster curing resins, with high viscosity gel too quickly and cannot sometimes impregnate the entire part [53].

In this study, the resin systems used were vinyl ester, polyester and epoxy resins. Even though vinyl ester and polyester resins are available cheaply in the market, styrene emissions is a problem, causing shrinkage in the parts resulting in stresses between the layers [53]. There were attempts to do VARTM with epoxidized soybean oil (ESO) but it proved to be unsuccessful because it could not crosslink. A detailed explanation of failures encountered in the use of ESO for VARTM has been explained in the Appendix.

In this study, the resins - Epoxy 2000 (hardener Epoxy Hardener 2120) and polyester and vinyl ester (with hardener: methyl-ethyl-ketone-peroxide) (MEKP) were procured from Fiberglast Corporation. The Epoxy 2000 resin was prepared by mixing with hardener with a weight ratio of 27/100. For example for every 1000 grams of epoxy resin, 270 grams of hardener was added and then stirred for effective cross linking. The pot life of the resin was 120 minutes due to the addition of Epoxy 2120 hardener used for mixing and therefore proved advantageous for larger samples. Polyester resin was prepared by adding hardener MEKP in the weight ratio of 1/100 while on the other hand for vinyl ester resin MEKP was added in the weight ratio of 1.25/100. Thus for every 1000 grams of polyester or for every 1000 grams of vinyl ester resin, 10 gm of MEKP and 12.5 grams of MEKP are added respectively. Since the curing temperature of both polyester and vinyl ester resins takes place at room temperature itself, the pot life for

these resins is as low as 20 minutes. A curing period of 24 hours was maintained to ensure complete curing for all resin types.

3.4.5 Measuring balance

A Mettler Toledo weigh balance was used to measure the accurate amount of resin and accurate amount of hardener mixture before infusion. The weigh balance needs to be accurate as improper ratios can cause uneven curing, change the properties of resin flow inside the preform and cause gel times to change [53]. A balance with an error range of 0.01 gm was used because the proportion of hardener to the resin should match exactly the manufacturer specifications.

During one of the experiments the amount of epoxy hardener to be added exceeded the specified amount, this lead to change of the color of the resin in the bucket from light pale brown to dark brown almost instantaneously. The bucket turned hot and dark fumes were emitted. Finally the bucket melted due to the heat produced by the resin therefore leaking the excess resin and causing a spill. In another incident MEKP added to vinyl ester resin was lesser in comparison to the specified amount; this lead to an uncatalyzed vinyl ester resin which did not get cross-linked and therefore remained uncured after the VARTM process. Since the cross-linking of resin is a highly exothermic process it is recommended to operate with great safety by measuring the appropriate amount of resin and hardener used; in turn using an accurate balance.

3.4.6 Resin Distribution media

The resin distribution media is used to accentuate the distribution of resin from the inlet piping to the preform and makes the resin moves faster due to the pressure gradient created. The resin resin distribution media used was "Greenflow 75" bought from Airtech International Inc. The resin resin distribution media efficiently distributes resin with little waste due to its low profile and tight construction.
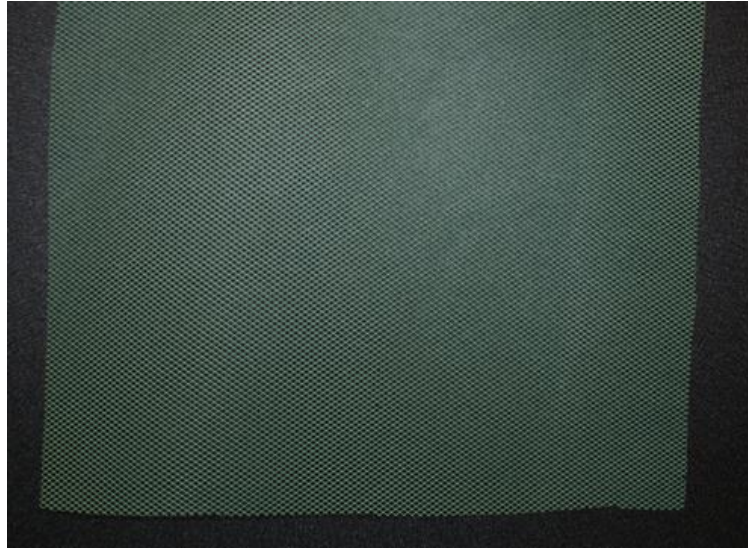
Fig. 3.5 An image of the resin resin distribution media used in fabrication process

Generally, the resin distribution media is placed from the inlet piping end to the outlet, without touching the outlet helix tubing. Generally, the gap between the outlet helix tubing and the resin distribution media is 31.75 mm (1.25 in) [53]. However in the scale-up of VARTM process, the resin resin distribution media covers the entire area including the outlet tubing. This would create micro voids in the composite panels fabricated. This is because there is always a possibility that some air gets trapped in the helix tubing and addition of the resin resin distribution media over the outlet tubing would aggravate the problem by actually trapping air in the micro - gradients created.

One of the main aims for scale-up of VARTM is to produce composites with excellent acoustic properties. Creation of micro-voids ensures that there is an increase in porosity which in turn results in improvement of acoustic performance of composites. Chapter 5 deals with acoustic characterization and the influence of porosity on the acoustic properties in detail.

3.4.7 Release film

The release film is cut according to the size of the sample and is placed on the top of the preform fabric. The pores in the release film contribute to bleeding of excess resin. The release

film used was the Wrightlon 5200B P - 3 bought from Airtech International Inc. This standard release film can withstand VARTM operations up to a temperature of 260 $^{\circ}$C (500 $^{\circ}$F). Even though release film is optional, it is a recommended part of scale-up of VARTM because it provides excellent release from all resin systems and allows for bleeding and breathing of resin.

3.4.8 Peel ply

The peel ply is a cloth like material that allows resin to flow through it but it does not let resin to stick to it. It also prevents the resin distribution media from sticking to the preform. The peel ply used in this study is Econo Ply J, bought from Airtech International Inc., a tight weave, finely - knit polyester which does not allow resin to adhere. The other important function of using a polyester peel ply is to avoid sanding or abrading the surface preparation for painting or bonding. Surface preparation of molds is a preliminary step in traditional VARTM process; however this can be replaced by using peel plies.

3.4.9 Breather Cloth

A lightweight breather cloth removes volatiles and allows breathing inside the vacuum bag. It is critical to have breather cloth inside the vacuum bag as it would help in maintaining efficient air – control, which is a necessary feature for scaled up VARTM as it is a target achieve good quality VARTM composites with micro voids. The breather cloth is placed above the resin resin distribution media and below the release film. This helps in keeping the vacuum bag away from resin thereby making it reusable.

3.4.10 Vacuum bag

The vacuum bag is made up of polyester, polyethylene or nylon material that does not allow the resin to stick to it or pass through it. The vacuum bag is easily one of the most vital components of VARTM because it covers all the components like fabric, peel ply, resin distribution media and inlet and outlet helix tubing. It withstands the negative pressure and contains resin in the set-up. There are different types of vacuum bags: non-stretch vacuum bags and flexible vacuum bags. There are some re-usable vacuum bags made of silicone, but they are

expensive. Of all the vacuum bags used, the non stretchable vacuum bag made of nylon was the best. Nylon film is preferred over polyethylene because polyethylene bags are recommended for smaller molds and also because Nylon bags can be used for higher temperatures..

3.4.11   Sealant Tape

This tape is used for the vacuum bag to stick to the mold; sticking the vacuum bag to the glass or mold. The primary use of the sealant tape is to seal the inlet and outlet joints. Sealant tapes are sold in various grades with respect to their use at different temperatures and are commonly referred as "tacky tape." Tack sprays can also be used instead of sealant tapes but it is difficult to have a good spray control for different shapes of composites. Also, the tack sprays give up their tackiness over a period of time.

Tacky tape does not stick on the surfaces coated with wax and hence care should be taken to avoid those areas as they might contain more leaks and spoil the entire setup.

3.4.12   Inlet and Outlet Piping

The inlet pipe is used to draw resin into the VARTM set up while the outlet pipe draws excess resin into resin trap and connects the resin trap to the vacuum pump. The inlet and outlet pipes used are generally PVC pipes that can hold 1 atm of vacuum pressure. However by experience it was learnt that less sturdy pipes which hold 1 atm of vacuum pressure are better than the sturdier vacuum pipes because they are easier to clamp and the escape of resin/air after clamping is low. The inlet and outlet PVC pipes of 1.27 cm I.D. (0.5 inch) were bought from Fiberglast Inc. and were cut according to the arrangement of the setup. Generally the inlet pipe is short to aid in quicker flow of resin into the setup while the outer pipe was a bit longer by 7 to 10 cms (around 3 to 4 inches) to allow better arrangement of the setup.

3.4.13   Helix tubing

The helix tubing is a spiral tube which is used on both inlet and outlet pipes for effective distribution of resin. The flow of resin being perpendicular to the helical tube gives maximum

resin distribution. Spiral tubing was bought from Fiberglast to fix them on the 0.5 inch pipes, the internal diameter of the tubing is critical because it needs to correctly fit on the inlet and outlet pipes. Omega tube is a variant of feed line-like helix tubing and serves the same purpose as helix tubing. Experience in VARTM found that there is little difference in performance between the omega tube and helical tubes.

The helix tubing may appear simple but it has many important characteristics -

- It is connected to the laminate but it is critical that the line does not get pressed into the laminate by the vacuum pressure.

- It is cut large enough and placed accordingly on the glass plate to transport the resin quickly to generate an even flow front across its length.

- It has grooves which allow an even outflow over its entire length.

- It does not collapse under vacuum pressure.

- It is critical that the outlet line helix tubing, part of the vacuum line should never touch the laminate because it leads to extraction of resin out of the laminate.

3.4.14   Clamping vice

Flat end clamping vices are used to clamp the inlet piping before the infusion to prevent air from entering the VARTM setup. Hence it is necessary that the vices used should be flat end and not the sharp end vices because they sharp ends might damage the clamped pipes. C-Clamps can also be used, provided if they have easy latch release system. The ease in latch release system is beneficial during the VARTM process because it would be easy for the composite technician to latch and un-latch the clamp whenever needed without letting it in any air into the setup.

3.4.15   Cutting tools

The cutting tools generally include scissors, dremel and a band saw. Scissors were used to cut the carpet, breather cloth, vacuum bag, release film, peel ply and the resin resin distribution media. However scissors become blunt if they are used excessively for cutting carpets. Special

carpet cutters do the job cutting carpets well with better cutting power. Thus it is necessary to use a carpet cutter to cut carpet layers. Also, the carpet layers used, can cut the carpet backing more easily and efficiently in such a way that it does not shear the Nylon fibers without the mess caused by a scissors. A Dremel and a band saw were used for cutting the resulting carpet composite and giving it a good finish. It was found that the carpet composite samples should not be cut immediately after curing, as it might still be uncured and might spoil the band saw if used at such a state.

3.4.16   Caul Plate

The caul plate is a hard or semi-flexible plate which is placed underneath a vacuum or silicone bag. The caul plate is used to change the surface of the part underneath the bag by creating a distinct profile that eliminates or reduces the need for finish work after demolding. Another use of caul plate is to define the geometry of a section; this feature was useful while making a curved shape composite panel by using an arch shaped caul plate underneath the vacuum bag. The caul plate in this study is a 0.2 inch thick aluminum plate with dimensions altered with respect to the size of the laminate desired. An aluminum caul plate helped in the process with an indirect application of a hot press. The aluminum caul plate stored energy generated by the exothermic curing of the composites for a long time. This resulted in giving a good finish to the resulting composites – almost as good as the finish obtained from hot press. Hence the use of caul plate helped in avoiding the use of hot press and is an important part of the scaling up of VARTM process.

3.5 EQUIPMENTS

The equipments used for the scaling up of VARTM have been detailed in this section.

3.5.1   Resin Trap

The resin trap is used with a sole intention of protecting the vacuum pump from the extra resin bleeding out of the sample. The resin trap is sealed so that there is no vacuum pressure lost. In this study, Fiberglast 1500 - A model of resin trap was used. This resin trap setup consists of a 9.46 liter (2.5 gallon) stainless steel tank mounted with a gauge (which measures the vacuum pressure and indicates the loss of pressure should there be a leak in the vacuum bag). Also, the resin trap acts like a vacuum reservoir which means that even if the pump is turned off the trap will not let the maintained vacuum pressure to be lost.

3.5.2 Vacuum Pump

The vacuum pump is the main driving force of the entire vacuum set up because it pulls the vacuum. The pump maintains a pressure of about 1atm under the vacuum bag. Generally pumps which maintain a pressure of 25 inch Hg pressure are considered to be good vacuum pumps. The minimum acceptable level of vacuum is 18 inch Hg.

The Becker VT 4.8 vacuum pump used in this study has a pressure range of 25.5 inch Hg, 0.56 Hp, 5.6 CFM rotary vane pump. This industrial single phase pump is ideal for applications like VARTM where the discharge is free of oil.

There is a common misperception that the Horse power of a pump is the real rating of the pump, but rather it is the flow capacity (stated as CFM – cubic feet per minute) that is used for rating of pumps. The rating of pump was investigated to address the problem if fabrication of larger samples in scaled up VARTM would need pumps with higher horse power or multiple pumps. It was found that there is no direct relation between horse power (Hp) of the pump and its VARTM capability, although a pump with higher Hp will have good CFM. So basically, a pump

with higher CFM will remove air from the vacuum bag more quickly for large size VARTM samples. Any pump with a CFM more than 3 CFM can be used for VARTM of 4 feet x 8 feet samples.

3.5.3 Ultrasonic Leak Detector

The vacuum pump makes a lot of noise during the VARTM process and therefore it is difficult to hear the leakages in the set-up. This problem is encountered even if a stethoscope is used. An ultra sonic leak detector helps in such cases to check leakages in the VARTM set up. The turbulence created by air or gas, forced through a small orifice, generates ultrasonic sound which gets located by the ultra sonic leak detector.

It should be noted that in this study, even though there is potential interest for creation of micro voids in the composite panels due to scale up VARTM there should not be any air leaks in the set up as these may result in defective samples with larger voids or macro-voidsin the composite. These macro voids would amount to reduction in mechanical properties like flexural strength of the samples significantly and hence these leaks should be arrested even before the infusion of resin begins.

3.6 SCALING UP OF VARTM PROCESS

The following section discusses in detail the changes made in order to achieve scale up of VARTM process.

3.6.1 Vacuum Degassing

Mixing of the resin and hardener cause air bubbles while mixing which get trapped in the resin. These air bubbles are the main reason for formation of micro - voids because these air bubbles stay in the resin, even after catalysis of resin and travel through the fabric during infusion and contribute to an increase in void volume fraction.
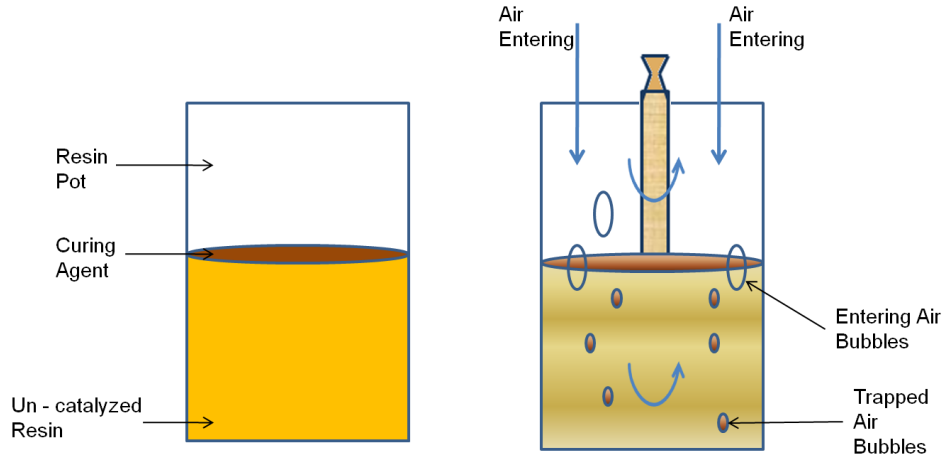
Fig. 3.6 An illustration to show formation of air bubbles due to mixing

Vacuum degassing set-up can address the arrest of these pre existing air bubbles in the resin pot after mixing of resin and hardener. The vacuum degassing set - up consists of a vacuum chamber in which the pre - mixed resin pot is placed. Vacuum is drawn into the chamber and therefore the air bubbles rise up to the top of the resin pot and get collected there. After a while there is reduction in the air bubbles. Literature suggests that the process of vacuum degassing creates micro bubbles which are not seen by naked eye and there is always scope for improvement in degassing, such as addition of nucleation agent [54-56].

However in this study, for scaled up VARTM process, it was intended to retain (or rather incorporate, if possible) micro - voids in the resultant composite. This is because of the unique research objective in the study to develop carpet composites with better acoustic properties. Literature suggests that in energy absorption testing, composite made out of higher void content out-performed a composite made of the same materials and a void content of less than 1% [57]. This indicates that the design of the composite structure should be made keeping in mind the product application intended for the composite. In this study, it was advantageous to have composite samples with higher void content for their use as highway noise barriers in terms of their superior acoustic characteristics. However, one of the recommendations for this study is to study the impact of these voids on the strength of the composite.

3.6.2   Resin Flow

The flow of resin in the laid up carpet layers played an important role in the final part configuration and properties. This was inferred with the observation of infusing un-catalyzed resin in the carpet which retained uncured properties post infusion. The fiber orientation, type and the thickness of the preform has a significant impact on the flow of the resin. Addition of distribution media creates a fairly complex 3-D flow where there is a significant flow gradient through-the-thickness of the reinforcement [47]. To understand the pattern of resin flow through the preform involves a thorough understanding of process physics of the capillary action of wetting fibers, the dynamic pressure gradients and the permeability of preform.

As discussed earlier, the 3-D architecture of different types of carpet (as illustrated in Fig. 2.3 to Fig. 2.6 in chapter 2) will have an impact on the resin flow, the capillary action of the resin flow and also the type of void formed due to the complexity of its construction. The resin flows around the fibers and not into it, therefore just partially wetting the fibers. The formation of micro-voids in the resultant composite is acceptable in this study because it helps in the porosity formation of the composite samples.

Another experiment included placing resin distribution media on both sides of the carpet that is above the top most layers and also on the bottom layer. In both these cases a peel ply was placed between the resin flow media and the carpet. The result observed was that even though the infusion occurred quickly, the surface finish was poor on both sides of the sample. Also the wetting of the fiber by resin was low. Literature suggests that use of resin distribution media has a higher chance of creation of micro-voids because the air bubbles in the resin retrace back into the fiber on encountering the overlapping distribution media at the outlet [53]. On the other hand, peel ply allows the vacuum bag to take its shape and acts like a natural throttle because it does not let the air bubbles trapped in it to retrace back [53]. However in case of our study there is a need

for improved porosity due to micro voids and hence the set up included deliberately placing the resin distribution media over the outlet pipe and helix tubing. This probably made the air bubbles retrace back into the sample and could have increased the thickness of the sample. Moreover the resin distribution media was useful for fabrication of large scale composites. During the infusion of resin with the resin distribution media, the resin flows preferentially across the surface and simultaneously through the preform thickness, thereby enabling large parts to be fabricated [44, 46, 47].

