Manufacturing and characterization of soy-based pultruded polyurethane composites

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MANUFACTURING AND CHARACTERIZATION OF SOY-BASED PULTRUDED POLYURETHANE COMPOSITES

by

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ABSTRACT

In the recent past, composites have been finding various applications in civil infrastructure, marine, transportation, automotive and non-automotive applications by replacing metals in structural components. Pultrusion is considered to be a cost effective method for manufacturing composite materials.

Polyurethane resin systems form a good alternative to the conventional styrene based systems in pultrusion due to their better physical, chemical and mechanical properties. Polyols derived from soybean oil along with isocyanates produce polyurethanes that can match in many aspects with one derived from the petrochemical polyols. Even though, polyurethanes have good properties there are lots of challenges like designing unique material handling and processing methods.

A two part polyurethane resin and a two part soy-based polyurethane resin system have been considered in the present work. Various issues like design of injection box, the component metering unit and die design which complicated the process of polyurethane pultrusion are discussed. Glass fiber reinforced composites were manufactured and mechanical characterization was performed. The properties of the soy-based polyurethane and base polyurethane pultruded parts are compared. It was found that soy-based polyurethane pultruded parts had good flexural properties and comparable impact properties than the base polyurethane system. In-core fiber reinforced composites are also manufactured using a polyester resin system. The process of manufacturing these pultruded composites are discussed in detail. Low velocity impact test was performed on these core filled parts and it was observed that ±45 fiber mat showed higher damage when compared to the random fiber mat pultruded part.

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1 INTRODUCTION

1.1 MOTIVATION AND OBJECTIVE

Composite materials have found importance not only in the high performance fields like aerospace industry but also in the basic industries like construction. In the construction industry, cost of production is one of the major factors that affect the profitability. Pultrusion can produce long parts of various cross-sections at a very fast, continuous pace, thus reducing the manufacturing costs.

Polyurethane (PU) has been used in foam manufacturing applications for many years. In the recent past, a lot of work has been done in the improvement of the chemistry of PU so that it can be used in the pultrusion process. PU has proved to be a very good alternative to the conventional pultrusion resins like polyester and vinyl ester resin systems [1-7]. The use of PU in pultrusion leads to various other challenges like design of an efficient injection box and metering unit. Polyols derived from soy-based products are a viable alternative to the polyols derived from the petroleum-based products especially at the time of oil crisis and global warming. PU synthesized using these bio-based polyols are environmentally friendly and can be used in the place of polyester and vinyl ester resin systems [5-9].

The objective of the present work is to address the challenges faced while using PU resin systems in pultrusion. Soy-based PU pultruded composites and conventional PU pultruded composites were manufactured. Performance evaluation was conducted on these two types of PU resin systems. In-core pultruded composites are manufactured using a polyester resin system. In-core pultrusion setup has been designed and core-filled pultruded samples were manufactured and performance evaluation was conducted.

1.2 PULTRUSION

Pultrusion is considered to be one of the simplest automated processes in manufacturing composite structures of constant cross-section. Unidirectional fibers, which are combined with the resin system, are pre shaped and pulled through a heated die thus processing the cured composite profile to its final shape. This process is also known as "Curing on the fly" [10]. Matrix resin used in pultrusion process can also contain other components like pigments, accelerators, internal release agents and fillers.

1.2.1 Process Equipment. The concept of pultrusion is pretty simple but its process is very complex [10-12]. Pultrusion processing has several steps to go through in a sequential manner:

(i) Reinforcement Delivery

(ii) Resin Impregnation

(iii) Preforming

(iv) Heating

(v) Pulling

(vi) Cutting

The Durapul 6000 pultrusion machine at UMR is shown in Figure 1.1. Figure 1.1 shows all the necessary requirements of a pultrusion machine. Pultrusion machine is also equipped with a ventilation system near the die which inturn helps in venting the emissions produced during pultrusion of polyurethane and polyester. There should be enough ventilation at the pultrusion setup in order to vent the harmful gases produced during pultrusion.

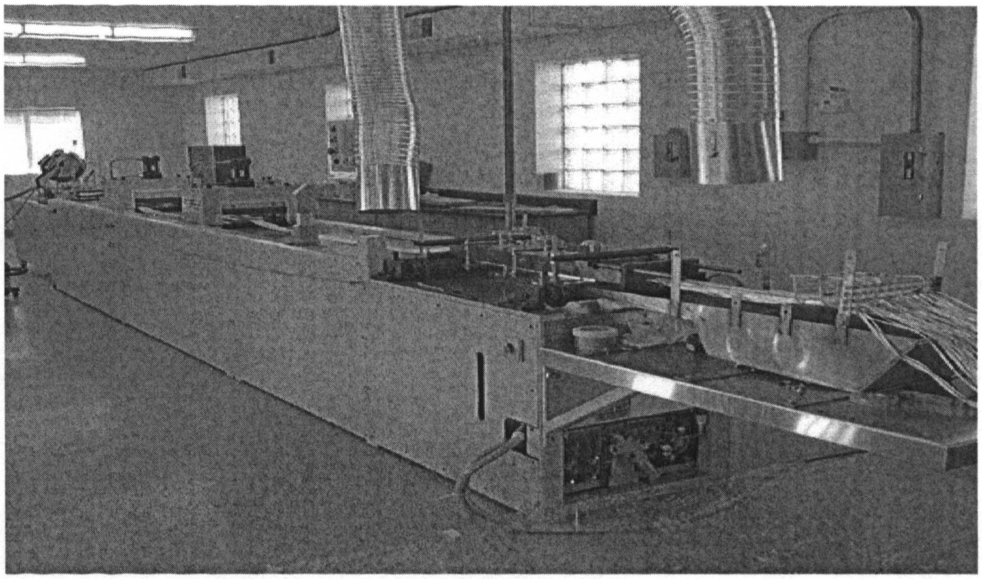


Figure 1.1. Durapul 6000 Pultrusion Machine at UMR

1.2.2 Reinforcement Delivery. Metal and wooden bookcases are commonly used as the reinforcement delivery stations. In order to minimize the damage of individual tows, they are pulled through eyelets. Inclusion of a tensioning mechanism for the individual tows has proved to increase the mechanical properties of the composite profiles [10].

1.2.3 Resin Impregnation. Proper wetting of the reinforcement by the matrix resin system is of great importance. The impregnation station is usually a container for the resin system. The reinforcements are pulled through a resin bath. Heaters and agitators can be included in the impregnation station while using special purpose resins.

The above setup is viable only for resins with long pot life. Polymers like polyurethane which typically have very short pot life (a few minutes) cannot be used in pultrusion along with the above mentioned setup. A specialized resin bath has to be designed to prevent the possible resin accumulation and early gellation. The wet fiber reinforcement then passes through the preforming fixtures to get an initial shape. These preforming fixtures are also used to consolidate the fiber/resin mixture.

1.2.4 Heating. After passing through the preform fixtures, the reinforcement is passed through the heated die for final processing to its shape and size. Generally, chrome plated metal dies are used due to the presence of high pressures and high temperatures. The dies can be heated in different ways which include use of electrical cartridges, strip heaters, and hot oil. Thermoset matrix resins usual cure exothermically. An effective heating system should account for both the energy supplied and the energy released during the exothermic reaction. A cooling system also forms an important part of the heating die assembly.

1.2.5 Pulling. The pulling section includes series of pullers or belts which pull the cured composite part from the die to the cutting mechanism. Pulling mechanism can be designed to be intermittent, continuous or both.

1.2.6 Cutting. Cutting of the pultruded panels is the final part of the pultrusion process. Pultruded profiles can be cut to the required lengths, using different types of cutters. Choice of the cutting saw depends upon the type of reinforcement and the matrix resin used. Generally, diamond cutting wheels are recommended. Care should be taken not to cause severe damage or weakening the composite while cutting.

1.3 MATERIAL SELECTION

Various types of reinforcements and resin systems can be used for the pultrusion process. The type of reinforcement and resin system depends upon the specifications of the final product.

1.3.1 Reinforcement. The greatest advantage of the pultrusion process lies in the feasibility of using almost all kinds of continuous fibers. Various kinds of reinforcements such as fiberglass, graphite fibers, carbon fibers, and natural fibers are generally used in pultrusion.

1.3.2 Resin System. Polyesters, epoxy resins, and vinyl esters form a major part of the resin systems used in pultrusion. Recent advancement in pultrusion technology enabled the usage of thermoplastic resin systems. This enables us to produce pultruded profiles with high process feasibility and toughness. Polypropylene, polyphenylene sulfide, polyesters, and polyimides are some of the thermoplastics which are used commonly for the process of pultrusion. For the present work, PU resin systems were used in the manufacturing of pultruded panels. By considering the complexity of in-core pultrusion, polyester was used as the resin system during core-filled pultrusion.

1.3.2.1 Polyurethane. The polyurethanes are sometimes called isocyanate polymers. They are characterized by the urethane linkage. Other functional groups, however, may be present in the polymer as well. Polyurethanes are carbonic acid derivatives. An older term for them is polycarbamate, from carbamic acid (RNHCO2H). Polyurethanes are used in a wide variety of products, including fibers (particularly the elastic variety), elastomers, foams, coatings, and adhesives [13].

