IMPACT OF NANOCLAY ON FIRE RETARDANCY AND ENVIRONENTAL DURABILITY OF POST CONSUMER CARPET COMPOSITES

By

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Title of Study: IMPACT OF NANOCLAY ON FIRE RETARDANCY AND ENVIRONMENTAL DURABILITY OF POST CONSUMER CARPET COMPOSITES

Major Field: MECHANICAL AND AEROSPACE ENGINEERING

Abstract: A simple vacuum assisted resin transfer molding (VARTM) process was previously used to scale-up the fabrication of large-size composite specimens from recycled post-consumer waste carpet. These composites exhibited superior mechanical and sound absorption properties compared to other types of infrastructure materials such as wood, concrete and particleboard. The process is simple and can be used with different resin types ranging in cost (polyurethane, polyester, epoxy, and vinyl ester). Environmental degradation and fire retardancy of these composites are potential limitations to their use as infrastructure materials. To enhance their fire retardancy and to protect against environmental degradation, the composites were coated with epoxy resin containing 4 % organoclay (I.28E) and also fabricated by VARTM infusion by infusing the carpet samples with epoxy resin containing 4 % nanoclay. Tests included fire retardancy tests using ASTM D 635 and exposure to moisture and alternating cycle of UV and condensation followed by mechanical testing. The fire retardancy and change in mechanical properties after UV/ moisture exposure of clay-epoxy-carpet composites were compared with baseline samples of carpet composites infused only with epoxy. It was observed that nanoclay coated and clay-epoxy infused carpet composites improved fire retardancy and resisted degradation due to UV and environmental exposure, as evidenced by nearly consistent mechanical properties.

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CHAPTER I

INTRODUCTION

1.1 Construction of carpet

Typical carpets consist of four different layers (figure 1). These are: 1) primary backing, 2) tuft or face fiber, 3) binder and 4) secondary backing. [1, 2]

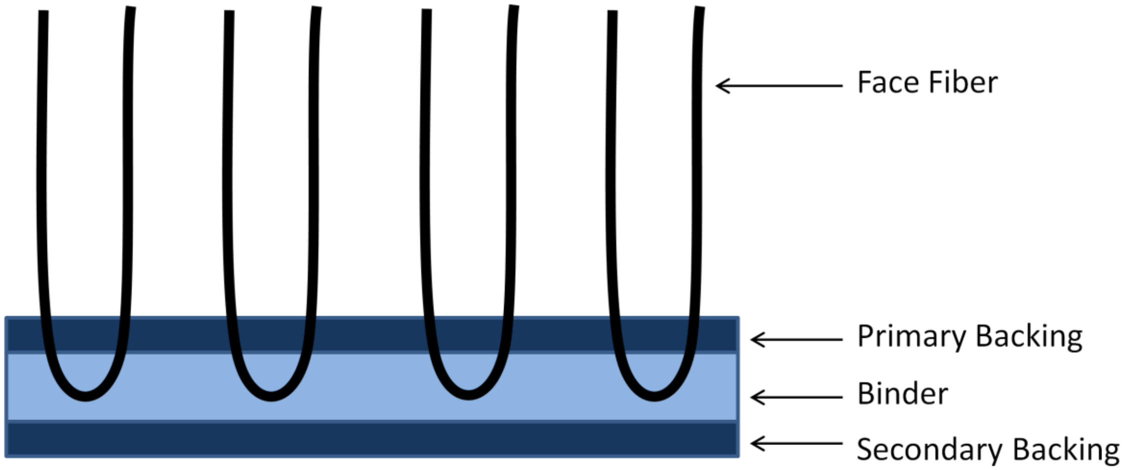


Figure 1.1: Schematic diagram of different component of carpet. Modified from [1]

The purpose of the primary backing is to hold carpet fibers. It can be woven or nonwoven, and is typically made of polypropylene. [1] Polyolefin and polyester are also used as the backing material. [2] Tuft or face fibers are tufted on backing material. Nylon has been the most commonly used material for face fiber because of its toughness and resilience. Almost 70% of the commercial carpets use nylon as face fibers. [2] The Other common materials used for tufted fiber are olefin, wool, polyester, acrylic, and others. [3] The purpose of the binder or adhesive is to hold the face fibers in place. The adhesive is generally styrene butadine copolymer with inorganic fillers such as $CaCO_3$ and $BaSO_4$. [4] Secondary backing is laminated to the back of the carpet and is generally made of the same material as primary backing. [1] Its purpose is to hold the face fibers, and improve the longevity of the carpet.

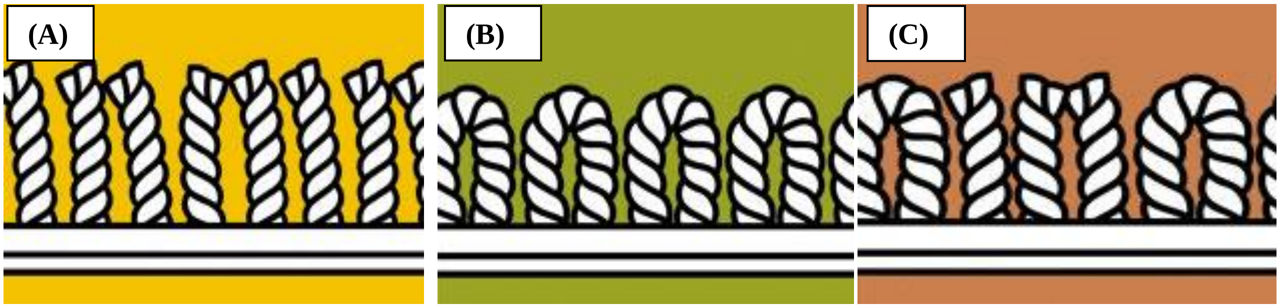


Figure 1.2: Types of carpet based on construction A) Cut pile, B) loop pile , C) Cut/ loop pile. [5]

Based on the face fibers construction, carpets can be classified in major three types: pile, Cut pile, and combination of the two known as cut-loop. [3] A very few varieties are seen in each type depending on the arrangement of the fibers.

1.2 Carpet recycling

Waste carpet can be categorized into two types : pre and post consumer carpet waste. [4] Pre consumer carpets are generated during edge cutting and trimming into different irregular shape. Automobile industry is the largest producer pre consumer waste carpet and overall amount of this manufacturing waste is 12% of the total production. [4]

Post consumer carpets are old carpets disposed in landfill after the use. The post consumer disposed carpet contains dirt, chemicals and other materials accumulated during the time of use. An average life span of carpet is in between 8 to 12 years, and the amount of contaminants in a post consumer carpet is 30% of its weight. [1]

The recycling process of carpet has been very limited due to different material components and accumulation of different contaminants. Mihut et al. [1] classified the traditional ways of carpet recycling into four major categories:

1) Primary recycling or depolymerization
2) Secondary recycling or separation of component
3) Tertiary or melt-blending
4) Quaternary or energy recovery

Primary recycling generally involves breaking of nylons into monomers which can be utilized for further re-polymerization. Solvent is used to selectively dissolve nylon and separate it from other components and contaminants of the carpet. [1] It is the most common method used for recycling carpet fibers. However, selection of appropriate solvent is the biggest challenge in this method. In some cases, physical separation of component is also employed.

In secondary recycling method, individual polymeric components are separated and used without converting into monomers. It requires step by step chemical processes to recover every single component. Different techniques are adopted for extracting components from carpets. The most common pathway of carpet component extraction is in the following order: grease and lubricants, binder or adhesive, backings, and finally face fibers. [1] After the recovery, polymeric components are useful for conversion into other product by injection molding.

Tertiary recycling technique utilizes disposed carpet without separating them into individual components. In this process, the carpet is shredded into small pieces (approximately half inch) , and is mixed with polymeric resin to hold them together. The mixture is then extruded to the final product. [1] The biggest disadvantage of this method is the lack of homogeneity of the materials. As a result, the mechanical properties of the material are not satisfactory. Melting process has also been applied to improve the homogeneity of the final product.

The quaternary recycling method is energy extraction by burning the disposed carpet. It has been the most debated process because of the environmental hazard created by burning of polymeric waste. During the burning process, CO_X, $NO_{X,}$ SO_X, volatile organic compounds (VOC), smoke/ particulate materials, particulate-bound heavy metals are released in the environment, which can create health hazard and long term environmental effect. [6]

The overall carpet recycling process involves separation, shredding, or complex chemical process. All these processes requires extra energy input which makes the recycling economically infeasible. As a result, only a small portion of the discarded carpets is being taken care for recycling process. The annual report published by CARE (Carpet America Recovery Effort) shows that almost 4000 million tons of carpet was discarded in 2011 in USA and only 7% of that was recycled. [7] So, a viable effort is demanded to make improvement in recycling process.

1.3 Carpet recycling by VARTM

Few years ago in Oklahoma State University, a new method was developed to recycle pre/ postconsumer waste carpet by VARTM (Vacuum assisted resin transfer molding) process. [8] Figure 1.3 illustrates carpet recycling by this Method. In this process, carpet pieces are layered in a mold and polymer resin is infused with the help of vacuum pressure~~.~~ The resin is then cured under vacuum. The final product in the process is a flat composite panels of polymer matrix and carpet fibers. Variation in the combination and orientation of the carpet layers such as bottom-top-top-bottom (BTTB), top-bottom- bottom-top (TBBT) is possible, and also different types of polymers can be used in this method. The main advantage of this recycling process is that it does not require any physical or chemical treatment of carpet and the carpet is used as received in the process. As a result, it eliminates the energy and cost barrier of the traditional recycling processes. Moreover, VARTM process with hand layup does not demand high initial investment and skilled workers.

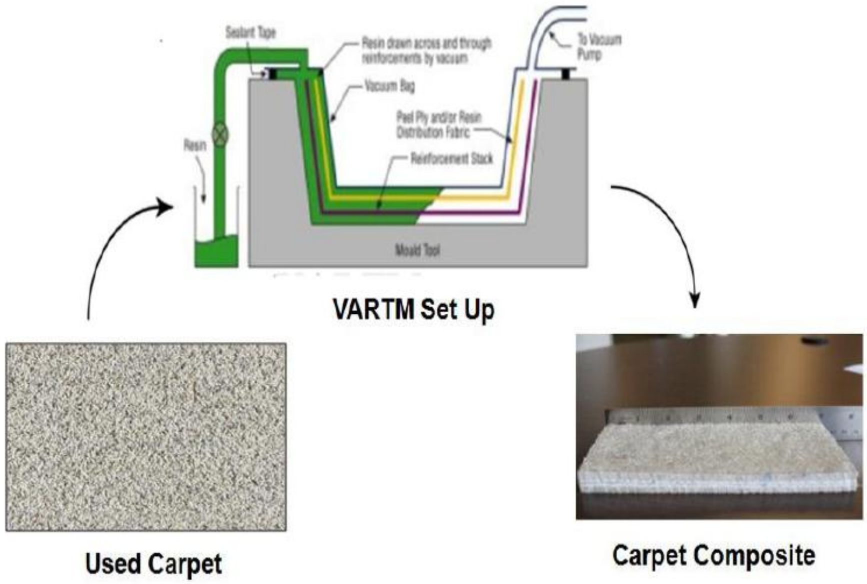


Figure 1.3: VARTM setup for carpet recycling. [9]

The new composites made from recycled carpet showed potential applications as sound absorbing panels for the highways. The primary criteria for application as a highway sound barrier are: 1) sound absorption capability and 2) strength to withstand wind. The static wind load test for BTTB carpet combination showed it required 448.11 kPa of static pressure to break the panels which was equivalent to 200mph of wind speed. [10] Acoustic characterization of the BTTB composite gave noise reduction coefficient (NOC) of 0.58 in third octave band ranging from 125Hz to 4000 Hz. On the other hand, most commonly used sound barrier panels such as concrete and wood of the same thickness demonstrated NOC of 0.12 and 0.37, respectively. [9, 11]

Figure 1.4: Carpet Composite with BTTB combination: Side view of flat sample (left) and cross sectional view of curve composite (right)

1.4 Environmental degradation of carpet composites

The performance of the carpet composite demonstrated high potential as a new material for highway sound barrier and other structural application in terms of acoustic and mechanical properties. However, during long-term outdoor type of applications, the composite panels would be exposed to UV, moisture, heat, wind, dust and other pollutants that could potentially deteriorate the properties of the composite panels. [12] Among all the environmental elements, moisture and UV play important roles in physical and chemical change or degradation process of polymers. [12]

The following section is about the possible degradation that the carpet composites may undergo due to the interaction with moisture and Ultra-violet (UV) radiation.

1.4.1 Effect of water on polymer

Chemical and physical changes are observed in polymers due to interaction with moisture. Chemical changes involve hydrolysis and leaching of additives. As a result, plasticization effect can be seen in polymers which lead to changes in mechanical properties. [13]

The water absorption kinematics in polymer is generally divided into two types: 1) Fickian and 2) non- Fickian. For the first kind, absorption follows the Fickian law of diffusion which in one dimensional case is governed by the following equation:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \text{ ………………………………….(1)}$$

This equation can be simplified in the following form relating mass gain to diffusivity and thickness h with time[14] :

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi h^2}\right)^{1/2} \text{ …………………………..(2)}$$

Taking initial mass M_∞ , thickness *h*, and diffusivity *D* as constant, mass gain becomes proportional to square root of time. As a result Fickian diffusion can easily be identified from linear relationship of mass change and square root of time. Fickian diffusion of polymers involves absorption through nano or micropores of the polymer, where non-Fickian indicates boundary separation in different polymer phase and causes swelling and residual stresses in polymers. [15]

Epoxy has strong affinity towards water. Absorption and transportation mechanism of water has been of interest for many researchers. Different techniques has been utilized to figure out whether the absorbed water molecules are in motion or in static. Most of the findings came to the conclusion that water is stable inside the epoxy and water molecules are attached to specific locations of the molecular chain of epoxy. It is assumed that nano voids open spaces for the water and polarity of the epoxy facilitates attachment of water molecules with polymer chain. NMR study by Fuller et al. indicated absorbed water molecules by epoxy is not in motion. [16] They also found hydrogen exchange in between water and epoxy. [17] Similar findings was reported by Ellis and Karasz and they suggested that one water molecule can interact with six OH sites of epoxy polymer. [18, 19] Along with the polarity, free void of epoxy facilitates water motion. During the formation of covalent bond in curing process, nanopores of 5-6 Å size are created which is big enough to occupy water molecule. [20] As the absorption process goes on, water absorption is slowed down not only because of the decrease of free void, but also for the hindrance created by the other water molecules strongly attached to the polar sites of the epoxy chain. [21]

However, epoxy can be saturated by 1 to 7% of water of its weight depending on the nature of epoxy. [22] Due to interaction with water, there can be change in physical and mechanical properties. One of the after effect of water absorption is depression of glass transition temperature (T_g) which is attributed to plasticization of epoxy. [23] Moy and Karasz reported that depression of T_g increases with the increase in amount of absorbed water. [24] Absorption of water leads to formation of microvoid and microcracking, as a result of which loss of mechanical properties is observed. [25]