Race-tracking is a problem that occurs in VARTM when the resin races around the edges of the mold and leaves large voids of dry fibers in the center of the mold [58]. The resin follows the path of least resistance, which is the edge of the mold where the fibers are not very tightly packed [59]. This causes dry spots to develop in the middle of the mold where the resin raced around the mold edge to the exhaust port making an unusable final product with dry spots [58]. The strength and existence of race-tracking is a function of operator skill, variability in preform architecture (different 3-D architectures of carpet), and the placement of preform in the mold [60]. Many approaches have been addressed to solve the problem of race-tracking, but it changes from part to another in size and extent and is not repeatable [61]. Most of the approaches in solving the problem involved use of process models and simulations [59, 61, 62] . In this study, this problem was faced in a few experiments involving large scale panels of rectangular shapes.

3.6.3 Large and Complex structures

In the conventional VARTM setup for fabrication of large scale composites, there is structural instability in the final part for composites of the size dimensions 1.22 m x 0.61 m (4 ft. x 2 ft.) and greater sizes. This is because the vacuum bag side is not smooth, which leads to structural instability due to thickness variation throughout the part [53]. Therefore it is quite often a problem to fabricate large scale composite by the conventional VARTM process. This problem

could also occur due to inability of the vacuum end in achieving greater compaction of stacked up carpet layers.

This problem was arrested in the scaled up VARTM process where the use of caul plate would ensure smoothness of surface on the vacuum bag side and thereby possibly minimizes the thickness variation throughout the part. Hence it was observed that it is advantageous to use scaled up VARTM process for fabrication of large scale composite panels.

For instance multiple inlet ports can be used for fabrication of large scale composites of the order of size 0.61 m x 1.22 m (2 ft. x 4 ft.) and greater sizes. This has been shown in the following Fig. 3.8 where multiple inlet ports were used for fabrication of large composites because the resin covers a larger area quickly.
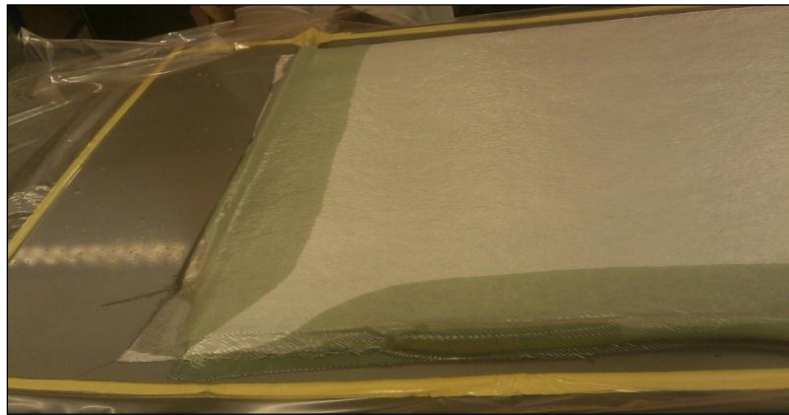
Fig. 3.7 A picture of VARTM process using multiple resin inlet ports

It was envisaged to demonstrate the feasibility of fabrication of complex structures using scaled up VARTM process. Therefore fabrication of complex shapes like arch was planned as an experiment. The mold prepared for this sample was an empty round shaped canister with an external flat base. One of the caul plates was stuck to the canister to form an arch shaped base of the mold. Carpet layers were stacked in the BTTB configuration. The scaled up VARTM process was rigorously followed and the mold was sealed with a vacuum bag on the top and a caul plate below the bag. Essentially there are two caul plates - in the top of the mold to give a shape to the

resulting composite and in the bottom of the mold for aiding in providing an arch shaped base for mold. The BTTB carpet layer configuration was placed between the caul plates after waxing and the standard procedure for fabrication of carpet composites by scaled up VARTM process was followed. During the resin infusion it was observed that the flow of resin is only because of the vacuum inside the bag and was not influenced by other forces like gravity. Post-infusion, a curved shape composite was observed as shown in Fig. 3.9 with an arch with inside diameter of 18 cm.
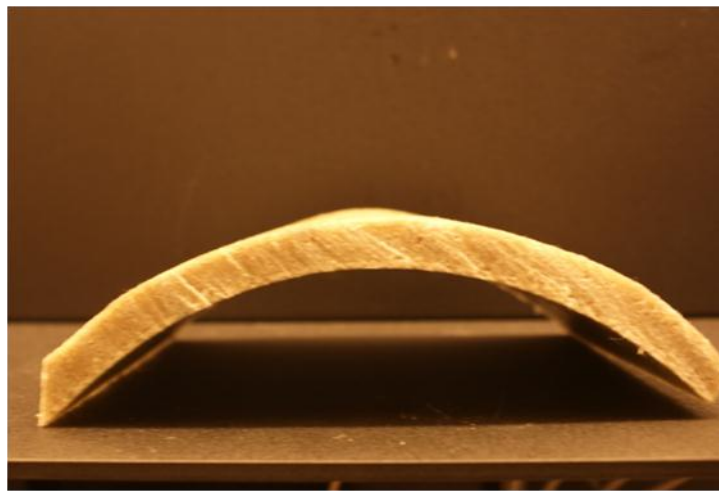
Fig. 3.9 Image of a curve shaped composite fabricated by scaled up VARTM process

3.7 COST ECONOMICS

A preliminary cost model has been developed by monitoring the VARTM process which has been regarded as a cost effective manufacturing method. VARTM provides significant savings in tooling cost because it requires only a one - piece mold and a vacuum bag is required to close the mold [63]. The total manufacturing cost (TC) consists of material cost (MC), direct labor cost (LC), equipment cost (EC) and the overhead cost (OC) as shown in the following equation 3.2.

$$TC = MC + LC + EC + OC \qquad (3.2)$$

Material cost is the major factor in the total manufacturing cost for this particular operation, mainly because the resin system and its curing agents used are expensive. The cost of resin required to fabricate a 0.0935 m^2 (1 ft. x 1 ft. panel) is around USD 11. This cost also involves the cost of the curing agent. There could be a maximum wastage of USD 3 of resin for this size of panel and the cost of curing agent therefore the total materials cost (MC) could be equal to USD 14 as per the current manufacturing practice of scaled-up VARTM process. However the cost of wastage could be optimized and therefore it the Total approximate cost of carpet composites prepared by the current manufacturing method could be USD 12.1.
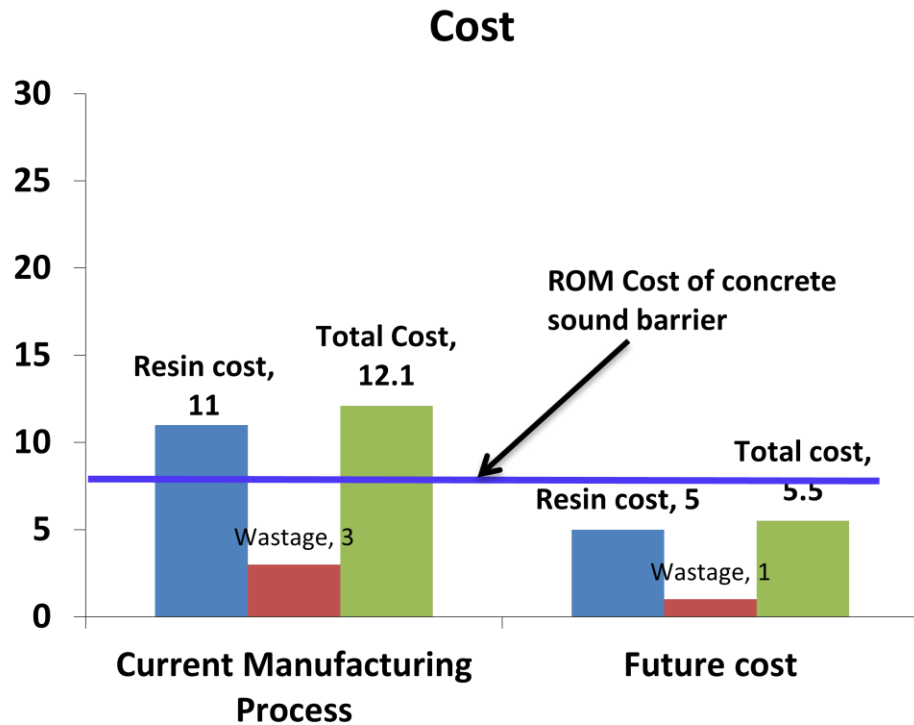
Fig. 3.10 Preliminary cost model

The future material cost could be low because of a regular bulk use of resin. The future cost is estimated to be around USD 5.5 for a carpet composite panel of the size 0.0935 m^2. The costs have been estimated on the basis of the material cost data obtained from the material supplier Fiberglast Inc., based in Ohio United States.

However it can be seen that the cost of concrete is low, about USD 7 for a 0.0935 m^2 sample because concrete is a cheap material. However the cost associated with concrete is mainly the cost of labor and its transportation. The cost of USD 7 for a concrete panel is a rough order of magnitude cost for the concrete panel of size 0.0935 m^2.

The cost analysis in this study has been non-conclusive and therefore it a judgement cannot be made on the basis of the data presented above. The material cost data suggested in this section is preliminary in nature and has been developed on the basis of lab scale experience. It is an attempt to give a precursor to the detailed cost estimation recommended for this study. A rough understanding of labor involved could be made due to experience in fabrication of composites in this study. VARTM method of manufacturing could be cheap but it is highly labor intensive. The primary labor cost would be the labor involved for 1 worker with 100 % presence for making a carpet composite panel of size 0.3045 m x 0.3045 m (0.0935 m^2). However as the size of the panel increases to 0.371 m^2 (0.609 m x 0.609 m) there will be a need for the presence of another worker at a 50 % presence factor. This understanding of the requirement of labor at various presence factors was developed during the fabrication of the carpet composites of different sizes in the laboratory.

The following table, Table 3.1 enlists the time taken for various process steps in the scaled up VARTM process for fabrication of carpet composites for a square panel with an area of 0.0935 m^2 (0.3045 m x 0.3045 m).

TABLE 3.1

A TABLE INDICATING TIME TAKEN FOR FABRICATION OF CARPET

COMPOSITES USING SCALED UP VARTM PROCESS

Sr. No.	Process Steps	Time (min.)
1	Mold Preparation	15 min
2	Cut materials (Carpet, Vacuum bag, breather cloth, resin resin distribution media, peel ply, release film and visually inspect each of these sheets)	45 min
3	Installation (stacking the carpet layers and adding clay films on its top), connection of vacuum pump to resin trap, cut inlet and outlet helix tubes and connecting outlet pipes to the resin trap.	20 min
4	Seal the vacuum bag and vacuum the system	40 min
5	Resin Preparation	15 min
6	Resin injection	Depends on resin (Generally less than 10 min)
7	Resin Cure	420 min
8	Part removal after resin cure	15 min
9	Cleaning	20 min
10	Cutting and Machining of the composite	15 min

3.8 SUMMARY OF COMPOSITE FABRICATION

In this chapter, VARTM process for recycling carpets was scaled up to fabricate carpet composites of larger size. The scale up was achieved in the process with an attempt to improve the porosity of the composites without making sacrifices in the mechanical properties of the resulting composite. This was achieved by forming micro-voids in the composite. This is not commonly practiced in the traditional VARTM process. Also various material parameters of VARTM were studied and it was inferred to include these materials to aid in creation of micro voids. It is now understood that avoiding vacuum degassing and including resin flow aids help in creating micro-voids. The scale up of VARTM manufacturing process was achieved by incorporating effective techniques to fabricate composites of large scale, complex shapes and higher porosity in comparison to traditional VARTM process.

CHAPTER IV

NANOCOMPOSITE FILLER

4.1 OBJECTIVE

One of the objectives of this study was to find an effective way of incorporating nanoclay in carpet composites to improve the properties of the carpet composite. This was achieved by incorporating clay based nanocomposite films in carpet composites without changing the scaled up VARTM process. The reasons for incorporating clay based nanocomposite films in the carpet composite are to improve the following:

1) Flame-retardant properties of the carpet composites, and

2) Resistance to environmental degradation in carpet composites.

4.2 INCORPORATION OF NANO-CLAY

Nanocomposite fillers have received a lot of attention in scientific and the industrial arenas because of the important role they play in modifying properties like thermal stability, barrier properties, mechanical properties and flame resistance of the composite [64]. There are different ways of incorporating nano-clay in the carpet composite:

1) *Mixing of nano-clay based solution or nano-clay with the resin, before the infusion stage of VARTM*. The high viscosities of the resin and the strong tendency of clay nanoparticles to agglomerate create a need for shear mixing in this mixing process [65]. Shear mixing reduces the high aspect ratio of the clay platelets from 200 - 1000 to 90 - 120 because the

clay platelets break during mixing [65]. The other problem in this approach is that the mixing can change the viscosity of the resin and alter the cross-linking parameters of the resin due to addition of foreign material like clay, accelerators and diluents.

2) *Wetting the fibers or painting the carpet with the clay based solution can also be used for incorporation of nano-clay.* In this technique there is a danger of losing the clay alongwith the extra resin bled in the resin trap. Also to wait for the carpet to dry after painting would increase process time and cost.

Hence to avoid these problems an attempt was made to use a novel film based approach to incorporate clay in the carpet composites .

4.3 HYPOTHESIS

The hypothesis of using a film based approach for incorporation of nano-clay is to achieve high distribution of clay in the carpet composite for improving the flame retardant properties of carpet composites. Also it is logical to assume that a well exfoliated film would ensure excellent distribution of clay in the film, which in turn would ensure effective distribution of clay in the resulting carpet composite.

Exfoliation of clay is a phenomenon which indicates breaking of the layered structure of clay and separation of the clay layers in the film. The amount of clay present in the polymer matrix affects the properties of the polymer - clay nano-composites [66]. Literature suggests that exfoliated nano-clay in nanometer level having very large stiffness and high aspect ratio in a polymer matrix could lead to very high mechanical performances of the nano-composite [64, 67, 68]. Hence exfoliation of clay is critical in the film based technique to ensure higher presence of clay in the carpet composite.

The perusal of literature in the use of film based technique for incorporation of nanofiller in composites is little explored and hence the improvement in properties needs further

investigation. However there is enough literature available on the property improvement due to addition of nano-clay which thrusts their use as nano-filler additives in composites [64-71].

4.4 THEORY

Nanocomposites are materials that comprise a dispersion of nanometer size particle (lamellar, fibrillar, shell like, spherical) in a matrix. Shaw (2001) [69] found the following advantages of using polymer clay nanocomposites as filler material:

1) Superior mechanical characteristics like high tensile strength (around 40% increase)

2) Heat and chemical resistance

3) Excellent results achieved at low concentration of clay filler (in the range of 0.1 to 10 wt. %)

The synthetic route of choice for fabrication of nanocomposite depends on whether the final material is required in the form of an intercalated or exfoliated nanocomposite. The phenomenon of intercalation and exfoliation of clay has been illustrated in Fig. 4.1 below.
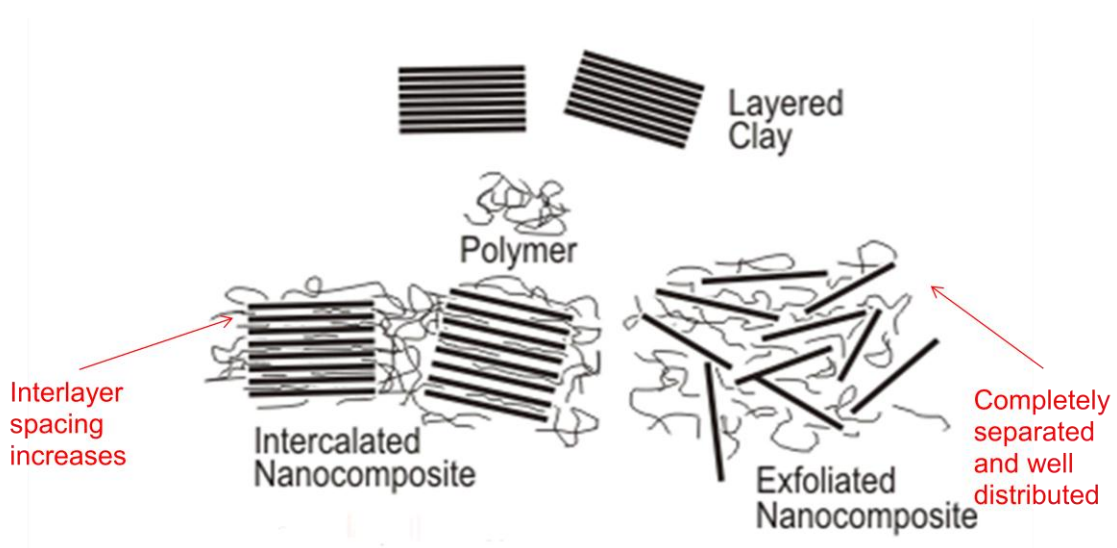
Fig. 4.1 Figure showing the formation of intercalated and exfoliated nanoclay [69]

In the case of an intercalate, the organic component is inserted between the layers of the clay such that the inter-layer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other. In an exfoliated structure, the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix. A third alternative is dispersion of complete clay particles (tactoids) within the polymer matrix, but this simply represents use of the clay as conventional filler. Many nanocomposite systems do not give the same degree of property enhancement like Polymer - clay nanocomposite and a low degree in property enhancement is also due to difficulty in achieving clay exfoliation [67]. In this study it was envisaged to prepare Polymer Clay nanocomposite films with complete exfoliation. The polymer chosen in this study was Polyvinyl-pyrrolidone (PVP) and the matrix was formed by dissolving it in ethanol solvent.

Nanocomposites are generally fabricated by three methods – Insitu Polymerization, Melt processing and Solution Induced Intercalation Method [70]. Insitu polymerization involves mixing clay layers with matrix with the help of a catalyst or initiator and thereby polymerizing to yield a good polymer nanocomposite. Fig. 4.2 below illustrating this commonly used fabrication method, in which a polymer precursor is inserted between the clay layers and then the clay layers are expanded and dispersed into the matrix by polymerization.

Clay layers ✚ Matrix ✚ Catalyst / Initiator $\xrightarrow{\text{Polymerization}}$ Nanocomposite with well dispersed clay
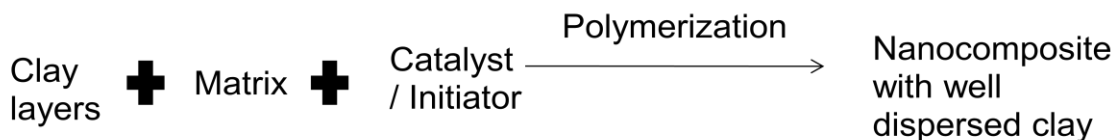
Fig. 4.2 An illustrative diagram to explain Insitu Polymerization fabrication method

The initial work in this area of Insitu polymerization was done byToyota research group to produce clay/nylon-6 nanocomposites. The drawback of Insitu polymerization is that it requires enough expertise in polymer science and understanding of compatibilization of materials

with respect to different temperature and pressures. Moreover the insitu polymerization would not be well suited for the objective of incorporating clay-films in composite.

