

EFFECT OF FIBER SURFACE TREATMENT IN CARPET
RECYCLING

By

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CHAPTER 1

INTRODUCTION

1.1 PROBLEM STATEMENT

Carpet is extensively used as a floor covering in households and commercial buildings. It is generally a pile of synthetic fibers tufted in a backing. Carpet is made to be very durable and long lasting, but after a certain period of time it needs to be replaced, and old carpet is disposed to landfills. In the United States, about 200 million metric tons (450 billion pounds) of carpet waste is generated every year. Only 2%, around 4 million tons (8.8 billion pounds) of this, is recycled [6]. Nearly all the rest of the waste is disposed into the landfills.

Post-consumer carpet accounts for approximately 1 wt.% and 2-vol.% of the municipal solid-waste stream in the United States, and this number is increasing every year [7]. Since the average life expectancy of a carpet is about 11 years [8], it has already become one of the largest components of post-consumer solid waste going to landfill. In addition, carpet is non-biodegradable, which diminishes the availability of landfills for other uses.

Apart from environmental problems, there are many economical aspects associated with carpet waste. These involve direct and indirect costs for the disposal of carpet waste. The direct cost includes the money given for discarding it to the landfill which is approximately equal to \$0.025/lb [9]. At present, carpet waste is discarded to landfills at a rate of \$100 million per year in the United States. The indirect cost associated with the disposal of carpet waste may include the discarding of valuable raw material in the form of high engineering value fibers going to landfills. These fibers involve Nylon 6,6, polypropylene, polyester, polyvinyl chloride etc.

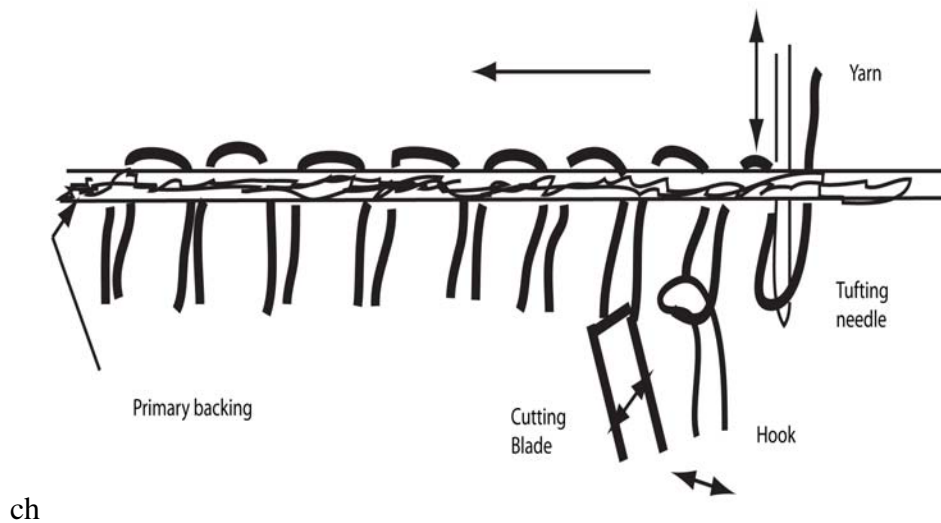
Mainly two types of carpet waste is generated, which can be broadly classified on their source of origin: pre-consumer carpet waste and post-consumer carpet waste. Pre-consumer carpet waste includes scrap generated during the process of making carpets for various consumer based applications, such as in automobiles, households or commercial buildings. As an example, in the case of automobiles, a considerable amount of carpet scrap is generated during the trimming and fitting process of cars. This scrap has a deformed and irregular shape and has no further use. Pre-consumer carpet waste accounts for about 12% of the total carpet discarded [7]. On the other hand, post-consumer waste includes used carpet generated due to exhaustion of its lifetime from the households and commercial buildings. In addition, used carpet from specialized sources, such as aircrafts, can contain chemical additives such as flame-retardents, stain resistant chemicals etc. This type of carpet waste contains various impurities, which makes its reuse or recycling process generally more complex.

Carpets are manufactured in various types and varieties, which are different from each other. So it becomes important to study the variety and types of carpet manufactured—their construction and how they are manufactured.

1.2 CARPET CONSTRUCTION

Broadly, carpet can be classified as per its construction and the face fiber materials used in carpet. Based on the construction, carpet is classified as cut-pile, level-loop, and multilevel-loop. Additionally, based on face fiber material, carpet is classified as Nylon 6, Nylon 6,6, polypropylene, olefin, polyester, and polyvinyl chloride. Generally, carpet consists of face fibers, primary backing, secondary backing, adhesive, and filler materials. Primary backing is the material into which yarn of face fibers is tufted. Secondary backing is the material laminated to the back of the carpet pile. The backings could either be woven or non-woven, and are generally made up of polypropylene or polyester. Tufting is the most common method used for manufacturing carpet. Tufting is a process of forming a loop of

fiber yarn across a woven textile backing material as shown in Fig. 1.1. In this process, the backing substrate is passed under a set of needles carrying fiber yarn. Then these needles are inserted through the backing and drawn back. This process is repeated several times to create a continuous loop of fibers tufted through the primary backing. This loop of continuous fiber yarn can be cut or sheared to form a cut pile or it can be left as it is to form a level-loop or multilevel-loop. Adhesive is used to bond secondary backing with primary backing tufted with the fiber yarn. Filler material is mixed with adhesive to cover the entire area of secondary backing. Figure 1.2 shows the application of secondary backing.



ch
Figure 1.1: Tufting method to manufacture carpet pile, adapted from [1].

The two most common types of carpet found in the US are cut-pile and level-loop as shown in fig 1.3. Generally household cut-pile carpet consists of 50% by weight face fiber. These are typically Nylon 6, or Nylon 6,6. The primary and secondary backing constitutes 10% of total carpet material, which is generally made up of polypropylene. Adhesive used for the adhesion of face-fibers and backings is styrene-butadiene and constitutes 9% of total carpet weight. Around 25–30 wt.% of the filler used in the carpet, is calcium carbonate. The other mostly used type of carpet is level-loop type of carpet. It has generally olefin as face fibers and polypropylene as the backing. It is also manufactured by using polypropylene as

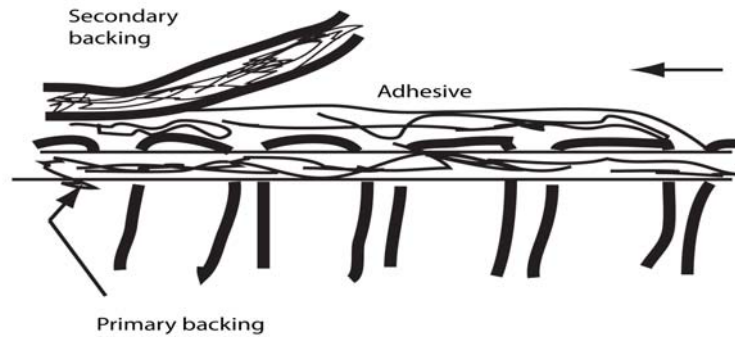
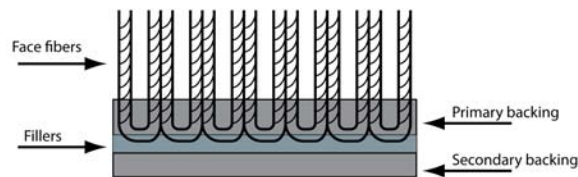


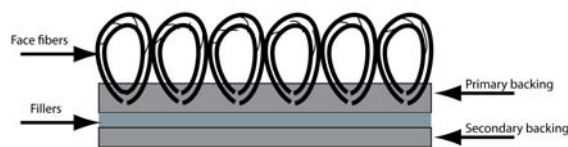
Figure 1.2: Application of secondary backing, adapted from [1].

the face fibers and the backing.

This chemical and physical diversity in carpet makes it very difficult to recycle carpet waste. Nonetheless, a lot of research work has been done to recycle carpet waste, which is discussed in next section.



(a) Typical construction of cut-pile type of carpet.



(b) Typical construction of level-loop type of carpet.

Figure 1.3: Architecture of the two most common type of carpet used.

1.3 CONVENTIONAL CARPET RECYCLING TECHNIQUES

There has been a considerable interest in developing techniques to recycle carpet waste. However, it is very challenging to recycle carpet because of its multicomponent structure which is chemically diverse in nature. Several recycling approaches have been proposed

so far, which differ by the type of process used and consequently by type and quality of the product generated. The recycling of carpet waste has been classified into four main categories [10]:

Primary recycling or depolymerization: This involves converting the constituents of carpet into their monomers. It is a chemical process which breaks down the polymers into monomers, which could again be polymerized.

Secondary recycling or polyamide extraction: This mainly includes the separation of individual components without breaking them down into their monomers. It involves separation of fibers and backing using shredders and choppers.

Tertiary recycling or melt-blending: This involves preparing a mixture of all the components of carpet by melt blending. It does not involve separation of face fibers and backing. The mixture thus obtained is used for making secondary low-cost plastic materials.

Quaternary recycling or incineration: This includes the recovery of energy by simply burning down the polymer waste in the kilns.

1.3.1 Primary Recycling or Depolymerization

Many researchers have studied this process in carpet recycling. It is a chemical process which converts face fibers into their monomeric form. This approach involves separation of the face fibers from backing and then chemically converting them into their monomers. Mainly the depolymerization of Nylon 6 occurs in an initiation or de-propagation step [11]. Water is used as the initiator of the process. Since this is an endothermic reaction, it requires high temperature, so superheated steam is used to provide high temperature. Water or steam also acts as a reaction initiator. The temperature is kept around 267 °C, which is the melting point for caprolactam. This process results in a heterogenous mixtures of polymer waste and gaseous phase caprolactam. The gas is taken out from the reactor along with

the steam. The reaction takes place at low pressure because it is easy to separate monomers. Sometimes catalysts such as Lewis acid, Brnsted acid and bases, are also added to accelerate the reaction [11].

Various polymers, and precursor can be extracted from this polymer waste. Mckinney *et al.* [12] have done recovery of hexamethylene diamine and adipic acid (monomers of Nylon 6,6) from the mixture of polymers using ammonolysis. The process takes place in the presence of ammonia at high temperature and pressure. One mole of ammonia is required for each mole of the amide group. The reaction temperature is kept between 300 °C to 350 °C, and pressure in between 500–2500 psig. The products formed from this process usually consist of hexamethylene dimine (HMD), 5-cyanovaleramide (CVAM), adiponitrile (ADN), caprolactam (CL), 6-aminocaproamide (6-ACAM) and 6-aminocapronitrile (6ACN). The monomers are separated into different stream. CVAM, ADN, and ACAM are converted into HDM by hydrogenation, which is the monomer for Nylon 6,6.

Hendrix *et al.* [13] developed a process to depolymerize polymers to monomers using at least one nitrogen containing compound. The nitrogen containing compounds could be ammonia, or primary, secondary or tertiary amines. The boiling point of the chosen material should be below the boiling point of amide (267 °C). They also discussed that catalysts like Lewis acids help in the reaction and product quality.

Depolymerization using acid-catalysts has also been tried in carpet recycling. This process was based on a process developed by Crescenti *et al.* [14] to recover caprolactam from cyclic oligomers of Nylon 6. However, it had a drawback that most of the acid catalyst was used up by calcium carbonate present as a filler in carpet. So separation of face fibers was necessary before feeding it to the reactor. But, Corbin *et al.* [15] carried out depolymerization of such mixture by using phosphoric acid. In this process no separation of fibers was needed. But the disadvantage of this process was that other components of carpet could not be recovered. This process involved the direct feed of carpet waste to the reactor having phosphoric acid 5 to 7 wt% concentration.

Boric acid and phosphate salts could also be used as catalysts. Superheated steam of temperature 250 °C to 280 °C was also used. Caprolactam was obtained as the final product from the reactor, while by-product such as polypropylene backing was fed to a kiln to recover heat energy. It is the preferred route of carpet recycling to recover the raw material, since it breaks down the carpet fibers into the corresponding monomers with quality as high as of commercially available nylon 6,6. Moran *et al.* [16] developed a process to depolymerize Nylon 6 and Nylon 6,6 fibers sheared from the carpet using carboxylic acid. In this process carboxylic acid acted as one of the reactants. Acetic acid and propionic acid were also used as the carboxylic acid. Nylon 6 required one mole of acid per two moles of repeating unit, while Nylon 6,6 required two moles of acid per mole of repeating unit. Nylon 6 is converted to caprolactam and Nylon 6,6 to adipic acid. The by-products of this methods were 6-alkylamidohexanoic acid and N,N'-hexamethylene bisalkylamide. To obtain caprolactam from these by-products they could be oxidized by air, oxygen or hydrogen peroxide.

Depolymerization using bases has also been used. Nielinger *et al.* [17] used potassium carbonate to obtain caprolactam from Nylon 6. In this process, potassium carbonate (0.5 to 2.5 wt%) and polyamides are heated up to 270–300 °C in an inert environment. The advantage of this process was that it avoided the use of water or steam, so no water removal step was required. The caprolactam was fractionated at the end of the process and was of purity as high as 90%.