Similar effect of moisture is observed in nylon. Nylon 66 can absorb up to 9% of moisture of its weight. [12] Reduction in tensile strength and modulus has been reported due to degradation by moisture. Reduction in elastic modulus may occur in nylon, and high temperature hygrothermal ageing can increase crystallinity. [26] Reduction in strength has been found as much as 82% after exposure to 100% relative Humidity in 100 °C up to saturation moisture absorption. [27]

In fiber matrix composites, interfacial bond between fiber and matrix is highly affected due to moisture absorption process. Debonding and weakening of the fiber-matrix bond is observed due to interaction with water. [27-29]

1.4.2 Effect of UV on polymer

Ultra violet (UV) radiation is responsible for chain scission, cross linking reaction, and photo-oxidation of polymer. UV exposure of epoxy leads to chain scission and surface cracking. [30] Due to irradiance of UV, surface damage and initiation of crack have been found in glass epoxy composites. [31]

Chemical, mechanical and physical changes in nylon are found when exposed to UV. Chain scission of the nylon by UV attack has been discussed by many authors. Figure 1.5 shows chain scission reaction in the most possible order [32]:

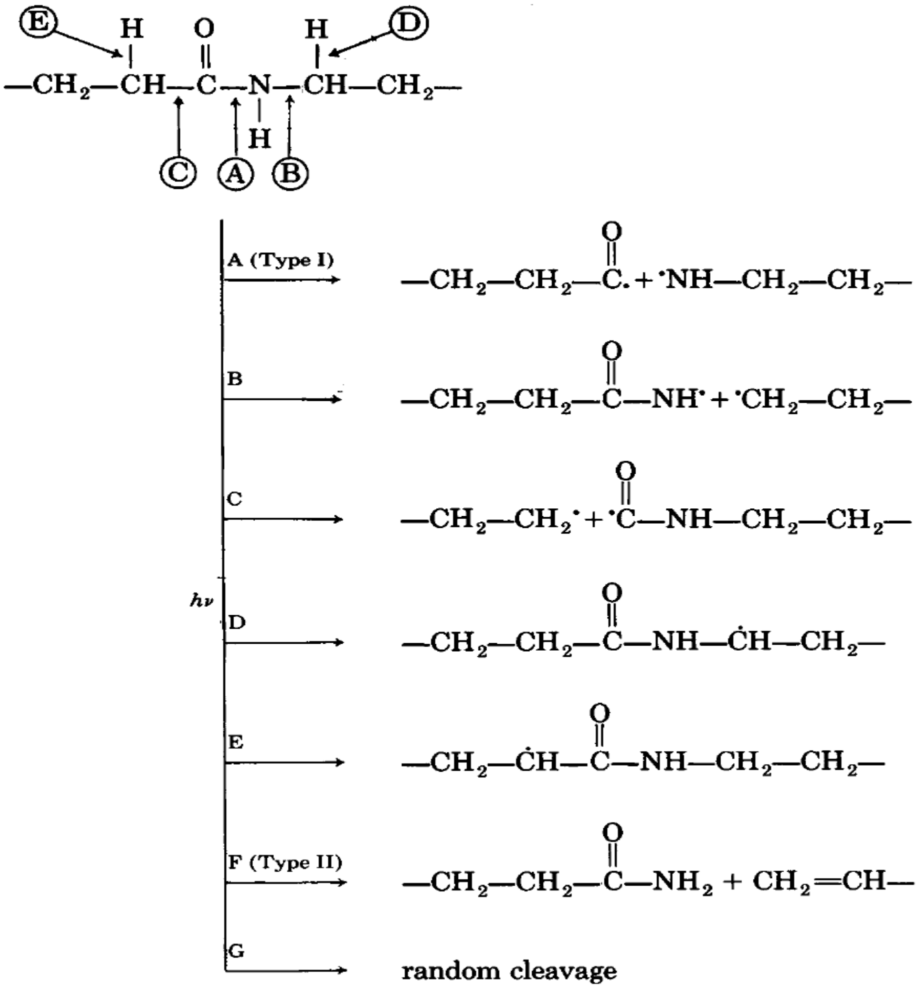


Figure 1.5: Possible chain scission reaction of nylon chain due to UV. [32] (Reused with permission from John Wiley and Sons)

FT-IR analysis showed that chain scission reaction of nylon 6,6 can be accompanied with emission of gases such as H_2, CO, NH_3, carbonyl compound. [32, 33]. Longer exposure of UV can lead to increased cross linking reaction. [34] Along with the chain scission and cross linking reaction, photo oxidation is another possible way of degradation of nylon in presence of UV. [35] Chain scission makes the polymer weaker and cross linking leads to brittleness and cracking.

Synergistic effect of UV and moisture is seen on polymer and polymer matrix composites. Kumer et al reported results of combined effect of UV and condensation on carbon fiber reinforced epoxy composites. Degradation process is accelerated and erosion can happen in polymer matrix by alternative exposure of UV and condensation. [36] It is assumed that the role of moisture in the combined effect of UV and moisture is to increases the mobility of the catalyst and thus enhance the degradation process.

1.5 clay- polymer nanocomposite

Clay is a montmorillonite mineral which has 2:1 sheet- layered smectite platey structure The elementary structure consists of 2 silica tetrahedron and 1 aluminum octahedral sheets. [37] These three sheets together make a clay layer whose thickness is 0.96nm. [38] High aspect ratio and high specific surface area have made nanoclay as an attractive nanofiller for polymers. The aspect ratio (thickness to diameter ratio) of nanoclay ranges 200 to 500, and specific surface area is more than 750 m^2/g. [37] Because of this high surface area, addition of small amount of nanocaly can contribute to significant improvement in mechanical properties as well as barrier properties against liquid and gaseous substants. To obtain the maximum performance of nanoclay, proper dispersion or exfoliation of nanoclay layers is extremely required. Based on the exfoliation or orientaion of clay layers in polymers, nanoclay- polymer composites are classified into three groups (figure 5) : 1) Conventional composite, 2) Intercalated Nanocomposite, and 3) Exfoliated Nanocomposite. [39] In conventional composites, there is no inclusion of polymer molecule in between the clay layers. In the second type, molecules of polymers enter in between clay layersand increse the distance of the layers. For exfoliated nanocomposites, individual clay layers are seperated from each other by polymer molecules.

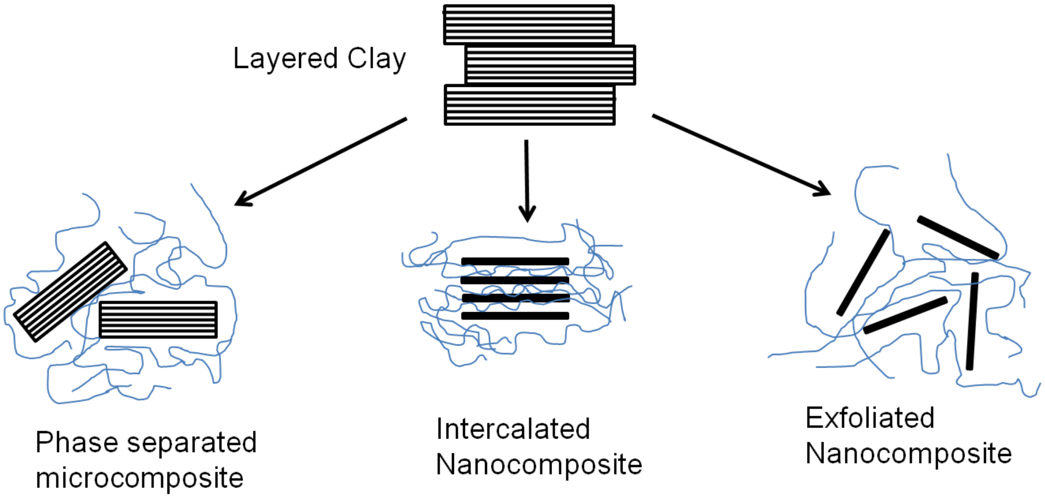


Figure 1.6: Schematic illustration of different clay- polymer composites. Modified from [39]

1.5.1 Effect of clay on properties of polymer and composite

Clay has been used with different polymers as a reinforcing agent. Proper mixing of clay restrains the movement of polymer chain, and enhancement in modulus is generally observed. Kojima et al. introduced use of clay polymer and reported enhancement of tensile strength, tensile modulus, flexural strength and modulus. [40] Lan and Pinnavaia found increasing trend of tensile strength and modulus in DGEBA epoxy with increasing amount of clay loading. [41] Chan et al. used different amount of clay and measured the strength and modulus. They found increasing trend of clay modulus and strength of epoxy up to 5% wt of clay loading and reduction in properties with higher amount of clay. According to their observations, clay platelets can hinder crack propagation in polymer matrix and thus help improving strength. On the other hand, higher loading creates agglomeration and works as discontinuity in matrix. [42] Similar effect of agglomeration has been found by Zerda et al. They reported improvement of properties up to 3.5% of clay loading and decrease with higher amount of clay. [43] Zaarei et al. found enhancement of microhardness, toughness and wear resistance for use of clay with epoxy as coating. [44]

1.5.2 Effect on barrier properties

Reduction in absorption and enhancement in barrier properties for liquid and gas have been obseved by addition of clay. These effects have been attributed to the tortuousity effect due to higher aspect ratio of clay platelets. Based on the tortuosity effect, Neilsen's model has been developed which predicts the permeability properties of clay composites against liquid and gaseous molecules by the following equation [39]:

$$P_{nanocomposite} = \frac{(1-\phi)P_{matrix}}{1+\alpha\frac{\phi}{2}}$$

Here α is aspect ratio, *Φ* is the volume fraction of nanofiller and *P* represents permeability. According to the model , because of the high aspect ratio of nanoclay, small volume fraction of nanoclay can provide significant improvement in barrier properties.

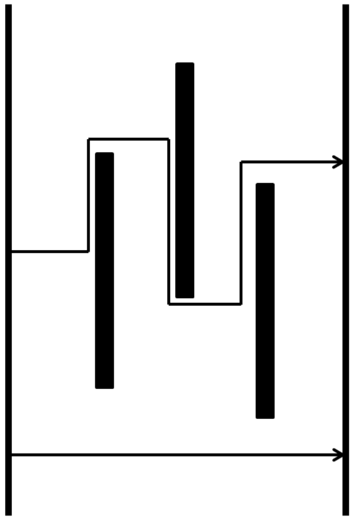


Figure 1.7: Illustration of Neilson's tortuous path model for reduction in permeability. Image modified from [39]

Experimental results show that the tortuousity effect significantly reduces the permeability of moisture and gas in nanoclay-polymer composites than the polymer itself. [14, 45, 46]

1.5.3 Impact of clay on degradation mechanism

Clay can bridge nanovoids and hinder degradation mechanism. This is the way it reduces the moisture absorption rate in epoxy. Not only that, by preventing formation of micro-crack due to environmental effect, it can reduce the effect of degradation on mechanical properties. Kim et al. used different types of clay and found reduction in moisture absorption while compared to neat epoxy. [14] Studies of effect of NO_x on the mechanical properties have also suggested that clay-polymer composites can retain tensile strength better than neat polymer after degradation. [47] Fractographic analysis by woo et al. indicated that initial degradation process by UV cannot be delayed by the use of clay, but effect of longer UV exposure is prevented. Clay can hinder diffusion of oxygen and other free radicals and thus prevents crack propagation along the thickness of the material. [30] Bagherzadeh et al. applied 60±5μ coating of epoxy-clay on metal and found better anti-corrosive behavior. [48] Singh et al. reported the effect of clay on retention of mechanical properties of epoxy against alternating exposure of UV and condensation. According to them, clay decreases the formation of cracks and micro-channels, and provides higher flexural strength and modulus after combined degradation. [49]

1.5.4 Effect of clay on fire retardancy of polymer

Polymers are more vulnerable than metal, ceramic, or concrete as construction material because of their flammability. Polymer can start a flame once the surface temperature reaches ignition point. For most polymers, ignition temperature ranges from 275°C to 475°C. [50] Norman Grassie proposed a simple model of fire propagation mechanism through polymer (figure 1.6). [51] According to the model, once the fire is ignited, because of the heat, polymer undergoes thermal decomposition and produces liquid and gaseous components which take part in the burning process.

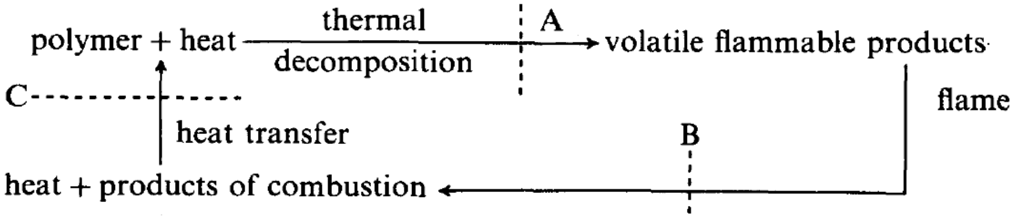


Figure 1.8: Flame propagation model proposed by Norman Grassie. [51] (Reused with permission from Elsevier Limited)

Different approaches to improve fire retardancy are targeted to discontinue the fire propagation cycle by breaking it on the point A, B, or C (figure 1.6).

Use of nanoclay or any other nanomaterial can create barrier against propagation of combustible product produced by heat and delay the flame propagation. Nanoclay hinders the physical movements of flammable product by two method: 1) Barrier effect and 2) formation of char. [52]

The network structure formed by nano particles create a thermal shield for heat, oxygen and other combustible product and reduce supply of fuel for flame. On the other hand, in many cases, use of nano components helps formation of robust char which prevents flow of combustible product produced by heat during burning process. [52] Kashiwagi used nanosilica, nanoclay, and carbon nanotube with PMMA, polyamide, and polypropylene, respectively, and observed fire properties in a cone calorimeter. It was reported that addition of nanoparticles can delay ignition time, reduces peak, and average heat release rate compared to neat polymers. The aspect ratio of the nanoparticle was attributed as the controlling parameter on the effect of flame retardancy. Analysis of the final burning product showed higher aspect ratio of the particle is favorable for formation of char and reducing crack during burning process. [53] Clay has been used in polymer with other flame redardant chemicals and reduced flammability was reported. Nazare et al used nanoclay in polyester with different flame retardants and found delay in ignition time and decrease in total and peak heat release. [54]

1.6 Objective

Previously it was discussed that carpet composites are vulnerable against environmental degradation for long term outdoor use. Based on the literature review, it can be hypothesized that addition of clay can reduce the degradation process. In the carpet recycling process by VARTM, carpet is used in as received condition. Addition of clay in epoxy can provide improvements in mechanical properties and reduce environmental degradation. Clay can be added in epoxy matrix in two ways:

In first method, clay can be dispersed in epoxy matrix before VARTM. It is expected that effect of clay in epoxy matrix will provide two important benefits:

1) Decelerate degradation mechanism in epoxy matrix by hindering formation of crack
2) Improve barrier properties against moisture to reduce degradation in fibers due to moisture absorption

In the second method, clay-epoxy can be used as a coating on the carpet composite. The UV degradation mostly effects the surface by initiating micro-crack and channels. By forming a clay/epoxy coating on the composites, the surface of the porous composites can be closed properly, and there is chance of having significant improvement in durability.