The melt processing technique induces the intercalation of clay and polymers during the melting. The efficiency of intercalation using this method is not as high as insitu polymerization and often the composite produced contains a partially exfoliated layered structure [70]. However this technology has industrial importance because by melt processing, traditional polymer processing techniques like extrusion and injection molding can be used for making clay based nanocomposites.

Solution Induced Intercalation method is the most preferred method for polymer clay nanocomposites since it uses solvents to swell and disperse clays into a polymer solution. The following Fig. 4.3 illustrates the mechanism of this fabrication of PVP clay nanocomposites used in this research.
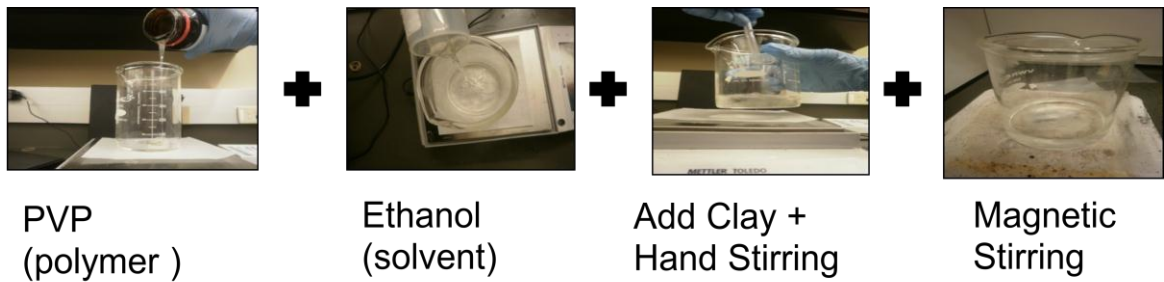
Fig. 4.3 PVP Clay films made using Solution Induced Intercalation method

Solution induced intercalation is applicable to water soluble polymers because of the low cost for using solvents for immediate dissolution and its low health and safety risks and its use in the production of nanocomposites [70].

4.5 SAMPLE PREPARATION

In this study 10 % of pure PVP K-60 of molecular weight 160 kDa (obtained from Sigma Aldrich Co.) was mixed with reagent ethanol (obtained from VWR Inc.) by hand stirring for 15

mins and later stirring on a magnetic stirrer for 45 mins. Organically modified montmorillonite clay, OMMT was used as organic filler in this study. Polymer to clay ratio of various combinations was later on used to determine the amount of clay to be added in the range - 0, 3,5, 10 and 30 wt. % were tested. The polymer solution was stirred in a magnetic stirrer for 2 h. Sonication can also be used instead of magnetic stirring, however, sonication made the films brittle after the evaporation of solvent. The film solution was poured into a boundary of about 0.12 m x 0.12 m made by tacky tape on a clean glass plate and left for drying for 24 h in fume-hood. The solid films were later dried at 90 ^{0}C for 8 h under vacuum and stored in a dessicator until used. Fig. 4.4 illustrates the materials used in fabrication of PVP Clay nanocomposite films [3].
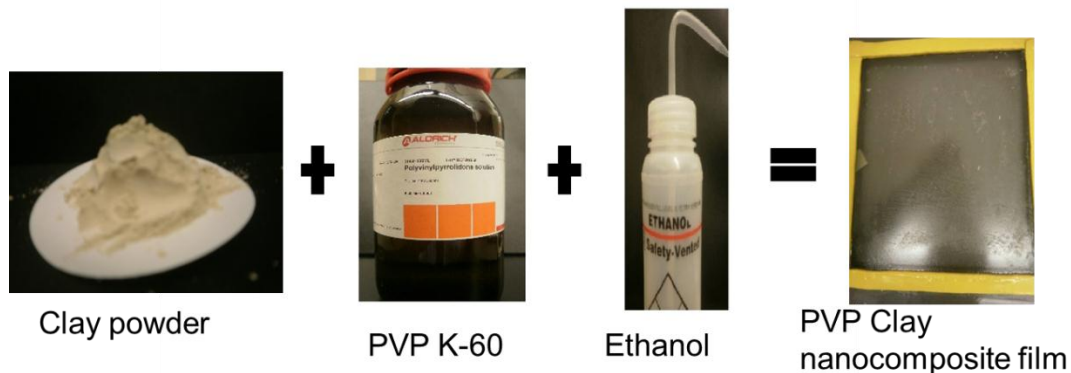
Fig. 4.4 An illustration of materials involved in the fabrication of PVP Clay films

Generally the properties for polymer clay nanocomposites depend on the following:

(a) *Type of clay and surface modification of clay -*

In this study, Nanomer I.28 E grade of Nanoclay, made by Nanocor Inc, was purchased from Sigma Aldrich Co. for its use in this study. This OMMT Clay is montmorillonite clay with its surface modified with 25-30 wt. % trimethyl stearyl ammonium. OMMT clay fillers are different from other commonly used clay minerals like talc and mica because OMMT clay has a

high surface area (>750 m^2/g) and a large aspect ratio (100-500) when delaminated or exfoliated completely [71]. This shows that it is highly advantageous to use OMMT clay as nanofiller.

   (b)   Selection of polymer (like PVP in this study)

   PVP is a water soluble polymer which mixes well and forms a polymer matrix on mixing with water or organic solvents. In this study reagent grade ethanol was used for dissolution of PVP in ethanol because ethanol vaporizes at room temperature. PVP is an amphiphilic (water loving and fat loving at the same time), nonionic polymer which adsorbs onto a broad range of different materials such as metals (like gold, silver, iron), metal oxides (like kaolinite, alumina), polystyrene, graphite, cellulose and silica [72]. Considering this advantage of ease in mixing of PVP by solution blending and the high adsorption characteristics of PVP made it as the choice of matrix for nanocomposite. The chemical structure of PVP is as shown in Fig. 4.5 below.
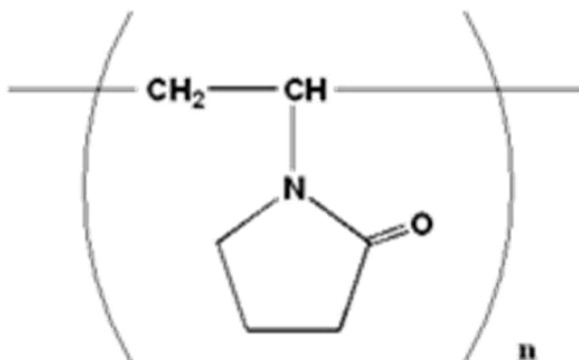
Fig. 4.5 An adapted image of the chemical structure of PVP [73]

   The ultimate aim of fabrication of nanocomposite films is for separation and dispersion of individual clay layers in a polymer. The strategy of fabrication of the nanocomposites depends upon the compatibility of clay and polymers. For clays which are not compatible with the polymer, it is necessary to have pretreatment of the clay and polymers before the intercalation. However the use of water soluble polymers like PVP and Poly-ethylene oxide (PEO) is an advantage because of excellent compatibility of clay layers with these polymers. This is because PVP and the clay silicate layers are hydrophilic. The dipolar or van der Waals forces between the

silicate layers result in easy absorption of hydrophilic molecules and aid in the ability to expand perpendicular to the layers [70]. Hence PVP was decided as a good choice for fabrication of nanocomposite films.

(c) The type of blending

Mechanical properties of the resulting nanocomposite film are strongly influenced by the thermo-mechanical agitation techniques employed in fabricating them. There are two types of mixing which are commonly employed in the fabrication of nanocomposite -

(1)   Distributed mixing - This method involves mixing by hand stirring and magnetic stirring. In comparison to dispersive mixing it was found that this type of mixing gave good exfoliation of clay in the film due to high degree of mixing.

(2)   Dispersive mixing - This involves mixing with the help of sonication after magnetic stirring. Sonication is a process of using ultrasonic waves for breaking the layered structure of molecules to aid in mixing. Even though it results in an ideal dispersion of clay in the film solution, it was seen that it made the film sample very weak. This problem can be solved with an understanding of an optimum amount of sonication needed for the samples.

In this study, dispersive method was used to achieve higher tensile strength and high modulus of the film to indicate good exfoliation of clay in the film.

4.6 RESEARCH FOCUS

Literature suggests that exfoliation of nanoclays in the nanocomposite film leads to enhancement of storage modulus [71]. Jeon et al. (2003) state the need for measuring storage modulus of nanoclay by stating that, "exfoliation of nanoclay sheets cause formation of physical connectivity or has a percolated network of nanoclay sheets at very small clay volume fractions because of their large aspect ratios ($\alpha > \sim 100$) and high surface areas (>750 m^2/g)." Yasmin et al.

suggest that the clay particles have an aspect ratio in the range of 200 to 1000 and the clay particles play a key role in confinement of polymer chain mobility under stress.

In this study the focus is on the incorporation of nanoclay into the carpet composites using the film based approach. The improvement in advanced mechanical properties of nanocomposite films is desirable but it is certainly not the primary goal of this study. Literature suggests that there will be a definite improvement in mechanical properties due to addition of nanoclay. But in this study the focus is on the well distributed presence of clay layers due to exfoliation in the nanocomposite film which would in turn lead to improved presence of clay in carpet composites. Hence the characterization of the nanocomposite films has been restricted to evaluating the degree of exfoliation of clay in nanocomposite films.

4.7 FILM CHARACTERIZATION

Characterization of polymers is carried out to analyze the performance of materials due to its properties such as strength, toughness, stiffness, thermal stability. In this study X-ray diffraction studies were carried out on the nanocomposite films and the clay nanofiller. The ultimate aim of the XRD characterization tests was to identify the nanocomposite film with the correct amount of clay which would exhibit properties of exfoliation.

4.7.1 XRD Test

X-ray Diffraction technique (XRD) is a technique capable of providing information about changes at molecular level. XRD tests were used in this study to investigate the structure of clay formed in the final composite was conducted on a CuKα source (λ = 1.5418 Å), an X-Ray generator of Bruker Discover operated at 40 kV and 40 mA.

In an XRD test, the change in the molecular orientation of the polymer solution or crystals can be tracked measuring the orientation order parameter in terms of "θ," which is defined as the angle between the molecular axis and specimen axis [74]. For this study, in the

XRD tests conducted, the powder samples were pressed on a glass holder and exposed to a wide angle X-ray beam. If an incident X-ray beam encounters a crystal lattice, general scattering occurs, which later gets eliminated on interference with itself [75]. This is known as destructive interference. Diffraction occurs when the scattering in a certain direction is in phase with scattered rays from other atomic planes, due to which, the reflections combine to form new enhanced wave fronts [75]. These wave fronts mutually reinforce each other and this phenomenon is known as constructive interference [75]. Because each crystalline material has a characteristic atomic structure it will diffract X - rays in a unique characteristic pattern [75]. OMMT Clay powder is crystalline by nature and hence it can be safely predicted that it would exhibit sharp peaks in the XRD test.

In this study, three film samples were characterized by XRD - PVP (0% Clay), PVP Clay 3% and PVP Clay 30%. In case of film samples, the in-plane structure can be inferred by using the azimuthal scan at an azimuthal angle after adjusting both equatorial scan and meridional scan. The equatorial scan is obtained by aligning the fiber axis or film longitudinal direction with the diffractometer axis and scanning on the surface parallel to the axis. Equatorial scan is different from that of a Meridional scan taken over the surface perpendicular to axis as shown in Fig. 4.6 [74].

M: Meridional scan (X = 90⁰)
E: Equatorial scan (X = 0⁰)
A: Azimuthal scan
X: Azimuthal angle (Chi)
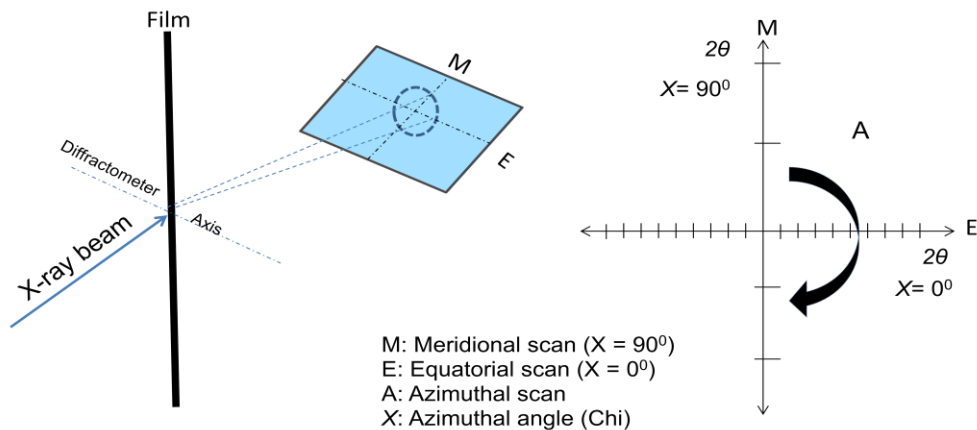
Fig. 4.6 Representation of meridional and equatorial scans for film sample [74]

The OMMT clay is a silicate with unit cell reactive sites due to the anions on silicate flat surface and hydroxyl (-OH) groups on edges. The clay has the chemical formula $M_x[Al_{4-x}Mg_x](Si_8)O_{20}(OH)_4]$, where M is a monovalent charge compensating cation Na^+ in the interlayer and x is the degree of isomorphous substitution (which means that elements are replaced in clay mineral without any alteration to clay crystals) [71]. Fig. 4.7 below shows the crystalline nature of OMMT clay.
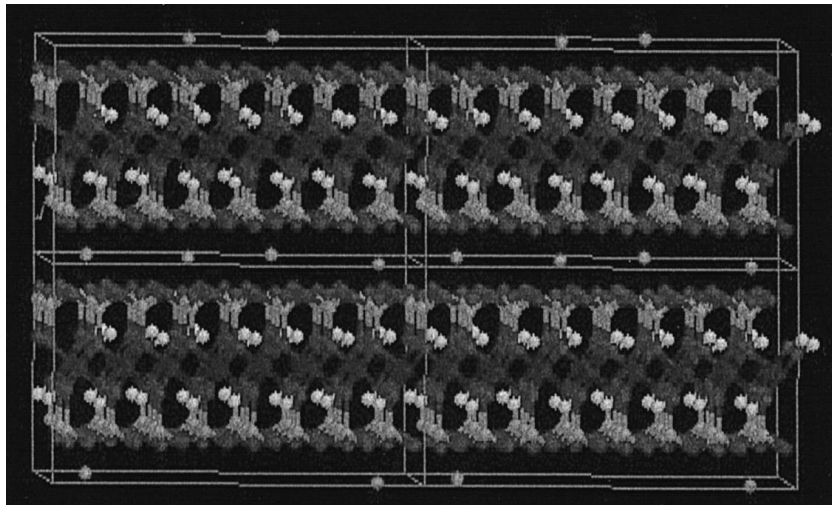
Fig. 4.7 An adapted figure of molecular representation of OMMT Clay, showing two aluminosilicate layers with the Na^+ cations in the interlayer gallery [76]

OMMT Clay is a metal silicate which tends to form small crystallites of lamellar structure made up of repeated sheets of two silica tetrahedral layers with an edge shared octahedral metal oxide layer [67]. Clay crystals have a constant interlayer distance which is determined by the type of counter ions present, for instance, smaller ions such as Na^+, K^+, or Li^+ lead to smaller interlayer distance and thus tightly spaced clay stack [67]. When this type of clay is added to the polymers, shear force is used to break the stacking of clay, and if the stacking order is completely lost, then the clay is identified as completely exfoliated [67].

OMMT clay is hydrophilic in nature and promotes dispersion of inorganic crystalline layers in water-soluble polymers such as poly(vinyl alcohol) and poly(ethylene oxide) [77]. Inspired from these studies this study focused on PVP/OMMT nanocomposite films.

Fig. 4.8 presents the diffractogram for the OMMT clay powder with some sharp peaks indicating the crystalline nature of nano-clay. As predicted earlier, the XRD results for clay in its powder form displayed results with sharp peaks. These sharp peaks are characteristic peaks of nano-clay [64].
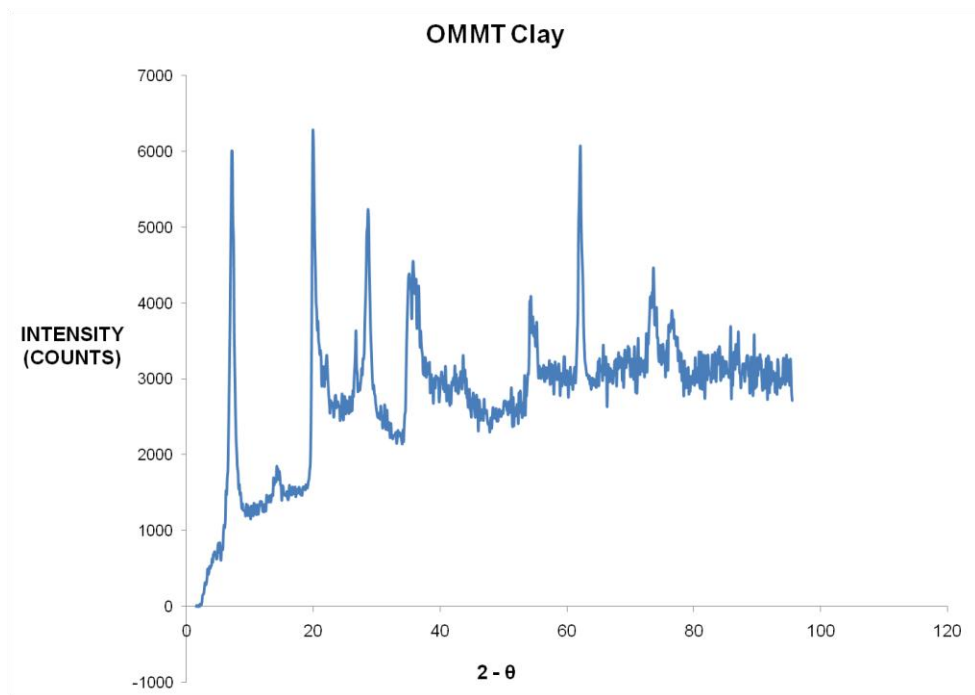
Fig. 4.8 OMMT Clay powder XRD results

In Fig. 4.9, the diffractogram indicates a few peaks which is a characteristic of a well dispersed PVP film (with 0% clay) in the organic solvent ethanol. The peaks indicate the characteristic amorphous nature of PVP because diffractograms of amorphous materials display a large hump created due to the scattering of X-rays [74]. The PVP was dispersed in ethanol by magnetic stirring and cast into a film which was characterized by XRD.
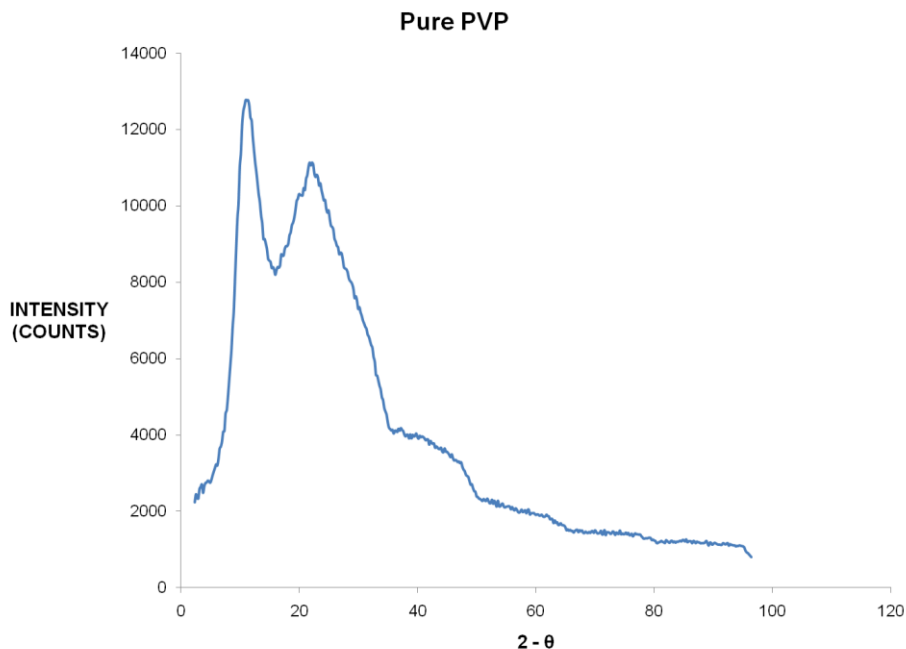
Pure PVP

Fig. 4.9 Pure PVP film XRD results

Addition of nanocomposite filler is expected to reduce the amorphous nature of the PVP polymer matrix. This would result in reduction of the area under the amorphous hump displayed by the characteristic PVP peaks. It is expected that there will be a significant reduction in the area under the hump made by amorphous PVP.