Apart from acid-base catalytic reactions, processes that uses only superheated steam have also been developed. Braun *et al.* [9] invented a process which employed superheated steam as a heat source. Unlike previous processes this process did not require separation of face fibers from the carpet. However, the carpet waste needed to be melted prior to the depolymerization. The melt carpet waste was sent to a contact reactor which was heated to 290–340 °C and pressurized to a pressure of 15 atm. Then the melt from the reactor was contacted with a jet of super heated steam. The heat from the steam helped in the

depolymerization reaction. The gaseous phase caprolactam was collected in an overhead duct and then condensed to caprolactam. Jenczewski *et al.* [18] used a high pressure pump to introduce the carpet waste melt into the reactor. Water was then injected in to the reactor and the mixture is heated to 250–350 °C and a high pressure was maintained up to 2700 psi. At the end of the process a mixture of monomers and insoluble wastes of carpet were left behind. Upon the cooling of the reactor the insolubles solidified and hence separated from the monomers which were in liquid phase.

Pyrolysis (reaction in the absence of oxygen at high temperature) was studied by Czernik *et al.* [19]. The group investigated the catalytic pyrolysis of Nylon 6 to caprolactam. The process employed a fluidized bed reactor in the presence of potassium hydroxide as a catalyst, at 300–700°C.

1.3.2 Secondary Recycling by Polyamide Extraction

This is a secondary recycling process that involves the recovery of the components of carpet without breaking them down to their monomers. It is also known as the physical approach. Usually fibers are separated from the backing using mechanical shredders. The fibers thus obtained are injection molded into other products. Subramaniam *et al.* [20] proposed a method which used organic solvents at high temperature to separate different components in different steps. The selection of the right solvent was the most important step in this method. Organic solvents such as polyol or an aliphatic carboxylic acid were used. On cooling the polyamide, dissolved in the solvent, could be separated out. The main disadvantage of this method was the possibility of solvents reacting with the polymer mixture. At such high temperatures, solvents might react with the polyamide causing depolymerization of polyamide. So quenching was used as an extra step to avoid any possible reaction.

Stefandl [21] proposed a method of using glycolic compounds to extract polyamides. This method was based on the solubility of polyamide as a function of temperature. Nylon 6 dissolves in glycerol at 155 °C, while Nylon 6,6 dissolves at 195 °C. The solution of

glycerol and carpet waste was heated to 160 °C then transferred to a separate vessel where it was collected by cooling it to a temperature of 40 °C. The precipitate of Nylon 6 was separated. Then the remaining solution was heated to 195 °C, then again by cooling it to 40 °C, the Nylon 6,6 residuals were collected.

Sikorski [22] used CO₂ as a supercritical fluid to dissolve carpet components. The components were dissolved in an increasing order of their melting point. Then they were transferred to a vessel where by decreasing temperature the components were extracted. Finally, Griffith *et al.* [23] used both solvent and super critical fluid to extract nylon 6,6 from the carpet. First the carpet waste was dissolved in an organic solvent, for example formic acid solution. Then super critical CO₂ was used to separate the nylon 6,6 from the solution. When fluid came in contact with the solution it diluted the solution and then it was redirected to the reactor. Nylon 6,6 was separated in powder form.

Apart from polymer extraction using organic solvents, many researchers have tried mechanical separation of carpet constituents, as this is one of the required step in depolymerization based recycling techniques. Haggquist and Hume [24] developed an apparatus for mechanical separation of Nylon fibers from the backing. In this process, the carpet was first sent to a conveyor belt, which passed it through a rotating blade. That sheared off continuous yarn of fibers from backings. Then the carpet was sent to a series of heat, water, and chemical treatments to separate the adhesives from the secondary backing. Then the carpet was treated with cup-brushes and then with the high-pressure rotating nozzle heaters to separate latex binder from the primary backing, leaving backing-fibers behind. Finally, the fibers from the backing were separated using rotating combs, which recovered fibers in a different chamber. The process was tedious and involved many steps.

Sharer *et al.* [25] developed a simpler and different approach to achieve the separation of the carpet materials. In this process the carpet was cut into small pieces of size two to four inches. Then these were sent to a granulator which ground the carpet pieces. This also started the separation of fibers from backings. Then high-pressure air stream was used

to recover Nylon fibers from the backing, which separated out in a chamber. The backing being heavier settled down and separated. This method however did not separate latex binder from the backing material.

Sferrazza *et al.* [26] developed a process using hammering after chopping the carpet into small pieces. A set of hammers was used to separate Nylon fibers from the backing, backing being more brittle than fibers helps in destroying the integrity of carpet. Then this material was sent to a air-separator. The fibers being lighter got separated in an overhead collector. The remaining material (backing and adhesive) was again sent to the unit to separate the remaining constituents.

1.3.3 Tertiary Recycling or Melt blending

This process does not require the separation of face fibers from the backing. In this approach the entire carpet is chopped into small pieces and then melt blended. Then this blend is extruded or injection molded to fabricate secondary plastic materials. Zhang *et al.* [27] shredded the carpet into the size of half square inch. The carpet pieces still contained adhesive and filler material. Then this shred was coated with a resin material such as phenolic or epoxy. The coated material was cured under a hot-press at a temperature around 150–190°C. The structural adhesive could also be used as a coating material. However, the final product obtained was of low quality and its properties depended on carpet's constituents and resin used.

Young *et al.* [10] developed a method to fabricate a thermoplastic homogenous material from waste carpet. The carpet was chopped into small size chunks and then transferred to twin-screw extruder. The extruder was kept at temperature around 210–230°C. But the product quality still remained low because of the incompatibility of Nylon 6,6 and polypropylene.

The compatibility of carpet's constituents has always been an issue in carpet recycling. Datta *et al.* [28] addressed this issue. Their study involved the effect of the compatibilizing

agents such as maleic anhydride grafted on polypropylene (PP). The properties of such blends of Nylon 6,6 and polypropylene was also studied. A similar study of using acrylic acid as a compatibilizer in blend of Nylon 6 and polypropylene was done by Dagli *et al.* [29]. This study showed that grafting acrylic acid on polypropylene could work as an effective compatibilization method. Mancosh *et al.* [2] first chopped or shredded the carpet waste and then the small size carpet waste was mixed or coated with a binder. This combination of carpet waste and binder was extruded to form a composite material. Later, in a following patent, the material was subjected to a high pressure and temperature under a press, along with the addition of some wood–flour fillers.

Wang *et al.* [30] tried to use waste carpet fibers to reinforce concrete and soil. The main disadvantage of this process was that it resulted in poor quality products that have lack of homogeneity. Albeit this process resulted in poor product quality, it is still assumed to be an attractive method due to the fact that the carpet ingredients need not to be separated.

1.3.4 Quaternary Recycling or Incineration

Other approaches that, have been studied, involve mechanical separation of the carpet fibers as well as incineration. The carpet used in incineration process is known as carpet derived fuel (CDF). The problems with the carpet derived fuels (CDF) are NO_x emissions and higher ash content than coal.

1.4 NEED OF AN EASY RECYCLING PROCESS

It is now clear that an optimal and low-energy process for carpet recycling is yet to be developed [31]. Some investigators have tried to simplify the method of manufacturing. However, the properties obtained from such composites were very low as compared to that of commercially available wood particleboard and other low cost plastic materials.

Given the challenges in recycling carpet, it would be advantageous to develop a technique that can achieve the following:

- Eliminate chopping, shredding, and energy intensive mechanical pre-processing steps.
- Use all types of carpet.
- Harness the three dimensional architecture of carpet.
- Provide flexibility and scalability to produce composites of various size as per the requirements.
- Ensure adaptability to components of various shapes and sizes.
- Produce products with high economic value and superior properties.

In this work we have utilized a different technique to fabricate composites from carpet waste directly, which does not require de-polymerization or mechanical separation. The waste carpet is taken and directly converted to the composite without any mechanical separation. Since this method needs no preprocessing like washing then separation of face fibers from the backing of the carpet and then chemical treatment, this fabrication technique saves the time and cost of recycling the carpet. Next chapter discusses the method used to fabricate composites from waste carpet, which fulfills all requirements listed above. It also focusses on the mechanical characterization of composites and their analysis.

CHAPTER 2

FABRICATION, CHARACTERIZATION AND ANALYSIS

The current investigation adopted a new technique to convert as-received carpet waste into structural composite laminates. This process involved the use of vacuum assisted resin transfer molding (VARTM) to infuse a polymer resin into the carpet face-fibers and the backing, as shown in Fig. 2.1. Then multiple such infused layers were stacked and cured under pressure so as to maintain a uniform thickness of the laminates. This process is a low energy process and comparatively easy to implement for various shapes and sizes. This technique also takes advantages of the mesh-like characteristics of the carpet backing, which helps in transferring the resin through out the carpet. Furthermore, vertical configuration of the face fibers helps in transferring the resin in Z-direction (along the face fibers, perpendicular to the backing).

2.1 FABRICATION OF CARPET LAMINATES

Two kinds of low-viscosity epoxy-based resins were used. The first was a two part (A+B), thermosetting epoxy resin system based on diglycidyl ether of bisphenol-A (DGEBA) (part A), commercially known as SC-79, that was acquired from Applied Poleramic Inc. (Benicia, CA, USA). This was a cyclo-aliphatic amine (part B, hardener) converted two-phase morphology epoxy which could be used for ambient VARTM processing. SC-79 required a cure cycle of 177 °C (350 °F) for one hour and room-temperature curing for 24 hours. The other resin used was vinyl ester (vinyl ester 1110, Fiber Glast Development Corp., Brookville, Ohio). Methyl ethyl ketone peroxide (MEKP) was used as the hardener, at

1.25% of the total weight of vinyl ester. The infused carpet layers with vinyl ester were cured at room temperature for 24 hrs. Then they were post cured at the temperature cycle of 80–100–120 °F for 6 hours, each temperature for 2 hours.

SC-79 is a high grade epoxy with high glass transition temperature, high toughness and is generally used for high temperature applications. On the other hand, vinyl ester is an ester based resin, which has good toughness and other mechanical properties but less than that of SC-79, but it is cheaper than SC-79. These two matrix materials were chosen to study the effect of epoxy and vinyl ester on the properties of the composites fabricated from waste carpet using same fabrication technique.

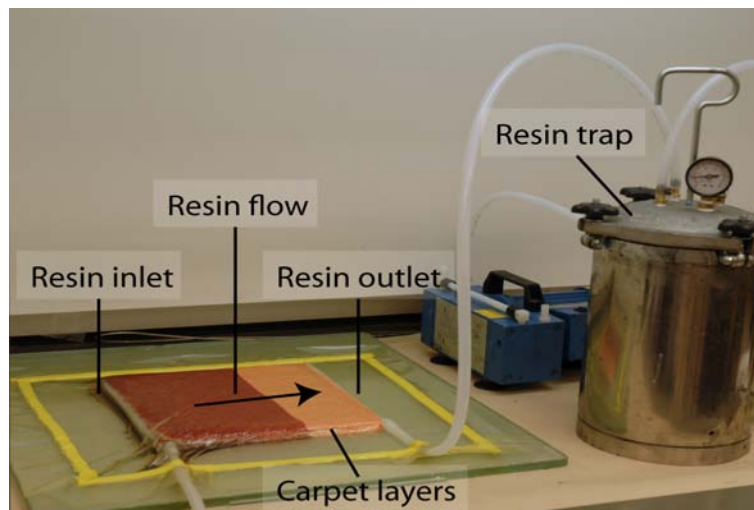


Figure 2.1: Vacuum assisted resin transfer molding of carpet laminates

The cut-loop type of carpet having Nylon 6,6 face fibers, and polypropylene backing, with a commercial designation Romper room / Orange cool-aid (Shaw Industries Group, Inc., Dalton, GA) was used. First, the carpet was cut uniformly in the sizes of 300×300 mm². Then one or multiple such layers of carpet were transferred under the vacuum bag in the set up of VARTM, in different orientations. For instance, face fibers of both the layers facing each other, backing of carpet layers facing each other, etc. In this method, no peel ply or transfer media were used, because the multi-dimensional structure of carpet helped in uniform infusion of resin. The resin infused carpet was directly taken to a press for

curing after the infusion process. The infused carpet layers were pressed to maintain the final thickness of the composite panel half of the initial thickness i.e. 12.7 mm.

Table 2.1 lists the layup sequences for the fabricated samples. Two configurations were fabricated for each kind of matrix system. In the case where the carpet backing forms the core, the composite was named as FBBF (face fibers, backing–backing, face fibers). On the other hand, in the case when the face fibers form the core the laminate was named BFFB (backing, face fibers–face fibers, backing). Finally, the fabricated composite panels were cut by using a simple table saw as recommended by the test standard ASTM D790-07 [32].