In addition, use of clay may provide better fire retardant properties. The advantages of using clay as fire retardant is that it reduces flammability without compensating the mechanical properties.

This study is focused on the effect of clay on the durability and flammability of the recycled carpet composite fabricated by VARTM process. Clay has been used as a nonofiller with epoxy matrix, as well as clay-epoxy coating was used on regular carpet composites. Effect of moisture and alternating exposure to UV and condensation on the carpet composites are studied. Flexural test has been utilized to quantify and compare the degradation process. Mass change is monitored for better understanding of the degradation process.

CHAPTER II

MATERIALS AND EXPERIMENTS

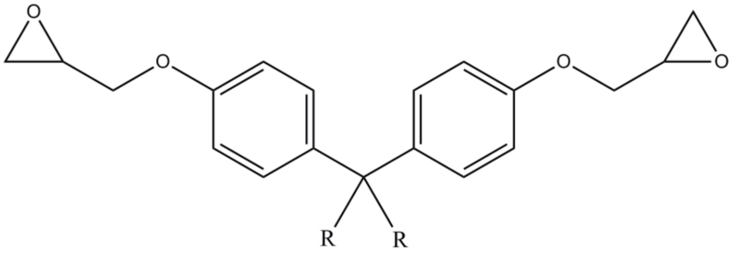
2.1 Materials

2.1.1 Resin System

The carpet composites were fabricated by vacuum assisted resin transfer molding (VARTM) process. The viscosity of the resin plays an important role for on the quality of the finished composites. Low viscosity may deform the composites. On the other hand, higher viscosity may lead to improper distribution of the polymer resin. [55] At the same time, higher pot life is desired for VARTM process to avoid the gelation before complete resin infusion.

The resin system used for this study is System 2000 epoxy purchased from Fibre Glast Corporation. This resin is mixture of epoxy with less than 0.8% of multifunctional acrylate. [56] Three different types of hardener are available for curing of system 2000 epoxy resin. For convenience of VARTM process, 2120 epoxy hardener which is a modified amine mixture was used because of its higher pot life,. The resin mixture was prepared with epoxy resin and hardner in the weight ratio of 100:27. The mixture has medium viscosity (925-975 cps) and 2 hours pot life at room temperature. [57]

The material data sheet has not provided the actual structure and formulation of epoxy resin. The epoxy could be either diglycidyl ether of bisphenol-A (derived from acetone) or diglycidyl ether of bisphenol-F (derived from formaldehyde). The general chemical structure of diglycidyl epoxy is shown in figure 2.1



When R= H, DGEBF
R= CH_3, DGEBA

Figure 2.1: Chemical structure of diglycidyl epoxy

2.1.2 Nanoclay

The nano-filler used in this study was Nanomer I.28 (Nanocor, Inc., IL, USA). This clay had been selected because of its compatibility with epoxy. This clay has particle size of 15 -20 micron. The clay surface was modified with trimethyl octadecyl ammonium chloride (figure 2.2) and modifier concentration is 25-30%. In order to allow the dispersion of clay in an organic medium, a surface modification was required to make it organophilic. I.28 clay has been chosen for the longer chain of modifier salt. Longer chain of the modifier helps better dispersion and higher mechanical strength of the nanocomposites than the clay modified with shorter chain. [58]

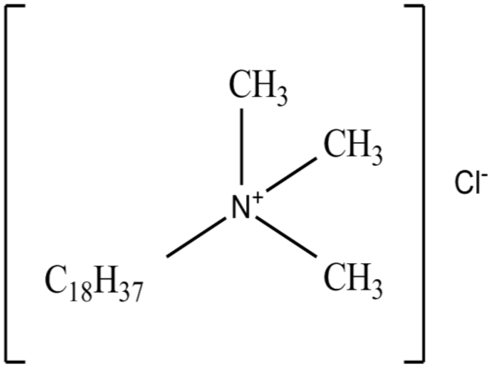


Figure 2.2 : Structure of nanoclay modifier

2.1.3 Carpet

In this study, orange color nylon cut loop type carpet was chosen (manufactured by Shaw Industries). The properties of the recycled carpet composite depends and varies on the life time of recycled carpet. In this studies, new carpet was used for baseline studies. Bottom- Top- Top-Bottom (BTTB) configuration of the carpet layup was chosen for composite fabrication as shown in figure 2.3.

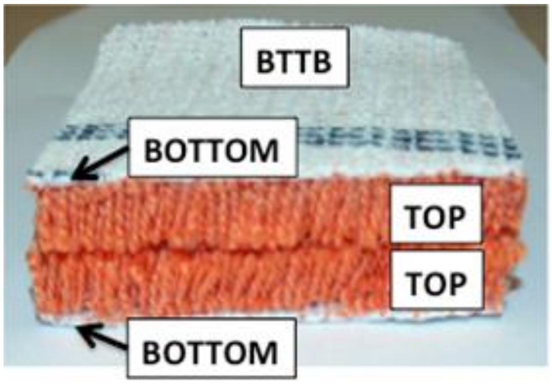


Figure 2.3: Configuration of carpet preform for fabrication of composite

2.2 Fabrication of carpet composites

Three different types of carpet composites have been fabricated for this study. These are- a) Neat epoxy carpet composite; b) Clay coated carpet composite; and c) Clay Infused carpet composite.

Fabrication of neat carpet composite with epoxy matrix has been elaborately described by Krishnan Lakshminarayanan. [9] Vacuum assisted resin transfer molding (VARTM) process has been used to fabricate carpet composites. In this process, layers of carpet were placed on a metal mold and it is completely sealed inside a vaccum bag with an inlet and outlet port for the resin to flow through the carpet layers (figure 2.4). Vacuum pressure of 75kPa has been utilized to pull the resin and infuse inside carpet layers. Different release medium and infusion fabric have been used as shown in figure 2.5 to facilitate uniform and faster infusion of the resin. After the infusion, resin was pre-cured in room temperature under the vacuum pressure. After demolding, composites were post-cured at 49 °C for 6 hours.

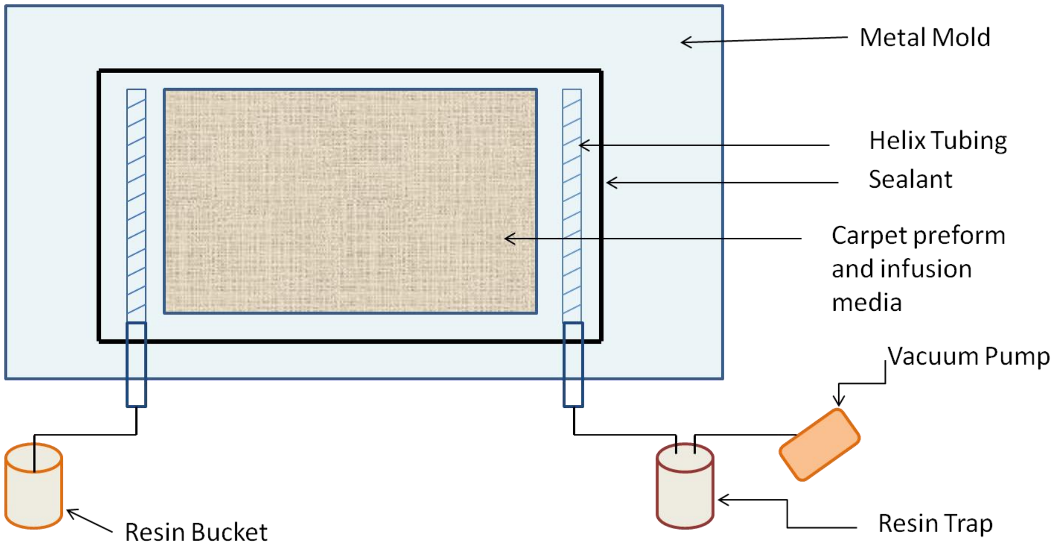


Figure 2.4: Schematic Diagram of the mold for VARTM process (Top view). Modified from [9]

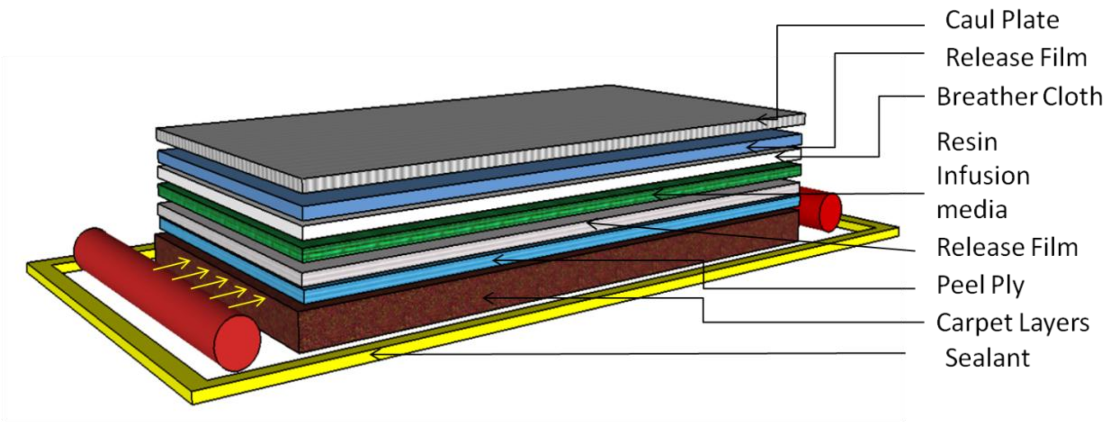


Figure 2.5: Schematic illustration of different infusion media and release fabric used in VARTM process

The same aforementioned VARTM fabrication process was used to make neat epoxy- carpet composites for our study. To fabricate clay coated composite, epoxy resin and clay in the weight ratio of 100:4 clay were mixed by magnetic stirring for 24 hours at 120 °C, and hardener was added in the mixture. Neat epoxy composite demolded from the vacuum mold was coated with this mixture by a paint roller (Figure 2.7). After coating, the coated material was pre-cured in room temperature for 24 hours and post- cured at 49 °C for 6 hours.

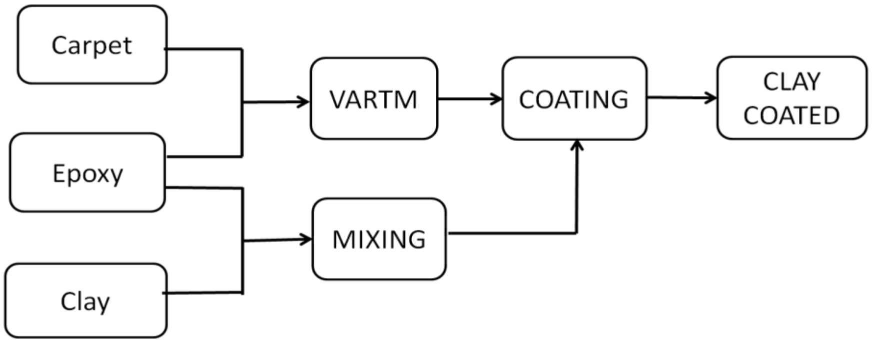


Figure 2.6: Flow chart of fabrication of clay coated carpet composites.

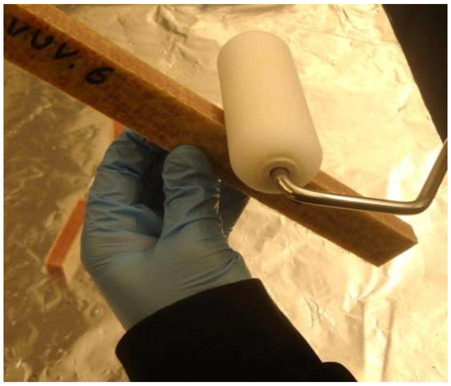


Figure 2.7: Coating of carpet composite with epoxy- nanoclay

For clay infused carpet composites, 4 wt% clay were dispersed in the epoxy by magnetic stirring for 24 hours at 120 °C, and the clay- epoxy mixture was infused through the carpet layers by VARTM process. The resin was pre-cured for 24 hours in room temperature, and then, post-cured at 49 °C for 6 hours.

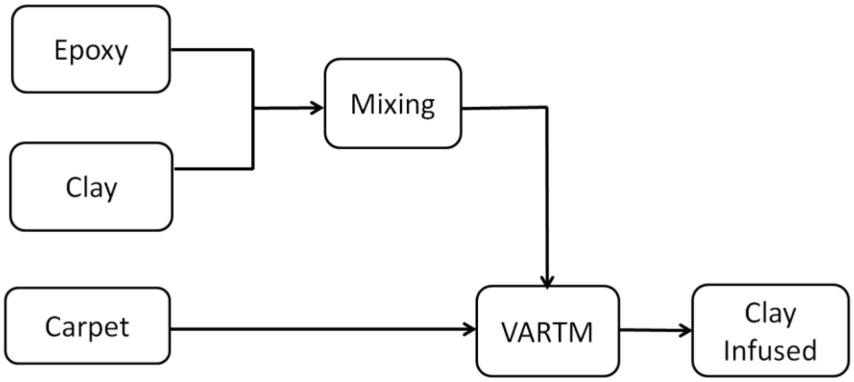


Figure 2.8: Flow chart of fabrication of clay infused carpet composites

2.3 Characterization test

The characterization tests were performed on the carpet composite for their environmental durability and fire retardancy. Two different environments had been applied on the composites for degradation studies. In the first case, composite panels were soaked in deionized water and the experiment had been termed as 'moisture absorption'. In the second case, cyclic exposure of the ultra- violet (UV) and condensed water vapor were applied on the composite. To observe the effect of environmental exposure, flexural test was performed for each type of the composite before and after the exposure. The mechanical test methods and the environmental degradation conditions used in this study are discussed in the following sections.

2.3.1 Flexural Strength and Modulus

Flexural strength and modulus were determined by three point bending test according to ASTM D 790 standard. [59] For this test Universal testing machine (Instron 5567, Norwood, MA) was used with a adjustable two support of anvils with radius of 4 mm and loading anvil of 10 mm radius.