There are two principal methods of forming polyurethanes: the reaction of bischloroformates (made from dihydroxy compounds with excess phosgene) with diamines as shown in Figure 1.2, and more important from the industrial perspective, the reaction of diisocyanates with dihydroxy compounds, which has the advantage of no byproducts, and is illustrated Figure 1.3.

Figure 1.2. Reaction of Bischloroformates with Diamines

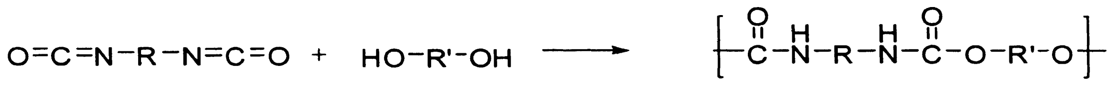


Figure 1.3.Reaction of Diisocyanates with Dihydroxy Compounds

Bischloroformates are less reactive than ordinary acid chlorides; nevertheless they react with diamines at low temperature under interfacial conditions. Polyurethane 23 prepared this way as shown in Figure 1.4 melts at about 180°C, compared with 295 °C for nylon 46. The reaction illustrated in Figure 1.3 is actually more complex because the urethane groups, once formed, can react further with free isocyanate as shown in Figure 1.5 to form allophonate groups, which leads to chain branching and crosslinking [14-15].

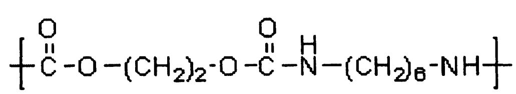


Figure 1.4. Polyurethane 23

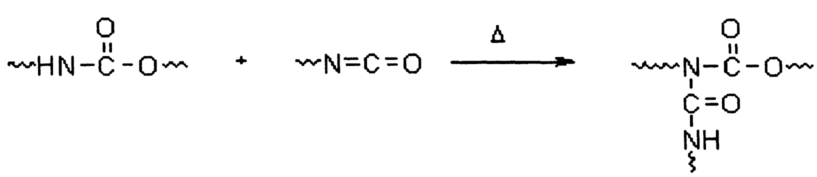


Figure 1.5. Reaction of Urethane Groups with Free Isocyanate

Industrial polyurethane production is based primarily on low-molecular-weight aliphatic hydroxyl-terminated polyethers such as poly (propylene glycol) or polyesters such as poly (diethylene glycol adipate). Poly (propylene glycol) and poly (diethylene glycol adipate) are shown in Figures 1.6 and 1.7, respectively. Low-molecular-weight diols such as 1,4-butanediol and 1,6-hexanediol are also used as chain extenders. The most important isocyanates are a mixture of 2,4-toluenediisocyanate and its 2,6 isomer (principally the former), methylene-4,4'-diphenyldiisocyanate (MDI), and polymeric isocyanate, which is derived from the reaction product of aniline with formaldehyde. Figures 1.8 and 1.9 represent MDI and polymeric isocyanate, respectively.

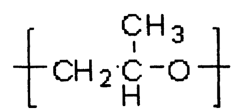


Figure 1.6. Poly (Propylene Glycol)

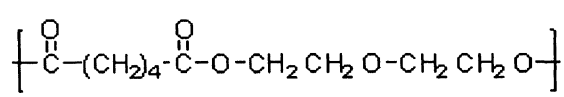


Figure 1.7. Poly (Diethylene Glycol Adipate)

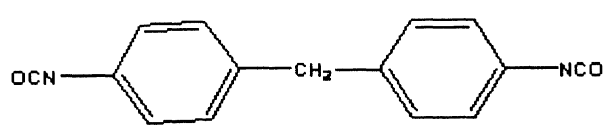


Figure 1.8. MDI

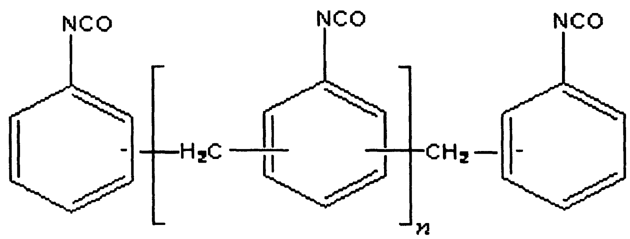


Figure 1.9. Polymeric Isocyanate

1.3.2.2 Polyester. Thermoset polyesters are the polymers with low molecular weight and contain carbon-carbon double bonds that can be used to form cross linking to create addition polymers. These polymers are usually liquids at room temperature and crosslinking polymers after the addition of intiator and heat. Even though polyesters are less rigid than phenolic and amino plastics, they are widely used due to their stiffness and brittle nature. Polyesters are mainly used in the manufacture of composites especially with glass fibers as reinforcement.

Thermoset polyesters can also be called as unsaturated polyesters due to the presence of unsaturated bonds in them [14-15]. The double carbon-carbon double bonds present in the monomers are not affected during the polymerization. Hence carbon-carbon double bonds can help in the cross linking of the polymer. Carbon-carbon double bonds react during the addition polymerization mechanism with the help of free radical. The free radicals can be obtained by heat-activated peroxide or some other source of free radicals. During the addition polymerization, the initiator reacts with a carbon-carbon double bond forming a new free radical on the carbon atom. The newly formed free radical then reacts with another carbon-carbon double bond thus forming a chain reaction. Byproducts are not formed during the condensation polymerization thus making it easier for the use when compared to phenolics and amino plastics. These solvents allow the molecules to move freely thus decreasing the steric hindrances in the polyester molecules which increases the cross linking of polyester.

Polyester is generally preferred to the other conventional resin systems in the pultrusion industry because of its process feasibility. Polyester can easily be pultruded by using the conventional pultrusion setup which does not involve complex parts like metering unit and injection box.

1.4 ADVANTAGES OF PULTRUSION

One advantage of the pultrusion is in terms of material costs and handling. Pultrusion process does not use costly prepregs and also combines different steps into one process, thus reducing the need to store a lot of materials in cold storage. The pultrusion process is a continuous process which decreases the production cost especially when mass production is taken into consideration [5, 17].

The second advantage deals with the design of a pultrusion die. One can produce more than one composite structure at the same time by having multiple cavities in the die. Cantilever mandrels enable the production of hollow composite structures. Usage of cantilever mandrels makes the process more versatile when compared to the other composite manufacturing processes. Pultruded parts do not need any secondary machining steps, due to the accurate shape and size of the closed mold.

1.5 LIMITATIONS OF PULTRUSION

Very complex profiles are more difficult to pultrude. Thus production of very complex profiles using pultrusion may not be economically feasible. There are many variables in the process of pultrusion which include pull speed, die temperature, and pull force. The effect of each variable has to be studied for each resin system separately in order to get the optimum set of variables for the high production rates. It is very time consuming to start a new process if interrupted.

1.6 APPLICATIONS

Initial pultruded profiles were simple in design. Pultrusion was initially used to produce fishing poles, bike flags, sucker rods, and various other products which had long length and small cross sectional area. Due to the significant improvement in pultrusion technology, production of complex profiles is made possible. New applications of pultrusion technology include the production of bus and car panels, fence posts, railing, graphite arrows, and bridge decking. The new technologies enabled in products with thicknesses ranging from one inch to nearly seventy inches.

2 MANUFACTURING

2.1 MANUFACTURING OF NEAT RESIN SAMPLES

The following process was adopted for the preparation of neat resin samples.

(i) Polyol was mixed well and then degassed to remove the air bubbles.

(ii) Well mixed polyol was then mixed with Part-B according to the recommended ratio for 10 minutes.

(iii) Mixed resin was then cast on a mold that had been preheated to 50^0C.

(iv) The mold was then cured for 1 hour at 50^0C and then post cured at 110^0C for another one hour.

2.2 MANUFACTURING OF PU PULTRUDED COMPOSITES

In the past, unsaturated polyesters and vinyl esters were considered to be the workhorse resin systems in the pultrusion industry [17]. But, limitations such as brittleness and slow reactivity helped polyurethane resin to compete with polyester and vinyl ester resin systems. PU systems exhibit high strength and superior damage tolerance relative to the conventional resin systems.

Use of PU resin system in pultrusion technique evolved new challenges such as design of injection box, materials handling, metering unit, and process conditions [18]. The present work lays importance on overcoming these challenges. The pultrusion setup with the injection box at University of Missouri – Rolla (UMR) is shown in Figure 2.1.

Figure 2.1. Setup for the PU Pultrusion at UMR

The basic polyurethane pultrusion system can basically be divided into four parts, metering equipment, injection box design, die design, and material handling.

2.2.1 Metering Unit. The basic limitation of the PU resin system is its very low pot life and its ability to foam very easily. Therefore, it was necessary to have a specialized system in which the two parts of the PU resin are mixed in correct proportions and transferred to the injection box without the inclusion of air during the mixing process. Metering unit consists of several basic subsystems: resin tanks, pumps, mixhead, mixing elements, and flushing mechanism.