Table 2.1: Specimen fabrication

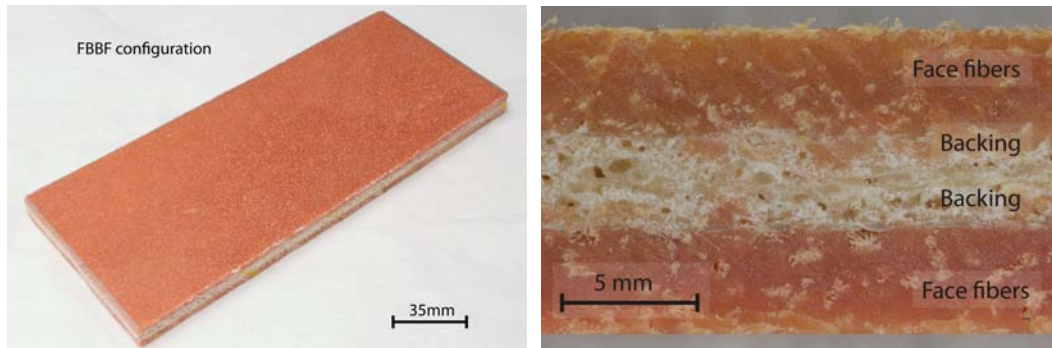
Sample no.	Face fibers	Configuration	Resin used
1–5	Nylon	FBBF – backing facing each other	SC 79
6–10	Nylon	BFFB – fibers facing each other	SC 79
11–15	Nylon	FBBF – backing facing each other	vinyl ester
15–20	Nylon	BFFB – fibers facing each other	vinyl ester

2.2 MATERIAL CHARACTERIZATION

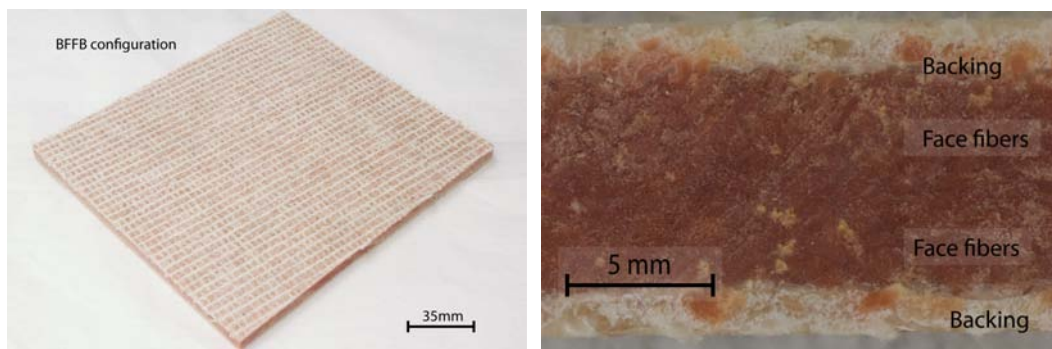
2.2.1 Optical Inspection

Figure 2.2 shows the surface and cross-sectional micrographs of Nylon based carpet composites. In this work, two layers were used for composite fabrication. A small piece was cut from a representative composite for optical inspection. These pieces were polished using an Ecomet 3 polisher (Buehler, Lake Bluff, Illinois, USA) using 800 grit paper to remove burrs that may have resulted from the cutting process.

It is evident, at this scale, that the laminates obtained from this molding process were smooth and well infiltrated by resin. Further porosity analysis proved the effectiveness of the infiltration this method. Furthermore, these variations in carpet layers could result in



(a) Top view of nylon based FBBF composite (b) Cross-sectional view of nylon based FBBF composite



(c) Top view of nylon based BFFB composite (d) Cross-sectional view of nylon based BFFB composite

Figure 2.2: Images of nylon based carpet composite panels prepared using VARTM process.

composites with different properties. In this fashion, more sequences can be designed to impart different properties to composites.

2.2.2 Density and Porosity Measurement

The density and porosity of the fabricated materials were determined, using the buoyancy method. The dry mass of the sample, W_a , was recorded. Subsequently, the composite sample was saturated using ultra-high purity water to fill all the open pores. A few drops of Photo-Flo[®] (Kodak Corporation, Rochester, New York, USA) were added to reduce the surface tension of water and aid in saturation. The apparent mass of the saturated sample while submerged in the fluid, W_b , was then determined using a density determination kit. The temperature of the saturation liquid was also recorded to compensate for the variations in the density of water, ρ_{fl} , as a function of temperature. Finally, the mass of the saturated sample, W_w , was determined by weighing in air. Any liquid that remained on the surface of the sample was removed with a damp sponge and the operation was performed quickly, to avoid loss of mass due to evaporation. Subsequently, the bulk density, ρ_{bulk} , was calculated as,

$$\rho_{bulk} = \frac{W_a}{W_w - W_b} \rho_{fl}. \quad (2.1)$$

The porosity of the samples was measured using an Ultrapycnometer 1000 (Quantachrome measurement). All the four types of samples were crushed using liquid nitrogen, into a powder form. Helium gas pycnometry was used to measure the solid or true density of the material. Then the total porosity was calculated using following equation,

$$Porosity(\%) = \frac{\rho_{true} - \rho_{bulk}}{\rho_{true}} \times 100 \quad (2.2)$$

where, ρ_{true} is the solid or true density of sample measured using the pycnometer.

2.2.3 Mechanical Characterization

The fabricated structural laminates were cut as per ASTM D 790-07 and tested for mechanical properties using the three point bend method. Flexural properties such as the flexural strength and flexural modulus were then evaluated. The samples were tested on using a table-top test frame (Instron[®] 5567, Instron Corporation, Norwood, Massachusetts, USA) as shown in Fig. 2.3.

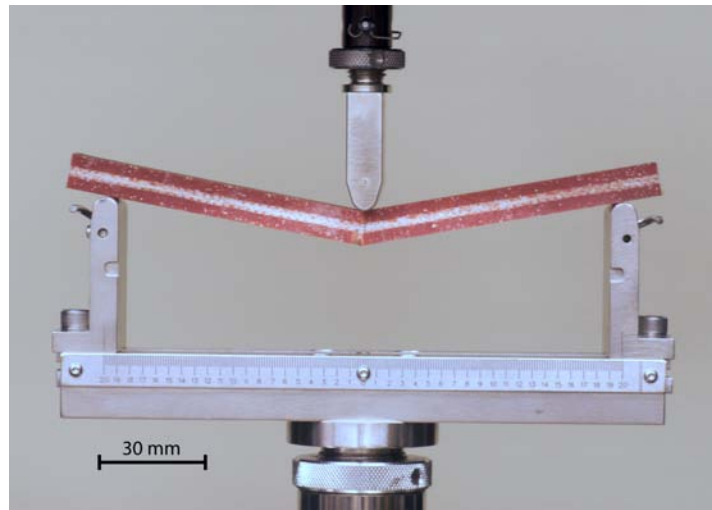


Figure 2.3: Three point bend flexure test of the carpet composite. A nylon based composite in FBBF configuration has been shown here at failure.

The loading rate for these tests was kept constant and was determined using the recommended standard as per Eqn. 2.3,

$$R = \frac{ZL^2}{6d} \quad (2.3)$$

where, R is the rate of crosshead motion (mm/min), L is the support span (mm), d is the depth of beam (mm), and Z is the rate of straining of the outer fiber measured in mm/mm/min. The straining rate of 0.1 mm/mm was chosen for these tests. In each of these experiments, a minimum of five samples were tested to ensure a fair representation of the test data. The results are presented in section 2.3.2.

The maximum flexural strength was determined using equation 2.4,

$$\sigma_{fmax} = \frac{3P_{max}L}{2bd^2} \quad (2.4)$$

where, σ_{fmax} is the maximum stress in the outer fibers at midpoint, P_{max} is the maximum load obtained in the load-deflection curve, L is the support span, b is the width of the beam tested, and d is depth of the beam tested.

Flexural modulus of the specimen is the ratio of flexural stress to corresponding flexural strain when constrained within the elastic limit. This was calculated using the Eqn. 2.5, where, the slope m is found on the steepest initial line on the load deflection curve.

$$E_B = \frac{L^3m}{4bd^3} \quad (2.5)$$

where, E_B is the modulus of elasticity in bending, L is the support span, b is the width of beam tested, d is the depth of beam tested, and m is the slope of the tangent to the initial straight-line portion of the load verses deflection curve.

2.3 RESULTS AND DISCUSSION

2.3.1 Density and Porosity

The density and porosity of the fabricated composites are summarized in Table 2.2. The densities of raw Nylon carpet, vinyl ester resin, and that of neat SC-79 were also measured using the same pycnometry technique. The density for Nylon carpet was 0.21 g/cc, for vinyl ester resin 1.03 g/cc and for SC-79 epoxy was 1.08 g/cc. As listed, the material constituents or laminate configuration did not have much effect on the material density. This is good as it allows flexibility in design. Thus different material strengths could be achieved by changing constituents or laminate configurations without compromising on the density.

It must also be noted that in the current fabrication technique, the laminates were pressed to reduce the thickness of the final composite to be half of the unpressed layers. In

Samples	Resin used	Configuration	Bulk density (gms/cm ³)	True density (gms/cm ³)	Porosity (%)
1–5	SC 79	FBBF	1.1±0.01	1.2±0.02	7±0.70
6–10	SC 79	BFFB	1.1±0.01	1.2±0.01	9±1.3
11–15	vinyl ester	FBBF	1.2±0.02	1.2±0.01	4±0.32
16–20	vinyl ester	BFFB	1.2±0.02	1.3±0.03	4±0.30

Table 2.2: Density and porosity values of carpet composites fabricated using the VARTM technique.

this regard, the density change from neat carpet may vary depending on such factors that may change based on final application desired. However, low porosities were obtained as shown in Table 2.2 which proves the strength of this technique. Vinyl ester based composites, however, has lower porosity than SC-79 based composites. This could be due to better fiber wetting by vinyl ester when compared with SC-79.

2.3.2 Flexural properties

Figure 2.4 shows typical load-displacement curves of composites in different configurations. It is apparent from the Fig. 2.4 that both type of composites underwent a brittle failure. However, vinyl ester resin based composites show ductility in the form of delayed failure. This difference in failure types could be due to the fact that SC-79 was cured at higher temperature (177 °C for one hour), which causes some brittleness in polypropylene backing. On the other hand, vinyl ester resin was cured at room temperature, so no brittleness in backing could be seen. In fact, the flexural stress at failure for both composites were comparable as presented in Table 2.3. The composites with face fibers on the outside sustains to higher loads than the other configuration.

Table 2.3 lists the flexural properties of prepared laminates as functions of face fibers and layup configurations. Both nylon and olefin fiber based carpet composites demonstrate

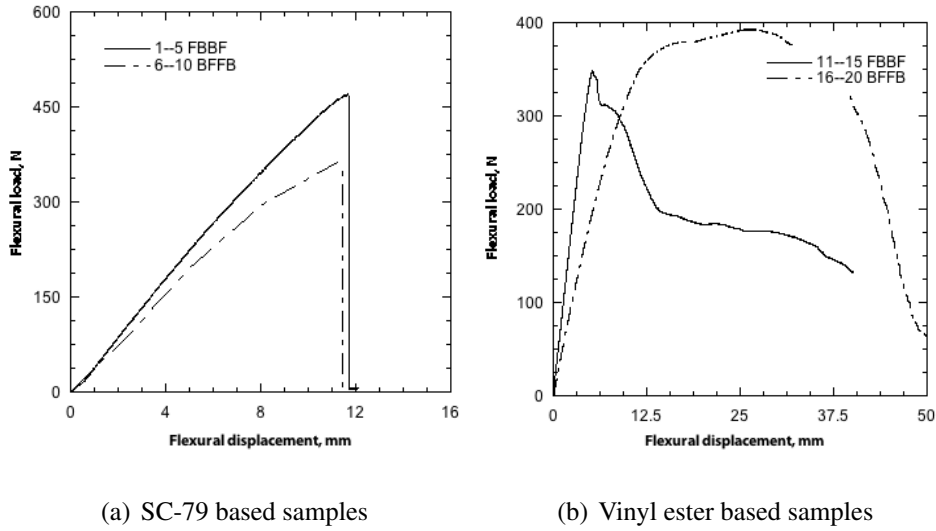


Figure 2.4: Load–displacement graphs for Nylon based carpet composite

better flexural performance as compared to other carpet based composites [2]. It is also evident from the table that the flexural strength of FBBF samples were higher than BFFB composites. This is because when the fibers are located away from the neutral axis as in the FBBF configuration, they have higher elastic modulus than that of backing (in BFFB). This shows, that, the reinforcement of resin with face fibers offers greater strength than with that of polypropylene backing combination. The load-displacement curve shows that composite materials exhibit sudden fracture.

Samples	Resin used	Configuration	$\sigma_{FL (avg.)}$ (MPa)	$E_{flexure}$ (MPa)	$\delta_{FL(avg.)}$ (mm)
1–5	SC 79	FBBF	34.9 ± 1.3	1748 ± 38	11.4 ± 1.1
6–10	SC 79	BFFB	23.6 ± 0.8	1437 ± 37	10.3 ± 1.0
11–15	vinyl ester	FBBF	28.2 ± 0.7	1722 ± 41	5.7 ± 0.3
16–20	vinyl ester	BFFB	24.0 ± 0.8	1634 ± 95	13 ± 0.5

Table 2.3: Mechanical properties of the composite fabricated.

As can be seen the flexural properties of the composites were mainly dominated by the type of matrix used. Flexural strength was dominated by the face fibers i.e. Nylon.

SC-79 based composites showed higher flexural strength in FBBF configuration than vinyl ester based composites, while both SC-79 and vinyl ester showed equal flexural strengths in BFFB configuration. This indicated that matrix dominated the flexural strength in FBBF configuration. Flexural modulus of both SC 79 and vinyl ester matrix composites were almost equal. This indicated that elastic deformation in both the cases were almost same. In case of BFFB, flexural modulus of vinyl ester based composites was higher than that of SC-79 based composites. This could be because of the high temperature curing of SC-79 epoxy, which diminishes the very elasticity of polypropylene backing, whereas in vinyl ester based composites no such higher temperature were used, which hence did not destroy the properties of polypropylene backing.