On addition of PVP to clay, a shift in the position of clay peaks would indicate an increase in the spacing between the layers of clay indicating intercalation. The disappearance of these peaks would suggest an exfoliated morphology [78]. In this study, the aim of achieving an exfoliated PVP clay film would mean a diffractogram without the characteristic peaks of clay [76, 78, 79].

This phenomenon of reduction of amorphous nature due to addition of nano-clay was observed in Fig. 4.10, which shows a diffractogram of PVP Clay 30 %. It can be clearly seen from the diffractogram that there is a significant reduction in the characteristic hump made by amorphous nature of PVP. This reduction of the hump in the peaks could be due to the influence of addition of clay to the polymer matrix [80]. It was also observed that there could be a case of

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characteristic clay peaks having a dominating presence in this film of PVP Clay 30 % due to agglomeration. By comparing Fig. 4.8 and Fig. 4.10, it was inferred that the intensity of clay peaks has lessened in the clay peaks present in the PVP Clay 30 % film but there might be a high presence of clay because of the high presence of clay peaks in the diffractogram.

The XRD peak analysis indicates that the presence of clay peaks maybe due to agglomeration of clay in the nanocomposite film and also because of the high levels of addition of clay. Intercalation of clay would have not occurred because there is no major shift in clay peaks seen on a comparison of the diffractograms of Clay and PVP Clay 30%.
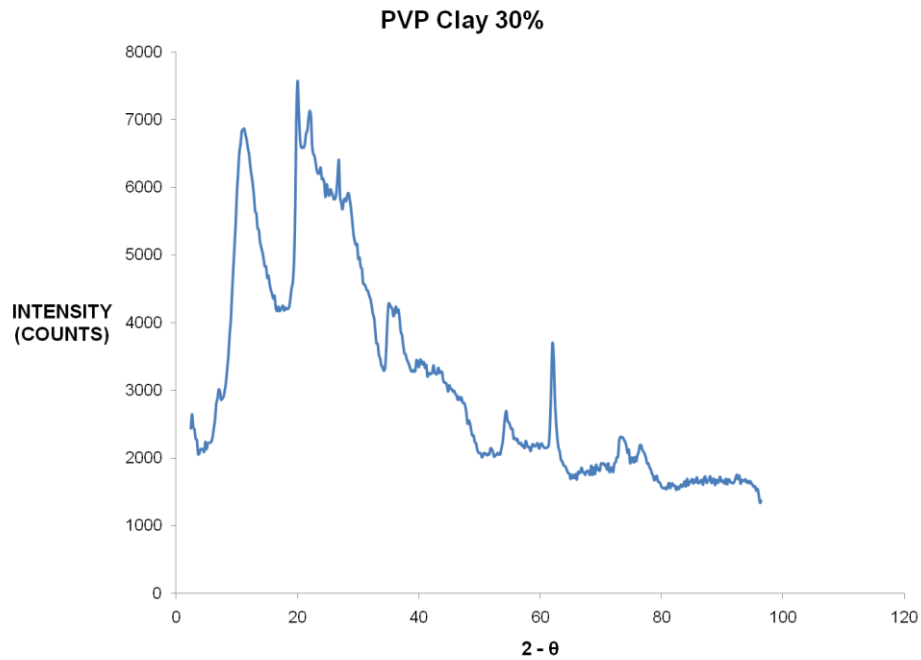
Fig. 4.10 PVP Clay 30% XRD results

In Fig. 4.10, the large hump created due to scattering of X-rays by the amorphous content in the sample is overlapped by the crystalline peaks and the shape shown in diffractogram in Fig. 4.9 might be independent of the degree of crystallinity of the clay, yet the relative area under the hump to the diffraction peaks appears to be proportional to the crystallinity.

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The XRD peak analysis of diffractogram for PVP Clay 3% revealed a high possibility of complete exfoliation of clay in the PVP Clay 3% film. While the amorphous peak of pure PVP (seen in Fig. 4.7) at 13000 counts had an approximate value of 6900 counts in the PVP Clay 30% (seen in Fig. 4.8), this value was now around 2900 counts for a small hump formed in the PVP Clay 3% diffractogram shown in Fig. 4.11. The area under the hump of the amorphous PVP curve is smaller in comparison to the characteristic amorphous hump in Fig. 4.9 and 4.10.
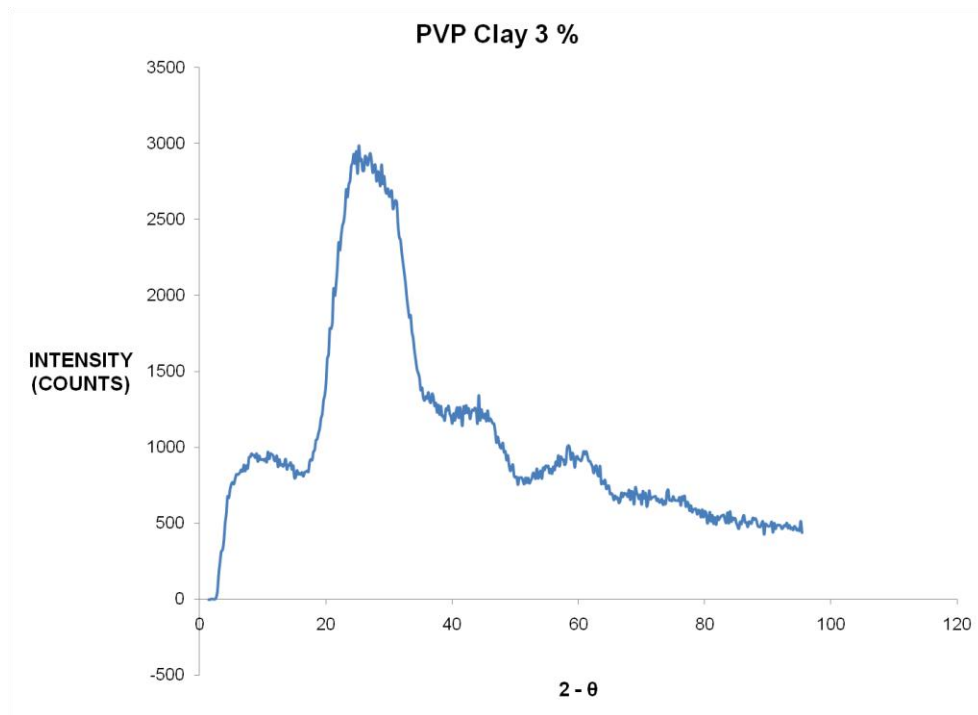
Fig. 4.11 PVP Clay 3 % XRD results

The clay peaks in Fig. 4.8 appear to have diminished to an extent that it suggests exfoliation of clay in the PVP Clay 3% film. This is because by the peak analysis of XRD results disappearance of clay peaks indicates exfoliation of clay. Therefore it would be appropriate to suggest the use of PVP Clay 3% as the nanocomposite film with better exfoliation as the nanocomposite filler for VARTM of carpet composites.

Because the intensity values (counts) of the diffractograms are close to each other in Fig. 4.8 to 4.11, overlaying of the diffractograms did not yield good results. Hence an offset value was

assigned to the intensity values (that is, y-axis) in Fig. 4.12 to get an overlay of all the diffractograms. Fig. 4.12 shows the comparison of all the XRD peaks which indicates disappearance of clay peaks in PVP Clay 3%. This indicates that exfoliation of clay is achieved at PVP Clay 3%.
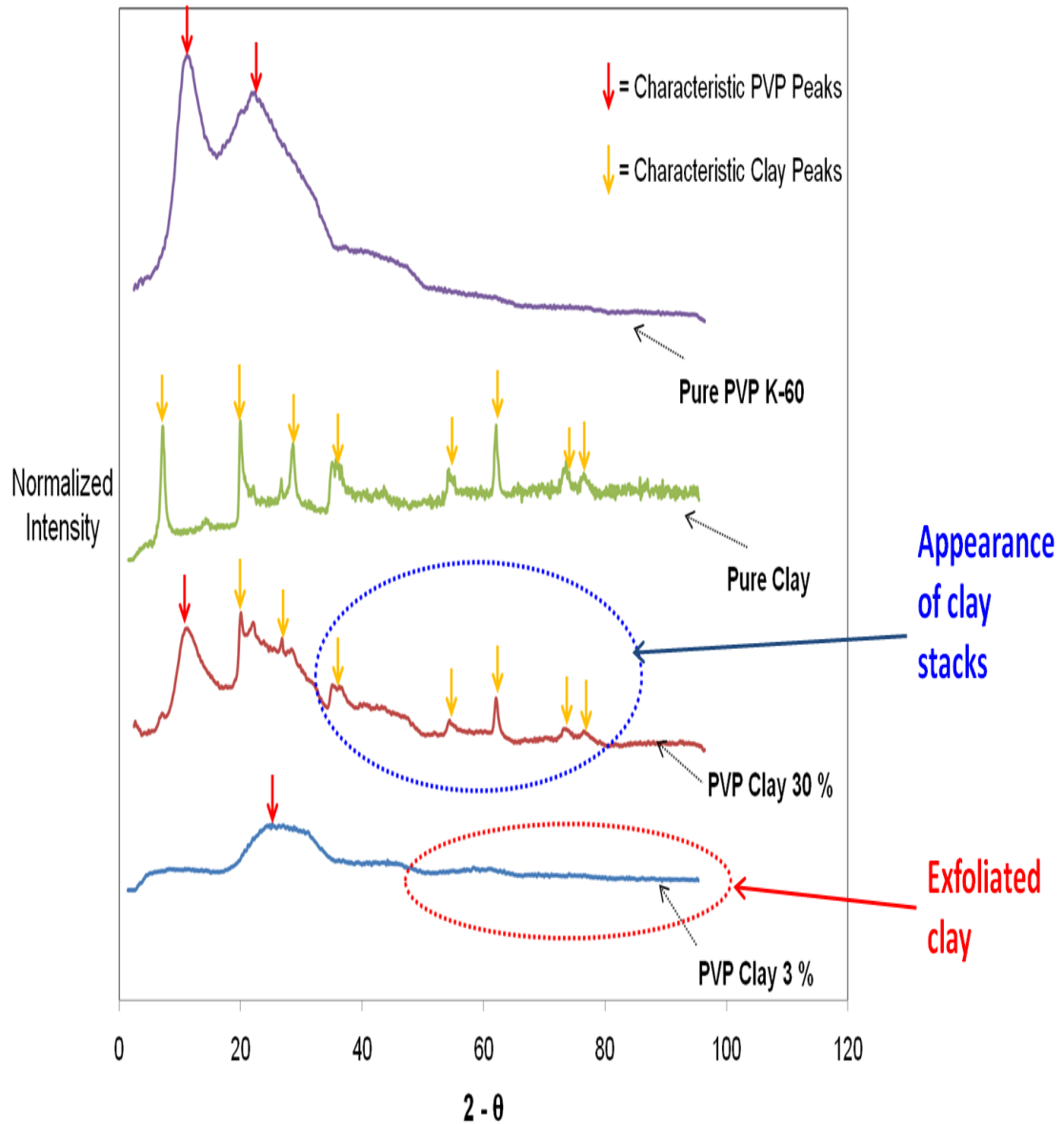
Fig. 4.12 Overlay of all XRD diffractograms indicating the exfoliation of clay platelets at 3%

PVP clay 3% film which has 3% of OMMT clay by weight is expected to have achieved exfoliation of clay in the nanocomposite film. However the PVP clay chemistry, like all polymer clay nanocomposites is driven by complex physicochemical mechanisms [81]. Therefore further investigation is needed to analyze chemical and micro-structural characteristics of PVP clay film formation in detail.

4.8 VARTM WITH NANOCOMPOSITE FILLER

Based on the characterization results of nanocomposite films, PVP with 3% clay was chosen as the filler for scaled up VARTM process of carpet composites. The PVP films were broken into smaller flakes and placed on the carpet layers uniformly, after the layup of preform. The films were placed on the top and the bottom of the preform layup (that is on the glass plate).

Fig. 4.13 shows an image of the nanocomposite filler incorporated carpet composite fabricated using the scaled up VARTM process. This panel was originally of the size 0.61 m x 1.22 m (2 ft. x 4 ft.), while the image shown in the picture below is after cutting out samples for characterization. The composite is machine-able and can be cut with a band saw, just like other carpet composites.
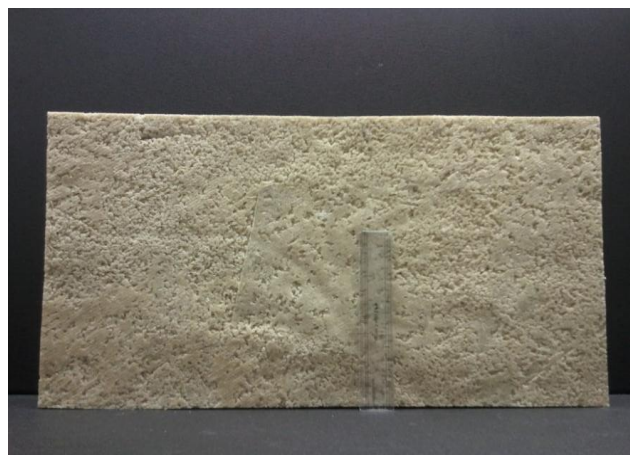
Fig. 4.13 An image of the clay filled carpet composite fabricated using the scaled up VARTM process

Though the VARTM of carpet composites with clay based nanocomposite film was primarily to incorporate the properties of clay, the organic polymer matrix of PVP film could also have an important role to play in the carpet composite. PVP was an ideal choice as the polymer matrix for nanocomposite films because of its high solubility in water and organic solvents. However literature suggests that PVP could also improve the toughness of the resin system and the hydrothermal performance of the resultant carpet composites [82]. PVP is used as a thermoplastic additive for selective toughening of epoxy resins because of the possible miscibility of PVP with epoxies [83]. The miscibility of PVP and epoxy could either arise from dipole-dipole interactions between the amido group of PVP and the oxirane groups of epoxy [83]. It was found in one of the studies that PVP exercises a stabilizing effect on epoxy by producing a retardation of its decomposition and hence can be assumed to be forming a protective layer in the carpet composites. Research studies also suggest that trace amounts of PVP have a dramatic effect in morphology of Nylon 6,6 due to lamellar modifications thereby improving mechanical properties [84]. Hence for VARTM of carpet composites with PVP Clay 3% filler would not only have the properties of clay but could also benefit from the use of PVP matrix layer of the film.

The property enhancement of clay additions have been analyzed in the following sections of this chapter.

4.9 FLAME RETARDANT PROPERTIES

One of the objectives of addition of nanoclay in the carpet composites was to make the carpet composites flame retardant. This is important because the flammability characteristics of infrastructure materials greatly affect the speed with which a fire grows [85]. In this section a brief review about the possible improvement in the flame retardant properties of the carpet composite due to addition of PVP - Clay film has been discussed.

In one of the attempts to understand the curing process of epoxy based carpet composites, BTTB composite sample was placed inside the vacuum oven at 210 ^{0}C. It was observed that the sample underwent a change in its color from light pale yellow to dark reddish brown. Since it is a BTTB carpet composite, which means, the Polypropylene is at the top and therefore the degradation could be because of the degradation of polypropylene. This suggested a need for flame retardant additives in carpet composites which can improve these types of degradation due to fire and high temperature.

Generally, the carpets (reinforcing fibers, in this study) imported or manufactured for sale in the United States need to meet the acceptance criteria of U.S. federal standard FF1-70 which specifies an acceptance criteria that the carpet used should be a fire retardant carpet [85]. Hence almost all carpets contain fire retardant coatings on their fibers for compliance with FF1-70. However carpets are made up of Polypropylene backing which are often susceptible to thermal degradation at temperatures more than its melting point of 165 ^{0}C [86].

In this study of carpet composites, the presence of Polypropylene backing and its weak resistance to thermal degradation indicate a need for protecting the polypropylene backing. The carpet composites were made up of thermo plastic resins like Epoxy, Polyester and Vinyl-ester resins which also have equally poor resistance to fire and are susceptible to high smoke densities associated with their burning due to their intrinsic chemical composition and molecular structure [68]. These problems clearly indicate the use of flame retardant additive in the carpet composites or use thermosetting resins with acceptable standards of flame retardant additives. However, to produce these resin systems with acceptable standards of flammability require high quantities of flame retardant additives (in the order of > 30% wt./wt.) [68]. The conventional flame retardant packages can be used which basically means use of halogenated flame retardants. Literature suggests that there have been some successful commercial approaches to remove conventional flame retardant package and replace it with clay based nanocomposites [87]. Also, the

environmental regulations in U.S. and worldwide have started to restrict the use of halogenated flame retardant additives, initiating research in alternative flame retardant additives [88].

Literature suggests that effective dispersion of functionalized clays in polymeric matrices yield nanocomposite structures which enable them to exhibit reduced flammability alongside improved mechanical properties compared to the conventional flame retardants [89]. This implies that the addition of PVP Clay 3% film can be a used a flame retardant layer to protect the carpet composites. The PVP Clay 3% nanocomposite film would form a thermal barrier of homogeneous char and therefore protects the resultant carpet composites. The following mechanism could be followed by the nanocomposite film incorporated in carpet composites:

High aspect ratio of clay platelets in the exfoliated PVP Clay 3% film would form a percolated jammed structure due to particle, particle interactions so that the melt by thermal degradation would behave rheologically like a gel [87].