2.2.1.1 Resin tanks. Two tanks are incorporated into the metering unit for isocyanate and polyol components of the PU resin. The two resin tanks are to be kept air tight to reduce the reaction of moisture with the chemicals. This factor is very important in the case of isocyanate resin tanks since isocyanate is highly reactive with moisture. The reaction of isocyanate with moisture results in the production of compounds which eventually clog the pump. An inline strainer is also included in the isocyanate hose in order to filter any debris entering the pump. During pultrusion, the soy-based PU resin tank containing polyol is agitated in order to keep the mixture of soy and polyol homogenous.

2.2.1.2 Pumps. Generally, gear or progressive cavity pumps are used for transferring the components from the resin tanks into the hoses at a certain pressure. Cylinder pumps can also be considered as they are rigid, rugged and have a more versatile variable ratio setup. The metering unit at University of Missouri – Rolla consists of two gear pumps run by a single motor.

2.2.1.3 Mixhead and mixing elements. The basic functionality of the mixhead is to control the volume of the mixed resin. The mixhead at UMR is electrically controlled. Check valves at the entrance of the mixhead will reduce the chance of backflow of the resin when there is a pressure differential. Static mixing tubes are generally used for the PU pultrusion. These mixing tubes help in the proper mixing of polyol and isocyanate without inducing any air during mixing. The length of the mixing tube depends on the mixing ratio of the resin system, component viscosity, component compatibility, and also the pressure with which the individual components are pumped from their tanks.

2.2.1.4 Flushing mechanism. Flushing is the most important part of PU pultrusion and involves flushing out all the excess raw materials that are present in the metering unit. Acetone and methyl ethyl ketone are used as the solvents to flush out the left over raw materials. The mixhead is flushed with the solvent as well as compressed air to remove any unwanted material in it. After flushing the mixhead, flushing of the rest of the metering unit is conducted. After flushing the whole metering unit, silicon grease is applied to the mixhead to block moisture.

2.2.2 Injection box. The injection box helps in the proper wetting of glass fibers or the reinforcement with the PU resin. The approach of Gauchel & Lehmann using a "tear drop'' [5] injection die is the most commonly used injection box design in the pultrusion industry. Steel and anodized aluminum will be more robust for a big pultruding environment. Use of metals for the injection boxes poses other obstacles like heat conductivity and corrosion. Usually high density polyethylene is used for making the injection boxes. The most important factor in the design of the injection box is the occurrence of 'dead spots' in the area of injection [15]. The solid model of the actual injection box at UMR is shown in Figure 2.2.

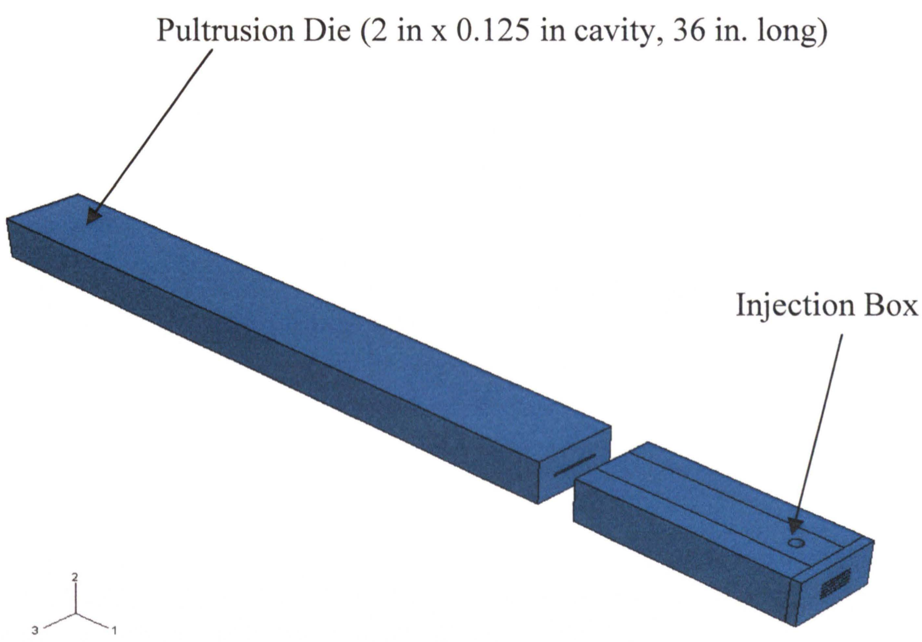


Figure 2.2. Solid Model of the Injection Box and the Heating Die

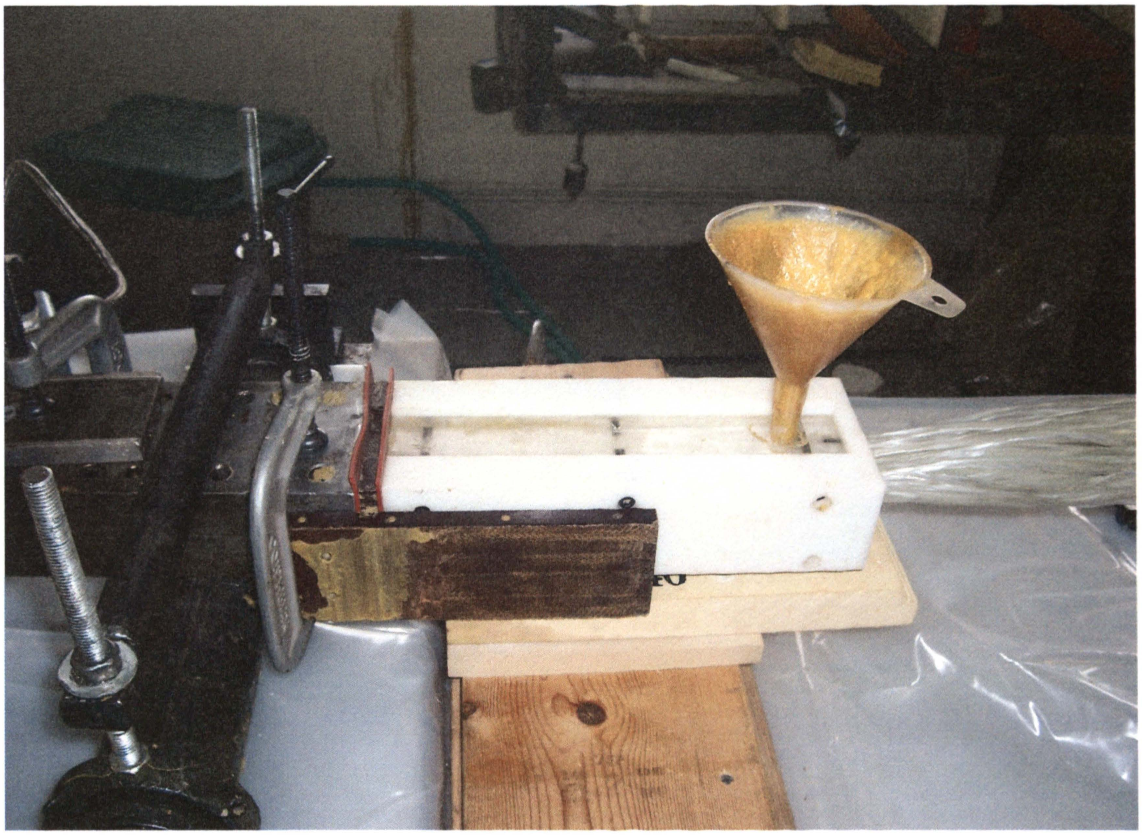


Figure 2.3. Injection Box and the Pultrusion Die Connected with a Connector

Before the pultrusion was started, the fibers where passed through the injection box and the die in a sequential manner to avoid the entanglement of fibers at the entrance of the injection box. After the fibers were passed, die was heated to the specified temperature range. Fibers were pulled continuously while the die was heated. All the hoses and lines in the metering unit are flushed with the solvent to avoid any obstruction to the raw materials while pultruding. After the die temperature reached the 270^0F, required quantities of the raw materials were poured in the resin tanks and the metering unit is started. Required amount of the mixed resin is poured into the injection box and the initial line speed was maintained at 0.5 foot per second. After some time, the line speed was increased to 2 feet per second. The pultruded parts were cut using the cutting saw.

2.3 MANUFACTURING OF IN-CORE COMPOSITES

2.3.1 Introduction. In-core pultruded parts are one of the many parts produced in the pultrusion industry. These pultruded components can be used as an alternative to the conventional wood panels used in the construction industry. A conventional core pultrusion setup and conventional in-core pultruded part are shown in Figure 2.4 and Figure 2.5, respectively.

The basic core-filled pultruded part consists of a foam core surrounded by fiber and resin matrix. Fiber mats can also be incorporated in the design of these pultruded samples to increase the surface finish. Figure 2.6 shows the in-core composite manufactured at University of Missouri-Rolla.