This variation in flexural properties could be helpful in multiple applications. As an example, in case of composites made using the FBBF configuration, the face fibers acted as tension and compression load bearing sides, so as to exploit the properties of face fibers in static load bearing applications. Also it was speculated that the out of plane orientation of the face fibers might help in low velocity impact protection. In the BFFB case the properties of polypropylene backing would be utilized so this orientation will provide better properties for application requiring graceful and not catastrophic failure. The polypropylene backing is supposed to have high strain to failure (ductile), so the area of applications where we do not want a catastrophic failure, this orientation will provide the desired properties. That means either of the resin system can be used to fabricate composites.

Figure 2.5 shows the comparison of flexural modulus of elasticity of the carpet based composite materials fabricated by Murdock *et al.* [2]. The fabrication technique incorporated by Murdock included chopping and shredding of carpet waste followed by coating of binders such as polyurethane, urea-formaldehyde etc. In addition, the composites were formed by the application of high temperature and pressure. In some of the composites wood flour was also used as a filler (25 %) in the composite. The modulus of elasticity of composites fabricated in current study has shown 200–250% increase, when compared

with Mancosh *et al.*.

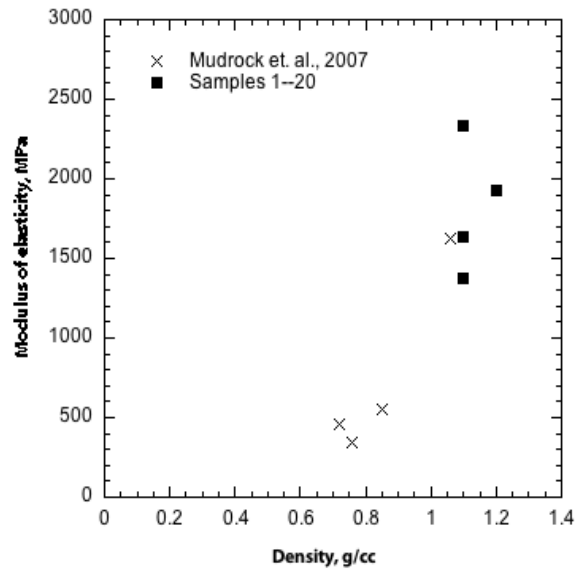


Figure 2.5: Comparison of modulus of elasticity of composites fabricated by Mancosh *et al.* [2] and the material fabricated under the current work.

2.3.3 Failure Characterization

SEM images were collected of the fibers at the cracked surfaces of the composites with vinyl ester as matrix. The micrograph in fig. 2.6 shows the image of a fiber at the fracture surface for a sample. It is apparent from the image there was no interaction between the resin and the fiber.

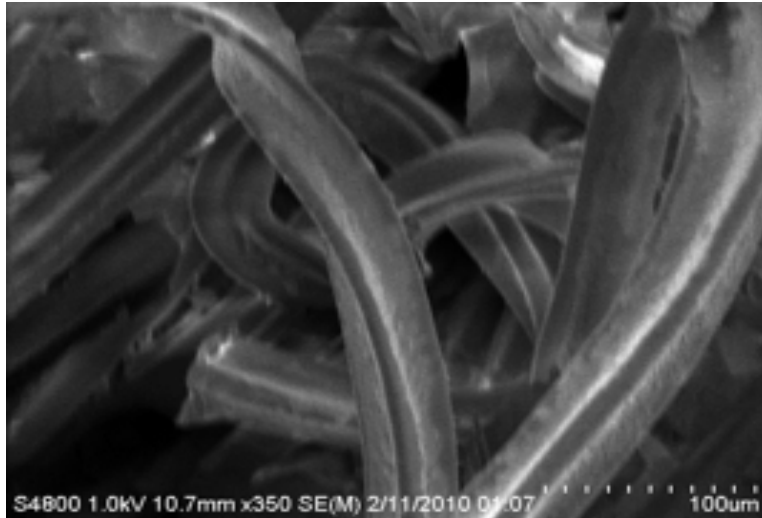


Figure 2.6: Scanning electron micrograph of a fiber at the fractured surface of the composite with vinyl ester as a matrix.

2.3.4 Conclusions

In the current work, vacuum assisted resin transfer molding (VARTM) method was used to fabricate engineered composite materials from post-consumer carpet waste. This fabrication technique did not require de-polymerization or melt blending, or any other processes. This method also avoided the requirement of mechanical separation of face fibers for raw material collection. Hence, the main advantage of this method was that, it was simple and required low amount of energy input. It also took the advantage of material architecture to provide properties that could be advantageous.

The composites fabricated using the VARTM based technique outperformed the previous preparation methods. As discussed above, the flexural strength of the composites was mainly dominated by the type of matrix used. Both SC-79 and vinyl ester gave almost equal flexural modulus in both type of configuration. That means either of the matrix system could be used to fabricate composites from waste carpet. It would be better to use vinyl ester because it is cheaper than SC-79 and it also does not require high temperature curing.

As can be seen in the Fig. 2.6 there was no adhesion between fibers and the matrix.

This could be because nylon fibers have high chemical resistance and also because they were pretreated with certain chemical and dyes. This makes it difficult for the matrix to interact with the fibers. So it becomes imperative to modify the chemistry or the surface properties of the fibers to enhance the bonding between the matrix and the fibers. In the next chapter, the surface treatment of nylon fibers using various solvents is discussed. Vinyl ester was chosen as the matrix and its adhesion with the treated fibers is discussed. FBBF was the configuration of interest, as it gave better properties than BFFB.

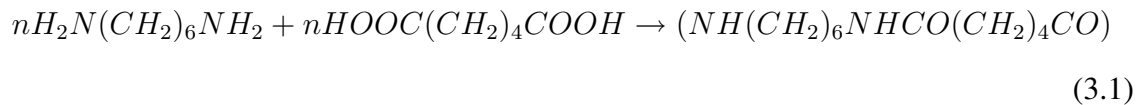
CHAPTER 3

SURFACE TREATMENT OF NYLON FACE FIBERS

3.1 NYLON FIBERS AND THEIR PROPERTIES

Properties of the fiber–matrix interface govern the load transfer from matrix to fibers, and hence the properties of composites. So it is very important to have good interaction between matrix and fibers. As discussed in previous chapter, when carpet pieces were infused with resin, SEM micrography showed almost no interaction between the resin and fibers. This necessitated the modification chemistry of the Nylon 6,6 face fibers, so as to have better bonding between resin and the fibers, and thus enhancement of mechanical properties.

To modify the surface chemistry it is necessary to understand the chemistry of the Nylon 6,6 fibers. This material is a polyamide formed from the condensation polymerization of hexamethylene diamine and adipic acid at high temperature and pressure as shown in eqn. 3.1. The name “6,6” comes from the fact that there are six carbon units in each monomer of the reactants. The step growth reaction results when the functional group of a monomer forms a dimer with that of another monomer, then reacts with other dimer, and so forth. After polymerization, the pressure of the reaction is reduced for the condensation of water. Then Nylon 6,6 is dried and extruded into the fibers. The glass transition temperature, T_g of the fibers can vary from 8 °C to 107 °C and the melting temperature (T_m) is equal to 250 °C. The applications of Nylon 6,6 commonly involve construction of textile materials, such as carpeting, upholstery, hosiery, and weatherproof outerwear. It is also used in parachutes and sails.



Nylon 6,6 has a chain-like structure in which the NH— group of one chain is hydrogen bonded with a C=O of the adjacent chain, as shown in Fig. 3.1. This structure and hydrogen bonding is responsible for good mechanical properties and chemical stability. Also this hydrogen bonding makes it nearly impossible to dissolve Nylon fibers. Many researchers have tried to modify the chemistry of Nylon 6 and Nylon 6,6 fibers. The next section would focus on the work done on modifying chemistry of the Nylon fibers.

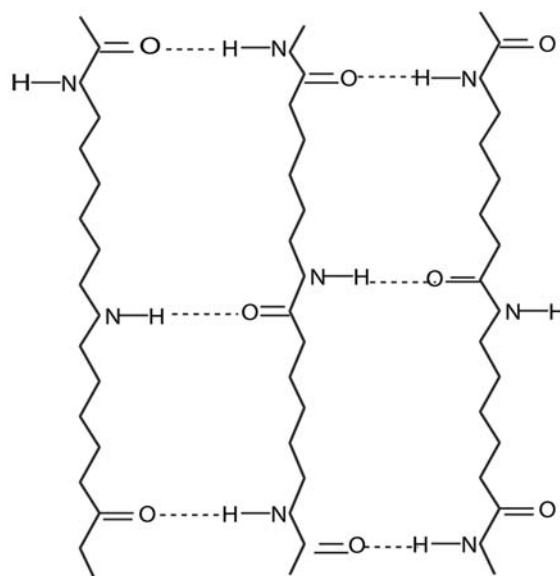
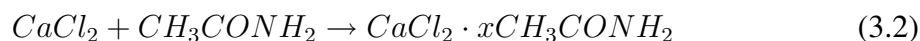


Figure 3.1: Intermolecular hydrogen bonding between two adjacent chains of Nylon 6,6.

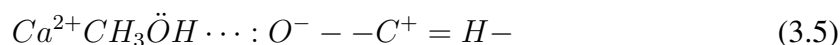
3.2 WORK DONE ON MODIFYING SURFACE CHEMISTRY

As shown in Fig. 3.1, the N–H group of one chain is hydrogen bonded with the C=O group of an adjacent chain. This hydrogen bonding provides high crystallinity, high melting point, good mechanical properties, and chemical stability. This hydrogen bonding, however, makes it very difficult to dissolve Nylon 6,6. Mainly there are two types of solvents

that have been developed to dissolve Nylon 6,6. Formic acid is one of them [33–35], but formic acid results in the polymer chain degradation of Nylon 6,6. Also it is difficult to work with formic acid [36,37]. Subsequently, Benhui [38] used a complex salt solution of CaCl_2 –Methanol (MeOH) to dissolve Nylon 6,6. It was observed that Nylon 6,6 is not soluble in methanol but soluble in CaCl_2 –MeOH by forming a complex as shown in eqn. 3.2. The number x depends on the temperature of the reaction [40]. So CaCl_2 salt plays an important role in dissolution of Nylon 6,6 by forming a complex with the amide group. In this process, CaCl_2 acts as Lewis-acid which accepts a lone pair of electrons while the amide group acts a Lewis base which donates a lone pair of electrons. This complex formation phenomenon is commonly known as “Lewis acid-base complexation”. Roberts *et al.* [39] also used gallium chloride as a Lewis acid to modify the properties of Nylon 6.



Benhui [38] explained the mechanism of Lewis acid-base complexation using FTIR (fourier transformation infrared spectroscopy). A sample of CaCl_2 /MeOH solvent mixed with Nylon 6,6 was prepared. The FTIR study shows a decrease of 15 cm^{-1} in frequency of amide I band which is dominated by the carbonyl oxygen group [41]. This decrease in frequency indicated the weakening of $\text{N-H} \cdots \text{C=O}$ hydrogen bond, while forming a complex at oxygen of carbonyl group. The possible mechanism proposed by Benhui [38] was as follows:

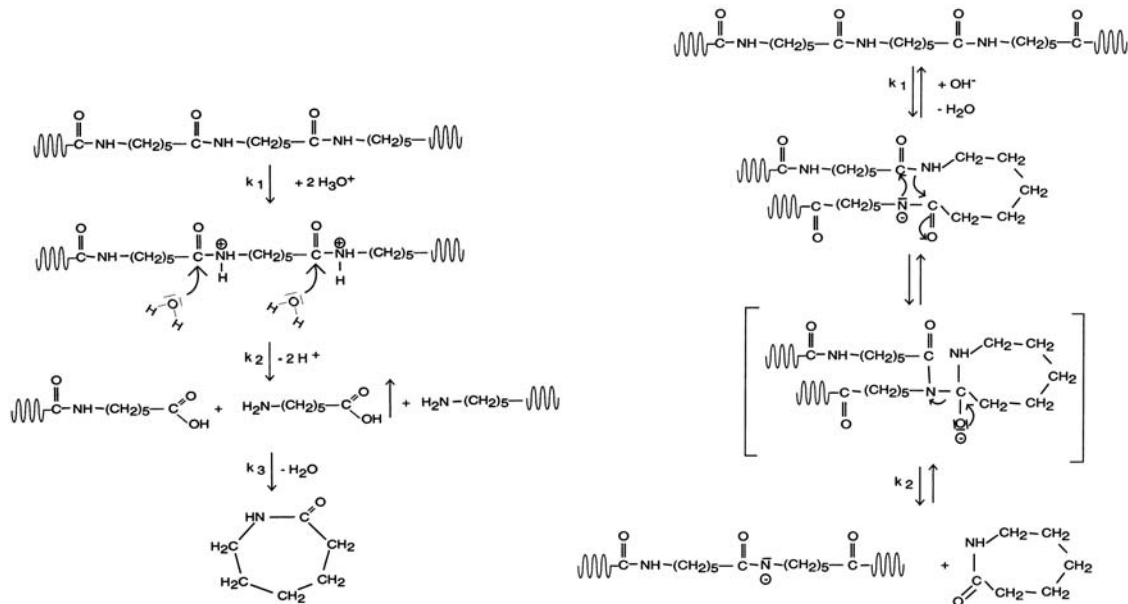


In other works, Garcia *et al.* [42] and Ensanian *et al.* [43] reported that stress bands of amide in Nylon would break if a concentrated solution of zinc or lithium chloride was

poured on it. Inspired from this phenomenon, Hamm *et al.* [44] and Hirschinger *et al.* [45] studied the interaction of metal ions with amide group in Nylon. Coleman *et al.* [46] and Dong *et al.* [47] reported in their separate works that the amide A band undergoes a blue shift i.e. an increase in the frequency in FTIR when gallium chloride was used as a Lewis acid. This shift in the peak position of the amide A band indicated the breakage of the hydrogen bond in Nylon 6,6. Wu *et al.* [48] also studied the effect of lithium salts on Nylon 6,6 using FTIR. The treated samples exhibited a red shift i.e. a decrease in the band frequency. That showed an increase on the bond strength of hydrogen bonding. Wu *et al.* also observed a change in amide I band. This could be because of the interaction of carbonyl group with lithium ions, and hence disturbing the chemistry of hydrogen bond. The change in the backbone chain of Nylon i.e. the methylene group, was also observed. This confirmed a conformational change in Nylon 6,6 with the introduction of lithium ions in the matrix of polyamide chain.