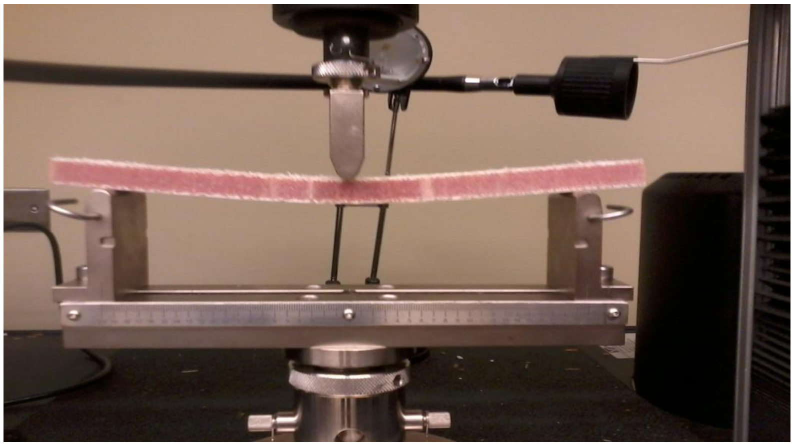


Figure 2.9: Flexural test of carpet composite

Rectangular bars were cut from carpet panels by bend saw. The width and length of the samples were kept 25 mm and 250 mm, respectively. The bars were rested on two nose supports and span length was kept at 200 mm. The specimen was then loaded in the middle of the supports with a constant strain rate (Figure 2.1). The cross head motion was calculated using equation 2.1 .

$$R = \frac{ZL^2}{6d} \quad \text{...(2.1)}$$

Where:

R= rate of crosshead motion, mm/min

L= support span, mm

d= depth of the beam, mm

Z= rate of straining of the outer fiber, mm/mm/min (equal to 0.01)

Based on the nominal dimensions of the specimen and the equation, the crosshead motion was maintained 5 mm/min for every specimens.

Equation 2.2 and 2.3 were used to calculate the flexural stress and strain from the applied load and midpoint displacement data.

$$\sigma_f = \frac{3PL}{2bd^2} \text{...(2.2)}$$

$$\varepsilon_f = \frac{6Dd}{L^2} \text{...(2.2)}$$

Where:

P= load

D= deflection of the midpoint of test span

The flexural modulus was obtained from the stress strain curve. For each type of sample, five specimens were used.

2.3.2 Moisture absorption

The samples were cut according to the required dimensions for the flexural test. The samples were then submerged in sub boiling deionized water for 1000 hours. Bulb condenser was attached on the hood of the water vessel to prevent water evaporation and to maintain constant water level (figure 2.10). Maintaining same water level helped to keep the temperature steady. Edges of the specimens were coated with high temperature wax to ensure uni-directional water diffusion. Before submerging the samples, the temperature of the water was kept stable at 80 °C ±2 °C by controlling the hot plate temperature. To reduce evaporation loss during the weight measurement, samples were placed at room temperature water for 10 min to bring them to ambient temperature before weight measurement. Before every measurement, specimen surface was wiped carefully to remove the surface water.

Figure 2.10: Moisture absorption of carpet composites

2.3.3 Cyclic Exposure of UV and condensation

The combined effect of Ultra-violet (UV) and condensation was studied by exposing several composite samples to alternating cycles of 8 hours UV radiation and 4 hours of water vapor condensation, as per ASTM G154-05. [60] An irradiance of 0.89 W/m^2 and a temperature of 50 °C was applied on the composite surface in the first step of the cycle. In the second step condensed air was applied at 50 °C for 4 hours. These tests were performed using a QUV/se Accelerated Weathering Tester, (Q-Panel Lab Products, Cleveland, Ohio, USA). After every 2 cycles (24 hours), the weight of the samples were recorded and the sample were rotated 180° before the next cycle. High temperature wax was applied on the edge of the composite to ensure unidirectional moisture diffusion.

Figure 2.11: Test chamber used for alternating exposure of UV and condensation

2.3.4 Fire Test

The flammability resistance of different types of composite was determined according to ASTM D 635-10. [61] In this set up, a composite bar of 125 ± 5 mm length was placed horizontally, and the free end of the samples were exposed to a standard test flame for 30 s and then flame was removed. The time of flame propagation in between two fixed position of the composite bar with 75± 1mm distance was recorded. From the recorded time flame propagation rate was measured in mm/min unit. An average of 11 samples were reported for each type of composite.

Figure 2.12: Test setup for determining flame propagation rate

CHAPTER III

RESULT AND DISCUSSION

3.1 Moisture Absorption

3.1.1 Gravimetric Analysis

Figure 3.1 represents comparison of the moisture absorption behavior in different carpet composites.

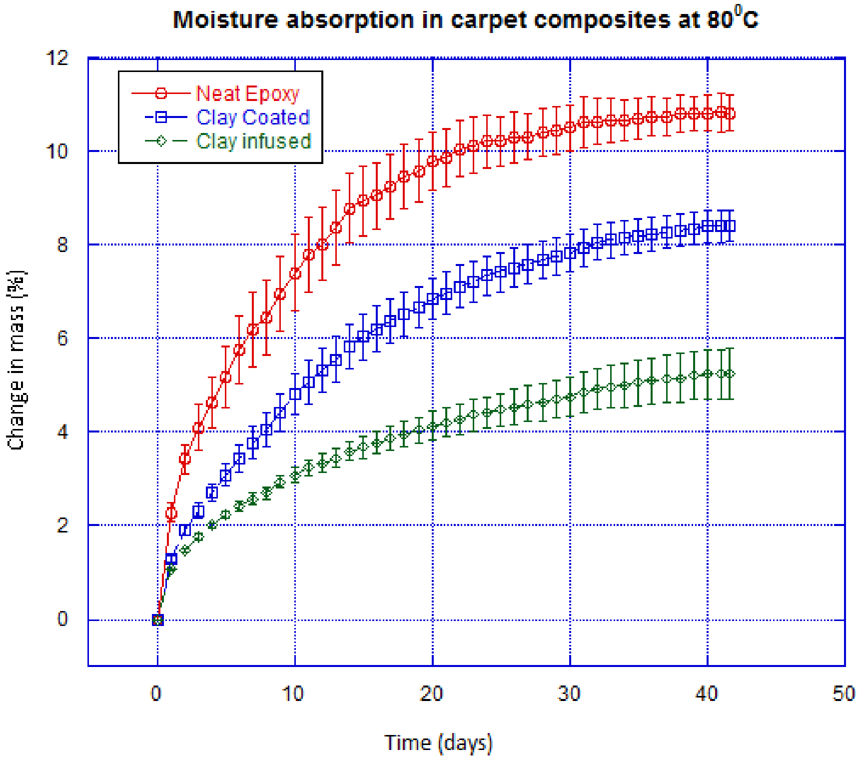


Figure 3.1 Moisture absorption behaviors of different carpet composites at 80°C. Error bar indicates standard deviation of five specimens.

From the curve, it can be inferred that after 1000 hours of moisture absorption, neat epoxy has reached the saturation or equilibrium water content. On the other hand, clay containing sample sets are showing slightly increasing trend at the end of the observed time period. Relative amount of moisture for the neat epoxy composites was about 11%, where as for clay coated and clay infused samples, it was around 8% and 5%, respectively. The maximum moisture absorption for epoxy and nylon are reported as 7% and 9%, respectively. [12, 22] On the other hand, carpet composites being porous absorb more moisture than the individual components.

It has been reported that clay enhances the saturation moisture level due to interface increase in the composite. [62] From the analysis of moisture absorption graph, it is difficult to predict if the clay increases or decreases water saturation level of carpet composites. However, it is seen that the addition of clay has reduced moisture absorption rate, and the absorption rate is observed in the following decreasing order: 1) neat epoxy, 2) clay coated, and 3) clay infused carpet composite.

For clay infused carpet composites, clay may effect on the overall moisture behavior of the composites in two ways:

1) Reduction in moisture diffusion rate in epoxy matrix
2) Reduction in permeability of epoxy matrix against moisture to reach nylon fibers

Reduction in moisture absorption rate or diffusivity constant by use of clay has been reported by many authors.[14, 62-64] Others reported that clay reduces moisture saturation level due to: I) bridging of microvoids, II) increased cross linked density around the clay platelets. [14, 64] Reduction in permeability is due to the tortuousity effect clay against water to pass through the matrix. [14] Because of the effect of clay throughout the matrix, clay infused carpet composites absorbed the lowest amount of moisture than the other two types of composites.

In the case of clay coated carpet composites, although the thickness of the coating is negligible compared to the thickness of the whole composite, a significant effect of clay coating in reducing the moisture absorption rate is observed. The neat carpet composite is highly porous. The coating on the composite with a thin layer of clay-epoxy mixture mends the pores, and acts as a clay reinforced diffusion barrier.

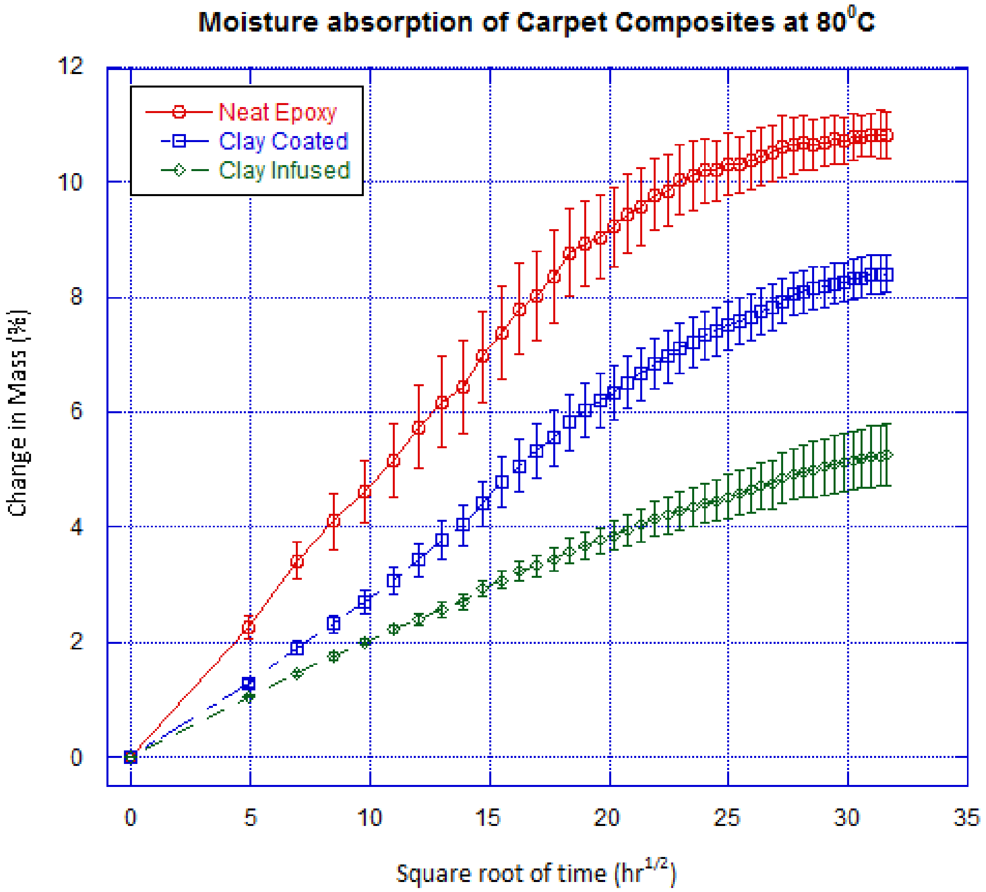


Figure 3.2: Change in mass in carpet composites as a function of square root of time. Error bar indicates ± standard deviation of five specimen

Change in mass due to moisture absorption as a function of square root of time is given in figure 3.2. The diffusion of water inside the composites was made unidirectional by blocking transport of moisture through the edges of the composites by coating with high temperature wax. In the plot, the initial straight line indicates the dominance of one directional Fickian diffusion.[65] Based on the Fickian diffusion, it can be assumed that the movement of moisture molecule is through the micro pores only. In this case, swelling, separation of different phases, and residual stress are not involved in the moisture diffusion process. [15, 65]

3.1.2 Mechanical Properties

3.1.2.1 Flexural Strength

Table 3.1 lists the flexural strength of different composites before and after moisture absorption. The flexural strength value of as prepared neat epoxy and clay coated composites are almost same. This shows that the thin clay layer coating did not show any effect in the flexural strength. On the other hand, increase in flexural strength in clay infused samples was around 13% compared to the neat epoxy composite. Similar enhancement of flexural strength has been observed in carbon fiber clay/epoxy [64, 66] and glass fiber clay/epoxy [67, 68] hybrid composites. This improvement in flexural strength for clay reinforced hybrid composites is attributed to the enhancement of strength in epoxy matrix and interfacial interaction of fibers and clay.

Table 3.1: flexural strength of different Carpet composites before and after moisture

Sample Type	Flexural Strength (MPa)
As Prepared Neat Epoxy	27.06854± 0.4417
As prepared Clay coated	27.93063± 0.17556
As prepared Clay Infused	30.67843±0.8963
Moist Neat Epoxy	20.92116±1.01040
Moist Clay Coated	22.69899±1.0525
Moist Clay Infused	25.86529±1.1385

Significant reduction of flexural strength of the composites has been noticed after the moisture absorption in comparison with the as prepared samples. For neat epoxy composite, reduction in flexural strength was 22.7%. On the other hand, reduction in strength was 18.7% and 15.7% , respectively for clay coated and clay infused composites. Reduction in flexural strength can be due to chemical degradation of both fiber and epoxy matrix, and also due to reduction in interfacial bonding between fibers and epoxy. [29] Reduction of flexural strength was minimum in. clay infused composite. It can be assumed that higher barrier property of the clay-epoxy matrix against water has slowed down the degradation process of nylon and fiber matrix interface. At the same time, presence of clay in epoxy matrix has maintained better mechanical properties of epoxy matrix after the degradation process.

3.1.2.2 Flexural modulus

Table 3.2 shows flexural modulus of different carpet composites before and after moisture absorption. As prepared clay infused composites has demonstrated 40.8% increase in flexural modulus in comparison with that of the neat epoxy samples. Increment in flexural modulus in clay- epoxy nanocomposite and for clay-epoxy- fiber composites has been reported by many authors. The increase in the flexural modulus is attributed to the motion restriction of the polymer chains by the clay platelets, and increase in the cross linking density of polymer around the clay platelets. Another possible explanation for modulus enhancement could be the increase in interfacial bonding between matrix and fiber by clay platelets.

Table 3.2: Flexural modulus of carpet composites before and after moisture absorption

Sample Type	Flexural Modulus (MPa)
As prepared Neat epoxy	1842.396± 96.91325
As prepared Clay coated	1877.732± 74.6482
As prepared Clay infuse	2594.19967± 64.0043
Moist Neat Epoxy	898.1166± 44.83102
Moist Clay Coated	1106.521± 44.2223
Moist Clay Infused	1392.555± 167.2172

Reduction in elastic modulus due to moisture absorption is observed (Table 3.2) in carpet composites. Reduction in modulus is directly related to scission of polymer chain. [69] For neat epoxy carper composites, reduction was 51.2%, while it was 41.1% and 46.32%, respectively for clay coated and clay infused composites. The improvement in modulus for moisture absorbed clay composites compared to neat composites is attributed to the less scission of polymer chains as a result of low moisture diffusion due to the presence of clay platelets.