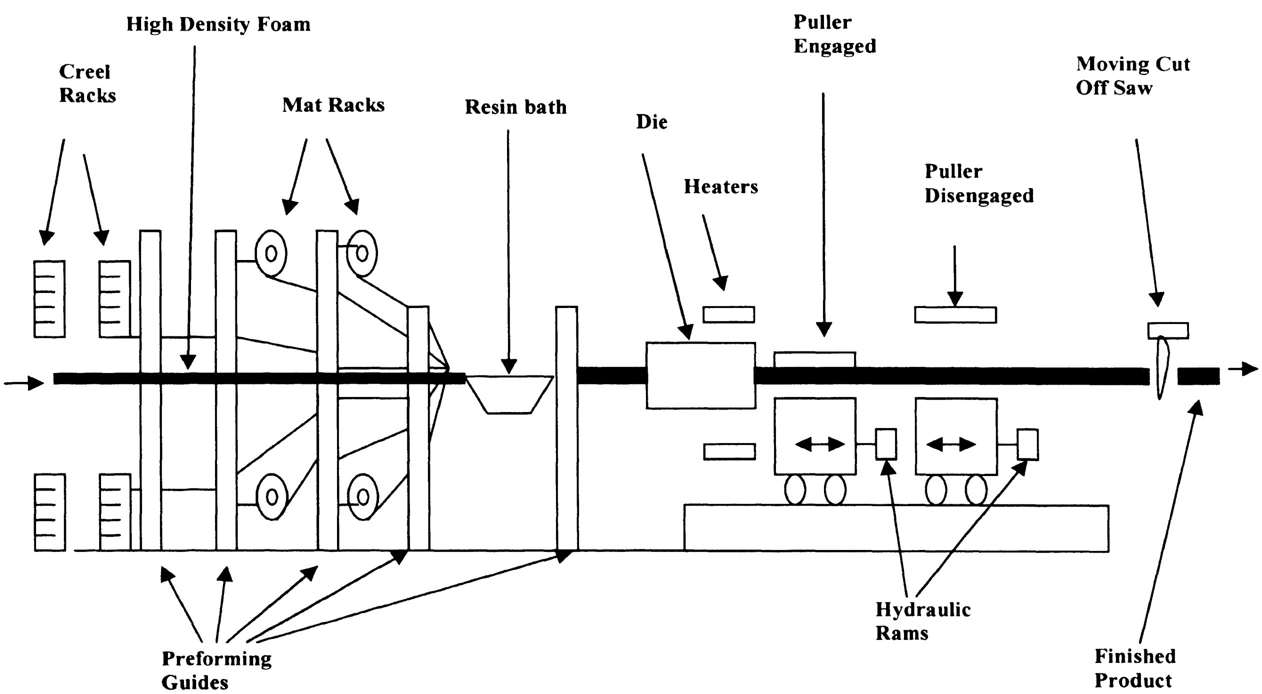


Figure 2.4. Setup of Core-filled Pultrusion Process

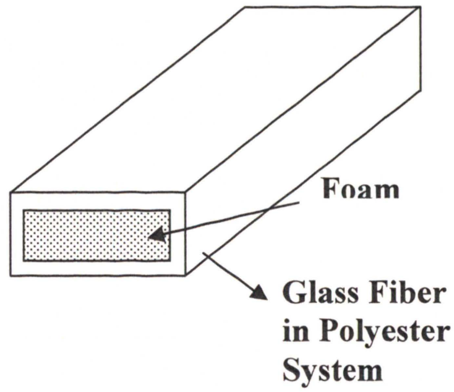


Figure 2.5. Core-Filled Pultruded Composites

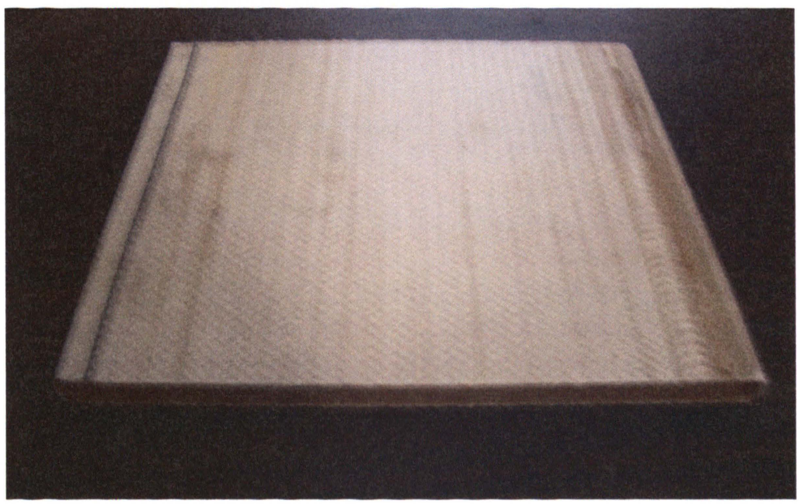


Figure 2.6. Core-Filled Composite Manufactured at UMR

Since the process of in-core pultrusion involves lot of complications, an easily pultrudable resin system like polyester was used. In the present work, two different types of fiber mats were used in manufacturing the in-core pultruded panels. They are

(i) ±45° woven mat

(ii) Random fiber mat.

2.3.2 Resin. Core-filled pultrusion process involves lot of complications. Hence, an easily pultradable resin can be considered during the initial stages of the work. Polyester was used as the resin system. Polyester is less viscous than epoxy and has a lower curing temperature which is favorable for pultrusion. Various intiators and fillers were added to the base resin system to improve curing. The weight percentage of the ingredients in the resin system is given in Table 2.1. For faster curing rates styrene can also be used. PU can also be used in core-filled pultrusion process by designing a specialized injection box which is similar to the core-filled pultrusion setup.

Table 2.1. Weight Percentages of the Individual Ingredients of Polyester Resin System

Serial Number	Name	Weight %
1	Polyester 31031 Resin	100
2	Promoter 15	0.15
3	Low Temp. Initiator (Esperox 570p)	0.75
4	High Temp. Initiator (TBPB)	0.1
6	Mold Release	1
7	Clay	10

2.3.3 Fibers. The fibers used include: Glass Fibers with yield-113, Random Glass Mats (7.5" width), and veils (7.5"width). The number of rovings and mats to be used depends on the net cross-section of the fiber (without the core) and the fiber volume fraction that is desired. PulGenie software was used to calculate the number of rovings and mats. The software calculates the fiber volume fractions based on the effective cross-sectional area of the die (internal area of the die – area of core) and by taking into account the number of rovings as well as the number of mats. 60 glass rovings and two random mats were used to obtain a fiber volume fraction of 60-64% with a core dimension of 7" x 0.4375". In addition to the mats, veils were also used (for a smooth surface finish and to soak up excess resin).

2.3.4 Die Mat and Veil Dimensions. The internal cross-section of the die was 7.0"x 0.55". This thickness was achieved by using shims. The dimension of the mat and veil are taken such that they drape over the sides, thus covering the entire perimeter of the pultruded sample. The width of the mat and veil were taken as

Mat - 7.5" wide

Veil - 7.5" wide

2.3.5 Foam. The initial dimension of the foam used was 0.4375" x 7.0" x 96". The initial thickness of the foam was found to be more than the required thickness therefore the thickness was reduced to 0.4375" by sanding. Density of the foam was found to be 6 lb/cubic ft.

2.3.6 Setup. Core-filled pultrusion setup is supported by wooden posts. Preforms are made of high density polyethylene. Preforms are then clamped to the setup using C-clamps. Other parts of the setup are explained below.

2.3.6.1 Creel. The creel setup along with mats, veils and fiber rovings setup is the key for good feeding. The upper veil and mat rolls are placed differently than the lower set of mat and veil. PVC tubing can be used to roll the mat or veil for usage.

2.3.6.2 Resin Baths. Two resin baths, one for the top set of fibers and one for the bottom set of fibers were used so that the foam core can be easily inserted into the die and to prevent the fibers from entangling. Fibers are passed through the resin baths before they enter preform1. Foam does not come in contact with the resin until it reaches preform 4. This arrangement makes sure that the fibers will not stick to the foam. Veils need not be soaked through both the resin baths. Fibers are placed in alternate fashion inside the resin bath for good flow and impregnation of the fibers. The fiber arrangement is shown in Figure 2.7.

2.3.6.3 Heaters. Six 750 watt heaters and two 600 watt heaters were used to heat the die to facilitate curing.

2.3.6.4 Die. The dimensions of the die are 0.55" x 7.0" x 30". Figure 2.8 shows the die used during core-filled pultrusion at UMR. The curing temperature of the polyester resin is around 250-270^{0}F, hence the temperature in the die was maintained in that range.

2.3.6.5 Pullers and cutting. The two pullers were run in continuous pulling mode, and pulled the fibers or the cured sandwich composite out of the die continuously.

Figure 2.7. Fiber Placement in the Resin Bath

The cutting saw located at the other end of the machine is used to cut the pultruded composite to desired lengths. A diamond cutter is used to cut the pultruded samples. This reduces the damage of the composite part during cutting.

2.3.7 Design of Preforms and Preform Guides. Preform guides are used to guide the fibers, mats, veils and core into the slot and ensure uniform distribution of the rovings. Preforms should be designed such that they distribute the fibers evenly and also prevent the fibers from entangling with each other.