4.10 WEATHER DEGRADATION RESISTANCE

Composites used in infrastructure applications like highway noise barriers undergo mechanical and thermal loading while being exposed to adverse environments including ultraviolet (UV) radiation, moisture (relative humidity), water vapor condensation and alkaline/salt environment [81]. Compared to other environments UV radiation and water vapor are considered to be predominantly responsible for degradation of composites [81]. UV degradation has dramatic effects on mechanical properties and it often causes a transition from ductile fracture to brittle fracture [90]. Fig. 4.14 gives a general plot of composites showing ductile behavior.
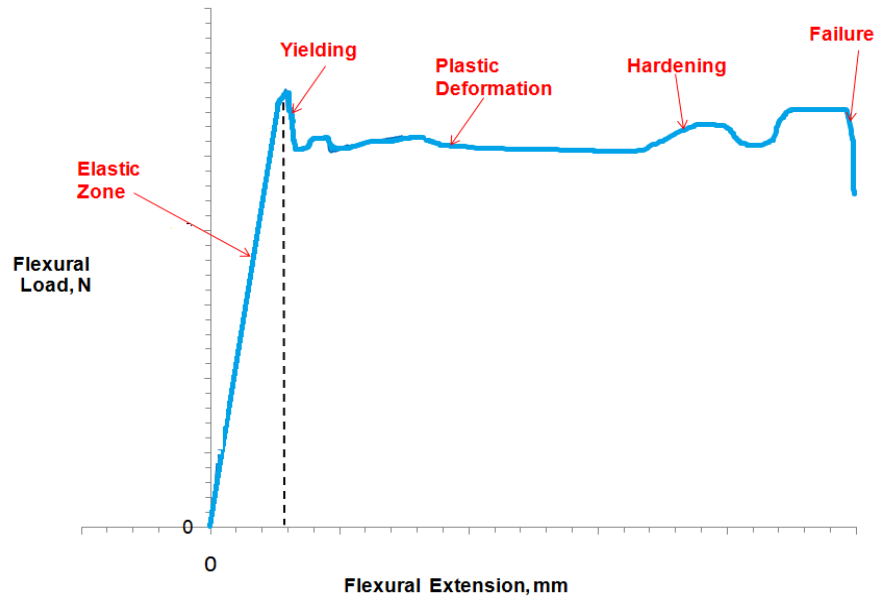
Fig. 4.14 General plot of force - extension results obtained from three point bend tests [74].

The incorporation of clay based nanocomposite film may improve the environmental degradation resistance of the carpet composites.

In this study an attempt was made to test the UV degradation of the composites after addition of nanocomposite filler and study their mechanical properties. This was carried out by exposing the clay based carpet composites to an alternate cycle of 8 hours of UV and 4 hours of moisture in an accelerated weather chamber known as weatherometer. Fig. 4.15 shows the image of the weatherometer used for exposing the samples to artificial weather cycles. The combined environment was simulated on a QUV Accelerated Weathering Tester. The weatherometer can house 16 samples of the size 7.6 cm x 10.16 cm (3 inch x 4 inch) in separate chambers.

Fig. 4.15 An image of the weatherometer (artificial weathering chamber) used.

The main aim of this experimental attempt was to check if the strength of the degraded material is equal to the strength of the non-degraded material. It is predicted that there would be transition in mechanical properties from ductile failure to brittle failure after degradation and evaluate this hypothesis 3-point bend test was carried out on Instron Universal Testing Machine.

This size specification of weatherometer had a negative implication on the three point test to be performed because as per ASTM D 4329-05 for measurement of flexural properties using three point bend test should have the length: depth ratio of 16:1. However this was a preliminary attempt to understand the embrittlement of carpet composites before and after exposure to UV. Six clay based carpet composite samples were cut in rectangular sizes of 7.6 cm x 10.16 cm (3 inch x 4 inch) and tested on the Instron. A strain rate of 0.1 mm/mm was chosen for the two tests conducted on each sample configuration used. The experiments were designed in the following ways: The first configuration of two samples consisted of unexposed samples without any exposure to UV and were tested as reference samples. Another configuration was to place the UV exposed sample to the compression side while the third configuration of the sample was to place the UV exposed sample on the tension face. As shown in the Fig. 4.16 below shows the arrangement in the compression and tension faces of the sample.
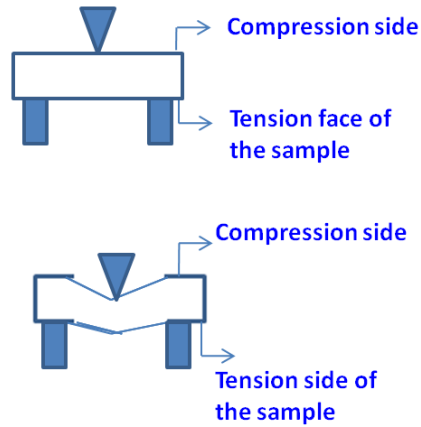
Fig. 4.16 A schematic of the arrangement of the sample for three point bend test

The samples were loaded on the as per the configuration as shown in Fig. 4.17 below.
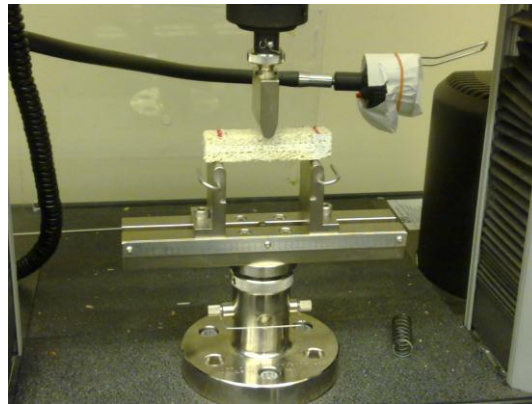
Fig. 4.17 An image of Clay - based carpet composite loaded on Instron machine

The results indicated immediate failure of the UV exposed samples which might be due to the brittleness induced in the samples due to exposure to UV and moisture. Fig. 4.18 shows an image of the carpet composite undergoing failure. Even though material properties like Young's modulus and yield strength can be obtained from the tensile test of the carpet samples these results are not conclusive because these were tested in non - ASTM standard size and hence it should be used only as a qualitative comparison.
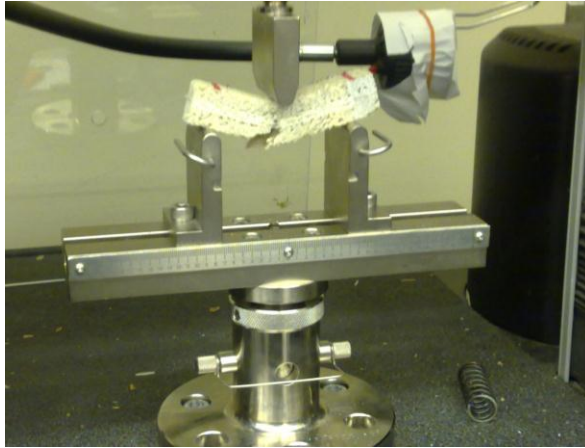
Fig. 4.18 An image of Clay-based carpet composite breaking on 3 point bend load

Fig. 4.19 presents the results obtained from the three point bend test performed on the clay based carpet composites (before and after degradation). It can be observed that though there is not much change in the linear elastic zone but the failure of samples exposed to UV and moisture in comparison to the unexposed sample show that the carpet composite samples behave like brittle materials.

Hence carpet composites appear to become brittle after exposure to UV and moisture. The area under the curve of a force extension plot is the work of fracture of the composite (W_f). The work of fracture is basically a sum of work due to yielding (W_y) and work due to necking (W_n). It can be clearly seen from Fig. 4.18 that there is a huge change in the necking behavior of the composite during its failure.
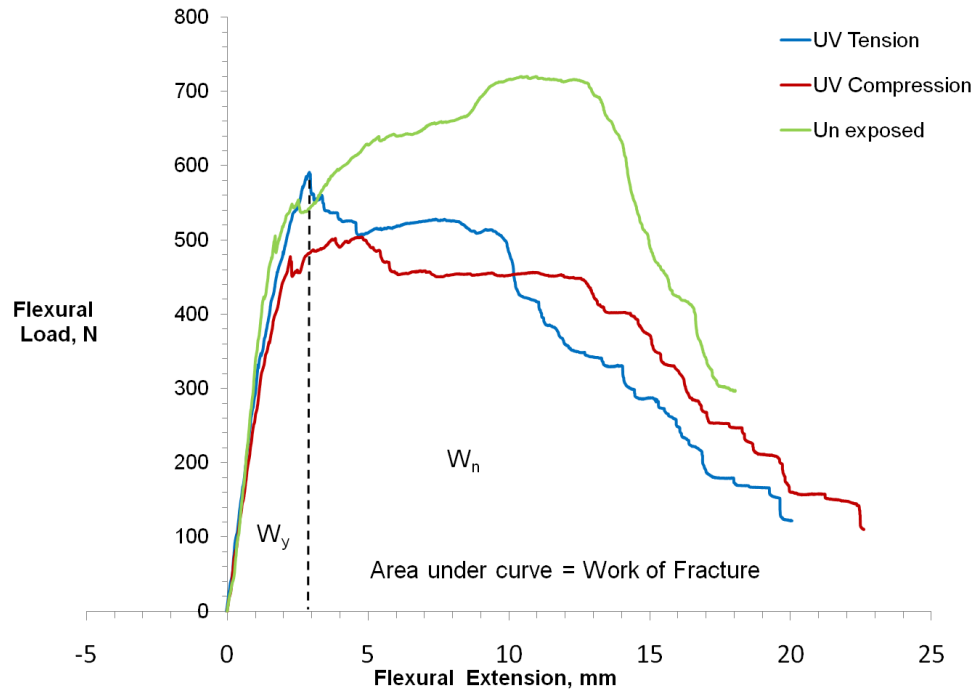
Fig. 4.19 Preliminary results of the three point bend tests conducted on the UV exposed samples indicating brittleness induced in the samples.

W_n has decreased drastically due to exposure of the composites to UV and moisture. In a quick comparison of Fig. 4.19 to Fig. 4.14 of an idealized flexure scan gives idea about the significant effect on the properties of the composite due to their exposure to harsh weather. The brittleness could possibly be due to the lower values of load at the "hardening" and "plastic deformation" area for the weather exposed samples in comparison to very high load values of the unexposed clay based carpet composite sample. Also the point of failure is very low for the weather exposed samples. The lowering of "hardening" region also known as "work hardening" or "strain hardening" could be because of post-curing of the composite samples on exposure to UV and moisture.

The area under the curve for the above force extension plot of Fig. 4.19 would give a much better understanding of the magnitude of reduction in the work of fracture of the weather exposed carpet composite sample.

The values for the area under the curve of Fig. 4.19 were calculated using the trapezoidal rule. Fig. 4.20 shows that the area under the curve is at its highest for the clay based carpet composite without any exposure to UV. A decrease in area under the curve for the weather exposed samples indicates a decrease in work fracture which in turn implies an increase in brittleness of the carpet composites on exposure to UV and moisture.

Fig. 4.20 presents information about the possible decline in work of fracture due to exposure of carpet composites to UV and moisture. A decline in the work of fracture indicates brittle nature of composites.
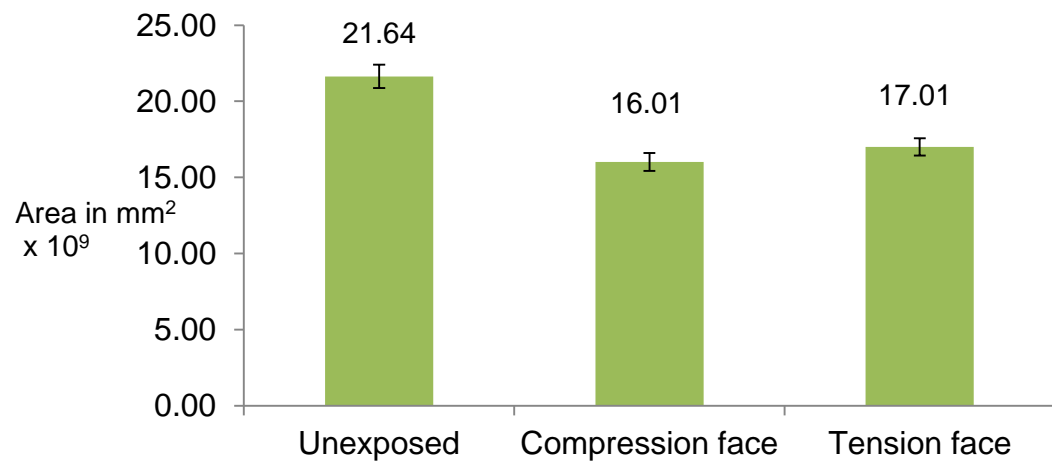
Fig. 4.20 Values of area under curve calculated using the trapezoidal rule.

Hence it can be safely hypothesized that the exposure of carpet composites to UV and moisture would degrade them to an extent of causing embrittlement in them.

4.11 NANOCOMPOSITE FILLERS SUMMARY

Exfoliated nanoclay based nanocomposite film was obtained by using the clay at 3% of the weight of PVP. The low filler range of nanoclay could show better mechanical performance and good exfoliation. This could be because addition of higher amount of nano-filler in the composite will increase the reinforcing load due to which the surface area of the silicate layer could lead to insufficient polymer molecules to wet. An attempt was made to understand the effect of addition of PVP-Clay films by doing preliminary studies on them. It can be safely assumed that there is some improvement in the carpet composites due to addition of clay based nanocomposite films to the carpet composites and there is immense scope for future work in this direction of research. In this study clay based polymer nanocomposite films were incorporated to improve the environmental degradation resistance properties of the carpet composites. The next chapter discusses the noise absorption results obtained by acoustic characterization of carpet composites.

CHAPTER V

ACOUSTIC CHARACTERIZATION

5.1 OBJECTIVE

The noise absorption coefficients of carpet composites were measured using the impedance tube method (ASTM C 384-04) to evaluate their feasibility as highway noise barriers.

5.2 BACKGROUND

Sound waves are longitudinal waves which require a medium for travelling, like air or water, and are measured in cycles per second or Hertz (Hz). The human ear can detect a wide range of frequencies from 20 to 20,000 Hz, but it is most sensitive to the sounds over a frequency range of 200 to 5000 Hz. The human ear does not respond in a uniform manner to different frequency sounds – a sound pressure level of 70 dB is perceived as much louder at 1000 Hz than at 100 Hz. The absorption of sound results from dissipation of sound energy as heat and this dissipation mechanism is mainly due to one of two phenomena:

1) Energy loss due to flexural vibrations in the specimen [41].

2) Porosity effects, where the energy is dissipated due to multiple reflections of sound waves within the voids in the structure [41].

For porous materials like sponge and mineral wool which have interconnected pores the incoming sound waves are reflected within the pores, causing them to vibrate and therefore convert sound energy into heat [41]. This is also true in the case of composites as concluded in the study by Hargrove that, "the mechanism that causes composites to reduce noise has been shown to be the reverberations of sound waves against the sides of many voids in the composite. This causes a transformation of acoustic to heat energy" [91]. The nature of composites is a multitude of minute voids in the material. Sound waves reverberate from wall to wall of these voids and are attenuated by the conversion of a large amount of noise to a relatively small amount of heat [91]. Also for a completely porous material, sound is lost isothermally near the walls of the voids and to a lesser extent in or near the center of the hollow spaces [91].

For homogeneous and isotropic materials, acoustic performance is defined by a set of five experimentally determined constants: noise absorption coefficient (NAC), pressure reflection coefficient (PRC), acoustic impedance, propagation constant and noise reduction coefficient (NRC) [41].

5.3 THEORY

The ability of a highway noise barrier to reduce noise levels depends upon a number of variables including the geometric factors like relative heights and distances of the noise source and receiver to the barrier, and the mass per unit area (surface density) of a wall type barrier [35]. There are two ways to characterize the acoustic properties of a material – by measuring its absorption coefficient or by measuring its transmission loss.

The noise absorption coefficient (NAC) is the most critical parameter in acoustic characterization of a material to determine how well it can absorb sound or noise. When a sound wave hits a material, a portion of it will be reflected or "bounced back." In simple terms, the lesser the sound energy reflected, the better the noise reduction property of the material [33]. A

value of NAC of 0 means the sound energy is being reflected completely, and a value of NAC of 1 means that all the sound energy is being absorbed, which is the best in noise reduction. The American Society of Testing and Materials (ASTM) issued a standard, ASTM C 384 -04, on how to conduct the test of noise absorption coefficient of a material.

In this experiment, sound waves are created with the use of a speaker connected to a function generator. The function generator sends an oscillating current signal to the speaker causing the speaker's diaphragm to vibrate. As the diaphragm moves outward or toward the sample, the air near the speaker is compressed creating a small volume at relatively high pressure, which propagates away from the speaker. As the diaphragm moves inward, away from the sample, it creates a low pressure area which propagates away from the speaker. As shown in the figure below in Fig. 5.1, an alternating signal into a speaker creates sound waves which propagate away from the speaker. The dark bands represent areas of high pressure while the light bands represent areas of low pressure [92].
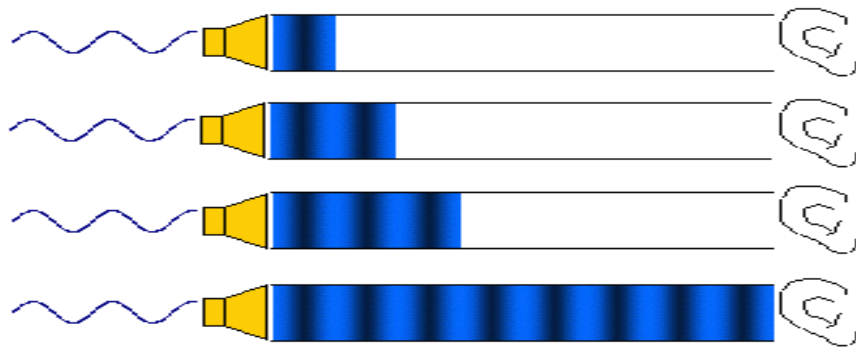
Fig. 5.1 A diagram illustrating the nature of unidirectional sound waves pumped into a impedance tube [92]

The process of compressions and rarefactions continues with a frequency equivalent to the input signal. The higher the input frequency, the more often the compression/rarefaction cycle would occur at each second. When sound waves move away from the speaker and are detected by the microphone, the entire cycle is reversed: the areas of high and low pressure cause the microphone's diaphragm to vibrate in both directions, and this creates small electrical signals

[92]. This electrical signal from the microphone can be recorded by a recording device or displayed on an oscilloscope [92]. In the method specified by ASTM C 384, "A plane wave traveling in one direction down a tube is reflected back by the test specimen to produce a standing wave that can be explored with a microphone" [93]. The normal incidence sound absorption (NAC), which is a function of the frequency, can be determined from the standing wave ratio at the face of the test specimen. Measurements were made with pure tones at a number of frequencies as described by the third octave band frequency specified in ANSI S1.6 [93].

5.4 SCOPE, STANDARD AND SIGNIFICANCE

ASTM C 384 – 04 mentions in its scope that, "This test method covers the use of an impedance tube, alternatively called a standing wave apparatus for the measurement of impedance ratios and normal incidence sound absorption coefficients of acoustical materials" [93]. The measurements specified in this test are significant because it is useful in basic research and product development of sound absorptive materials [93].