3.2 Cyclic exposure of UV and condensation

3.2.1 Gravimetric Analysis

Variation in mass in neat and clay carpet composites due to the cyclic exposure to Ultra Violet (UV) and condensation is shown in figure 3.3. It is observed that during 1000 hours alternative exposure, neat epoxy composites gained more weight than clay composites. Among the clay composites, clay infused composites has more weight change than clay coated composites. The reason is attributed to the number of voids present on the surface of composites. The neat composites gained more weight because of the presence of numerous voids. These voids are minimum for clay coated composites as a result of thin coating of clay- epoxy on the composites' surface. The voids are not closed for infused carpet composite, but the weight gain is lower than neat composite because moisture diffusion is hindered due to tortuousity by clay platelets. No erosion or decrease of weight has been noticed during exposure of 1000 hours.

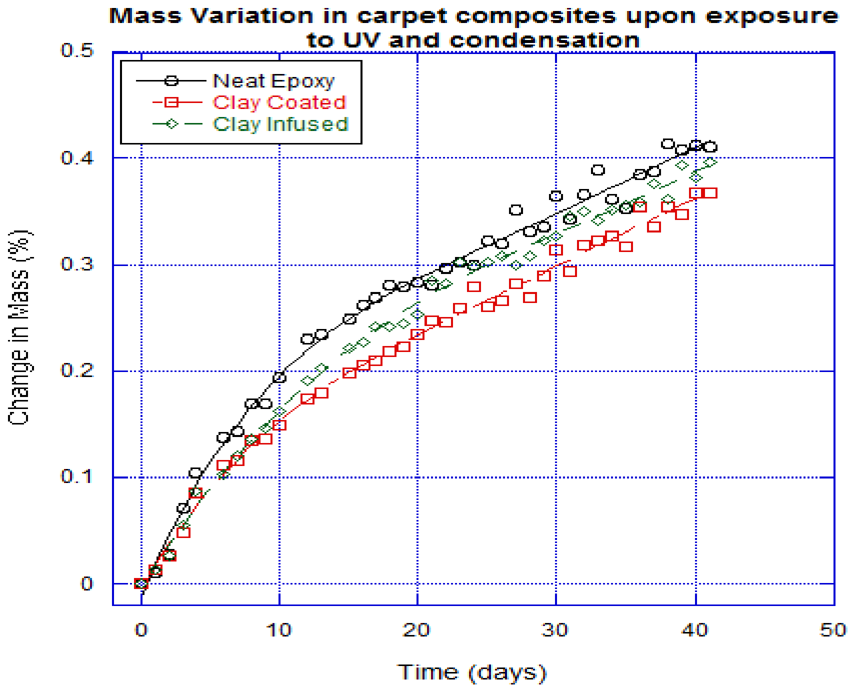


Figure 3.3: Change in mass of carpet composites due to alternating environmental exposure

3.2.2 Mechanical properties

3.2.2.1 Flexural Strength

The flexural strength of different carpet composites before and after cyclic exposure to UV and condensation is shown in table 3.3. The results show an unexpected Increase in flexural strength after alternating environmental exposure. The possible explanation for this could be an increase in the cross linking density in epoxy matrix due to high temperature in the degradation chamber. The degradation effect on the mechanical properties as a result of cyclic exposure is not observed

This is due to the high thickenss of the carpet composite, and 1000 hrs exposure time is not sufficient to significantly change the mechanical properties as a result of degradation . UV degradation is surface phenomena. Liau et al. exposed glass fiber composite in UV and effect of UV was not found for the composite with more than one lamina after 180 days exposure. [31] Kumar et al. used sample thickness of 1.27 mm of epoxy carbon fiber composites for UV and cyclic exposure to observe the change in properties, and as a result, found some decrease in the mechanical properties. [36] Allen et al. used nylon test samples of 100 μm thickness to observe the significant effect of exposure. [70] In the case of carpet composite, 14 mm thick composites were used for exposure. Due to the high thickness of the composite, and less exposure time, the UV exposure effect is limited only the surface layer. As a result, significant contribution from degradation is not observed in the strength reduction of the carpet composites.

Table 3.3: Flexural strength of carpet composites before and after exposure to UV and condensation

Sample Type	Flexural Strength (MPa)
As Prepared Neat Epoxy	27.06854± 0.4417
As Prepared Clay Coated	27.93063± 0.1756
As Prepared Clay Infused	30.67843± 0.8963
Degraded Neat Epoxy	37.38847± 8.5581
Degraded Clay Coated	43.48824± 1.0962
Degraded Clay Infused	36.92608± 1.9672

It is seen that clay coated composites possess the highest strength after alternating degradation in comparison to other samples of carpet composites. This is attributed to the low absorption of water and hence low degradation of the clay coated composites. Clay acted as a strong barrier against moisture penetration, and protected the composite panels degrading from UV radiation and condensation.

3.2.2.2 Flexural Modulus

The flexural modulus of composites before and after cyclic UV and condensation is given in table 3.4. The neat and clay coated composites show an increase in flexural modulus after alternating environmental exposure. Higher cross linking density restricts molecular movements. Increase in flexural modulus after alternating degradation indicates higher cross linking density of epoxy matrix during the degradation process. But, the flexural modulus of clay infused composites is decreased after cyclic exposure due to unknown reason.

Table 3.4: Flexural modulus of carpet composites before and after exposure to UV and condensation

Sample Type	Flexural Modulus (MPa)
As Prepared Neat Epoxy	1842.396339± 96.9133
As Prepared Clay Coated	1877.731891± 74.6482
As Prepared Clay Infused	2594.19967± 64.0043
Degraded Neat Epoxy	2032.447225± 213.7068
Degraded Clay Coated	2183.034141± 40.58722
Degraded Clay Infused	2173.147697± 40.34234

3.3 Fire test

Figure 3.4 shows comparison of the linear flame propagation rate for different carpet composites. 20% and 34% reduction in the average linear burning rate for clay-coated and clay infused samples, respectively are observed when compared to neat composites.

Clay coated samples have clay only on the surface and it can be assumed that clay-epoxy coating delayed the ignition time to initiate the flame propagation. The formation of initial flame is important in flame propagation in absence of any other external heat source. Delayed ignition time can be attributed to the thermal stability enhancement of epoxy/ clay coating composites. [71] Among all the prepared composites, lowest flame propagation rate is observed in clay infused composite. This indicates that the presence of clay platelets throughout the matrix in the clay infused composite reduces the flame propagation in the bulk sample. The result is in accordance with the reported observation of reduction in flammability of clay-polymer compared to neat polymer. [53] Nano particles, like clay, when present in the polymer matrix help in forming network like structure against decomposed flammable product and hinder the burning process.

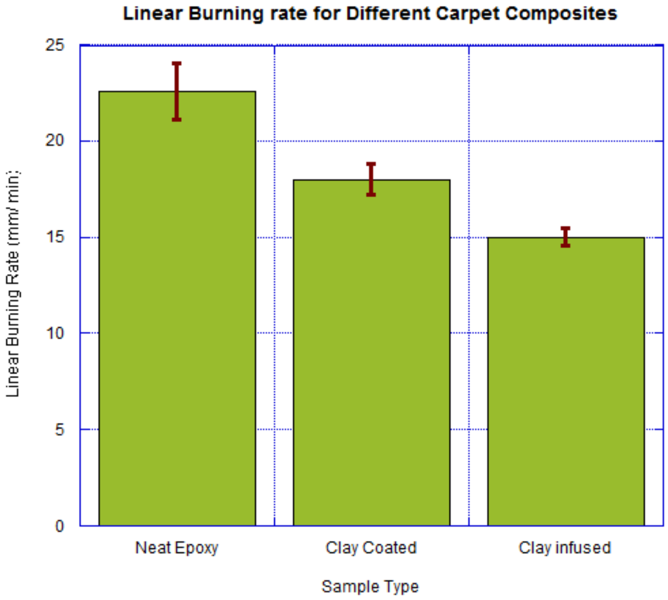


Figure 3.4 : Linear burning rate of neat and clay carpet composites. The error bar shows ± standard deviation of eleven specimens.

CHAPTER IV

CONCLUSION

Composite panels were fabricated from recycled post-consumer carpet materials. These composites were fabricated with neat epoxy, and further coated with a mix of epoxy and I.28E nanoclay. Composite samples were also fabricated by infusing them with a mixture of epoxy and 4 % I.28E. Composites were exposed to moisture and cycling exposure of Ultra violet and condensed vapor. Flexural properties were tested before and after each degradation process/

Significant reduction in flammability in the carpet composites was observed due to use of clay. The linear burning rate as per ASTM D 635-10 was reduced by 20 % for composite samples coated with the epoxy-clay coating, while it was reduced by 34 % for composite samples infused with 4 % nanoclay.

Moisture exposure for these samples indicated that both clay coating and clay infusion reduced the deleterious effect of moisture on the composites. Significant reduction in diffusivity was found in clay coated and clay infused composites. All the composite showed reduction in flexural strength and modulus, where severity of degradation was less in clay coated and clay infused carpet composites. After 1000 hours exposure of moisture clay infused carpet composite demonstrated higher strength and modulus than other other two composites. It was also observed that moisture absorption was a Fickian diffusion mechanism.

For alternating moisture and UV exposure cycles, the clay-coated samples exhibited the lowest change in mass, while the neat epoxy recycled carpet composites showed the highest mass gain. However, It was also observed that the combined moisture/UV exposure resulted in an increase in strength in the case of all composite types. It can assumed that , high temperature exposure of composites lead to higher cross linking of the polymer and exposure time for cyclic environmental condition was not long enough to observe the effect of degradation. Longer exposure and molecular analysis can be conducted to determine the effect of UV on the carpet composite.

REFERENCES

[1] C. Mihut, D. K. Captain, F. Gadala-Maria, and M. D. Amiridis, "Review: Recycling of nylon from carpet waste," *Polymer Engineering & Science,* vol. 41, pp. 1457-1470, 2001.

[2] V. Moody and H. L. Needles, *Tufted Carpet: Textile Fibers, Dyes, Finishes, and Processes*: William Andrew, 2004.

[3] G. Heisterberg-Moutsis, R. Heinz, T. F. Wolf, D. J. Harper, D. James, R. P. Mazzur, V. Kettler, and H. Soiné, "Floor Coverings," *Ullmann's Encyclopedia of Industrial Chemistry,* 2001.

[4] D. C. Young, S. J. Chlystek, R. Malloy, and I. Rios, "Recycling of carpet scrap," ed: Google Patents, 1998.

[5] C. Bremworth. (2010, Sep 9, 2012). *Style/ Texture*. Available: http://www.cavbrem.com.au/buying-guide/styletexture.aspx

[6] S. Al-Salem, P. Lettieri, and J. Baeyens, "Recycling and recovery routes of plastic solid waste (PSW): A review," *Waste Management,* vol. 29, pp. 2625-2643, 2009.

[7] C. A. R. Effort, "Carpet America Recovery Effort's Annual Report in 2011," ed, 2011.

[8] A. K. Singh, G. Pandey, R. Vaidyanathan, and R. P. Singh, "FABRICATION METHOD OF MULTI-FUNCTIONAL COMPOSITES FROM PRE/POST-CONSUMER CARPET," ed: Google Patents, 2010.

[9] K. Lakshminarayanan, "Scaling up of manufacturing processes of recycled carpet based composites," Oklahoma State University, 2011.

[10] R. V. K. Lakshminarayanan, M. S. High, A. Abbaszadeh, T. Ley, "Scaling Up of Manufacturing Processes of Recycled Carpet Based Composites," in *SAPME,* Long Beach, CA, 2011.

[11] H. Zhu and D. D. Carlson, "A spray based crumb rubber technology in highway noise reduction application," *Journal of Solid Waste Technology and Management,* vol. 27, pp. 27-32, 2001.

[12] A. Davis and D. Sims, *Weathering of polymers*: Springer, 1983.

[13] H. Abeysinghe, W. Edwards, G. Pritchard, and G. Swampillai, "Degradation of crosslinked resins in water and electrolyte solutions," *Polymer,* vol. 23, pp. 1785-1790, 1982.

[14] J. K. Kim, C. Hu, R. S. C. Woo, and M. L. Sham, "Moisture barrier characteristics of organoclay–epoxy nanocomposites," *Composites Science and Technology,* vol. 65, pp. 805-813, 2005.

[15] T. Alfrey Jr, E. Gurnee, and W. Lloyd, "Diffusion in glassy polymers," 1966,

pp. 249-261.

[16] R. Fuller, R. Fornes, and J. Memory, "NMR study of water absorbed by epoxy resin," *Journal of Applied Polymer Science,* vol. 23, pp. 1871-1874, 1979.

[17] R. T. Fuller, S. Sherrow, R. Fornes, and J. Memory, "Hydrogen exchange between water and epoxy resin," *Journal of Applied Polymer Science,* vol. 24, pp. 1383-1385, 1979.

[18] L. W. Jelinski, J. J. Dumais, R. E. Stark, T. S. Ellis, and F. E. Karasz, "Interaction of epoxy resins with water. A quadrupole echo deuterium NMR study," *Macromolecules,* vol. 16, pp. 1019-1021, 1983.

[19] L. Jelinski, J. Dumais, A. Cholli, T. Ellis, and F. Karasz, "Nature of the water-epoxy interaction," *Macromolecules,* vol. 18, pp. 1091-1095, 1985.

[20] C. L. Soles, F. T. Chang, B. A. Bolan, H. A. Hristov, D. W. Gidley, and A. F. Yee, "Contributions of the nanovoid structure to the moisture absorption properties of epoxy resins," *Journal of Polymer Science Part B: Polymer Physics,* vol. 36, pp. 3035-3048, 1998.

[21] C. L. Soles and A. F. Yee, "A discussion of the molecular mechanisms of moisture transport in epoxy resins," *Journal of Polymer Science Part B: Polymer Physics,* vol. 38, pp. 792-802, 2000.

[22] C. L. Soles, F. T. Chang, D. W. Gidley, and A. F. Yee, "Contributions of the nanovoid structure to the kinetics of moisture transport in epoxy resins," *Journal of Polymer Science Part B: Polymer Physics,* vol. 38, pp. 776-791, 2000.

[23] T. Ellis and F. Karasz, "Interaction of epoxy resins with water: the depression of glass transition temperature," *Polymer,* vol. 25, pp. 664-669, 1984.

[24] P. Moy and F. Karasz, "Epoxy-water interactions," *Polymer Engineering & Science,* vol. 20, pp. 315-319, 1980.

[25] H. Hahn, "Hygrothermal damage in graphite/epoxy laminates," 1985, p. 1985.

[26] R. Seltzer, P. M. Frontini, and Y. W. Mai, "Effect of hygrothermal ageing on morphology and indentation modulus of injection moulded nylon 6/organoclay nanocomposites," *Composites Science and Technology,* vol. 69, pp. 1093-1100, 2009.

[27] Z. Ishak and J. Berry, "Hygrothermal aging studies of short carbon fiber reinforced nylon 6.6," *Journal of Applied Polymer Science,* vol. 51, pp. 2145-2155, 2003.