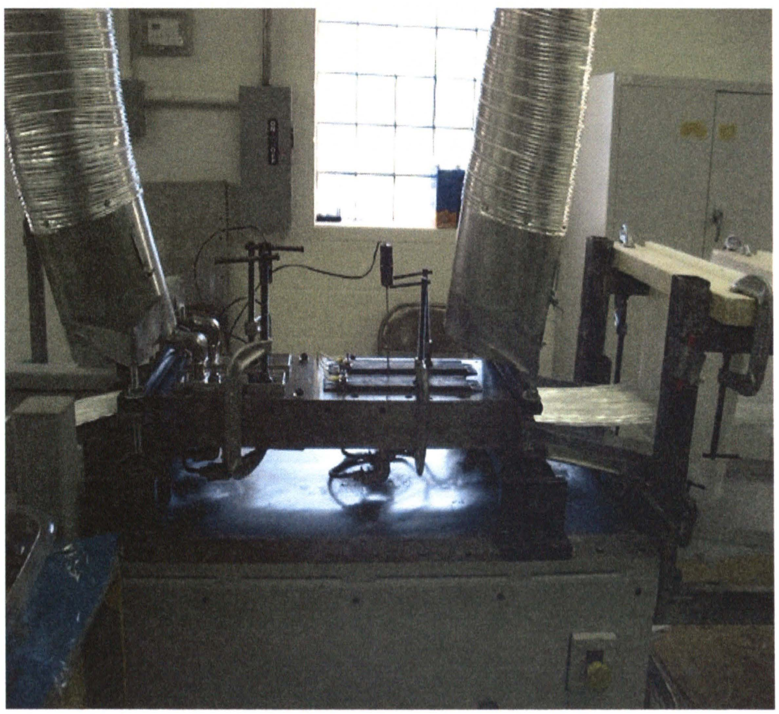


Figure 2.8. Pultrusion Die and the Heaters at UMR

2.3.7.1 Preform f1 (farthest from the die). The first preform is designed such that twenty five fibers pass through the holes on the top, twenty five through the bottom and five fibers through each side. The foam passes through the slot in the middle. The mats pass through the slots next to the center slot. The top veil is passed through the extreme top slot. The bottom slot was passed through the other extreme slot.

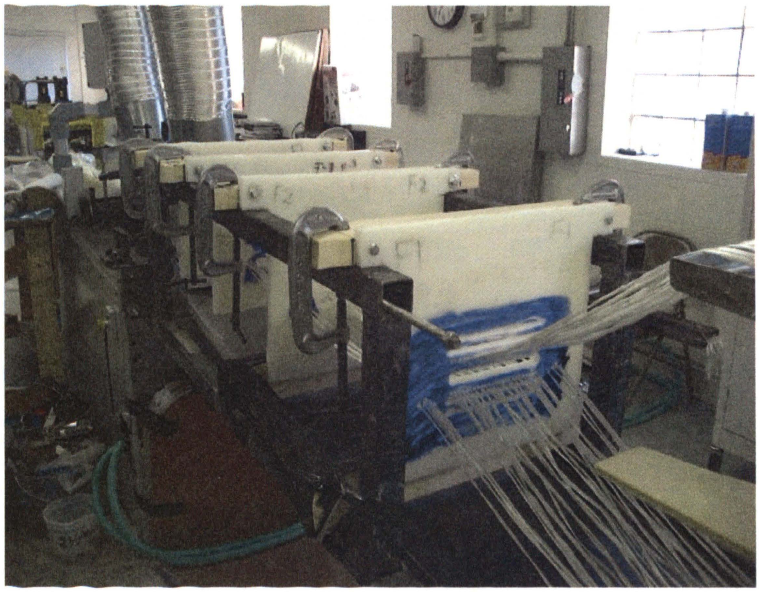


Figure 2.9. Setup of Preforms in the Core-Filled Pultrusion Setup

The bottom veil was passed below the bath drip tray. There is also a risk of the bottom mat getting entangled with the resin bath due to the small clearance. Figure 2.10 shows the arrangement of mat, fibers and the core which are passing through preform 1.

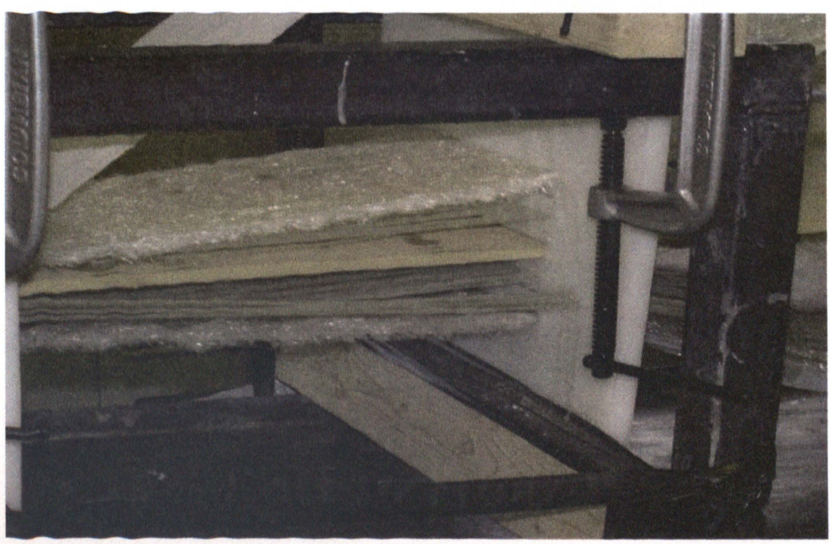


Figure 2.10. Arrangement of Mat, Fiber and Core in Preform 1

2.3.7.2 Preform f2. In the second preform, the fibers on the top along with top mat and veil are passed through one slot on the top. The bottom fibers along with the bottom mat and veil are passed through one bottom slot. The foam passes through the slot in the center and the fibers on the sides pass through the holes on the sides. Figure 2.11 shows the second preform in the pultrusion setup. The side slots were arranged in such a way that they move towards the foam. This arrangement enables the fibers to keep the mats and veils to drape the foam perfectly. All the preforms were made of high density polyethylene.

2.3.7.3 Preform f3. In the third preform, the top layer (veil + mat + rovings) passes along with the foam through one slot. One preform guides are fixed just above this slot to guide the rovings, mat and veil into the slot. The bottom layer (rovings + mat + veil) and the fibers on the side still pass through separate slots. Preform 3 is shown in Figure 2.12.

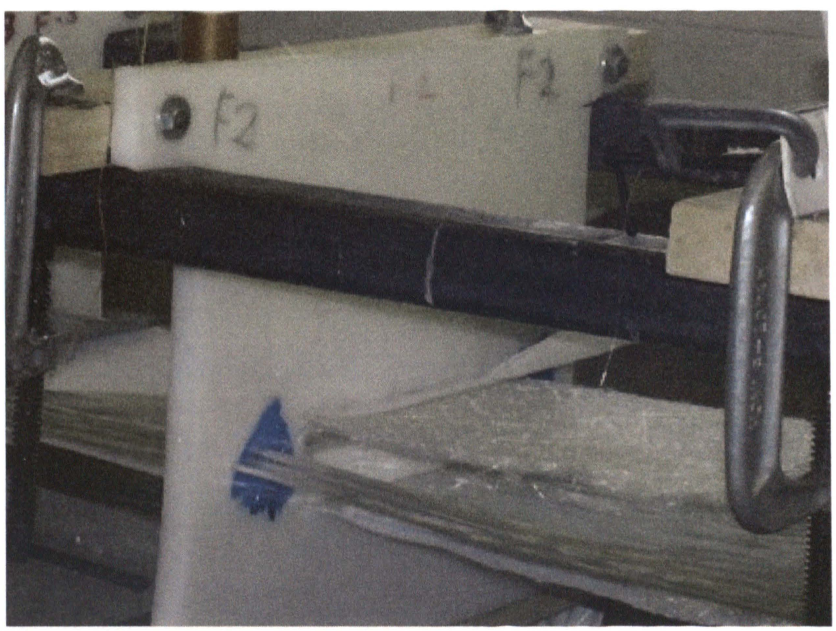


Figure 2.11. Arrangement of Fibers, Core, Veil and Mat through Preform-2

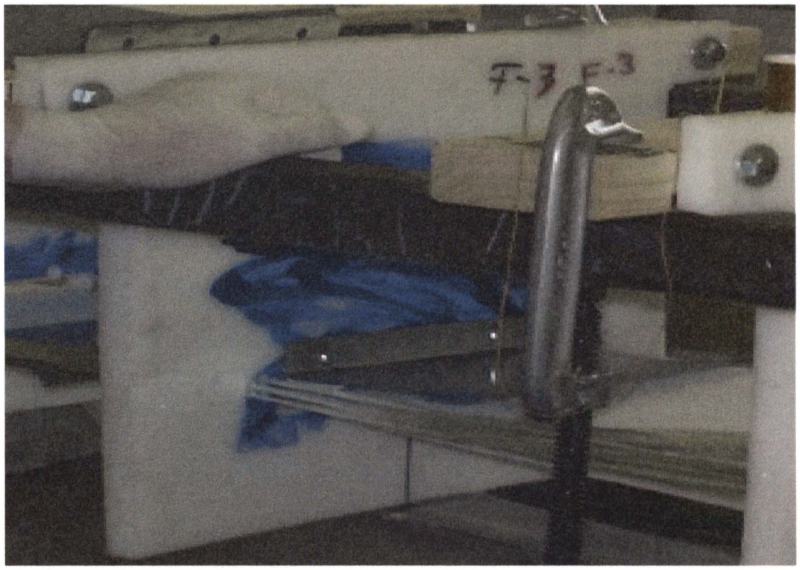


Figure 2.12. Setup of Preform-3

2.3.7.4 Preform f4 (closest to the die). In the last preform, all the layers (top + foam + bottom) pass through one slot except the fibers on the sides. Two preform guides, one on top and one on bottom are used to guide the fibers and foam into the slot. The two preform guides are clamped together. The fibers on the side still pass through separate holes. The last preform should be placed as close to the die as possible. Figure 2.13 shows the final preform.