The sound absorbing performance of the material is the ratio of un-reflected sound intensity at the surface to the incident sound intensity, and is known as Noise absorption coefficient (NAC). Other important acoustic parameter include the pressure reflection coefficient (PRC) which is a ratio of total reflected pressure (sound intensity) to the total incident pressure at the face of the specimen [93]. NAC and PRC vary with frequency and are also a function of material thickness, density and pore sizes.

The standing wave apparatus used for the testing of ASTM C 384 is a simple and less complex method which yields the noise absorption coefficient of the material being tested. The test method can be applied for measuring NAC at normal incidence that is 00. NAC calculated by ASTM C 384 is useful in basic research and product development of sound absorptive materials like carpet composites. This method involves the use of impedance tube (with two microphones), a digital

oscilloscope, and measurement of complex pressures using the microphones, from the source

speaker which has an input from the frequency generator as shown in Fig. 5.2 below.
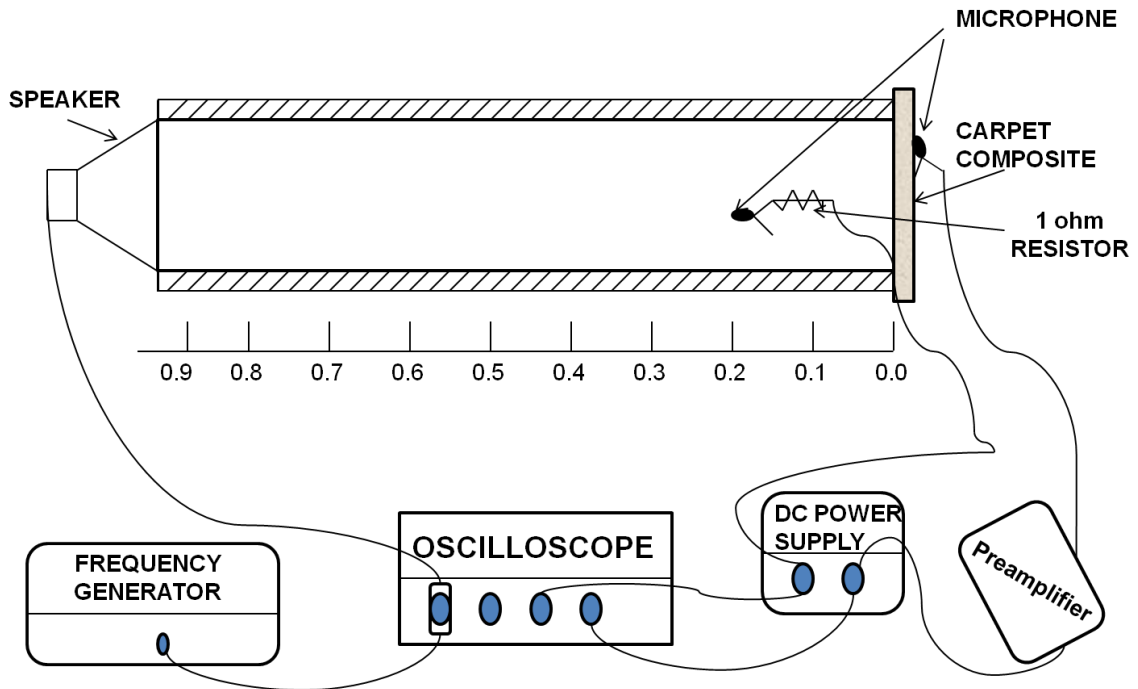
Fig. 5.2 A schematic diagram to show the apparatus used for acoustic test based on ASTM C - 384 to obtain noise absorption coefficient

The approach adopted for this study was to build an acoustic set up rather than purchasing an

integrated acoustic set up which is expensive. The tube used as an impedance tube was a

rectangular aluminum tube with polished inner ends. The tube is straight 1m in length to ensure

that the plane waves are fully developed. The rectangular tube had a cross - section of 0.0762 m x

0.0762 m. The general formula for rectangular cross section as per the ASTM standard is as

mentioned in the following equation 5.1.

$$d = \frac{4 \times Area}{Perimeter} \qquad (5.1)$$

The tube should be maintained free of dust to main low tube attenuation. Tube attenuation is

calculated using the following equation 5.2. Kirchoff developed and Beranek modified the

formula for estimating the attenuation constant as given below,

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$$A = \frac{0.02203\, f^{0.5}}{C \times d} \qquad\qquad (5.2)$$

Where, f = frequency in Hz.

C = velocity of sound in m/s.

d = diameter (length of one side of the rectangle) in m.

The wavelength of the sound transmitted from the frequency generator is developed using the following equation 5.3.

$$W = \frac{C}{f} \qquad\qquad (5.3)$$

The velocity of sound is in turn, dependent on the room temperature T in which the experiment has been conducted and is given by the following equation 4.4.

$$C = 20.05\,(T + 273.1)^{0.5} \qquad\qquad (5.4)$$

Hence the velocity of sound was found to be stable at 345.76 m/s during the experiment process because of a steady atmospheric temperature maintained at 24.24 ^{0}C.

The microphone is placed at regular intervals of 0.1 m inside the impedance tube with a marking of 0.1 m to 0.9 m on the aluminum tube. A correction factor was used to analyze the distances was used as shown in the following equation 4.5.

$$x_{cor} = x_{1/4} - x_{mr} - \frac{W}{4} \qquad\qquad (5.5)$$

Where,

x_{cor} = Correction factor for distance, m.

$x_{1/4}$ = 0.1 m = observed scale reading with microphone probe at the first minimum, m.

$x_{mr} = 0.005$ m = observed scale reading with probe touching face of metal backing plate, m.

The correction factor for distance x_{cor} was found to be 0.078 m.

This was incorporated in the routine measurements by the following equation 5.6 used to subtract correction factor.

$$x = \left(x_{obs} - x_{sf}\right) - x_{cor} \tag{5.6}$$

Where,

x = true distance from the specimen surface, m

x_{obs} = observed scale reading, m, and

x_{sf} = observed scale reading with probe touching specimen face, m.

For the standing wave within the tube it is necessary to know the distance from the sample face at which each pressure is being measured. The exact location of the mounted sample within the tube can be determined by gently advancing the probe until it makes contact with the sample face and noting the scale reading of the point of contact [93]. The exact location however requires a correction factor applied to the observed scale reading because the acoustic center of the microphone or the microphone probe does not necessarily correspond to its geometric center [93].

The microphone voltage at its minimum voltage should be at least 10 times more than the voltage of the background noise voltage. This would ensure that the noise level would be atleast 10 db more than the noise level of background noise. This can be observed from the following image taken from oscilloscope reading while performing the acoustic test. The sound waves are generated at various frequencies by placing the microphone at a particular distance from the specimen. This can be seen in Fig. 5.3 where the frequency generator was set to produce a sound of 500 Hz and the microphone was placed at the specimen face. The peak to peak voltage was

noted at every frequency at different distances from the specimen to obtain a standing wave. Fig 5.3 shows that the noise voltage in green – no.4 is less compared to the microphone voltage observed in the wave no. 3 in purple.
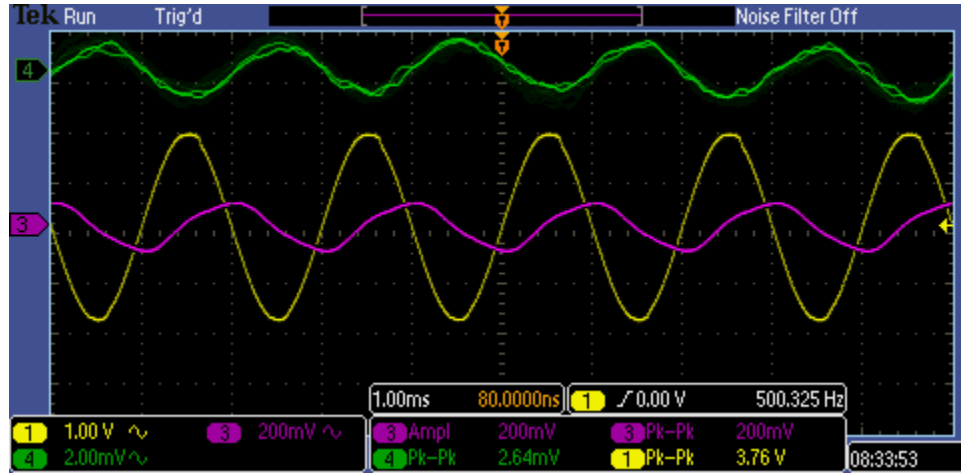
Fig. 5.3 An image of the oscilloscope reading

The standing wave ratio (SWR) at the specimen face is calculated using the extrapolation method by measuring the voltages (corresponding pressure levels) at various frequencies and at various distances.

The standing wave ratio at specimen face is measured using the following three cases -

When two or more minima are present in the sine wave obtained

$$V_{min}(0) = V(x_1) - x_1 \frac{[V(x_2) - V(x_1)]}{x_2 - x_1} \tag{5.7}$$

One minimum and one maximum present

In this case, the maximum voltage at the sample face is $V_{max}(0)$. In this case there is only one minimum and a graphical extrapolation back to the specimen face cannot be used. A valid approximation can be given by the following equation.

$$V_{min}(0) = V(x_1) - A \times x_1 \times V_{max}(0) \tag{5.8}$$

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where, A can be calculated from equation 5.2.

Only one minimum and no maximum present

When there is no actual maximum measured in the tube, a maximum level can be inferred from a measurement of the sound pressure level at W/8 distance on either side of the minimum as per the ASTM C - 384 Standard. The following equation 5.9 is suggested in the standard for this kind of situations.

$$V_{max} = \left(2 \times V_{W/8}^2 - V_{min}^2\right)^2 \qquad (5.9)$$

Thus when no maximum and only one minimum can be measured, an additional voltage measurement at a distance of W/8 from the measured minimum should be taken and used as $V_{W/8}$ in 5.9 to arrive at an estimated V_{max} value.

Hence using any of the above three conditions the values can be substituted to calculate SWR (0) at the specimen face.

The impedance tube is used to generate a standing wave in the tube which is enclosed with a speaker at one end and a specimen on the other end. The interference of an incident wave and reflected wave from the specimen creates a standing wave in the impedance tube, which is measured as standing wave ratio (SWR). SWR is a function of the distance between the speaker and the microphone (*x*), and is given as,

$$SWR\ (x) = \frac{V_{max}(x)}{V_{min}(x)} \qquad (5.10)$$

Where SWR(*x*) = standing wave ratio at location *x*, a dimensionless, positive, real number greater than or equal to 1.

In this experiment voltage has been correlated to the change in pressure level and hence the standing wave ratio mathematically indicates,

$$SWR\ (x) = \frac{P_{max}(x)}{P_{min}(x)}$$

(5.11)

Where P_{max}, P_{min} are the maximum and minimum sound pressures in the impedance tube.

The ASTM C - 384 states that, "The primary purpose for making the measurements described in this test method is to find the standing wave ratio at the face of the specimen, that is, SWR (0)." SWR (0) is determined indirectly by extrapolation of the maximum and minimum voltages actually measured in the tube and its value is critical in this experiment.

 The pressure reflection coefficient can be calculated from SWR (0) by the following equation:

$$PRC = \frac{SWR(0)-1}{SWR(0)+1}$$

(5.12)

The noise absorption coefficient is a dimensionless, real number which is directly related to the pressure reflection coefficient by the following equation:

$$NAC = 1 - |PRC|^2$$

(5.13)

5.5 MATERIAL CHARACTERISTICS

The 11 materials tested for acoustic characteristics and their surface properties are mentioned in Table 5.1. These surface properties were measured using the weigh balance and ruler because of their dimensional stability.

Amongst all the carpet composites the 4 layer carpet composite has the highest specific gravity (SG) of 12.07 while the PE carpet closely followed this number with a specific gravity of 10. The BTTB carpet composite had an SG of 3.611 making it the lowest amidst all the carpet composites tested for acoustic characterization. The TBBT carpet composite had an SG of 6.667

while the carpet with clay configuration which has addition of clay layers in a TBBT carpet composite has an SG of 7.143, indicating just a marginal improvement in SG. This indicates that the use of clay as nanofiller increases the specific gravity of the composite.

"PS" foam was the lightest material tested with an SG of 0.4167 and concrete on the other hand has the highest SG of 24.61.

The choice of the 12 materials was not restrained by thickness or composition as ASTM C 384 has no specifications about thickness and compositions of the sample.

TABLE 5.1

A TABLE OF 11 SOUND ABSORBING MATERIALS AND THEIR SURFACE PROPERTIES

Sr. No.	Materials	Mass (kg)	Volume (m^3)	Specific Gravity
1	Virgin Carpet	0.08	0.52	1.54
2	Virgin Carpet BTTB	0.08	0.52	1.54
3	Epoxy Matrix	0.21	0.12	1.75
4	TBBT Carpet Composite	0.24	0.36	0.67
5	BTTB Carpet Composite	0.13	0.36	0.36
6	4 layer Carpet Composite	0.35	0.29	1.21
7	VE Carpet	0.11	0.17	0.65
8	PE Carpet	0.17	0.17	1.00
9	Concrete	0.96	0.39	2.46

10	Wood	0.14	0.19	0.73
11	Carpet with Clay	0.15	0.21	0.71
12	PS Foam	0.01	0.24	0.04

5.6 RESULTS

The NAC measurements were conducted using the ASTM C - 384 standards at the 3rd octave band frequency range from 125 Hz to 4000 Hz. The 3rd octave band frequencies chosen for this test were - 125 Hz, 250 Hz, 500 Hz, 1000 Hz, 2000 Hz and 4000 Hz.

Fig. 5.4 shows the result obtained for 11 different materials tested for noise absorption coefficient (NAC) using ASTM C 384-04 and it can be concluded from the result that the virgin carpet (which means carpet without any resin treatment or usage) has the highest noise absorption at low frequencies of 125 Hz but drops down in absorption at frequency range of 250 – 500 Hz. Polystyrene ("PS") foam is the best absorber material among all the other materials compared in the frequency range of 250 – 500 Hz. However it can also be seen that PS foam gives up at frequency above 500 Hz that is, in the higher frequency range of 1000 Hz to 4000 Hz it performs poorly.

The following observations were made based on the results displayed in Fig. 5.4 for NAC obtained at different frequencies -

- The four layer carpet composite performs exceptionally well in the frequency range from 1000 Hz to 4000 Hz. This proves that among all the materials the best material best suited for a highway noise barrier is the four layer carpet composite material. The material is robust in its noise absorption in the low frequency range of 125 Hz to 500 Hz. This is because it is only third to virgin carpet and PS foam in the low frequency range.

- Virgin carpet BTTB was tested to check if the properties had any difference in properties in comparison to the other virgin carpet sample which has a configuration of TBBT. Results from Fig. 5.4 indicate that probably the backing surface of the carpet is very weak due to lesser porosity in comparison to the carpet fibers. A porous medium can be looked at as a mixture of two phases, air and solid material, both of which react

differently to the sound wave. Hence there is a higher NAC indicating greater noise absorption in porous materials like Virgin carpet than in the flat Virgin carpet BTTB.
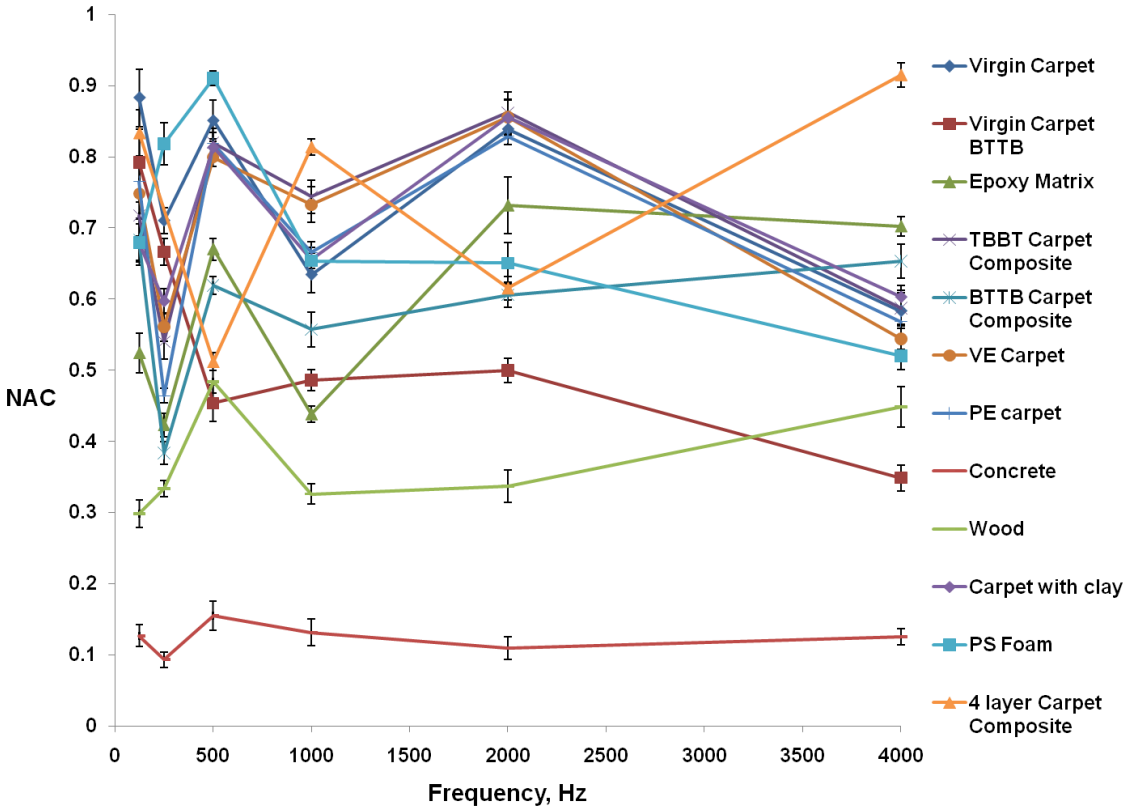
Fig. 5.4 Noise Absorption coefficients of various noise absorbing materials calculated at the third octave band range of frequencies using ASTM C 384 -04

- The material which performed the poorest among the 11 materials is concrete. Concrete has a steady absorption rate of around 0.125 at all frequencies which is significantly low.

- There was a steady trend observed at 500 Hz where all the materials displayed high sound absorption. A similar trend was observed for a dip in acoustic absorption for all materials at 1000 Hz. This could probably be because the frequencies could be harmonic frequency of the materials.