[28] A. Bergeret, I. Pires, M. Foulc, B. Abadie, L. Ferry, and A. Crespy, "The hygrothermal behaviour of glass-fibre-reinforced thermoplastic composites: a prediction of the composite lifetime," *Polymer testing,* vol. 20, pp. 753-763, 2001.

[29] J. Arnold, "Environmental effects on crack growth in composites," *Comprehensive Structural Integrity, I. Milne, Ed., Elsevier,* vol. 428, 2007.

[30] R. S. C. Woo, Y. Chen, H. Zhu, J. Li, J. K. Kim, and C. K. Y. Leung, "Environmental degradation of epoxy–organoclay nanocomposites due to UV exposure. Part I: Photo-degradation," *Composites Science and Technology,* vol. 67, pp. 3448-3456, 2007.

[31] W. Liau and F. Tseng, "The effect of long-term ultraviolet light irradiation on polymer matrix composites," *Polymer composites,* vol. 19, pp. 440-445, 1998.

[32] C. Do, E. Pearce, B. Bulkin, and H. Reimschuessel, "FT–IR spectroscopic study on the photo-and photooxidative degradation of nylons," *Journal of Polymer Science Part A: Polymer Chemistry,* vol. 25, pp. 2301-2321, 2003.

[33] C. Stephenson, J. Lacey, and W. Wilcox, "Ultraviolet irradiation of plastics III. Decomposition products and mechanisms," *Journal of Polymer Science,* vol. 55, pp. 477-488, 2003.

[34] J. Zimmerman, "Degradation and crosslinking in irradiated polyamides and the effect of oxygen diffusion," *Journal of Polymer Science,* vol. 46, pp. 151-162, 2003.

[35] N. Allen and J. McKellar, "The photochemistry of commercial polyamides," *Journal of Polymer Science: Macromolecular Reviews,* vol. 13, pp. 241-281, 2003.

[36] B. G. Kumar, R. P. Singh, and T. Nakamura, "Degradation of carbon fiber-reinforced epoxy composites by ultraviolet radiation and condensation," *Journal of Composite Materials,* vol. 36, pp. 2713-2733, 2002.

[37] F. Uddin, "Clays, nanoclays, and montmorillonite minerals," *Metallurgical and Materials Transactions A,* vol. 39, pp. 2804-2814, 2008.

[38] J. H. Koo, *Polymer nanocomposites: processing, characterization, and applications*: McGraw-Hill New York, 2006.

[39] P. C. Nanocomposites, "Pinnavaia, TJ, Beall, GW, Eds," ed: Wiley Series in Polymer Science, 2000.

[40] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, and O. Kamigaito, "Mechanical properties of nylon 6-clay hybrid," *Journal of Materials Research(USA),* vol. 8, pp. 1185-1189, 1993.

[41] T. Lan and T. J. Pinnavaia, "Clay-reinforced epoxy nanocomposites," *Chemistry of Materials,* vol. 6, pp. 2216-2219, 1994.

[42] M. Chan, K. Lau, T. Wong, M. Ho, and D. Hui, "Mechanism of reinforcement in a nanoclay/polymer composite," *Composites Part B: Engineering,* vol. 42, pp. 1708-1712, 2011.

[43] A. S. Zerda and A. J. Lesser, "Intercalated clay nanocomposites: morphology, mechanics, and fracture behavior," *Journal of Polymer Science Part B: Polymer Physics,* vol. 39, pp. 1137-1146, 2001.

[44] D. Zaarei, A. A. Sarabi, F. Sharif, M. M. Gudarzi, and S. M. Kassiriha, "The Impact of Organoclay on the Physical and Mechanical Properties of Epoxy-Clay Nanocomposite Coatings," *Journal of Macromolecular Science, Part B*, vol. 49, pp. 960-969, 2010.

[45] G. Choudalakis and A. Gotsis, "Permeability of polymer/clay nanocomposites: A review," *European Polymer Journal*, vol. 45, pp. 967-984, 2009.

[46] S. Pavlidou and C. Papaspyrides, "A review on polymer–layered silicate nanocomposites," *Progress in Polymer Science*, vol. 33, pp. 1119-1198, 2008.

[47] J. Shelley, P. Mather, and K. DeVries, "Reinforcement and environmental degradation of nylon-6/clay nanocomposites," *Polymer*, vol. 42, pp. 5849-5858, 2001.

[48] M. Bagherzadeh and F. Mahdavi, "Preparation of epoxy–clay nanocomposite and investigation on its anti-corrosive behavior in epoxy coating," *Progress in Organic Coatings*, vol. 60, pp. 117-120, 2007.

[49] R. P. Singh, M. Khait, S. C. Zunjarrao, C. S. Korach, and G. Pandey, "Environmental degradation and durability of epoxy-clay nanocomposites," *Journal of Nanomaterials*, vol. 2010, p. 6, 2010.

[50] A. B. Morgan and C. A. Wilkie, *Flame retardant polymer nanocomposites*: Wiley-Interscience, 2007.

[51] N. Grassie, "Polymer degradation and the fire hazard," *Polymer Degradation and Stability*, vol. 30, pp. 3-12, 1990.

[52] A. Castrovinci and G. Camino, "Fire-retardant mechanisms in polymer nano-composite materials," *Multifunctional Barriers for Flexible Structure*, pp. 87-108, 2007.

[53] T. Kashiwagi, "Flammability of Nanocomposites–Effects of the Shape of Nanoparticles," *Fire Retardancy of Polymers. Royal Society of Chemistry, London*, pp. 81-99, 2005.

[54] S. Nazare, B. Kandola, and A. Horrocks, "Flame-retardant unsaturated polyester resin incorporating nanoclays," *Polymers for advanced technologies*, vol. 17, pp. 294-303, 2006.

[55] A. Dhyani, *VARTM process with some modifications*: ProQuest, 2008.

[56] F. D. Corporation. (2012, October 20). *System 2000 epoxy MSDS*. Available: http://cdn.fibreglast.com/downloads/PDCT-MSDS-00130.pdf

[57] F. G. D. Corporation. (October 20). *Product Data Sheet System 2000 Epoxy Resin*. Available: http://cdn.fibreglast.com/downloads/00343-A.pdf

[58] G. I. Nakas, "Use of different alkylammonium salts in clay surface modification for epoxy-based nanocomposites," *Polymer composites*, vol. 30, pp. 357-363, 2008.

[59] A. International, *Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials*:

ASTM International, 2007.

[60] A. International, *Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials*: ASTM International, 2006.

[61] A. International, *Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Plastics in a Horizontal Position*: ASTM International, 2006.

[62] T. Glaskova and A. Aniskevich, "Moisture absorption by epoxy/montmorillonite nanocomposite," *Composites Science and Technology,* vol. 69, pp. 2711-2715, 2009.

[63] S. U. A. HAMIM, "VARIATION OF MECHANICAL PROPERTIES DUE TO HYGROTHERMAL AGEING AND PERMANENT CHANGES UPON REDRYING IN CLAY/EPOXY NANOCOMPOSITES," MASTER OF SCIENCE, Oklahoma State University, OK, USA, 2011.

[64] Y. Zhou, M. Hosur, S. Jeelani, and P. Mallick, "Fabrication and characterization of carbon fiber reinforced clay/epoxy composite," *Journal of Materials Science,* pp. 1-11, 2012.

[65] M. G. Mcmaster and D. S. Soane, "Water sorption in epoxy thin films," *Components, Hybrids, and Manufacturing Technology, IEEE Transactions on,* vol. 12, pp. 373-386, 1989.

[66] Y. Xu and S. V. Hoa, "Mechanical properties of carbon fiber reinforced epoxy/clay nanocomposites," *Composites Science and Technology,* vol. 68, pp. 854-861, 2008.

[67] J. L. Tsai and M. D. Wu, "Organoclay effect on mechanical responses of glass/epoxy nanocomposites," *Journal of Composite Materials,* vol. 42, pp. 553-568, 2008.

[68] N. H. M. Zulfli and C. W. Shyang, "Flexural and Morphological Properties of Epoxy/Glass Fibre/Silane-Treated Organo-montmorillonite Composites," *Journal of Physical Science,* vol. 21, pp. 41-50, 2010.

[69] B. De'Nève and M. Shanahan, "Water absorption by an epoxy resin and its effect on the mechanical properties and infra-red spectra," *Polymer,* vol. 34, pp. 5099-5105, 1993.

[70] N. S. Allen and A. Parkinson, "Ultraviolet derivative absorption spectra of nylon 6, 6: Effect of photolysis versus photo-induced oxidation," *Polymer Degradation and Stability,* vol. 4, pp. 239-244, 1982.

[71] S. J. Park, D. I. Seo, and J. R. Lee, "Surface modification of montmorillonite on surface acid–base characteristics of clay and thermal stability of epoxy/clay nanocomposites," *Journal of colloid and interface science,* vol. 251, pp. 160-165, 2002.

APPENDICES

APPENDIX A: RELATED WORK ON CARPET RECYCLING

The following paper was presented in SAMPE Spring Conference in Baltimore, MD in May, 2012. This is included here because it discusses about application of the carpet composite fabricated by VARTM process.

LOW-COST COMPOSITE TOOLING MATERIALS BASED ON RECYCLED POST-CONSUMER CARPET

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ABSTRACT

Post consumer carpet waste is both an environmental and economic liability because of the cost involved in its disposal and 90% of post-consumer carpet is dumped into landfills. It is therefore necessary to develop sustainable post-consumer carpet-based products for high-value engineering applications such as composite tooling. To be considered as an acceptable composite tooling material, a composite has to meet several property requirements such as low coefficient of thermal expansion, reasonably good compressive strength, accurate tool dimensions after repeated exposure to curing cycles as well as the ability to withstand several curing cycles without change in mechanical properties. Recently, Oklahoma State University has developed a modified vacuum assisted resin transfer molding (VARTM) process for recycling carpet materials into large-scale composite panels with excellent mechanical and acoustic properties. In this paper, we present an application of these composite materials for composite tooling applications. Material properties such as glass transition temperature, hardness based on Shore Durometer D scale, mechanical properties as well as tooling accuracy as a function of composite fabrication cycles have been presented. The results indicated that this tooling material based on recycling post-consumer carpet waste has the potential to be a low-cost composite tooling alternative for the industry.

1. INTRODUCTION

The use of advanced fiber reinforced composites in commercial aircraft has become a necessity to achieve higher performance and greater fuel efficiencies. Boeing's 787 and Airbus's A350 are two such aircraft that exemplify the push to achieve aircraft made from > 50% performance composite instead of traditional aircraft alloys. To ensure the best material quality and reliability, aerospace composites are processed inside autoclaves that combine heat and pressure to fully bond multi-layered composites. The tooling used to support/shape composite prepregs during the layup and cure process key component in the manufacturing process in terms of function, logistics, and in terms of cost. A large opportunity exists for innovative materials to displace existing Invar and carbon composite tooling.

Metallic alloys have been the traditional engineering class of materials from which structural and thermal systems are manufactured. However, newer platforms such as those developed for the department of defense (DoD) as well as newer aerospace components tend to operate at higher temperatures, faster speeds, in order to achieve better performance. These needs push the limits of conventional alloys that have significant weight penalties compared to next generation materials. Increasingly, engineers are trying to incorporate advanced fiber reinforced composites in a larger fraction of platforms to benefit from their high specific strength and stiffness.

Manufacturing Fiber Reinforced (FRP) Composites are fundamentally different than metal or plastics. Metals are typically cast into molds directly from the liquid state or CNC machined from bulk stock. Plastics can be cast, injected, or thermo-formed. High performance composites (with continuous fibers) exhibit exceptional strength and stiffness values due to engineered orientation of continuous fibers/fabrics. They must be formed using operations that can maintain these specific fiber orientations. Fibers and resins must be supported with a “tool” or “mandrel” to impart shape during the lay-up process and while the resin system cures and sets the fibers in place.

Lay-up tools and techniques vary by the application, final composite geometry, and desired process conditions. For open geometries without trapped features, parts are formed against a tool in using the either the Outer Mold Line (OML) or Inner Mold Line (IML). Figure 1 (left) illustrates vacuum forming around a male tool using the IML. Composite “prepreg” (pre-impregnated fabric) is layered around the tool, bagged, and put under vacuum to laminate and consolidate fabric layers. Once the part is cured, it is removed from the tool.

Hollow geometries, such as pressure vessels, may be filament wound with continuous fibers as shown in Figure 1 (right). In the pressure vessel case, the support tool/mandrel may be a liner that will stay inside the composite vessel or it may be a removable mandrel. [1]

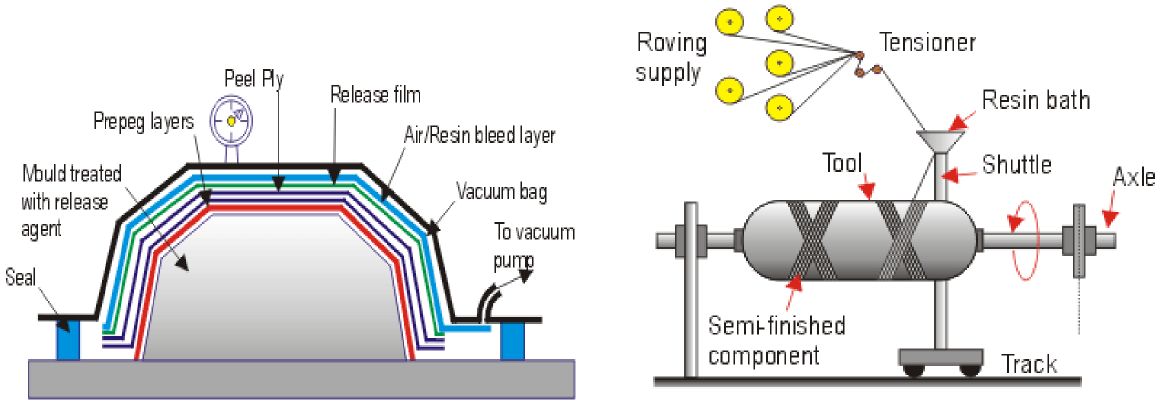


Figure 1: (Left) Vacuum forming around a male tool (Right) Filament winding around a male tool [1]

Tooling materials can be broadly classified into IML, OML, and removable (for seamless, hollow/trapped configurations that do not allow a tool to be pulled out). In addition, these can also be subdivided into single-use and multi-use. Figure 2 shows a schematic representation of the different tool types. [1] Materials and applications used in OML/IML process vary greatly within the composites industry. Low cost tooling materials are plasters (easily castable) and resin boards can be CNC machined. These materials tend to be used in low cost applications and in single use / prototyping manufacturing runs. In high performance applications, carbon fiber based composites are used to manufacture parts and it is often desirable to have a tool/mandrel with a similar CTE (coefficient of thermal expansion). Therefore, the use of Invar and carbon-carbon tooling/mandrel materials is prevalent in the industry for matching the properties of [1].