2.3.8 Other Considerations. The mats and the veils should be stitched along with the roving. Care should be taken that the fibers, mats and rovings remain dry before stitching and then should be uniformly wetted with resin after being stitched. Non-uniform wetting of the rovings will cause the rovings to cure in the die first and these cured rovings will be subjected to a higher stress that might cause them to break. Figure 2.14 shows the procedure for stitching the mat and the veil.

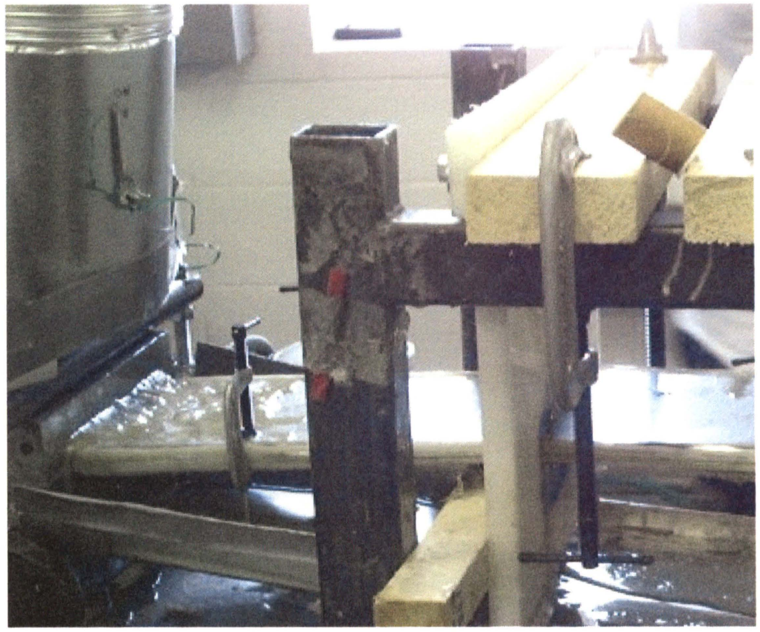


Figure 2.13. Setup for Preform-4

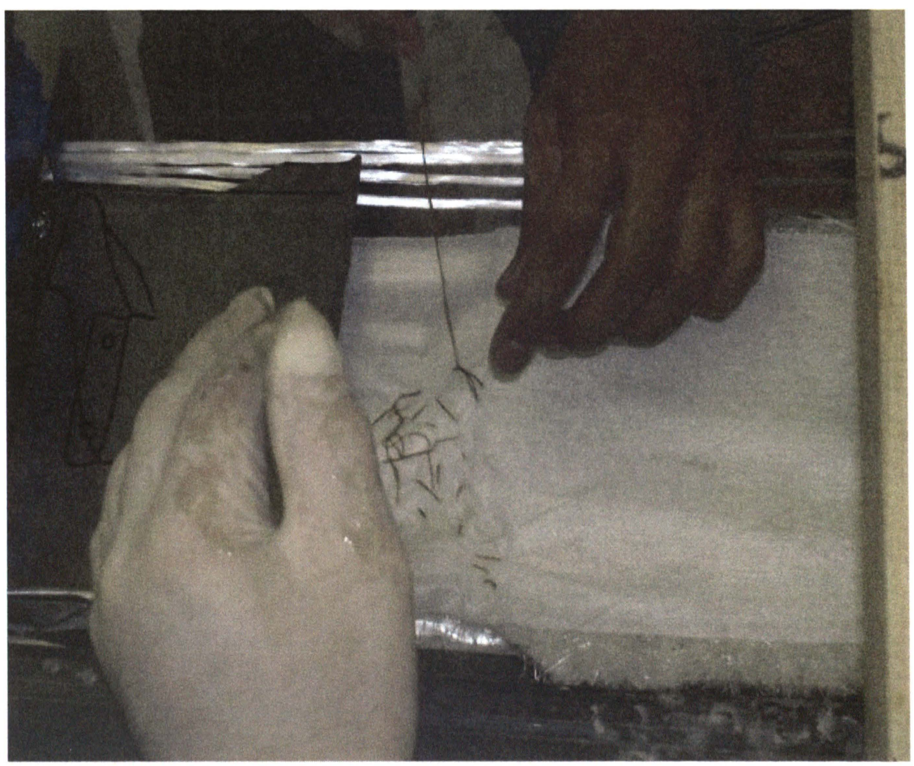


Figure 2.14. Stitching Mat and Veil with Rovings

- The resin baths, guides in the resin bath, preforms and preform guides should be clean and free of sharp edges to prevent entangling of the fibers.
- The preforms should be designed properly and the dimensions of the slots and holes should be accurate. The slots and holes should also be chamfered and smoothened.
- Appropriate line speed (around 12"/min) and temperature control should be maintained.
- The fibers can easily be inserted into the holes by wetting the ends in water.
- If the fibers are to be laid on top and bottom, like layers, then they should be fed from the performs in the same profile i.e. The first perform should have 25 holes for top and 25 holes for bottom all aligned together and should not be changed like 10 and 15 separately as different number of holes leads to entanglement.

2.3.9 Machine Shutdown. Before stopping the machine, mold release should be applied on the fibers to clean the die and the resin baths, preforms, etc. should be cleaned. The final product after curing is shown in Figure 2.15.

Figure 2.15. Cured Core-filled Pultruded Part

2.4 DIFFICULTIES FACED DURING PU PULTRUSION

• A heat resistant material was needed to secure the injection box to the die. This heat resistant material had to be structurally strong in order to withstand the thermal and structural stresses during pultrusion. A phenolic composite was chosen to make the attachment but during the process, the phenolic composite cracked. Another reliable material has to be found.

• Perfect sealing of the injection box and the pultrusion die was not achieved. Bad design of the connector resulted in the leakage of the PU resin from the injection box and the attachment.

• After the pultrusion process, the lines have to be purged very rigorously. Hoses carrying the raw materials were clogged during the initial runs. An economical and reliable flushing agent has to be chosen for pultrusion process.

• Discarding the left over raw materials i.e., polyol and isocyanate has to be very precise since the raw materials are harmful to human health. Cat litter was used to soak up the isocyanate during chemical spills.

• Care has to be taken not to come in contact with the monomeric isocyanate raw materials. Masks and goggles have to be worn by the pultruders during pultrusion to avoid contact.

2.5 FUTURE IMPROVEMENTS IN THE PU PULTRUSION AND CORE-FILLED PULTRUSION

• Monitoring for the in-core and the PU pultrusion process in future runs

• During the in-core process, the veil was passed from below the drip bath through a gap. Instead, a slot with a lip can be made in the drip bath and the bottom mat and veil can be passed through it.

- Excess resin dripped to the floor immediately in the region before the die due to improper drip path design. This has to be studied in detail for both the processes.
- Flexi glass for the cutter can be used in the place of the presently used cutter.

3 PERFORMANCE EVALUATION

Soy-matrix polyurethane neat resin from Urethane Soy Systems was tested for tensile and flexural properties. The resin and the curing agent are mixed according the suggestions given by the company. The cure schedule provided by Bayer has been used for manufacturing.

3.1 FLEXURE TESTING

Three samples dimensions 0.5 in x 6 in were used for testing. Each sample was tested using an Instron testing machine with a three point loading system (Figure 3.1) and ASTM D 790, "Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials." Support span and a cross head speed of 2 in and 0.1 in/min, respectively were used for the testing.