It was necessary to understand the behavior of different carpet composites and the effect of different resin systems; layup arrangements that is, TBBT, BTTB, 4 layer; addition of nanocomposite fillers and other general comparisons on the acoustic performance of the

composites. Hence a comparison of 6 different carpet composites has been presented in Fig. 5.5 from which the following observations were made -

- The 4 layer carpet composite is the best material among all carpet composite configurations tested. The 4 layer carpet composite performs exceptionally well for high frequency range sound from the range of 1000 Hz to 4000 Hz. This is the range of noise created by the friction of tires on highway roads. The low frequency noise is created by the engine noise of the cars and vehicles. It can be observed that in general the carpet composites do a good job of absorbing the noise at both low and high frequencies. However it is the 4 layer carpet composite that has the highest noise absorption at the high frequency range qualifying it for a product as a highway noise barrier.
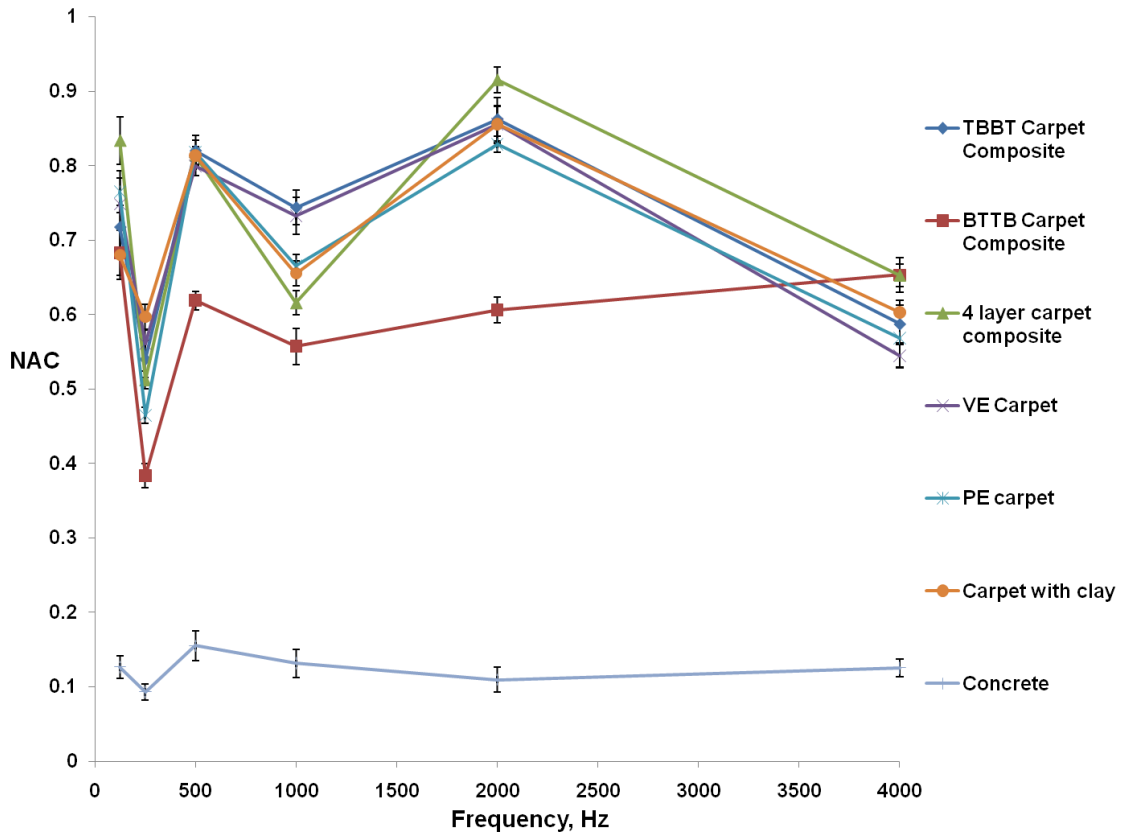
Fig. 5.5 Comparison of Noise Absorption coefficients different carpet composite materials calculated at the third octave band range of frequencies using ASTM C 384 -04

- Addition of clay to the composites has a marginal effect on the noise absorption properties of the carpet composites. Although it is difficult to arrive at conclusion considering the thin margin of difference in the acoustic performance of composites but the comparison suggests that addition of clay has no impact on acoustic performance of carpet composites.

- In an attempt to highlight the difference between the proposed highway noise barrier material, the current highway noise barrier material that is, concrete was tested and used in this chart for a direct comparison. Fig. 5.5 clearly highlights the poor noise absorption qualities of concrete in comparison to the carpet composites. Also an interesting observation is the difference in the pattern in which the NAC varies with respect to a change in the frequencies. The NAC variation in concrete is completely different from other carpet composites. For instance the carpet composites have a huge reduction in NAC at 1000 Hz which suddenly increases in 2000 Hz, while this is not observed in concrete. This is interesting in the material science perspective and therefore it is necessary to compare the properties with the parent material, as shown in Fig. 5.6.

A comparison of noise absorption coefficients of carpet composites with its parent materials - virgin carpet and the epoxy matrix is as shown in Fig. 5.6. The following observations were made from the Fig. 5.6.

- It can be observed that the 4 layer carpet composite performs better than the virgin carpet material and the epoxy matrix at higher frequencies, in the range of 1000 Hz to 4000 Hz, which is the most critical sound frequency range for a highway noise barrier.

- It can be observed that the 4 layer carpet composite tries its best to mimic the superior noise absorption properties of virgin carpet.
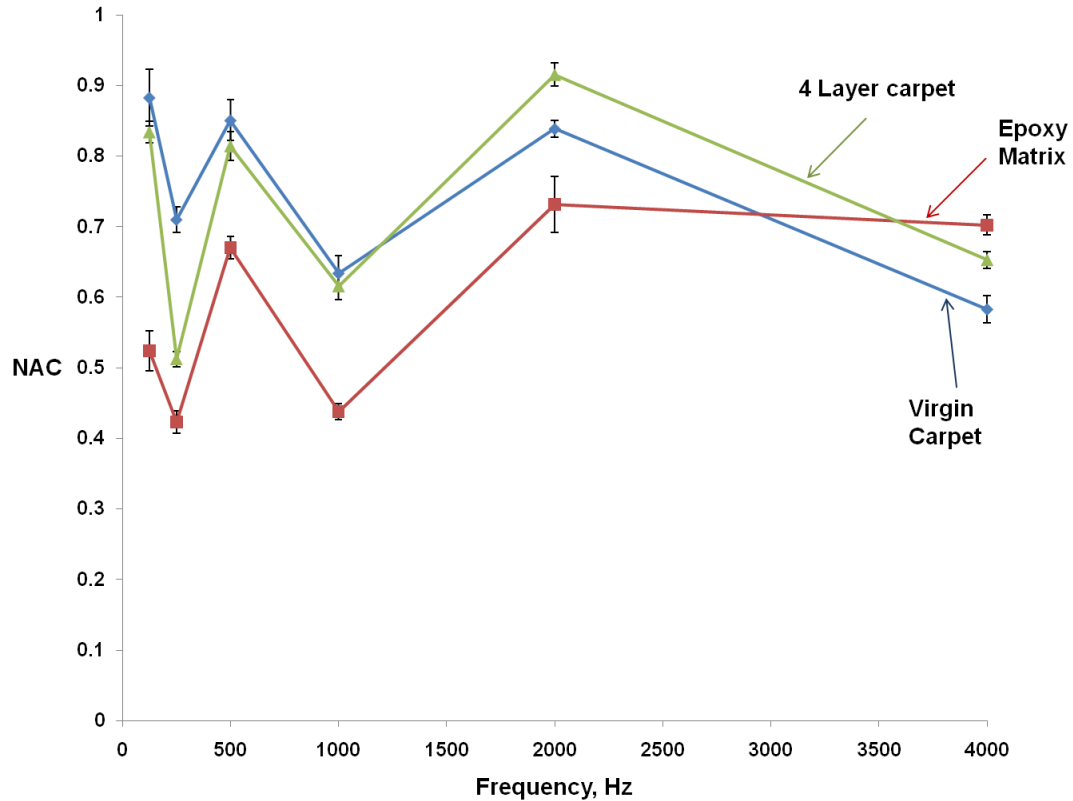
Fig. 5.6 Comparison of Noise Absorption coefficients of 4 layer carpet composite with its parent material calculated at the third octave band range of frequencies using ASTM C 384 -04

- The 4 layer carpet composite behave closely to the nature of variation of NAC for carpet and epoxy matrix at lower frequency range. But at higher frequency range it behaves like virgin carpet, rather with higher NAC. The epoxy matrix in itself is poor in noise absorption at higher frequencies like 1000 Hz and 2000 Hz and therefore has minimal influence on the behavior of 4 layer carpet composite NAC variation.

A similar observation can be made for BTTB carpet composite which mimics the NAC behavior of Epoxy matrix over the range of frequencies from 125 Hz to 4000 Hz. This has been presented in Fig. 5.7 to give a comparison of NAC's of epoxy matrix and BTTB carpet composite.

- The acoustic performance of BTTB Carpet composite is lesser than epoxy matrix in the third octave band range of frequencies but the nature of the plot is similar. It can be

clearly seen that the BTTB carpet composite mimics the NAC behavior of Epoxy matrix at both low and high frequency ranges.
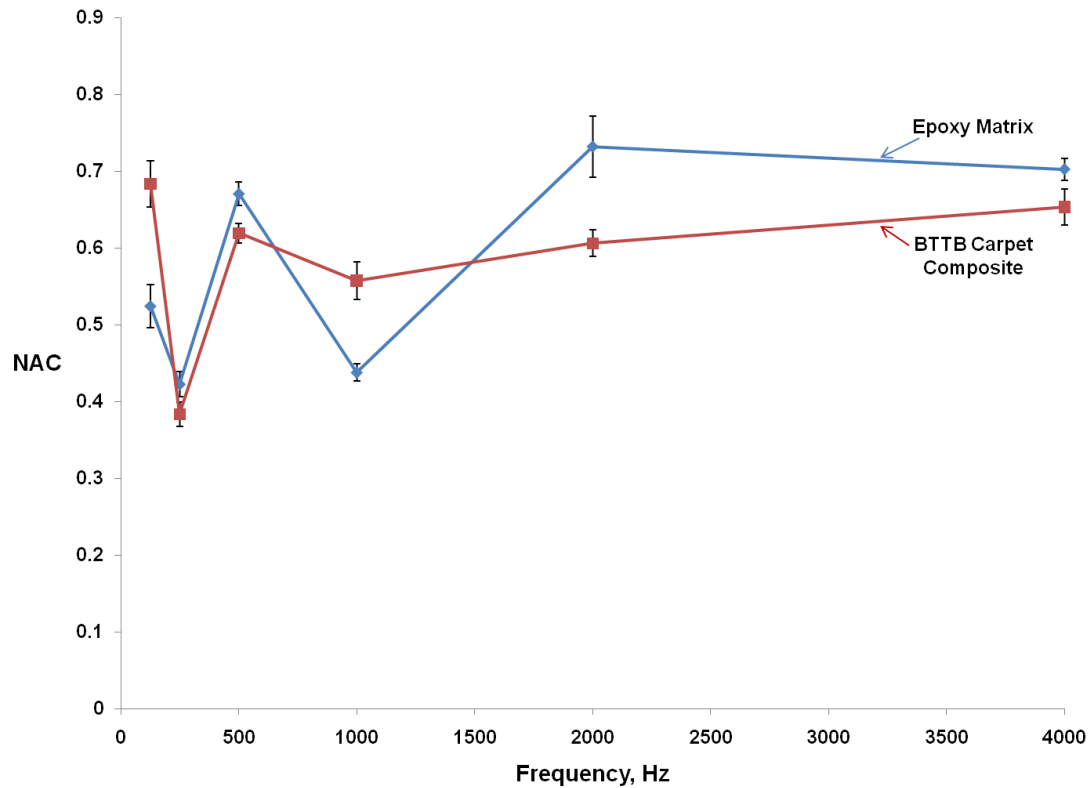
Fig. 5.7 Similarity of acoustic behavior of BTTB carpet composite material and Epoxy Matrix calculated at the third octave band range of frequencies using ASTM C 384 -04

- BTTB carpet composites have the poorest acoustic performance in comparison to the acoustic performance of all the carpet composites. Because BTTB arrangement has Bottom - Top - Top - Bottom, type of arrangement the reinforcement for BTTB carpet composites is provided by the Polypropylene backing of the carpet instead of the nylon fibers. The Polypropylene backing is the flat end of the carpet and therefore has no obstruction for the resin flow during VARTM. This could be a potential reason for the epoxy matrix to play a dominant role in influencing the acoustic performance of the

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carpet composites instead of the virgin carpet. Hence the BTTB carpet composites mimic the NAC variation behavior of epoxy matrix composites.

- ▪ Therefore it is safe to conclude that amongst all the carpet composite configurations, it is safe to avoid BTTB carpet composite, because it would not make good highway noise barriers due to poor noise absorption characteristics.

Hence from the test it can be concluded that the noise absorption coefficient of proposed highway noise barrier that is, carpet composites is high in comparison to the currently used concrete highway noise barriers. Fig. 5.8 presents a comparison of noise absorption between the 4 layer carpet composite (the best noise absorption material) and concrete (the worst noise absorption material). The superior noise absorption characteristic of the 4 layer carpet composite is evident from Fig. 5.8.
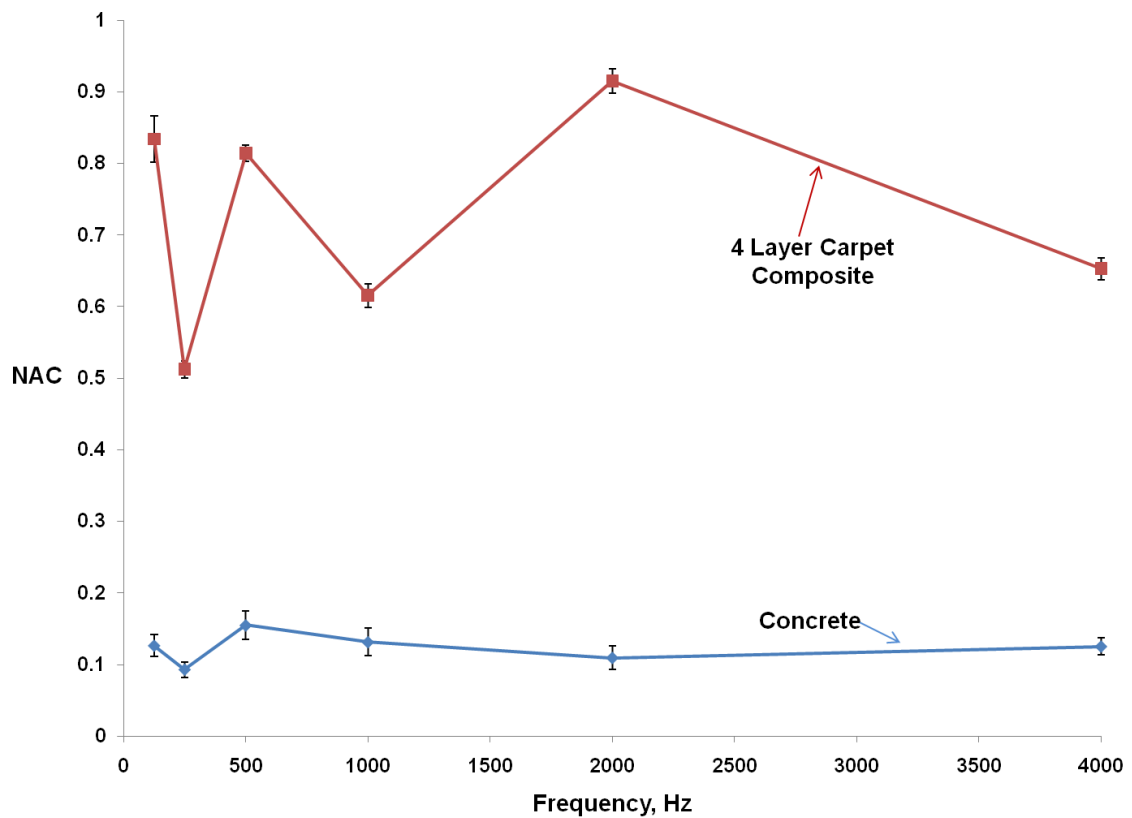
Fig. 5.8 Acoustic property comparison of concrete and 4 layer carpet composite

NAC gives a detailed comparison of the noise absorption of the material over a broad range of frequencies. However there is a need for a parameter which helps in direct comparison of noise absorption of all the materials. Noise Reduction Coefficient (NRC) represents a single number, which is the average of value of all the absorption coefficients of the material at the frequencies 125, 250, 500, 1000, 2000 and 4000 Hz. NRC was calculated for all the materials and the plot in Fig. 5.9 illustrates the difference in NRC's for all the 12 materials tested for noise absorption.
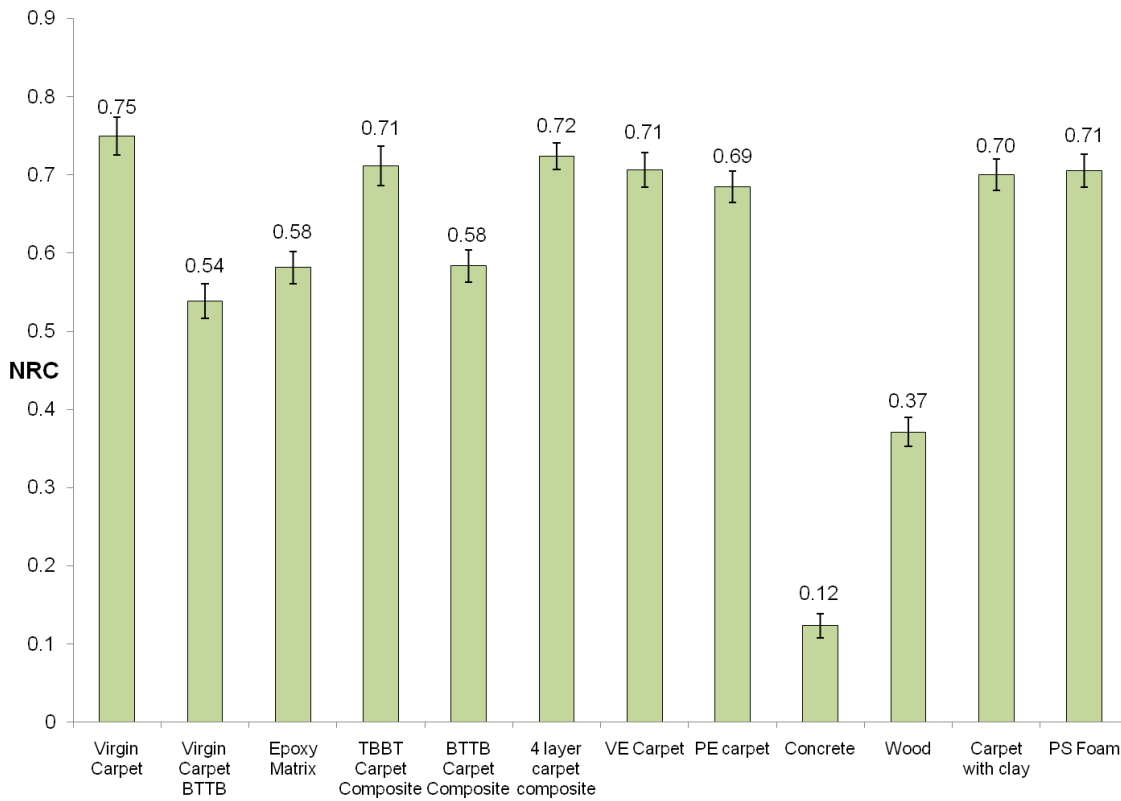
Fig. 5.9 Noise Reduction Coefficients of all the materials calculated at the third octave band range of frequencies using ASTM C 384 -04

The following observations can be made on the basis of analysis of the values of NRC from Fig. 5.9 -

- It can be seen that the NRC of 4 layer carpet composite (best absorbing material) is the highest and the NRC of concrete (worst absorbing material) is the lowest.