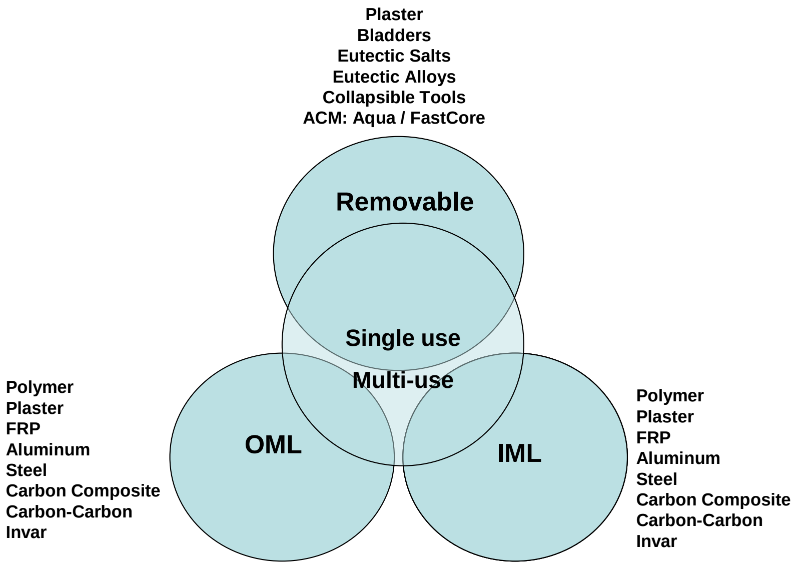


Figure 2: Tool/Mandrel Classification

Selection of tooling materials is driven by resin/fabric system, production methods, production quantity, costs, required tolerances, composite geometry (size/contour severity), and manufacturing experience. Based on typical aerospace requirements, lost cost tooling options rarely suffice. Key aerospace drivers are thermal stability and thermal expansion behavior. Performance carbon fiber reinforced composites have very low CTE’s and tooling materials are often selected to minimize mismatch with the layup tool. According to discussions with aerospace composite manufacturers, the ideal CTE should lie between or close to that graphite/BMI, Invar 36, graphite/epoxy, graphite or carbon foam. [1] This should match that of the composite system being fabricated. [2]

Table 1 shows a list of ideal target properties desired in a composite tooling material and compared them with properties for several commonly used tooling materials, as per several composites manufacturers. [1, 3]

Recently at Oklahoma State University (OSU), a new technique was developed to recycle post-consumer waste carpet into composite panels based on a modified vacuum assisted resin transfer molding process. [4] The manufacturing process was further scaled up to manufacture large-scale (approximately 1 m x 1 m or 3 ft x 3 ft in size) composite panels with excellent sound absorption capabilities and mechanical properties. [5]

Table 1. Properties of existing tooling materials and target properties

Property	**Invar**	**Composite**	**Epoxy**	**Polyurethane**	**Target**
CTE [10^{-6} K^{-1}]	1.3		32	50	1.3
Density [g/cc]	8.1		0.67	0.85	<1
Max. Thickness [cm]	N/A		15	15	>30
Temperature Capability [°C]	>260		141	142	160 and 260
Compressive Strength [MPa]	-		57	72	21
Cost [$/L]	300		25-38	25-35	<20

It is important to understand why it is necessary to recycle carpet materials. In the United States alone, about 200 million metric tons (450 billion pounds) of carpet waste is generated every year. Only 2%, around 4 million tons of carpet waste is recycled while the rest is disposed into the landfills [6]. Post-consumer carpet accounted for approximately 1-wt% and 2-vol% of the municipal solid waste stream in the United States in 2008, and this number has been increasing steadily [7]. Nylon is utilized in 65% of the carpet sold in the US market. It has excellent performance characteristics and is very durable, especially in heavy foot traffic conditions. Nylon based carpets have either the nylon 6 face fibers or the premium nylon 6, 6 face fibers. However these carpets fail to perform after their shelf life of 11 years and are either incinerated or sent to landfills after their useful service. [8]

In the technique developed at OSU, the panels were fabricated with different low cost room temperature cured polymer resins (epoxy, polyester and polyurethane) infused through the nylon fibers with good surface quality and large sizes. A big advantage of the OSU process is that it is possible to fabricate the composites without having to remove the parts of the composite other than the nylon fibers. During this process, it was observed that it was also possible to fabricate carpet composite with complex surface profiles, which is a necessary requirement for composite tooling. This option leads to the opportunity of recycling carpet materials to manufacture composite tooling articles with a high temperature resin system.

In this paper, we present the preliminary data for the fabrication process of tooling using nylon-based carpet and a high temperature epoxy resin and its properties such as density, compressive strength, surface hardness, and dimensional accuracy as a function of number of cure cycles.

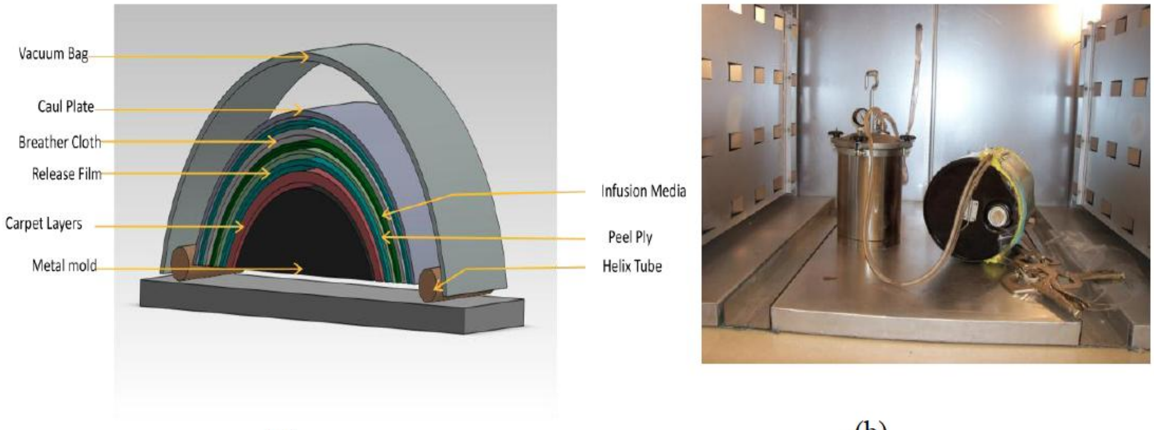
2. EXPERIMENTATION

Materials

In this study Nylon, cut loop type of carpet of the commercial name Orange Cool Aid by Shaw Industries was chosen. These carpets of size 60 cm x 144 cm were bought from M/s Georgia Carpet Industries Inc., Atlanta, Georgia, and then pieces of different sizes were cut from the carpet for preparing the samples. The epoxy resin used for this study was SC-79 (low viscosity cycloaliphatic amine), supplied by Applied Poleramic Inc. This two part resin system is of high temperature use and preferable for VARTM infusion with 5 hours pot life at room temperature. New carpet materials based on nylon 6,6 fibers were used to fabricate the composite. New carpet was used to develop baseline properties of recycled carpet-based composites so that the effect of carpet life on the properties could be eliminated. This carpet consists of nylon fiber and polypropylene as the backing material. The peel ply, resin infusion media, breather cloth, release film, breather cloth, spiral tubing, and resin traps were purchased from Fibreglast Development Corporation.

Tooling Fabrication

Samples were fabricated using a simple, vacuum assisted resin transfer molding fabrication technique. Any of two different combinations of layers viz. Top-Bottom-Bottom-Top (TBBT) and Bottom-Top-Top-Bottom (BTTB) can be used for the tooling fabrication. The carpet fiber side is the top and the carpet backing side is the bottom. For this particular study, a BTTB configuration was used. In the modified VARTM fabrication process use of caul plates and green mesh cloth (similar to SCRIMP process) are an addition. Additional details of the process have been described in references 4 and 5. The vacuum mold was prepared on a cylindrical metal container to provide a contour to the final component. Wax and PVA (polyvinyl alcohol) were applied for ease of de-molding after curing the composite (tooling) and two layers of carpet in BTTB configuration was placed on top. A schematic as well as the actual molding in progress is shown in Figure 3. Release film, peel ply, resin infusion media, breather cloth and caul plate were used on the carpet preform as shown in Figure 1. Helix tubes were placed along the width in inlet and suction side to ensure uniform distribution of resin flow throughout the width of the carpet.



(a) (b)

Figure 3: VARTM setup for tooling Fabrication (a) Schematic Diagram, (b) Setup inside oven

The SC-79 resin part A and Part B were mixed and infused utilizing a vacuum pump and resin trap. The mold was then kept at 60 °C for 4 hours at a vacuum pressure of 75 kPa to complete the curing process. After demolding, the composite part was post cured at 121 °C for 4 hours as per the instructions of the resin manufacturer. Flat samples were also prepared for the characterization of density and mechanical properties, prepared under the same conditions.

Characterization of Mechanical Properties

The fabricated tooling piece was subjected to fifteen (15) autoclave cycles of 154 °C at 1 hour, based on the manufacturer recommended curing cycle for SC-79 resin. Compression test samples of size 25.4 mm x 25.4 mm x 12.7 mm thickness were machined from flat panels, according to ASTM C365 [9]. Compression tests were performed on an INSTRON 8802TT servo-hydraulic machine. Differential scanning calorimetry was carried out after 0, 1, 5, 10 and 15 cure cycles using a Q2000 (TA Instruments). Shore D durometer hardness was measured using an AD-100-D Durometer (Albuquerque Industrial) while dimensions were recorded using a shop caliper after every cure cycle. The density of the composite was calculated by measuring the dry weight and the volume displaced by the sample after immersion in distilled water.

3. RESULTS

Thermo-mechanical and physical properties

An image of the tooling fabricated is shown in figure 4. The approximate dimension of the tool was 250 mm x 200 mm. The average thickness of the tooling was 13.09 ± 0.321 mm. The density was measured to be 1.1785 gm/cc. The tooling material was machinable. It is possible to adjust the thickness, density and fiber:resin ratios.

Figure 4: Recycled carpet based composite tooling

Figure 5 shows the DSC data for the tooling samples after 0, 1, 5, 10 and 15 cure cycles. For the first few cure cycles, two endothermic peaks were visible. The low temperature peak was in the range of 45-55 °C representing the glass transition temperature of nylon 6,6 fibers. However, after the tooling material was exposed to additional cure cycles, the low temperature endothermic peak was not apparent, indicating that the T_g was only dependent on the T_g of the SC-79 resin. With additional curing cycles, the T_g appeared to increase for the tooling material, which would be an advantage. Many researchers have studied the Increase in T_g of semi crystalline materials after high temperature exposure. [10] The upward shift in T_g is attributed to a reduction of mobility of the amorphous phase. It is also speculated that the interaction between nylon 6,6 and SC-79 after high temperature curing may have contributed to the increase in T_g.

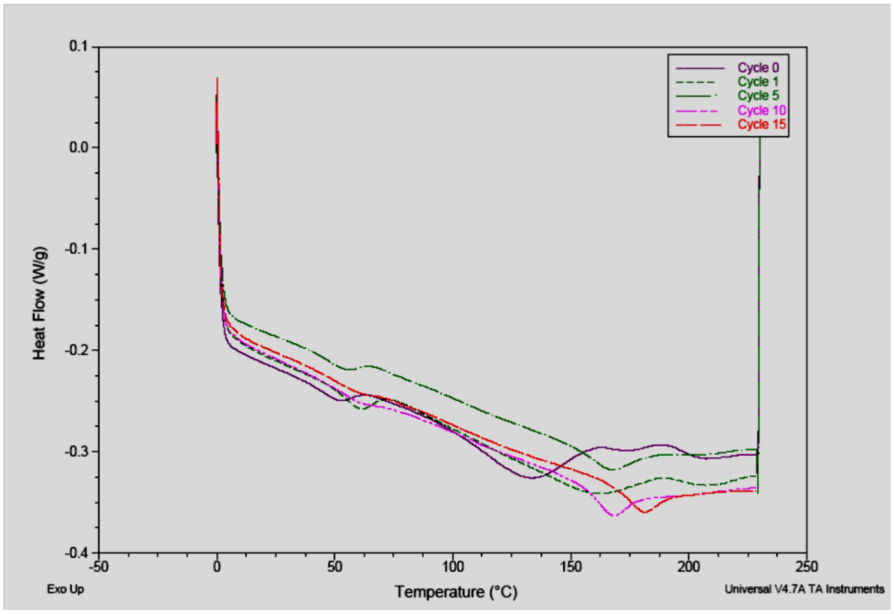


Figure 5: DSC data for composite tooling materials after exposure to different number of cure cycles (data acquired at 10 ˚C/min)

Dimensional Accuracy

Dimensional accuracy of the tool was also measured using a shop caliper having an accuracy of ± 0.005 mm. Five different positions were marked on the concave surface of the tool and distances from a fixed reference point were measured as shown in figure 6 after every cure cycle. Figure 7 shows the distances from the reference point as a function of the number of cure cycles. It can be observed that the relative dimensions of the tooling remained approximately stable. More accurate measurements will be required to demonstrate the tool accuracy.

Mechanical Property Measurements

The Shore D hardness values of the tooling surface are shown in Figure 8 as a function of number of cure cycles. It was seen that the tooling surface demonstrated a slight increase in surface hardness with increasing cure cycles, indicating that the tool would be accurate and will not lose its strength or hardness after exposure to every subsequent cure cycle. This phenomenon is expected due to the cross linking of polymer constituents of the composite. Figure 9a shows a typical stress-strain curve for the as-prepared tooling material, while figure 9b shows the compressive strength of the tooling material as a function of number of cure cycles. It was observed that the compressive strength decreased initially and stabilized with increasing number of cure cycles. The total reduction in compressive strength was less than 10% and was still above the required compressive strength, as per Table 1.