It has certainly been understood that divalent salts play an important role in modifying the surface chemistry of the Nylon 6,6 fibers. In a recent study Vasanthan *et al.* [49] tried to disturb the interchain hydrogen bonding in Nylon 6,6 during its processing by the application of Lewis acid-base complexation. The Lewis acid used was gallium chloride. Electrolytic interaction was also studied by Wall *et al.* [50].

Bockhorn *et al.* [3] worked on the pyrolysis of polyamide 6 in presence of acid and basic catalysts. Then the results of this study was used in reutilization of carpet to recover caprolactam. Acid catalyst used was 10 wt% orthophosphoric acid (H_3PO_4), while a 10 wt% eutectic mixture of sodium hydroxide (60% molar) and potassium hydroxide (40% molar) was used as basic catalysts. Figure 3.2 shows the proposed mechanism of the reactions with acid and base catalysts. It was also found that the rate reaction of depolymerization with NaOH/KOH as a catalyst was higher than that of H_3PO_4 acid or just simple thermal degradation. This implies that strong bases such as NaOH/KOH might act as a good surface treatment agents for Nylon 6,6..



(a) Acid hydrolytic scission of the amide linkage. (b) Anionic chain reaction of polyamide 6 degradation in presence of bases.

Figure 3.2: Depolymerization of polyamide chain using acid and catalyst [3].

All work to modify the surface chemistry of Nylon 6 and Nylon 6,6 was done on either the polyamide matrix or pure Nylon 6,6 fibers. However, Nylon fibers used in carpet are pre-treated several times. The fibers used in carpeting are dyed with different colors which are further coated with stain resistant chemicals to avoid any staining of carpet fibers. The following section discusses the dyes and chemicals used in forming carpet face fibers.

3.3 DYES AND STAIN RESISTANT CHEMICALS IN CARPET

To provide good aesthetic look, the face fibers of carpet are colored using various dyes. Dyes are basically unsaturated organic molecules which impart color. The dyes can be physically or chemically bonded to the fibers [1]. There are various types of dyes used in coloration. They can be classified as:

1. Dyes containing anionic functional groups, including acid and mordant dyes,
2. Dyes containing cationic groups, such as basic dyes,

3. Special colorant class, such as disperse dyes.

Acid dyes mainly contain sulfonic or carboxylic acid salt as their functional groups. To impart these dyes onto fibers an acid solution is used. This acid solution helps in developing a positive charge on the fiber, which further helps in the diffusion of dye onto the fiber. Mordant dyes are acid dyes which have an anion group that forms a complex with the dye. Then this complex gets attached to the fiber. Mordants are basically polyvalent metal ions salts, such as, salts of chromium, aluminum, copper, iron, tin, and cobalt [1]. These metal ions forms a coordination complex with the dye, which is a colloidal solution. This solution is then diffused onto the fibers.

Basic dyes are cationic salts which migrate towards the negative charges on the fiber. Generally basic dyes are used impart color on protein, Nylon, acrylic, and specially modified synthetic fibers [1].

Disperse dyes are some small polar molecules, which usually contain anthraquinone or azo groups that do not have any charged group, such as cationic or anionic groups. These dyes are water-soluble, and must be dispersed with the aid of a surfactant in the dye bath. Dispersed dyes are used for hydrophobic thermoplastic fibers that include Nylon fibers, polyester, acrylic, and polypropylene [1].

Both acid and basic dyes can be used to impart color onto the polyamide fibers such as Nylon 6 and Nylon 6,6. This is driven by the fact that polyamides have both carboxylic acids and basic amino groups. This structure of Nylon fiber makes it very easy to use a number of different dyes. So there is a large variety of dyes available for dyeing carpet fibers. The dye used may affect the properties of the fiber, and hence the properties of the composites fabricated from them.

In addition to dyes, many chemicals are used to prevent soiling and staining of the carpet fibers. Though, during the dyeing process most of areas of fibers are covered with dyes, nonetheless some spots remain unfilled by the dyes. These spots generally get attacked by spilled over liquids, which cause stains on face fibers. So to avoid this staining, carpet

fibers are chemically treated after the dyeing process. There are many complex mixtures known as sulfonated aromatic aldehyde condensations that are used as post-treatments for dyed fibers. The main attractive forces between the stain resistant chemicals and the fiber are hydrogen bond. The uncharged polar hydroxyl groups of the stain resistant chemical bonds with the amide linkages in Nylon. The other type of attractive force between the fiber and chemical are electrostatic attraction between the sulfonic groups in the stain resistant chemical and the protonated amine end groups of the fiber [1]. This type of bonding between the chemicals and fibers could be advantageous to change the surface and chemical properties of the fiber.

To have the knowledge of all these chemicals used in carpet making was useful in surface treatment of the fibers prior to epoxy infusion. Removing or changing the surface chemistry of the Nylon fibers was important to have better adhesion between the resin and the Nylon face fibers, and different chemicals were used for surface treating the fibers.

3.4 INDUCTIVE COUPLED PLASMA ELEMENTAL ANALYSIS

Since the dye and stain resist treatments are proprietary, inductive coupled plasma (ICP) elemental analysis technique was used to determine the elements on the fibers. Three types of samples were prepared.

1. Entire carpet, as it is, was cut into small pieces and dipped into acetone, in a small glass vile.
2. Face fibers were separated from the backing, then dipped into acetone.
3. The remaining material, i.e. backing and filler, was cut into small pieces, and then dipped into acetone.

Table 3.1 shows the elements and their quantity present in carpet. It can be seen that mostly divalent metals, such as barium, calcium, magnesium etc. were found. As can be

seen that Ca and Mg are present in large quantities as compared to other metal elements. The abundant quantity of these metal ions indicates that fillers used in carpet were CaCO_3 mixed with salts of Mg and Cd. A decent amount of sodium was also found in this sample. This may be either from fibers or filler materials.

Table 3.1: ICP data showing the elements and their amount present in carpet.

Analyte	Entire carpet	Face fibers only	Backing and fillers
	mg/L	mg/L	mg/L
Ag	0.000130×10^6	0.000094×10^6	0.000094×10^6
Ba	0.022031×10^6	0.076531×10^6	0.023060×10^6
Ca	2.9384×10^6	0.027701×10^6	28.307×10^6
Cd	0.000043×10^6	0.000061×10^6	0.000061×10^6
Mg	2.9415×10^6	0.010193×10^6	10.193×10^6
Zn	0.10332×10^6	0.010627×10^6	0.040525×10^6
Na	0.79425×10^6	0.40469×10^6	2.1258×10^6
Fe	0.043944×10^6	0.000571×10^6	0.42590×10^6

The elements presented on the Nylon fibers are of utmost importance. So fibers were separated from the carpet and dissolved in acetone. As can be from from Table 3.1, sodium was the most abundant element present on the face fibers. This could be because of the orange dye used to impart color on the fiber. Similarly the remaining material i.e. fillers and adhesive were also tested using ICP. As can be seen, Ca and Mg were present in large quantity as compared to other elements. It can be clearly seen that calcium was found in abundant quantity. This could be because of the presence of CaCO_3 as filler. The other metal presented was magnesium.

Based on the understanding of the chemistry of the Nylon fibers (and the chemicals used to treat them before carpet manufacturing) and the work done on the modification of the chemistry of the Nylon fibers, several classes of compounds were selected for surface

treatment studies. Of these, two alcohols, methanol and isopropanol, and two bases sodium and potassium hydroxide, have been studied. FTIR was used to analyze and optimize the change in the structure of the fibers.

3.5 FTIR OF PURE NYLON 6 AND NYLON 6,6

As shown in Fig. 3.3 there are mainly three bands in the FT-IR of Nylon 6,6. Amide A, amide I, and amide II.

1. Amide A gives a sharp peak at the 3300 cm^{-1} frequency, corresponding to N–H stretching of the amide group present in Nylon 6,6 [51]. It is important to study the change in the position of this peak because this change gives the information about the change in the interchain hydrogen bonding. The amide A band shows a blue shift i.e. a shift of the band towards higher frequency, on melting [52, 53].
2. Amide I band has its peak around 1636 cm^{-1} . It mainly includes the C=O stretching of the carbonyl group. This band can be considered as conformational so as to characterize the change in Nylon 6,6 structure [54].
3. Amide II has its peak around 1540 cm^{-1} which mainly shows C–N stretching and N–H bending [4].

Figure 3.3 shows the FTIR image of pure Nylon 6 and 6,6.

3.6 EXPERIMENTATION

3.6.1 Surface treatment, Fabrication and Characterization

These studies were conducted on Nylon face fiber carpet. The carpet used was of cut-loop type (fibers facing up), which commercially known as Romper room/Orange cool-aid. As-received carpet was cut in to nominal sample size of $200 \times 200\text{ mm}^2$. These samples were then soaked in four different treating agents, methanol, isopropyl alcohol,

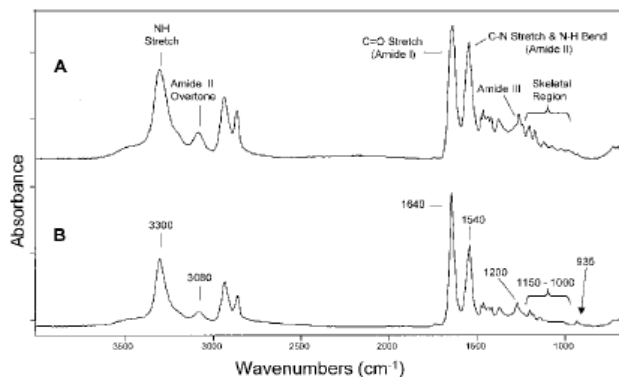


Figure 3.3: Infrared spectra of Nylon 6 and Nylon 6,6 fibers. **(A)** nylon 6 ; **(B)** nylon 6,6 [4].

sodium hydroxide (0.5 molar), and potassium hydroxide (0.5 molar) (99% pure, Sigma Aldrich, St. Louis, MO.) for three hours, and then for twelve hours. After the soak period, the carpet samples were air dried at ambient temperature. The pH of the solvents after treatment was also measured prior to treatment and after the treatment using a Hanna pH electrode. Surface treated carpet fibers were used in the collection of FTIR spectra using an AVATAR 360 FT-IR spectrophotometer. This IR spectroscopy data was compared with that generated for untreated carpet samples to determine change in the surface chemistry of the carpet fibers. Omnic 5.0 software was used for the data analysis. Atomic Force Microscopy (AFM) was used to observe any change on the surface of the fibers.

After soaking, the carpet pieces were dried in air at room temperature. Then the VARTM method was used to infuse the treated carpet pieces with vinyl ester resin. Two infused laminates were stacked together, such that the backing of the carpet pieces facing each other (FBBF), and allowed to cure under nominal pressure at room temperature for 24 hours. The applied pressure was used to compress the laminate to a final thickness of 12.5 mm and hence achieve a total compression of 50% from the original thickness. In this case post-curing of laminates was done in an air circulating oven using a 80–100–120 °F cycle with a two hour hold time at each temperature.

The resulting composite panels were cut using a band saw to prepare samples for de-

termination of density, porosity, flexural strength and tangent modulus as per the ASTM standard D790-07 [32]. Finally, scanning electron microscopy of the fracture surfaces was conducted to investigate the effect of surface treatments on fiber–matrix adhesion.

3.7 RESULTS AND DISCUSSION

3.7.1 pH Measurement

To observe the change in the chemistry of the solvent after the carpet has been soaked for 12 hours the pH of the samples was measured using a Hanna pH electrode. The pH values are listed in Table 3.2.

Table 3.2: The pH values of the solvents before and after soaking.

Surface Treatment	pH before soaking	pH after soaking
Isopropylalcohol (IPA)	5.3	4.3
Methanol (MeOH)	5.6	4.7
Sodium hydroxide (NaOH)	9.8	12.1
Potassium hydroxide (KOH)	10.1	12.5

The pH values obtained with IPA and MeOH samples suggest acidic conditions of the solvents after the treatment. This indicates that the carpet fibers went under a change in chemistry, leaving behind positive ions. This could be due to the weakening of interchain hydrogen bonding in the Nylon 6,6. On the other hand, an increase in basicity was observed in case of the basic solvents. This could be explained by the capability of the amide group to exist into resonating structure [55]. According to which amide group can exist as both–a hydrogen bond donor and hydrogen bond acceptor, structures.

3.7.2 FTIR Spectrometry

First the carpet pieces were soaked only for 3 hours. The treated carpet fibers were overlaid on that of virgin fibers (untreated fibers) it was noticed that two almost overlaid on the top of one another indicating no significant change in the chemistry of carpet fibers, as shown in fig. 3.4. It was believed that it may require more time for the solvents to interact with the fibers.