- The NRC of BTTB carpet composite is close to the NRC value of epoxy matrix and therefore confirms the influence of epoxy matrix in determination of noise absorption characteristics of BTTB carpet composite. This also indicates that there is no significant acoustic contribution by the reinforcement which has occurred in the BTTB composite formed by VARTM of carpet in BTTB lay - up with epoxy matrix as the thermoset matrix.

- The NRC of virgin carpet is the highest amongst all the 12 materials tested for noise absorption. But poor mechanical properties of the virgin carpet would disqualify it as a good highway noise barrier. Hence the 4 layer carpet composite which is only next to virgin carpet with a high NRC value of 0.72 can be proposed as a good highway noise barrier.

- The carpet composites have good noise absorption properties compared to wood and concrete which are the traditional highway noise barrier materials.

An attempt was made to understand the correlation between the specific gravity of the material and its acoustic properties. It can be roughly said that the acoustic properties are better for a material with higher specific gravity. This can be inferred from Fig. 5.10 below, where the 4 layer carpet composite material with highest specific gravity of 12.07 also had the highest NRC of 0.72 among all the carpet composites tested for acoustic characterization.
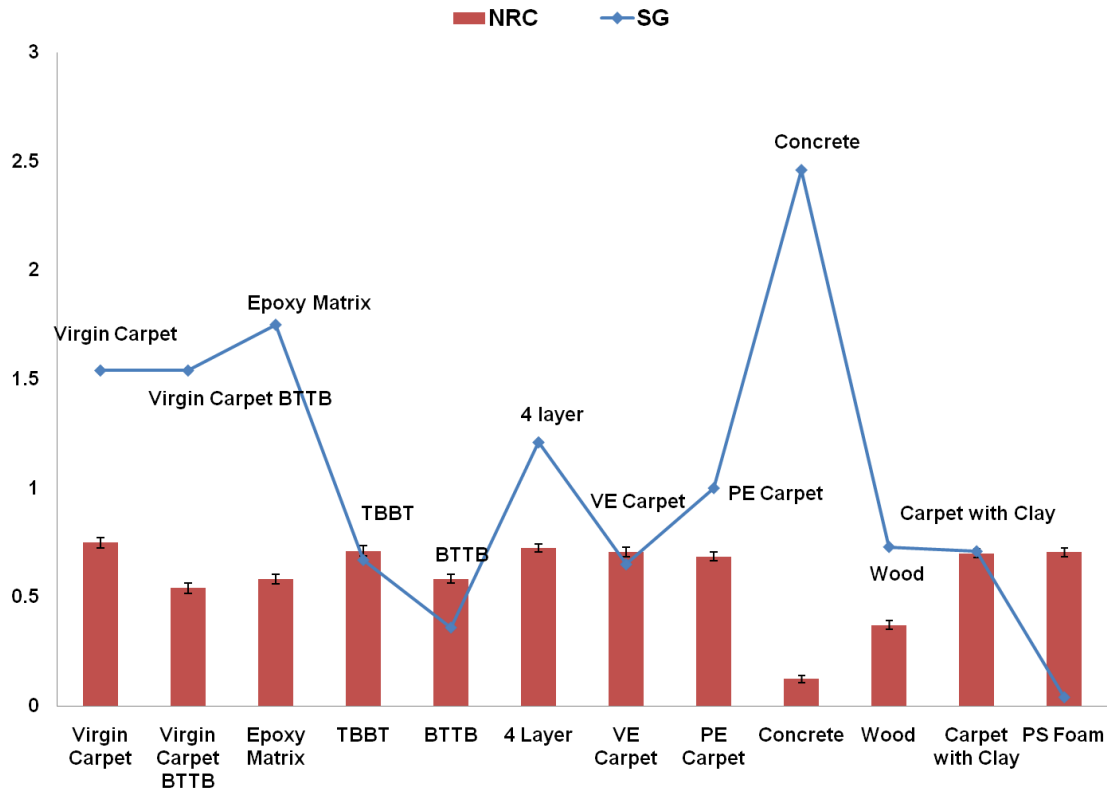
Fig. 5.10 Correlation of Noise Reduction Coefficients (NRC) with Specific Gravity (SG)

The following observations can be made from Fig. 5.10 -

- A material with higher specific gravity would have lower noise reduction coefficient. This can be seen on a comparison of high specific gravity material like Concrete with a low specific gravity material like PS Foam, where PS Foam yielded better noise reduction characteristics in comparison to concrete.

- Carpet composites have lower specific gravity and therefore have higher noise reduction coefficient in comparison to materials like concrete and wood. Hence it can be concluded that carpet composites have better noise reduction capabilities than concrete or wood.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

This work focuses on the acoustic testing of carpet composites manufactured by scaled up VARTM fabrication process. The acoustic results for six different set of carpet composites indicated excellent absorption properties of the carpet composites and therefore it could have a potential application as highway noise barriers. The contributions of this work include:

1) Scaling up of VARTM process for fabrication of large scale carpet composites. The capabilities of the scale up include:

    1. Feasibility of making large composites of size more than 0.61 m x 0.61 m with uniform thickness.

    2. Fabrication of curved shaped panels by the scale up of VARTM process.

    3. One of the powerful features of the process scale-up of VARTM practiced is the exclusion of hot press used in VARTM process. Hot press restricts the size and shape of the final part of the composite and by avoiding it, the scaled up the process.

2) Product scale up included the addition of PVP-clay 3% nanocomposite films in the carpet composite by the scaled up VARTM process. The clay nanofiller can act as a fire retardant and probably prevent the carpet composites from undergoing environmental degradation by UV and moisture. The PVP Clay 3% nanocomposite film used as filler was a well exfoliated film.

3) Application of the carpet composites prepared by scaled up VARTM process as Highway Noise Barriers:

    a. It was demonstrated that Carpet composites have excellent absorption properties with a noise absorption coefficient in the range of 0.70.

    b. Addition of clay to the carpet composites did not make a significant difference in the noise absorption capabilities of the carpet composites.

    c. Changing the resin system did not make any significant improvement of decline in the noise absorption of carpet composites.

    d. The BTTB carpet composites have an acoustic performance similar to the epoxy matrix – which indicates that the noise absorption properties of carpet have no contribution in this type of configuration of composites.

    e. The acoustic test results indicated that the carpet composites could have an acoustic performance better then the epoxy matrix, but they do not seem to match the sound absorption capabilities of virgin carpet material. However on the basis of the experiments, the performance of the carpet composites is estimated to be better than both the virgin carpet and the epoxy matrix at higher frequencies.

    f. On the basis of the acoustic measurements of concrete and other materials it can be estimated that the carpet composites can absorb more sound than concrete. Hence there is a possibility for carpet composites as alternative highway noise barrier material.

6.2 RECOMMENDATIONS

In this section, remedial actions for preliminary characterization tests conducted like the UV degradation test, incorporation of clay nanofiller and some future investigations desired in this study have been discussed.

The following are recommended as valuable future work for this study:

1) To conduct wind load tests to check the wind load bearing capacity for the structures made out of carpet composites. This work is being currently worked at OSU Civil Engineering.

2) Investigation of change in mechanical properties of carpet composites due to incorporation of voids. It is recommended to measure the porosity and its effect on the strength of the carpet composites.

3) Effect of PVP-Clay film incorporation on the mechanical properties of the carpet composites. To paint the carpet with clay-PVP films before the VARTM process. It has been seen in similar studies for incorporation of POSS nanofillers in carbon fiber composites that the flexural strength and fracture toughness of the composite increases if the painting approach for incorporating nano-fillers is preferred over the film based approach. It can therefore be believed that a similar strategy could be used for this study.

4) The carpet composites can be attached to the already existing concrete noise barriers for a period of nine months and be tested for their endurance to weather and handling involved in mounting and demounting. Also the measurement of roadside noise levels for the carpet composite can be achieved if this is done. The measurements can be made for six 10 minute periods by placing microphones at various heights above the ground. There have been studies which have conducted similar studies for different materials. Freezing and thawing approach could be used to analyze the damage caused to the carpet composites by capillary action of salt water. Considering acid rain effects and effects due to water mixed with salt sprayed on roads, there is a high possibility of this water attacking the carpet composite walls.

5) Detailed cost analysis and economic feasibility for efficient technology transfer of the scaled up VARTM process is a recommended future work in this study.

6) The ASTM C 384-04, noise absorption test while typical of those conducted for acoustical materials on one hand and concrete highway use products on the other, is not necessarily the best or only test for this application. There are several other ASTM standard tests like the ASTM E 90 for instance which measures the transmission loss in dB, thereby aiding in to calculate the A-weighted noise absorption by the materials as per Department of Transportation (DOT) and American Association of State Highway and Transportation Officials (AASHTO) specifications.

Hence there is immense scope for innovation in the study and the technology transfer of carpet composites made by scaled up VARTM process and enhanced research in this area would help understand its improvisation.

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APPENDIX A: CASE STUDIES IN VARTM

Apart from the variations in VARTM methods to understand VARTM processability and scale - up there were a few other experiments carried out during this study which even though did not yield convincing results but could be crucial in setting forth new pathways in this study. This appendix enlists such attempts made during the course of the study.

A.1 PVC-Carpet Hybrid Composites

An attempt was made to recycle both PVC and nylon based carpets into unique hybrid carpet composites. As seen in the Fig. A.1 the PVC sheet was sandwiched between two layers of carpet and VARTM was carried out.

Fig. A.1 An image of PVC - Carpet Hybrid composite

The sole purpose of fabrication of this composite was to recycle the PVC in landfills which is equally a menace as waste carpet. However this attempt was not successful because the carpet composite easily delaminated and had low strength.

Hence a preliminary investigation for non - compatibility was carried out. By analyzing the individual material properties of PVC and nylon, it was seen that PVC softens at its glass transition temperature but it does not melt, rather contracts at higher temperatures. While carpet, due to nylon melts at 210 $^{\circ}$C, it does not bond with PVC. Compatibilizers are available in the market for polymer blending of polymers in extruded powder forms or in ground state. However compatibilization did not work for the VARTM technique used for fabrication of composites of PVC - carpet hybrid composites. The compatibilizers tried were Polyethylene - graft - maleic anhydride (PE-g-MAH) and Polypropylene-graft-maleic anhydride (PP-g-MAH). An alternate terpolymer, ethylene-n-butyl acrylate-monoxide grafted maleic anhydride (EnBACO-g-MAH) might work because it is used for alloying of PVC with Nylon in the powder form. EnBACO-g-MAH was sold by DuPont by the commercial name Elvaloy Terpolymer in its Fusabond family of chemicals; however this product has now been discounted by DuPont which was the sole manufacturer of this chemical. It was decided that this research dimension would not be probed any further due to lack of any results.

A.2 Soy bean oil resin

An attempt was made to try a non-petrochemical based resin to make the VARTM process completely green. Soy bean oil resin can be used to make composites, however for VARTM of soy based resins there were some problems. Soy based resins are tri-glycidyl esters and therefore for curing these resins there is a need to cross link them with styrene (which in turn is a petrochemical product). Since the aim was to avoid petrochemical products completely and therefore improvise the process of making greener recycling techniques more green. Epoxidized soybean oil (ESO) resin was tried as an alternative, which has epoxy rings at the ends of the soy bean oil composition. The thought process behind selection of this resin was to check if the epoxy curing agents could be used directly for curing and thereby avoiding the use of styrene to crosslink the resin. This was unsuccessful because the resin did not cure using the epoxy curing

agent. Attempts were made to cure ESO with a combination of Jeffamine curing agent with Cobalt Napthenate (Co Np), Dicumyl peroxide and Tung Oil. However even then, the resin did not cure because styrene is needed to copolymerize the resin. It was decided to further modify the resin or choose a resin which is already modified, and hence acrylated epoxidized soy bean oil (AESO) was chosen. The problem with this resin was the same as Styrene was still needed to copolymerize the resin.

A.3 Resin Specifications

The following are the specifications of the Epoxy 2120 resin hardener used as shown in the following table

TABLE A.5

A TABLE INDICATING THE PHYSICAL PROPERTIES OF THE EPOXY HARDENER

	Epoxy 2120
Color	Amber
Viscosity @ 77 ^{0}F, centipoises	200 - 250 cps
Specific gravity, g / cc	0.95
Mix ratio, by wt.	100:27 by weight or 3 to 1 by volume
Pot Life	2 hour

APPENDIX B: STATISTICAL ERROR TABLES

The following table, Table B.1 to Table B.12 give information about the statistical standard error occurred in the experiment conducted as per ASTM C-384 04:

TABLE B.1

A TABLE INDICATING THE STATISTICAL STANDARD ERRORS IN NAC
MEASUREMENTS OF VIRGIN CARPET TBBT

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.88	4.04
2	250	0.71	1.83
3	500	0.85	2.86
4	1000	0.63	2.50
5	2000	0.82	1.22
6	4000	0.58	1.91

TABLE B.2

A TABLE INDICATING THE STATISTICAL STANDARD ERRORS IN NAC
MEASUREMENTS OF VIRGIN CARPET BTTB

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.80	4.62
2	250	0.66	1.86
3	500	0.45	2.53
4	1000	0.49	1.48
5	2000	0.53	1.76
6	4000	0.35	1.83

TABLE B.3

A TABLE INDICATING THE NAC VALUES STATISTICAL STANDARD ERRORS
IN ACOUSTIC MEASUREMENTS OF EPOXY MATRIX

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.52	2.83
2	250	0.52	1.61
3	500	0.80	1.54
4	1000	0.73	1.14
5	2000	0.86	3.97
6	4000	0.63	1.39

TABLE B.4

A TABLE INDICATING THE NAC VALUES STATISTICAL STANDARD ERRORS
IN ACOUSTIC MEASUREMENTS OF TBBT CARPET COMPOSITE

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.74	2.89
2	250	0.42	2.46
3	500	0.69	2.03
4	1000	0.45	2.37
5	2000	0.73	2.89
6	4000	0.69	2.52

TABLE B.5

A TABLE INDICATING THE NAC VALUES STATISTICAL STANDARD ERRORS
IN ACOUSTIC MEASUREMENTS OF BTTB CARPET COMPOSITE

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.68	3.05
2	250	0.35	1.58
3	500	0.62	1.25
4	1000	0.56	2.44
5	2000	0.60	1.75
6	4000	0.61	2.35

TABLE B.6

A TABLE INDICATING THE NAC VALUES STATISTICAL STANDARD ERRORS
IN ACOUSTIC MEASUREMENTS OF 4-LAYER CARPET COMPOSITE

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.83	3.20
2	250	0.51	1.21
3	500	0.82	1.16
4	1000	0.61	1.64
5	2000	0.91	1.71
6	4000	0.65	1.53

TABLE B.7

A TABLE INDICATING THE NAC VALUES STATISTICAL STANDARD ERRORS
IN ACOUSTIC MEASUREMENTS OF VE CARPET COMPOSITE

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.74	3.54
2	250	0.56	1.97
3	500	0.79	1.25
4	1000	0.73	2.51
5	2000	0.86	2.41
6	4000	0.52	1.51

TABLE B.8

A TABLE INDICATING THE NAC VALUES STATISTICAL STANDARD ERRORS
IN ACOUSTIC MEASUREMENTS OF PE CARPET COMPOSITE

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.77	1.59
2	250	0.47	2.46
3	500	0.82	2.03
4	1000	0.67	2.37
5	2000	0.83	0.90
6	4000	0.49	2.52

TABLE B.9

A TABLE INDICATING THE NAC VALUES STATISTICAL STANDARD ERRORS
IN ACOUSTIC MEASUREMENTS OF CONCRETE

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.13	1.53
2	250	0.09	1.07
3	500	0.16	2.01
4	1000	0.13	1.92
5	2000	0.11	1.64
6	4000	0.12	1.18

TABLE B.10

A TABLE INDICATING THE NAC VALUES STATISTICAL STANDARD ERRORS
IN ACOUSTIC MEASUREMENTS OF WOOD

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.30	1.94
2	250	0.33	1.12
3	500	0.48	1.58
4	1000	0.34	1.43
5	2000	0.33	2.28
6	4000	0.45	2.86

TABLE B.11

A TABLE INDICATING THE NAC VALUES STATISTICAL STANDARD ERRORS
IN ACOUSTIC MEASUREMENTS OF CLAY BASED CARPET COMPOSITE

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.68	3.27
2	250	0.57	1.73
3	500	0.82	1.15
4	1000	0.64	1.72
5	2000	0.85	2.56
6	4000	0.63	1.63

TABLE B.12

A TABLE INDICATING THE NAC VALUES STATISTICAL STANDARD ERRORS
IN ACOUSTIC MEASUREMENTS OF PS FOAM

Sr. No.	Frequency, Hz	NAC	Std. Error (in %)
1	125	0.69	2.57
2	250	0.82	3.00
3	500	0.92	1.04
4	1000	0.63	1.11
5	2000	0.65	2.89
6	4000	0.51	1.92

VITA

Krishnan Lakshminarayanan

Candidate for the Degree of

Master of Science

Thesis: SCALING UP OF MANUFACTURING PROCESSES OF RECYCLED
CARPET BASED COMPOSITES

Major Field: Chemical Engineering

Biographical:

Education:

- Completed the requirements for the Master of Science in Chemical
  Engineering at Oklahoma State University, Stillwater, Oklahoma in July,
  2011.

- Completed the requirements for the Bachelor of Science in Chemical
  Engineering at University of Mumbai, Mumbai, India in 2007.

Experience:

- Worked as an Operations Engineer Trainee at Indian Oil Tanking, Goa,
  India, 2007.
- Worked as a Senior Research Associate at Avalon Global Research,
  Mumbai, India, 2007-2009.
- Employed at Next Generation Materials Lab at OSU - Tulsa, as a
  Research Assistant, 2010 - present.

Professional Memberships: AIChE

Name: Krishnan Lakshminarayanan   Date of Degree: July, 2011

Institution: Oklahoma State University   Location: Stillwater, Oklahoma

Title of Study: SCALING UP MANUFACTURING OF RECYCLED CARPET BASED
                COMPOSITES

Pages in Study: 128   Candidate for the Degree of Master of Science

Major Field: Chemical Engineering

Scope and Method of Study:

This study focused on "Scaling up manufacturing of recycled carpet based composites" for recycling waste carpet by Vacuum Assisted Resin Transfer Molding (VARTM) process. The process was modified to fabricate large scale composites of larger size for its potential application as a highway noise barrier. The scope of this thesis included fabrication, characterization and analysis of the carpet based composites and their feasibility as highway noise barriers.

Findings and Conclusions:

This work focuses on the feasibility of recycling carpet into carpet composites which have a potential use as a highway noise barrier. A novel scaled up technique of VARTM was devised to fabricate the carpet composites. Large scale composite panels of the size 1.22 m x 0.61 m were made using the technique of scaling up of VARTM process. Acoustic characterization of the carpet composites revealed excellent noise absorption characteristics of the material.

ADVISER'S APPROVAL: Dr. Martin High