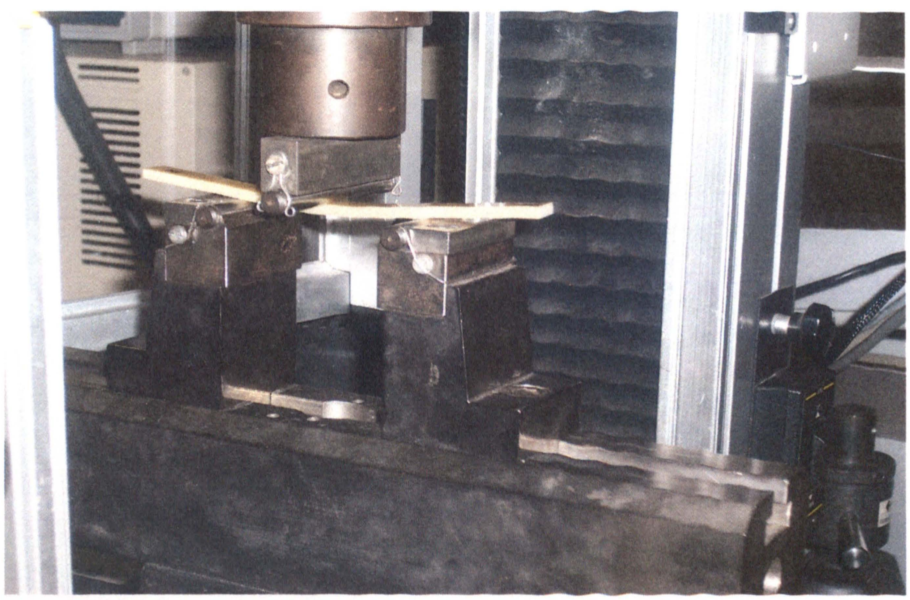


Figure 3.1. PU Flexure Sample and Instron Testing Machine

3.2 IMPACT TESTING

A Dynatup Instron Model 9250 Impact Testing Machine (Figure 3.2) with impulse control and data system was used to carry out the low velocity impact tests. The maximum physical drop height of the machine is 1.25 m but can simulate a drop height of 20.4 m. The impact test instrument has a motor and twin screw drive for rapid crosshead retrieval after impact. The impulse control and data system includes impulse software controller panel for test set-up and high-speed impulse signal conditioning unit. The impulse data software can calculate the total energy, contact force, impactor displacement and impactor velocity as a function of time. A typical impact test lasted for around 12 milliseconds. Measurement of the contact force, transient deflection and impact energy can be used to assess the extent of damage in composite structures. The fixture in the impact testing machine has the capability to test 7 in. x 10 in. specimens supported over a 5 in. x 5 in. opening.

As the pultruded PU samples were only 2 in. wide, a fixture with an opening of 1.75 in. x 1.75 in. was used for the impact tests. The fixture opening was kept to 1.75 in. to ensure that the test specimens are clamped along all four edges. The core-filled pultruded parts were 7 in wide. Therefore, the usual setup was used during the impact characterization of these samples. The impactor had a mass of 6.48 Kg and a diameter of 0.5 in. Three different energy levels of 10 J, 15 J and 20 J were considered. Four specimens were tested for the ordinary and the soy-based PU resin formulation at each energy level. The specimen was first clamped in the fixture. The impactor mass was then raised to the desired drop height corresponding to the energy of impact.

The impactor is dropped onto the clamped specimen. As the impactor makes contact with the specimen, the impulse control data acquisition system is triggered to start acquiring data.

Figure 3.2. Impact Testing Machine

4 RESULTS AND DISCUSSION

4.1 FLEXURE CHARACTERIZATION OF PU SAMPLES

The flexure tests conducted on neat resin samples indicate that the flexural modulus and flexural strength of soy-PU are higher than those of the base PU. The values are tabulated in Table 4.1. The flexural results for the pultruded samples are shown in Figure 4.1. Flexural strength increased from 889.4 MPa to 1,343.8 MPa by the addition of soy into the base PU resin. A considerable increase in the modulus was observed when soy was added to the base resin. Area under the curve for soy-PU was higher than that of the base PU. The increase in the area indicates that the soy PU has high toughness when compared to the base PU resin system. Higher modulus of soy-based PU suggests its high resistance to stresses and deformation.

Table 4.1. Neat Resin and Pultruded Flexure Results

	Modulus (GPa)	Flexure Strength (MPa)
Base PU	2.8 ± 0.3	54.8 ± 5.5
Soy-PU	3.1 ± 0.2	69.1 ± 8.9
Pultruded Base PU	35.2 ± 4.2	889.4 ± 89.5
Pultruded soy-PU	45.1 ± 4.5	1343.8 ± 161.2

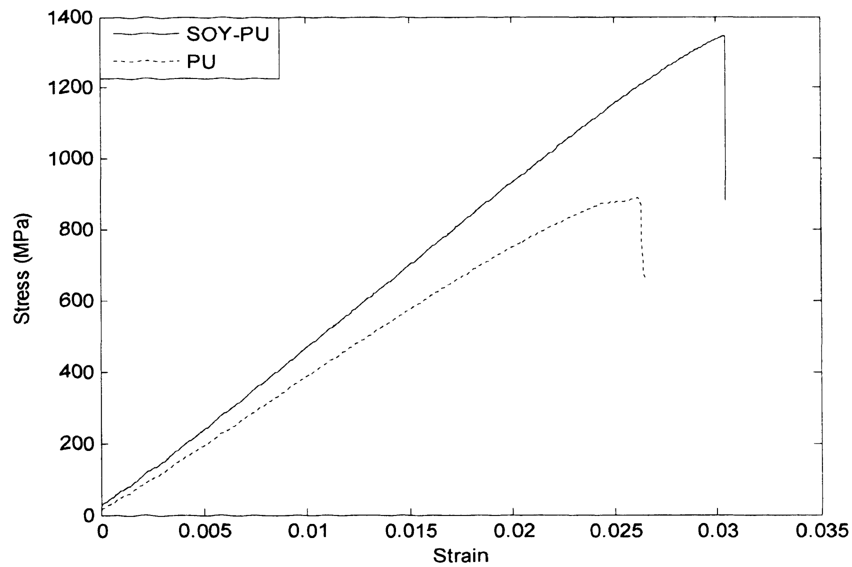


Figure 4.1. Comparison of Flexural Properties of Polyurethane and Soy-PU

4.2 IMPACT CHARACTERIZATION OF PULTRUDED PU SAMPLES

The effect of impact force at various energy levels with the addition of soy in the PU resin is shown in Figure 4.2. The addition of soy increased the maximum load on the specimen. Increase in the maximum load resulted in an increase in the stresses and the localized damage developed during the impact and is not desirable for a good impact resistant material; however, the increase in the maximum load was very less. When the errors during manufacturing and testing are considered, this increase in load would be much less than the obtained value. The increase in the maximum load is more for the 15 J, whereas the increase in maximum load is very less for 10 J and 20 J impact energy levels. The time taken to reach the maximum load was approximately the same for both the PU resin systems at all the energy levels.

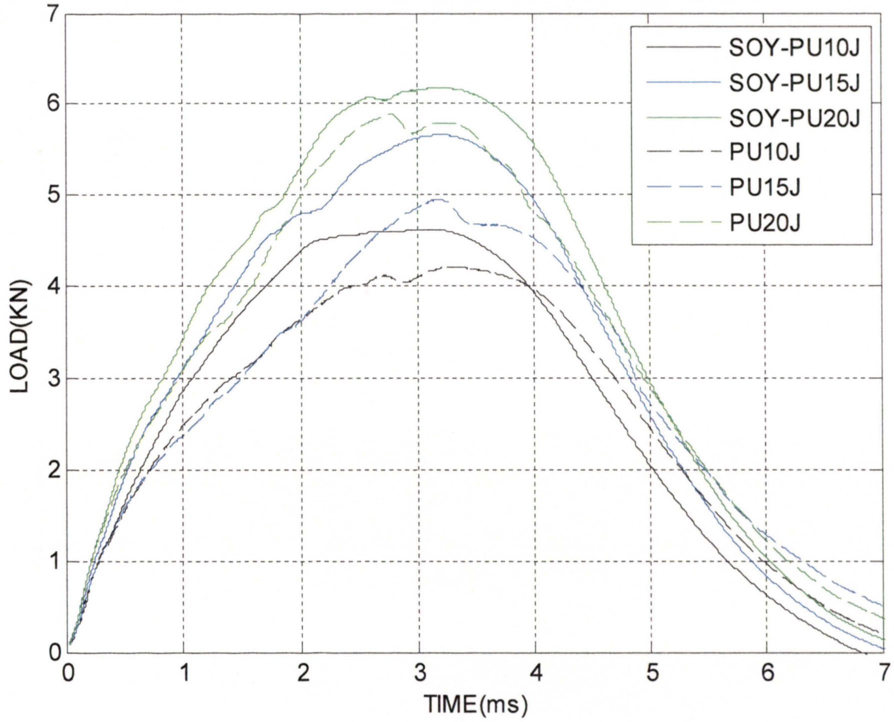


Figure 4.2. Contact Force Versus Time Plots at Different Energy Levels

Variation of impact energy with respect to the time is shown Figure 4.3. The curves can be divided into three phases. The first phase of the curve indicates the transfer of energy from the impactor to the specimen while the second part shows the transfer of energy from the specimen back to impactor. The final phase shows the flat region after the energy transfer from the specimen. This region indicates the energy absorbed by the specimen [19-21]. Base PU showed the higher energy absorbing capacity than the soy PU. Figure 4.4 shows the velocity versus time plot for both the PU resin blends. Higher rebound velocity indicates that the material is more elastic and can absorb higher energy. The change in the energy absorbing capacity by the addition of soy into the base PU resin was very little. The variation of velocity versus time supports the plots of energy versus time and load versus time. The rebound velocity for the soy PU is higher than that of the base PU resin.