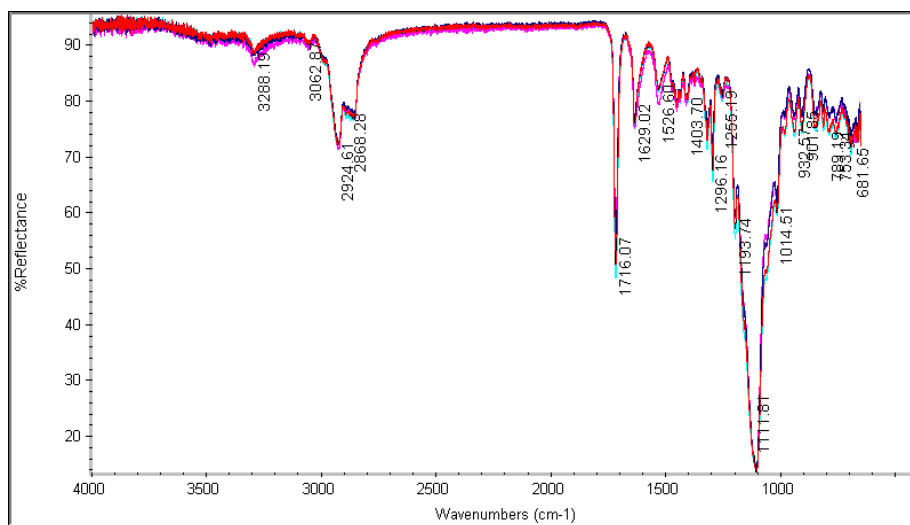
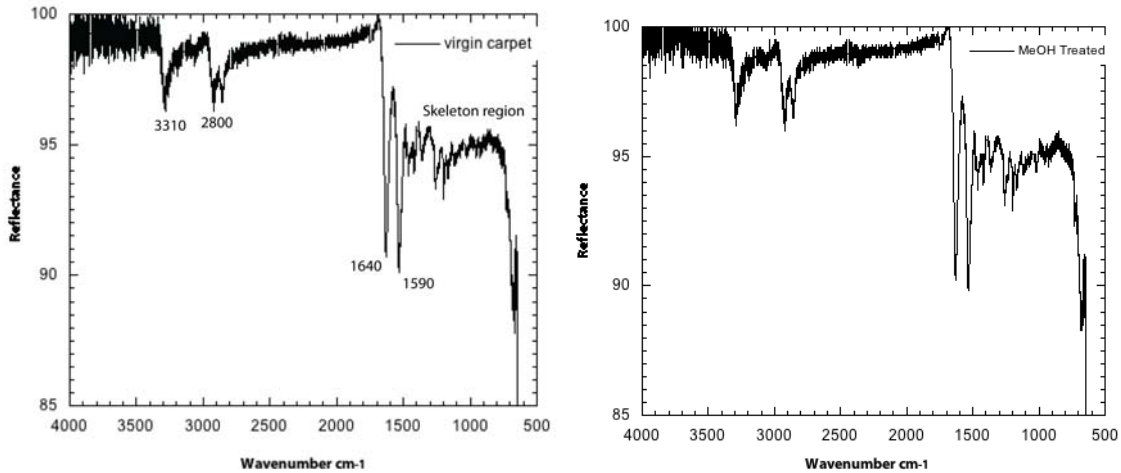


Figure 3.4: Superimposed IR spectra of virgin fibers against fibers treated with isopropanol, methanol, sodium hydroxide, and potassium hydroxide.

In the second experiment, the fibers were soaked with the same solvents for a period of 12 hours and then air dried at ambient temperature. Figure 3.5 shows the stacked spectra of virgin carpet fibers and carpet fibers soaked for 12 hours in methanol. There were significant differences in the region 3500 to 2500 cm^{-1} and 1500 to 500 cm^{-1} .

More precisely, amide A and amide I bands i.e. at frequency around 3300 and 1640 cm^{-1} has showed changes. Table 3.3 shows the change in the frequency after treatment. The change could be explained on the basis of the Lewis acid-base complexation. The calcium ions (Ca^{2+}) present in the filler material acted as a Lewis acid, while the amide group of Nylon 6,6 fibers acted as a Lewis base. When the carpet was dipped in the bath of



(a) FTIR spectra of virgin carpet fibers. (b) FTIR spectra of the carpet fibers treated with MeOH.

Figure 3.5: FTIR spectra comparison of untreated and treated carpet fibers with MeOH.

methanol, first methanol reacted with the Ca^{2+} ions forming a complex molecule $\text{Ca}^{2+}-\text{CH}_3\text{OH}$.

Table 3.3: FTIR spectra assignment of untreated and treated carpet fibers (cm^{-1})

Sample	Amide A	Amide I
Untreated	3310	1640
Treated with methanol	3290	1626

This molecule was formed by the hydroxyl ions of methanol interacting with the Ca^{2+} ion. Now this molecule approached the Nylon 6,6 molecule to interact with $\text{C}=\text{O}$. The capability of calcium cation to form a complex with carbonyl group was more than that with hydroxyl group [56]. Therefore in the end, a complex of $\text{Ca}^{2+}-\text{Nylon 6,6}$ was formed. Figure 3.6 shows the complex formed at the end of the reaction.

Under the same experimental conditions, the FTIR spectra of the IPA soaked fibers was collected and the spectra is stacked with that of virgin fiber is shown below in fig. 3.7. No major changes were observed in the spectra. Specifically in the regions 3400 to 2800 cm^{-1} and also on the regions 1800 to 500 cm^{-1} .

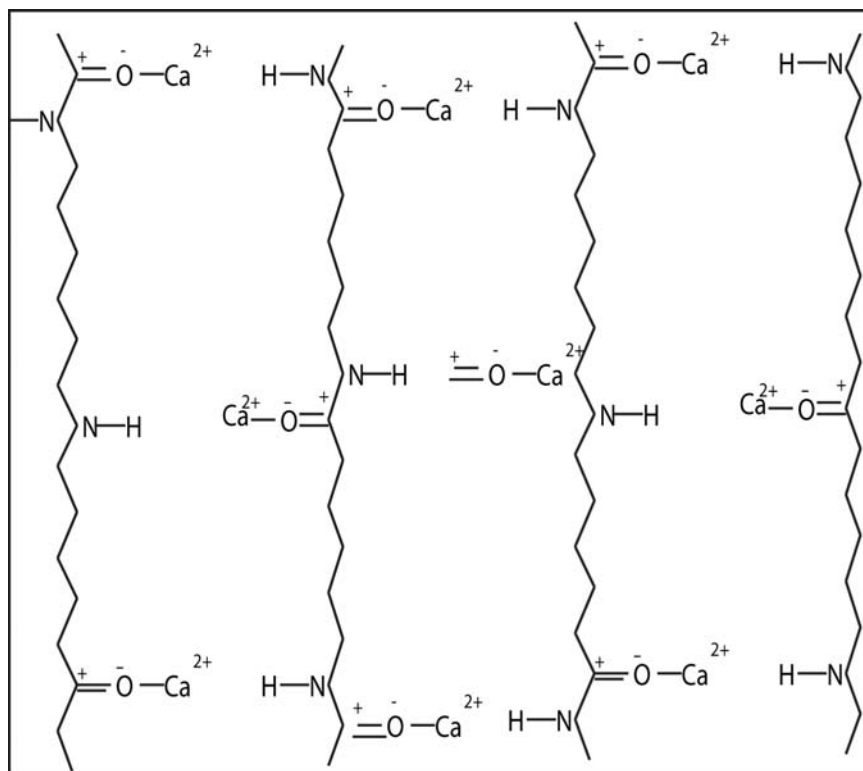


Figure 3.6: Lewis acid-base complexation mechanism scheme.

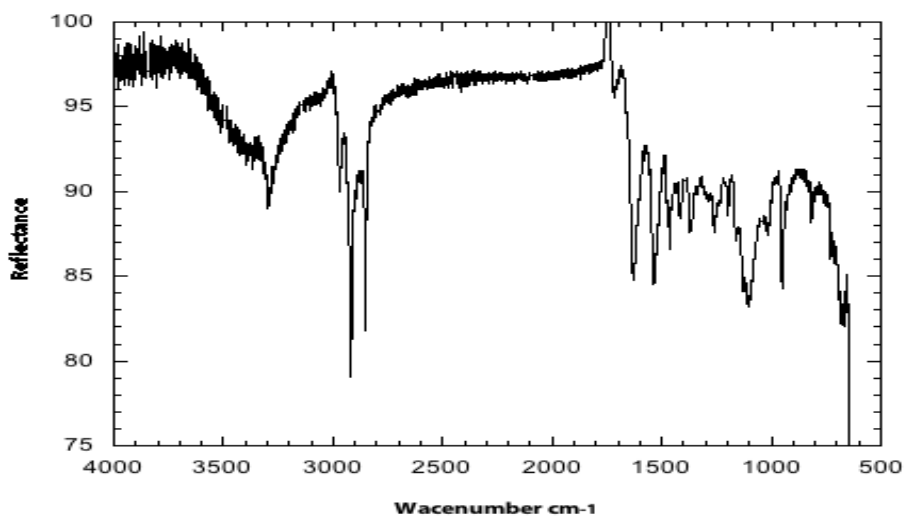


Figure 3.7: FTIR spectra of the fibers treated with Isopropylalcohol

The effect of bases such as sodium hydroxide and potassium hydroxide on the face fibers was studied. 0.5 M of NaOH was taken and carpet pieces were soaked for 12 hours. Figure 3.8 shows the FTIR spectra of the face fibers treated with sodium hydroxide. The amide A band peaks seemed to broaden. This could be due to the vibrations of the O–H group for the characteristic absorption in the region 3300 to 3400 cm^{-1} . Practically every O–H has the same shape intensity and the position of the O–H stretch absorption is very uniform. Amide I peak still could be found around 1640 cm^{-1} , which corresponds to the carbonyl group. But the peaks beyond it could not be seen as expected for Nylon 6,6. Amide II i.e. C–N stretching could not be found and the skeleton region peaks for C–C (methylene group) were also missing. This change indicates a polymer chain degradation of Nylon 6,6. Similar observations were noticed when fibers were treated with potassium hydroxide, as shown in fig. 3.9. Increase in the intensities of the peaks can also be seen. This could be due to excessive hydroxyl group present on the surface of fibers, even after drying.

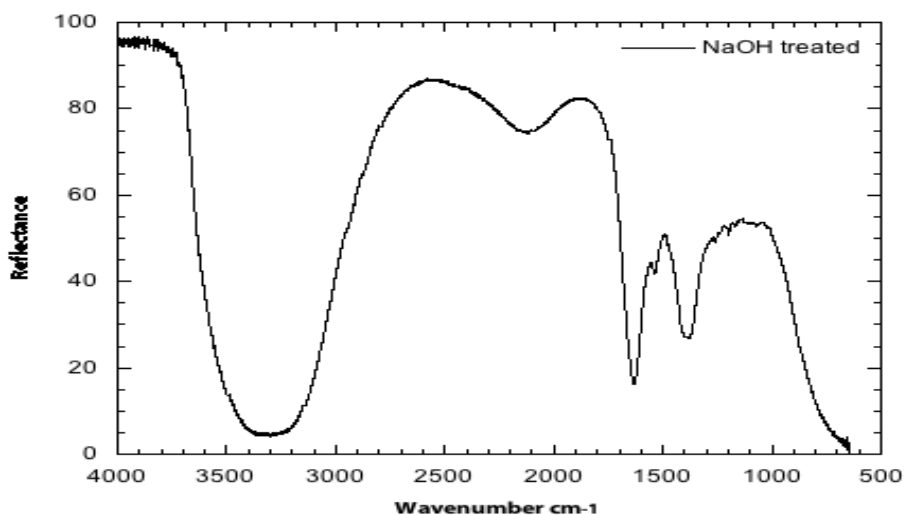


Figure 3.8: FTIR spectra of fibers treated with sodium hydroxide.

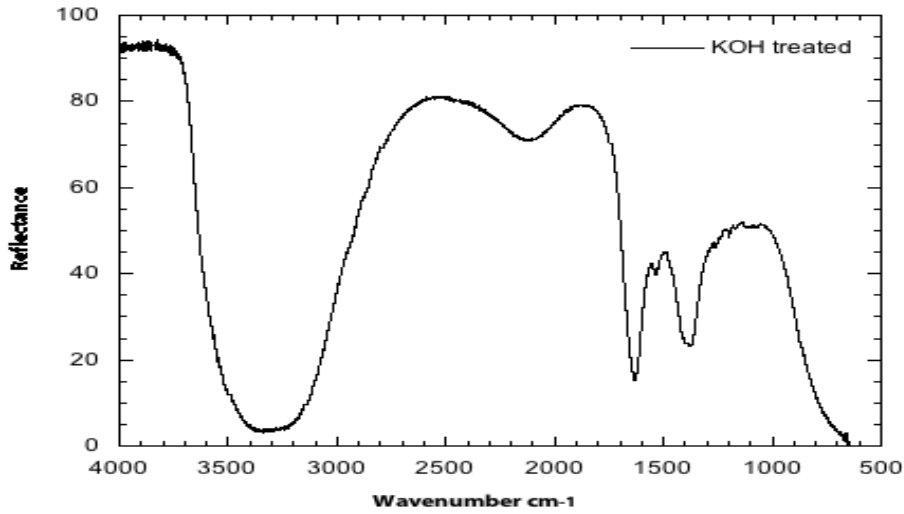


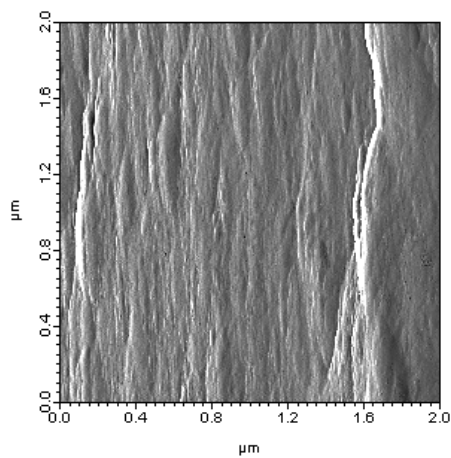
Figure 3.9: FTIR spectra of fibers treated with potassium hydroxide.