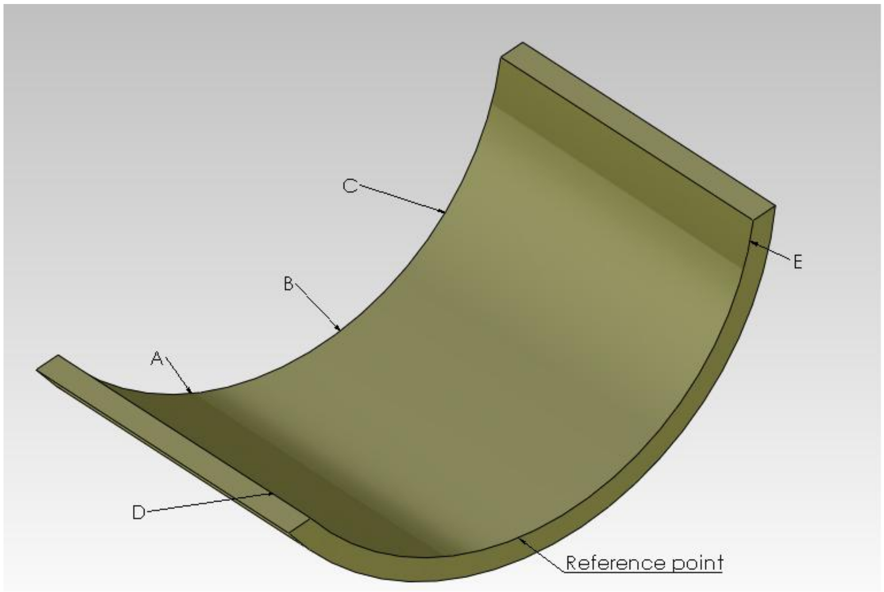


Figure 6: Different points for dimensional measurements

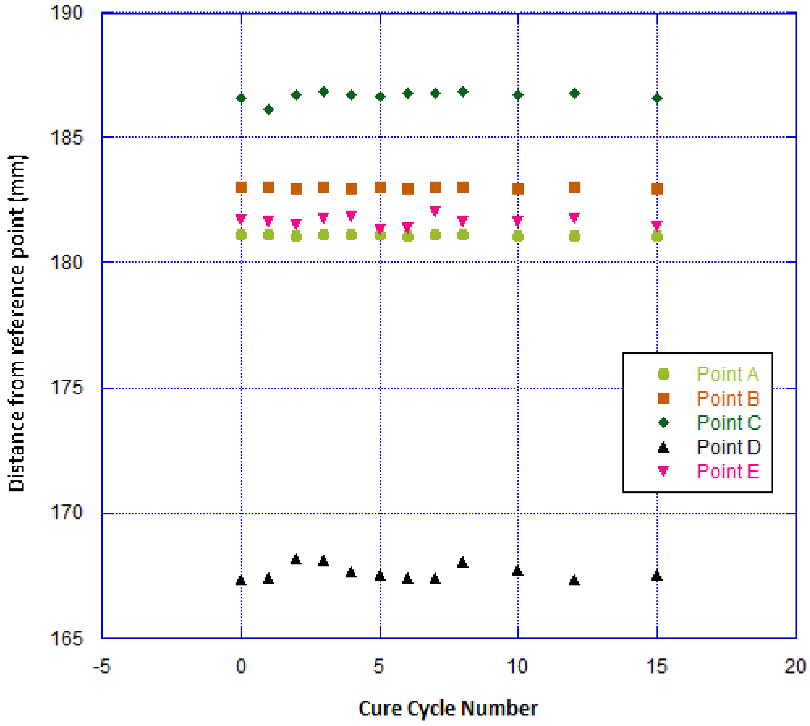


Figure 7: Dimensional accuracy as a function of number of curing cycles

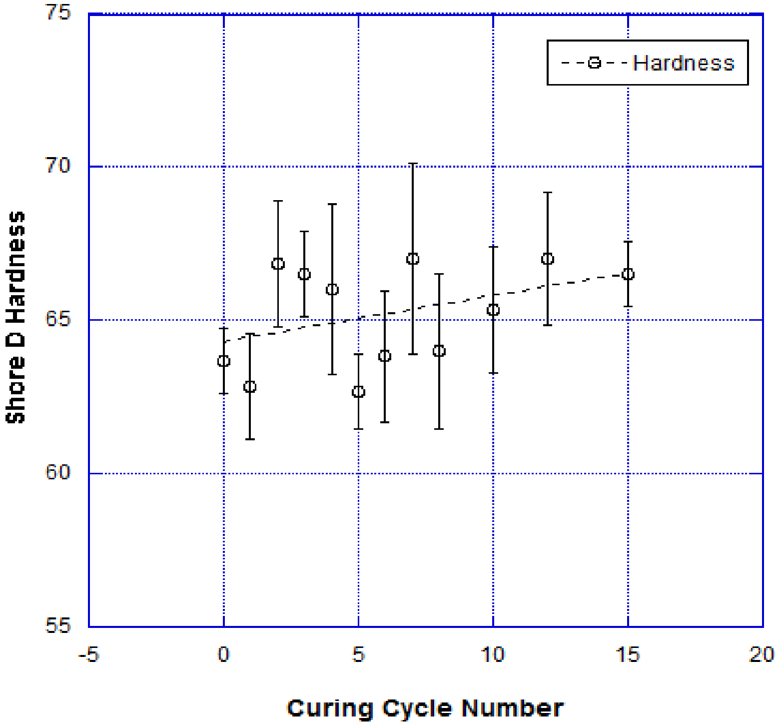
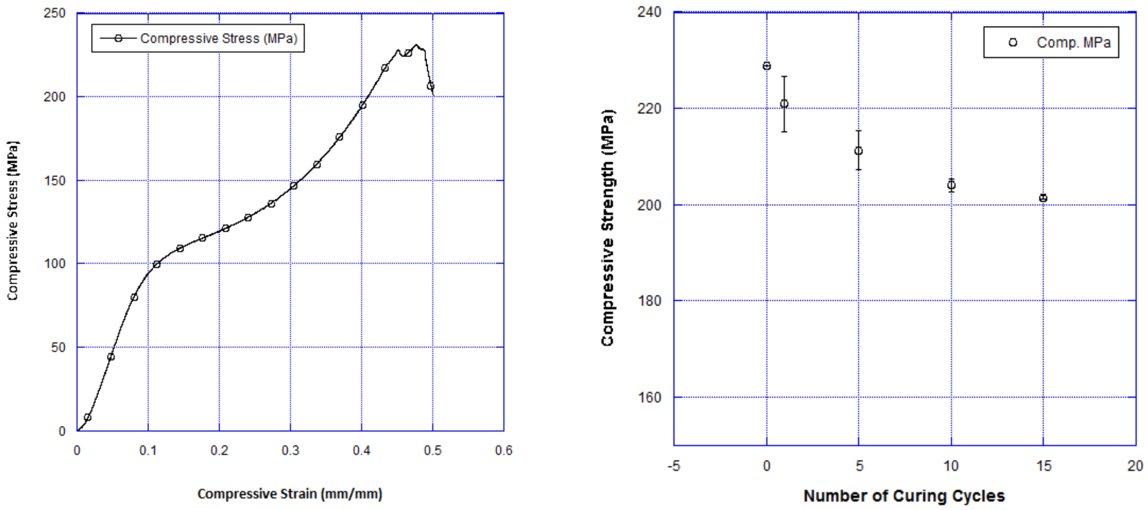


Figure 8: Shore D hardness as a function of curing cycles



(a) (b)

Figure 9: a) Compressive stress-strain curve for as prepared sample and b) Change in the compressive strength of the carpet composites after exposure to cure cycles

Preliminary Cost Calculations

Assuming that recycled carpet would be almost free, the only cost contributor to the tooling material would be the cost of the resin as well as the cost of supplies for fabrication. At current volumes, the cost per 1 m x 1m composite tooling would be approximately $40, which is comparable to the cost of polyurethane and epoxy types of tooling materials. The major advantage of the recycled carpet tooling materials would be in its ability to recycle a major waste material into a high-value end product. Further cost reductions with lower cost resins are perhaps required for this tooling material to be cost-competitive compared to other tooling materials.

4. CONCLUSIONS

A low cost composite tooling has been developed from waste carpet and its mechanical and physical properties have been investigated. It was observed that the dimensional accuracy, compressive strength and surface hardness were maintained as a function of the number of cure cycles. Preliminary cost calculations indicated that the cost of the tooling with the recycled carpet materials would be comparable to epoxy and polyurethane type of materials. Further cost reductions are required for this tooling material to be cost-competitive compared to other tooling materials.

Acknowledgements

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References

1. Private communications with Z. Wing, Advanced Ceramics Manufacturing LLC, Tucson, AZ, January 2012.

2. B. Boursier, R. Callis, J. Porter, “A new composite tooling material and concept for aerospace composite structures,” *Proceedings of the Annual Society for Advanced Manufacturing and Processing Engineering*, Long Beach, CA, April 30 - May 4, 2006. CD ROM – 15 pages.

3. M. Wallen, J. Rossfeldt, C. Aune, Z.N. Wing, “Washout Tooling for Hollow Composites: Toward Rapid, Low Cost Production Technology,” Presented at the Society of Manufacturing Engineers, Composites Manufacturing Conference & Exhibits 2011, Dayton, OH.

4. A. Jain, G. Pandey, A. K. Singh, V. Rajagopalan, R. Vaidyanathan, R. P. Singh, "Fabrication of structural composites from waste carpet," *Advances in Polymer Technology*, available online October 2011, available at http://dx.doi.org/10.1002/adv.20261.

5. K. Lakshminarayanan, R. Vaidyanathan, M. S. High, A. Abbaszadeh, T. Ley, "Scaling up of manufacturing processes for recycled carpet based composites," *Proceedings of the Annual Society for Advanced Manufacturing and Processing Engineering*, Long Beach, CA, May 23-26, 2011. CD ROM – 9 pages.

6. http://www.carpetrecovery.org/, accessed on January 15, 2012.

7. "Municipal solid waste in the United States," available at http://www.wastexchange.org/upload_publications/MSWintheU.S.2010.pdf, accessed on 15th November 2008.

8. Mcintyre D et. al, "PROCESS FOR RECYCLING FIBER MATERIAL AND BINDER WITH NOVEL INJECTION MOLD AND PARTS MADE THEREBY", *United States Patent Publication*, US 2007/0212531 A1, Sep 13, 2007.

9. ASTM Standard C365/C365M – 11a, 2011, "Standard Test Method for Flatwise Compressive Properties of Sandwich Cores," ASTM International, West Conshohocken, PA, 2011, DOI: 10.1520/C0365_C0365M-11A, www.astm.org.

10. R. Picciochi, Y. Wang, N. M. Alves, "Glass transition of semi-crystalline PLLA with different morphologies as studied by dynamic mechanical analysis," *Colloid Polym. Sci.*, **285**, pp. 575-580, (2007).

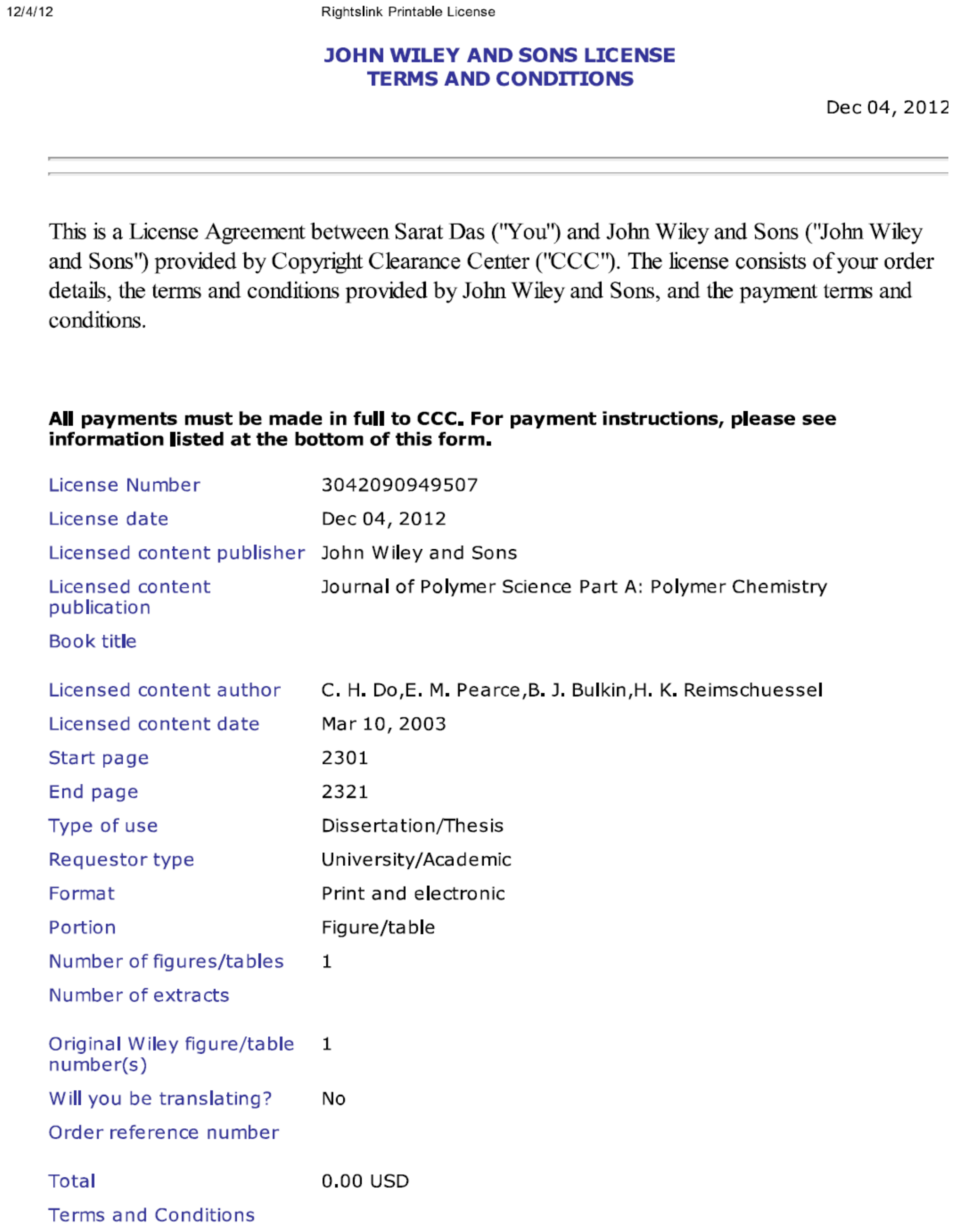
APPENDIX B: CALCULATION OF EFFECTIVE AMOUNT OF CLAY IN CLAY COATED CARPET COMPOSITE

In this study, it was found that reduction in degradation in clay coated composite was significant and comparable with clay infused carpet composite. In the clay coated carpet composites, clay was only present in the coating and weight percentage of clay with respect to total amount of epoxy matrix may be of interest. The following section present the calculation of clay content with respect to total amount of epoxy in clay coated sample.

Weight and dimension of 'neat epoxy' and 'clay coated' composites were taken from four samples of each type. Also weight per square inch of two layers of raw carpet was measured. After that, amount of epoxy in neat epoxy, as well as amount of clay- epoxy mixture in the coating were calculated. Finally, total amount of epoxy and clay in the clay coated composite were determined. The calculation and results of this is given below:

Weight of two layer of carpet	3.36 gm/ in^2
Average weight of neat epoxy carpet composite	10.0845 gm/ in^2
Amount of epoxy in neat epoxy carpet composite	6.7245 gm/ in^2
Average weight of clay coated carpet composite	10.9836 gm/ in^2
Calculated weight of clay-epoxy coating	0.8991 gm/ in^2
Calculated amount of clay in clay coated composite	0.03458 gm/ in^2
Calculated amount of epoxy in coating in clay coated composite	0.8646 gm/ in^2
Total amount of epoxy in clay coated carpet composite	7.8491 gm/ in^2
Percentage of clay in comparison to total amount of epoxy in clay coated carpet composite	0.46%

APPENDIX C: LICENSE FOR REUSING FIGURE



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Graduate Teaching Assistant in Materials Science Laboratory, Oklahoma State University, Stillwater, Oklahoma