3.7.3 Surface Roughness

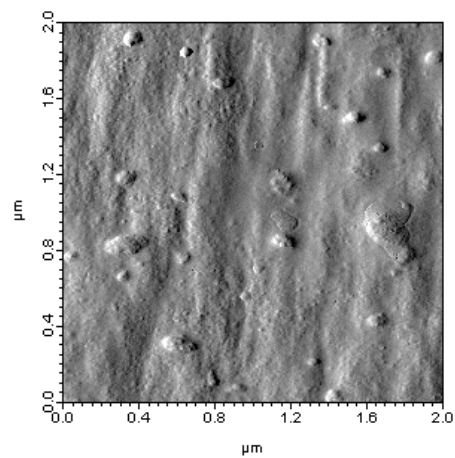
Atomic Force Microscopy (AFM) was used to observe the change in the surface roughness of the fibers after treatment. An MFP-3D™ Stand Alone AFM (Asylum Research, Santa Barbara, CA), was used to take images in the dual-AC mode. Figure 3.10 shows the roughness of a virgin fiber and a fiber treated with methanol and sodium hydroxide. A significant change on the surface of the fibers was seen. It could be seen that the fibers were more rough after the surface treatment. The root mean square (RMS) values of the height of the surface roughness of the virgin fiber was 13.9 *nm*, whereas RMS height values for methanol and sodium hydroxide treated fibers were 15.4 *nm* and 20.1 *nm*, respectively. This could help in an increase in the friction between matrix and the fibers, and hence results in better load transfer from matrix to fibers. So, not only the change in the chemistry of the Nylon 6,6 fibers was observed, but the surface roughness was also changed.

3.7.4 Density and Porosity of Fabricated Laminates

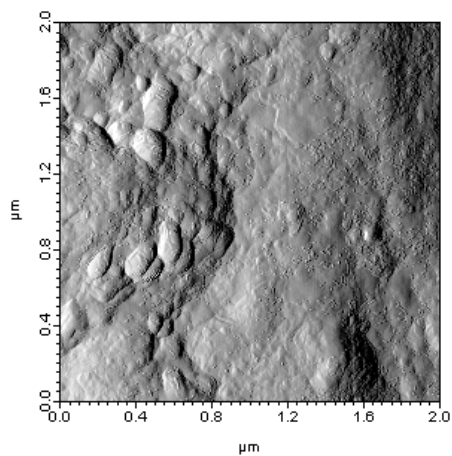
The density and the porosity of the samples fabricated after surface treatment were measured using the same method as discussed earlier in chapter 2. Table 3.4 shows the bulk



(a) AFM image of a virgin fiber.



(b) AFM image of a fiber treated with methanol.



(c) AFM image of a fiber treated with sodium hydroxide.

Figure 3.10: Atomic force microscopy image comparison of the roughness of a virgin fiber and a fiber treated with Methanol and sodium hydroxide (0.5 M).

density, solid density, and porosity of the composites fabricated.

Table 3.4: Density and porosity values of carpet composites fabricated using the VARTM technique after surface treatment.

Samples	Treating agent	Bulk density (gms/cm³)	Solid density (gms/cm³)	Porosity (%)
FBBF	-	1.2±0.01	1.16±0.01	4±0.7
MEOH-FBBF	Methanol	1.4±0.02	1.369±0.02	2±0.08
IPA-FBBF	Isopropylalcohol	1.2±0.01	1.17±0.01	2.4±0.08
NaOH-FBBF	Sodium hydroxide (0.5 N)	1.4±0.02	1.372±0.03	2±0.06
KOH-FBBF	Potassium hydroxide (0.5 N)	1.3±0.03	1.27±0.02	2.3±0.06

The density measurement shows that an increase in density of the samples was achieved after surface treatment. The reason for this could be more resin material was infused through the carpet fibers, which resulted into less amount pores in the composite. The porosity also decreased, which further indicated the increase in the wetting of the fibers by the resin material. The improvement in wetting of the fibers could be due to the chemical change in the fibers or the increase in the surface roughness.

3.7.5 Flexural properties

The mechanical properties are listed below in the Table 3.5 and Fig. 3.11 shows the stress-strain behavior of the composites fabricated after the surface treatment. The results showed an increase in the values of flexural strength and the modulus. Composites treated with methanol has shown an increase of ~28% in flexural strength and ~38% increase in flexural modulus. Similar results were obtained in case of treatment with potassium hydroxide. The composite treated with sodium hydroxide had shown an increase of ~39% in flexural strength and an increase of ~52% in flexural modulus. This increase in flexural modulus indicated the better fiber wetting and more and more resin sticking around the fiber. The

porosity in case of sodium hydroxide seemed to have lowered, which substantiated this increase in flexural modulus.

Table 3.5: Mechanical properties of the composite panels.

Sample name	Treating agent	Flexural strength (MPa)	Flexural modulus (MPa)
FBBF	None	27.4±0.7	1722±41
MEOH-FBBF	Methanol	35.2±0.5	2364±29
IPA-FBBF	Isopropylalcohol	32.5±0.6	2152±37
NaOH-FBBF	Sodium hydroxide (0.5 N)	38.6±2.1	2631±65
KOH-FBBF	Potassium hydroxide (0.5 N)	35.6±1.1	2348±38

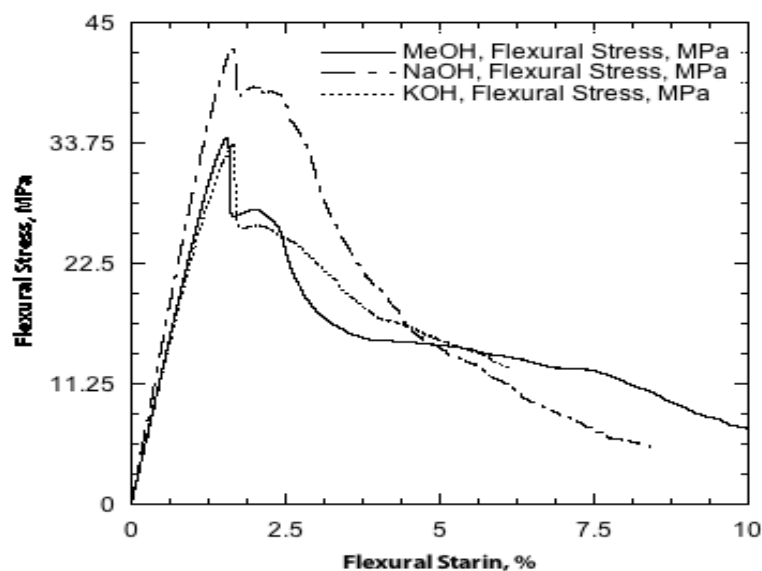
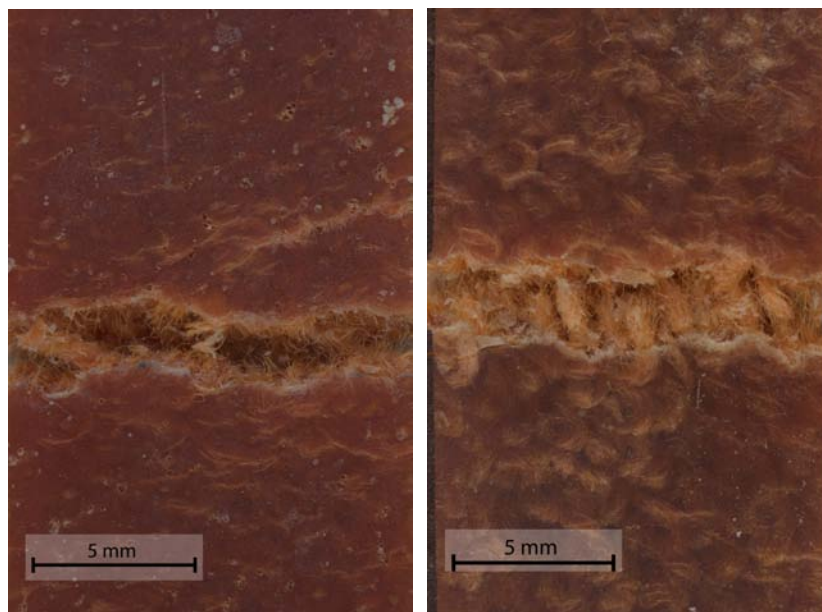


Figure 3.11: Stress-strain curves of the composites fabricated after surface treatment.

3.7.6 Failure Characterization

Figure 3.12 shows the difference in the crack developed in two composite samples, treated and untreated, when loaded to failure in a three-point bend test. The composite which was

not treated prior to resin infusion, Fig. 3.12, had no interaction with resin, while the composite which was treated after before resin infusion, showed a fiber alignment even after failure indicating, a better interaction of fibers with matrix. This lead to a higher modulus of the composites fabricated after the surface treatment. SEM images were collected of the fibers at the cracked surfaces of the composites with surface treatment and without the surface treatment. The micrograph in Fig. 3.13 show the image of a fiber at the fracture surface for a sample with surface treated fibers. It is apparent that the fiber was surrounded by the resin material indicating a better adhesion between the fiber and the resin. So an improvement in the extent of fiber wetting has been obtained by surface treatment which has helped in improving the mechanical properties of the composites.



(a) Crack developed in the composite (untreated), when loaded to the failure in three point bend test. (b) Crack developed in the composite (treated), when loaded to the failure in three point bend test.

Figure 3.12: The crack developed in the composite samples when loaded to failure in a three-point bend test.

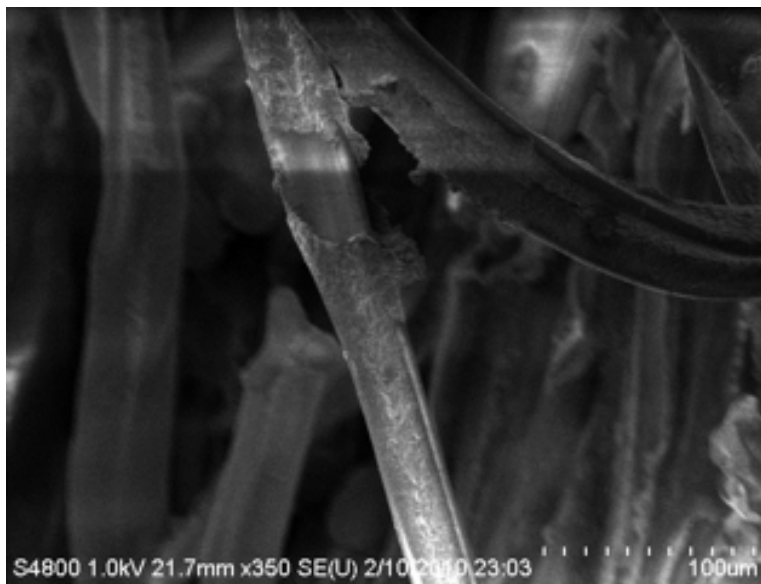
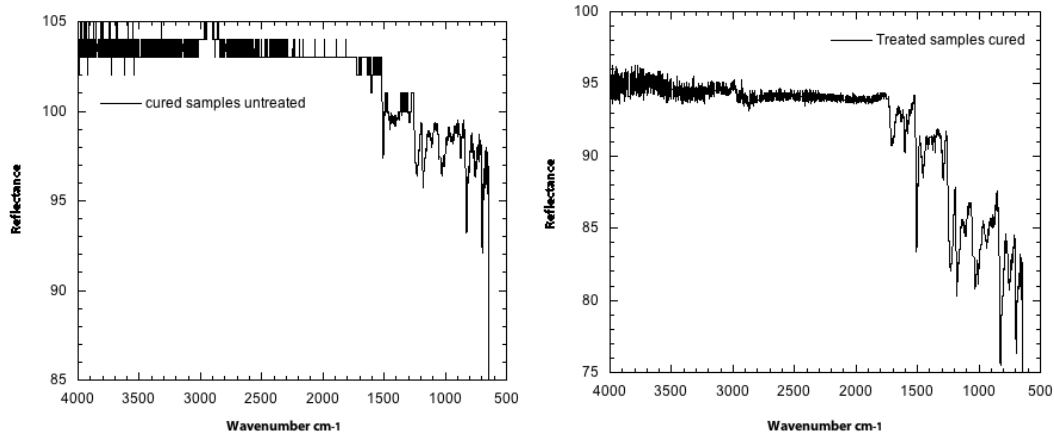


Figure 3.13: Scanning electron micrograph of the treated fibers composite at the fractured surface.

3.7.7 Possible Mechanism

For an aftermath of all the surface treatment work above, FTIR of the cured samples with and without surface treatment were taken, to see any differences in the chemical interaction between the vinyl ester matrix and the fibers. Small pieces of nylon fibers cured with vinyl ester resin samples were crushed using liquid nitrogen into powder form. Then the FTIR of these samples were collected. A noticeable change in the region from 2000 to 500 cm^{-1} was observed. Figure 3.14 shows the two FTIR spectrum of the two treated and untreated samples.

To put together a proper mechanism of interaction between fibers and matrix, the structure of vinyl ester had to be determined. Since the resin used was proprietary, the exact structure could not be known. So the FTIR of the resin was also taken to compare it vinyl ester resin generally used and whose structure is known. Figure 3.15 shows the comparison of the FTIRs taken for the resin used in current study and the vinyl ester resin used by Rosu *et al.* [5]. It was reported that generally vinyl ester resins are manufactured by addition



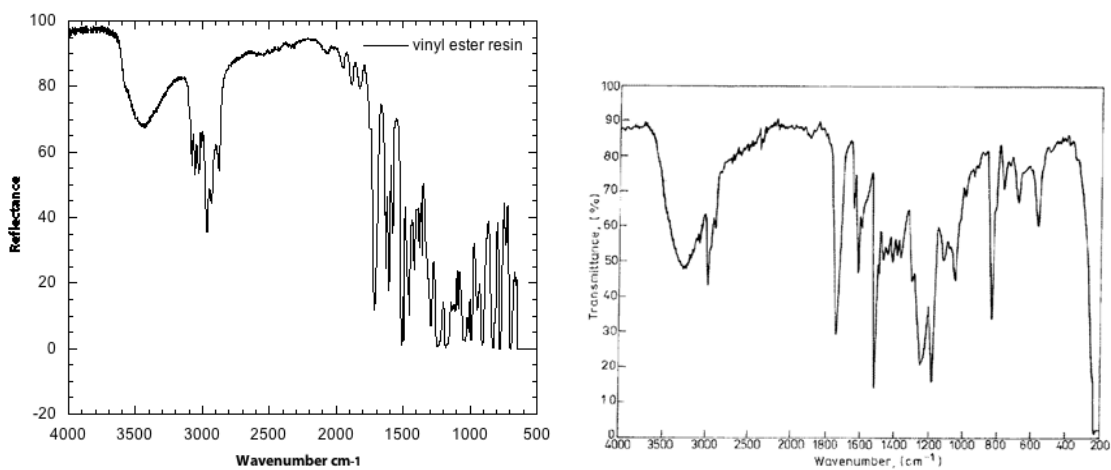
(a) FTIR spectra of the untreated nylon fibers, (b) FTIR spectra of the treated nylon fibers, vinyl ester cured samples.

Figure 3.14: FTIR spectra comparison of untreated and treated fibers, when cured the vinyl ester resin.

of unsaturated monocarboxylic acids to an epoxy backbone, in presence of a basic catalyst [5]. Equation 3.16 shows the structure of the vinyl ester resin proposed in the paper. The FTIR spectra shown by Rosu *et al.* has absorption peaks due to the carbonyl group at 1718 and 1180 cm^{-1} . Also it has C=C stretching and wagging vibrations peaks at 1636 and 944 cm^{-1} respectively. The peak at 1636 cm^{-1} obtained is overlapped by the peak due to styrene double bond absorption peak. The broad absorption around 3200–3600 cm^{-1} was due to hydroxyl group. All these peaks could be found in the FTIR spectra of the resin used in current study. So we could predict the structure of resin used having a carbonyl group, C=C group, and styrene group.

Methyl ether ketone peroxide (MEKP) was used as a hardener to begin the curing of resin. Now a possible mechanism of bonding between the fibers and matrix could be proposed in which the C=C group at the ends of the chain took part in the reaction with the carbonyl group in amide group. Figure 3.17 shows a crude approximation of the interaction of vinyl ester resin and the amide group after the treatment with methanol. The C=C interacted with the Ca ion which had formed a complex with amide group.

Another possibility of reaction is shown in Fig. 3.18, in which the carboxylic group of



(a) FTIR spectra of the vinyl ester resin used in current study. (b) FTIR spectra of the treated nylon fibers, vinyl ester cured samples.

Figure 3.15: FTIR spectra comparison of vinyl ester resin used in current study and the vinyl ester resin used by Rosu *et al.* [5] to confirm the structure of the resin.

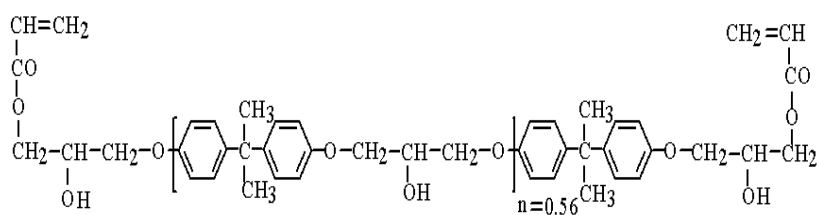


Figure 3.16: Structure of the resin proposed by Rosu *et al.* [5], prepared by addition of monocarboxylic acid and an epoxy backbone.

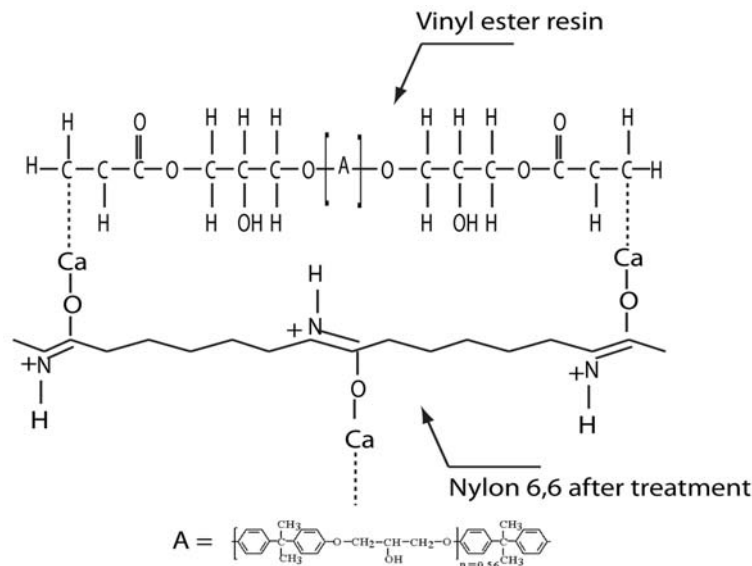


Figure 3.17: A proposed possible mechanism of interaction of vinyl ester resin with the nylon 6,6 molecule treated with methanol.

vinyl ester formed a bond with Ca ion present on the amide chain.

There was no heat provided to the system while soaking any of the surface treating agent. It was believed that the longer duration of soaking period might have helped in modifying the surface chemistry. There is another possibility of methanol forming a methoxide group with calcium i.e. $\text{CH}_3\text{—O—Ca}$. Then this methoxide forming a complex with the carbonyl group of amide, hence breaking the —C=O—NH— hydrogen bond. This complex might then interact with the vinyl ester resin as shown in Fig. 3.19.

3.8 CONCLUSIONS

The effect of the surface treatment of the carpet fibers on the mechanical properties prior to resin infusion was studied. It was found that treating fibers with alcohols such as isopropyl alcohol, methanol, and ketones such as acetone improves the flexural strength, around, by 30%. Also the FTIR spectra of the treated fibers were collected and it was observed that, surface treatment modifies the surface chemistry resulting in the better adhesion between

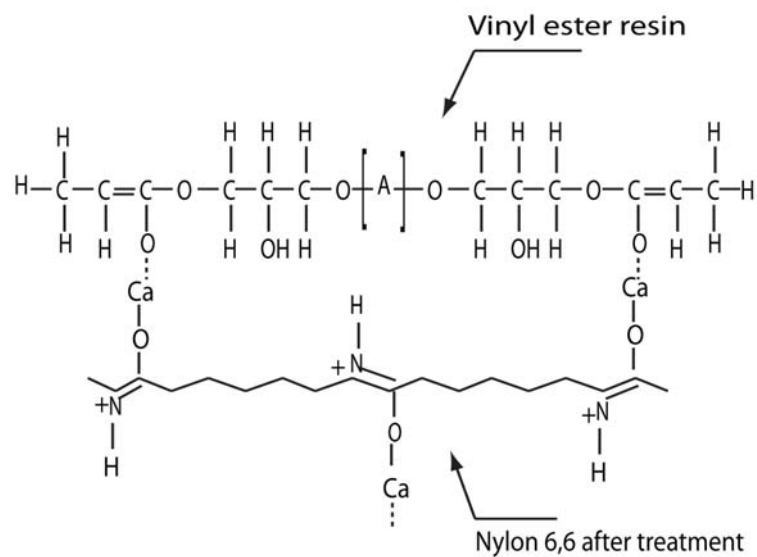


Figure 3.18: Second proposed possible mechanism of interaction of vinyl ester resin with the Nylon 6,6 molecule treated with methanol.

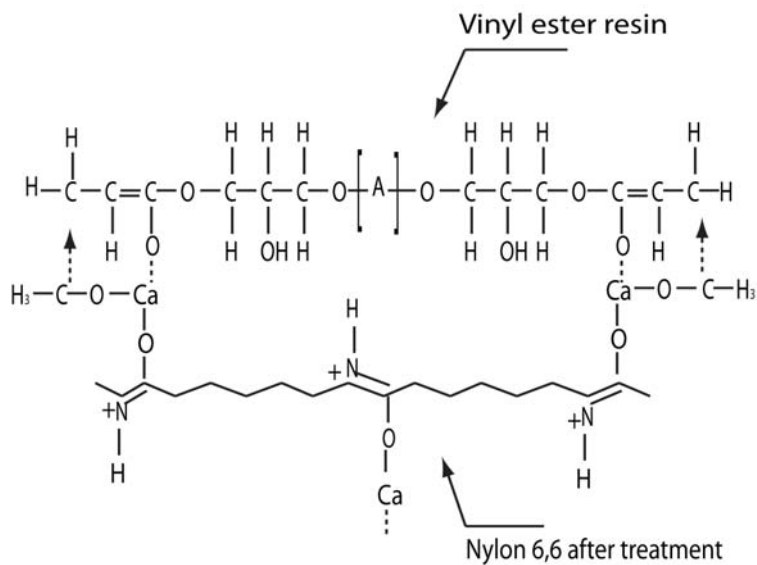


Figure 3.19: Third proposed possible mechanism of interaction of vinyl ester resin with the Nylon 6,6 molecule treated with methanol.

matrix and the fiber. SEM micrographs clearly showed the difference in the texture of the fibers at the crack surface of treated composites and untreated composites.

CHAPTER 4

CONCLUSIONS

In the current work, vacuum assisted resin transfer molding (VARTM) was used to fabricate engineered composite materials from post-consumer carpet waste. This fabrication technique did not require de-polymerization or melt blending, or any other processes. This method also avoided the requirement of mechanical separation of face fibers for raw material collection. Hence, the main advantage of this method was that it was simple. It also took the advantage of material architecture to provide properties that could be advantageous.

The composites fabricated using the VARTM based technique outperformed the previous preparation methods. The flexural strength of the composites was mainly dominated by the type of matrix used. Both SC 79 and vinyl ester gave almost equal flexural modulus in both type of configuration. That means either of the matrix system could be used to fabricate composites from waste carpet. It would be better to use vinyl ester because it is cheaper than SC 79 and it also does not require high temperature curing.

Failure characterization of the composites showed that there was no adhesion between untreated fibers and the matrix. This could be because nylon fibers have high chemical resistance and also because they were pretreated with certain chemical and dyes. So it became imperative to modify the chemistry or the surface properties of the fibers to enhance the bonding between the matrix and the fibers. So the carpet was treated with various solvent before resin infusion. FTIR of the fibers showed considerable changes in the chemistry of the fibers. This lead to a better bonding between fibers and matrix. A small increase in the density, and around 50% decrease in porosity was also seen. The decrease in porosity

showed better wetting of fibers. Atomic force microscopy was done to observe any change on the surface of the fibers, and an increase in the surface roughness was seen. Surface treatment of fibers seemed to improve the flexural strength by 38% and flexural modulus by 52%, through better fiber-matrix adhesion.

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Vacuum assisted resin transfer molding (VARTM) has been used to fabricate engineered composite materials from post-consumer carpet waste. The process is unique, and applicable to any type of carpet. The technique can be used to make laminated structures for load-bearing applications. The mechanical properties of the composites obtained are 200% higher than that of other carpet based composites. Failure characterization of tested material shows no fiber-matrix adhesion, so various surface treatment methods have been used to modify the surface chemistry of the fibers so as to improve the fiber-matrix bonding. Solvents such as, methanol, isopropanol, sodium hydroxide, and potassium hydroxide are used for surface treatment. Carpet pieces are soaked in these solvents for 12 hours, and then air dried at room temperature. FTIR spectrometry is used to determine the change in the chemistry of the fibers. A considerable change in the chemistry is observed. Atomic force microscopy is used to determine any change in the surface morphology of fibers after surface treatment. An increase in the surface roughness is observed. Composites fabricated after surface treatment show 38% increase in flexural strength and 50% increase in flexural modulus. A decrease of 50% in porosity is also observed. This increase in mechanical properties is attributed to the modification of fiber chemistry, and also, the change in surface morphology.

ADVISOR'S APPROVAL: _____