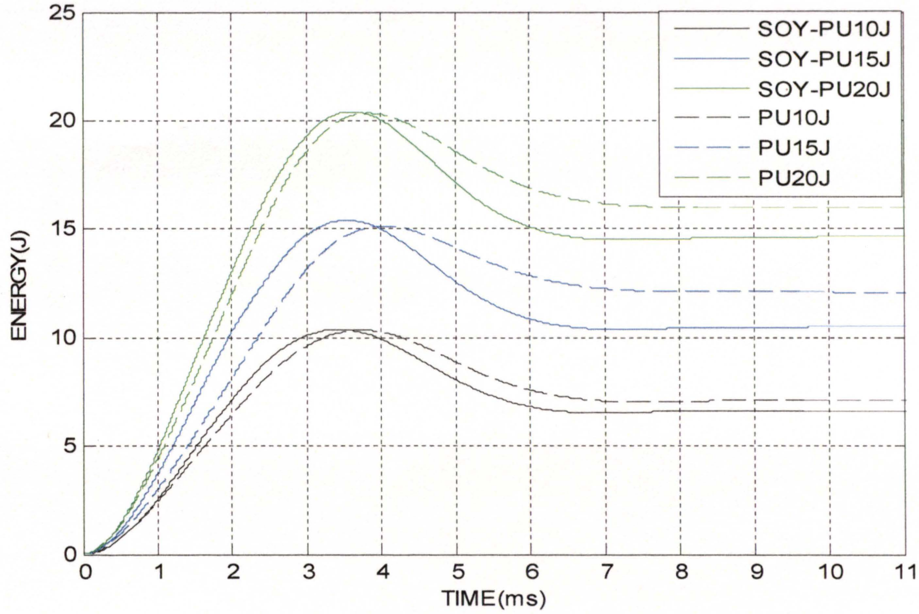


Figure 4.3. Energy Versus Time Plots at 10J, 15J, 20J

This indicates that soy PU absorbs less amount of energy when compared to the base PU blend. From Figure 4.4; the velocity reaches zero for base PU much earlier than the soy PU pultruded composite samples.

Figure 4.5 shows the variation of load with respect to the displacement of the specimen during impact. Figure 4.6 shows the plot of displacement versus time. The slope of the loading phase in Figure 4.5 indicates the stiffness of the material. The slope for the soy PU curve in Figure 4.5 is higher than the base PU curve. Soy PU pultruded specimens were much stiffer than the base PU pultruded samples. The area under the curves represents the energy absorbed. Minimal changes were observed in the variation of displacement when soy was added into the PU resin system.

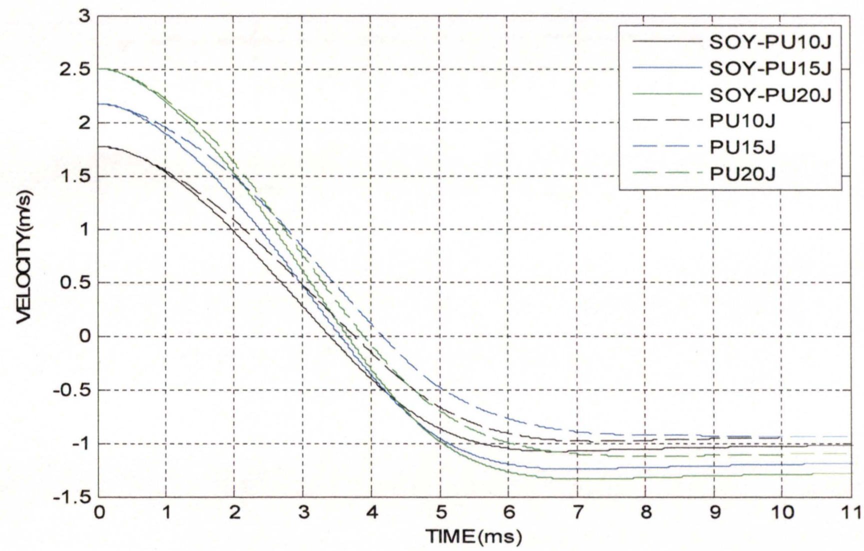


Figure 4.4. Velocity Versus Time Plots at 10J, 15J, 20J

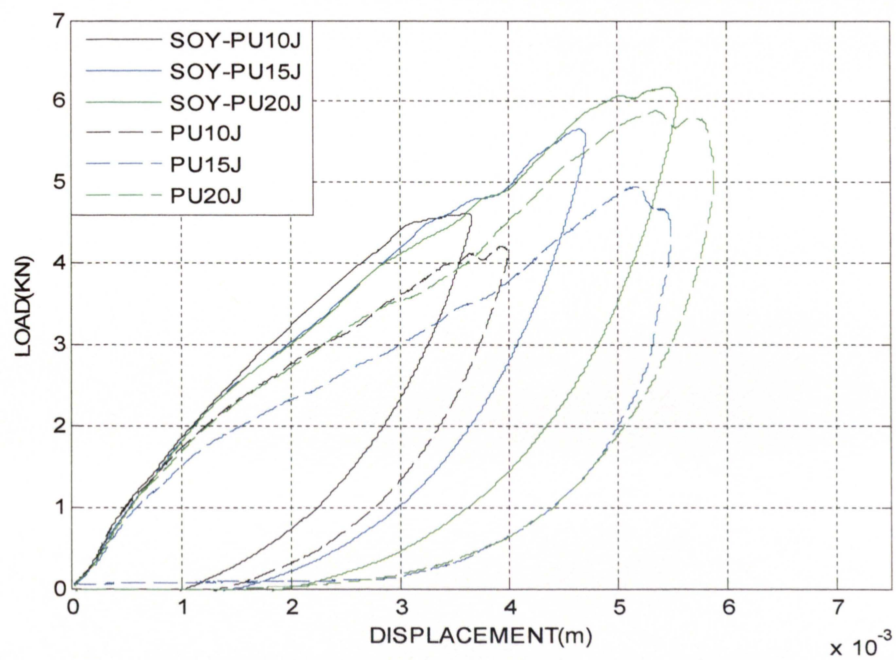


Figure 4.5. Load Versus Displacement Plots at 10J, 15J, 20J

Figure 4.6 shows the variation of displacement of the pultruded sample with respect to time. Base PU pultruded samples showed higher displacement than that of the soy PU samples, indicating that base PU samples are more flexible than the soy PU pultruded samples.

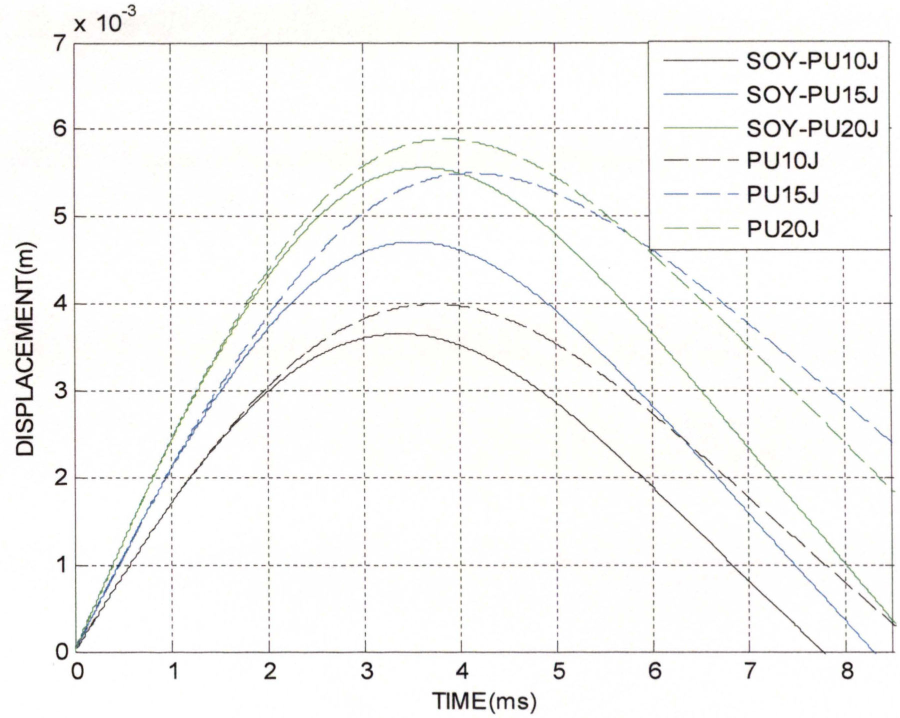


Figure 4.6. Displacement Versus Time plots at 10J, 15J, 20J

4.3 IMPACT CHARACTERIZATION OF CORE-FILLED PULTRUDED COMPOSITES

Figure 4.7 shows the variation of contact force as a function of time for in-core pultruded panels with two different types of fiber mats (±45° woven mat and random fiber mat). From Figure 4.7, the in-core pultruded panel with random fiber mat has lower contact force than the core-filled pultruded panel with woven mat. The maximum load reached during the impact was 4.1 KN for the ±45° woven mat pultruded samples while the maximum load for the random fiber mat samples was approximately equal to 3.4KN. Figure 4.8 shows the energy absorbed by the in-core pultruded panels. The energy absorbed by the in-core panels does not change a lot with the change in the type of mats.

The damage induced by the impact on the woven mat in-core panel and random fiber mat in-core panel can be seen in Figures 4.9 and 4.10, respectively. However, the damage induced in the in-core panels with the ±45° woven mat is much severe when compared to the random mat. The fracture in the ±45° woven mat pultruded samples tends to propagate in the direction of the fiber placement. Whereas, in the random fiber mat pultruded samples the damage was concentrated within a certain area.

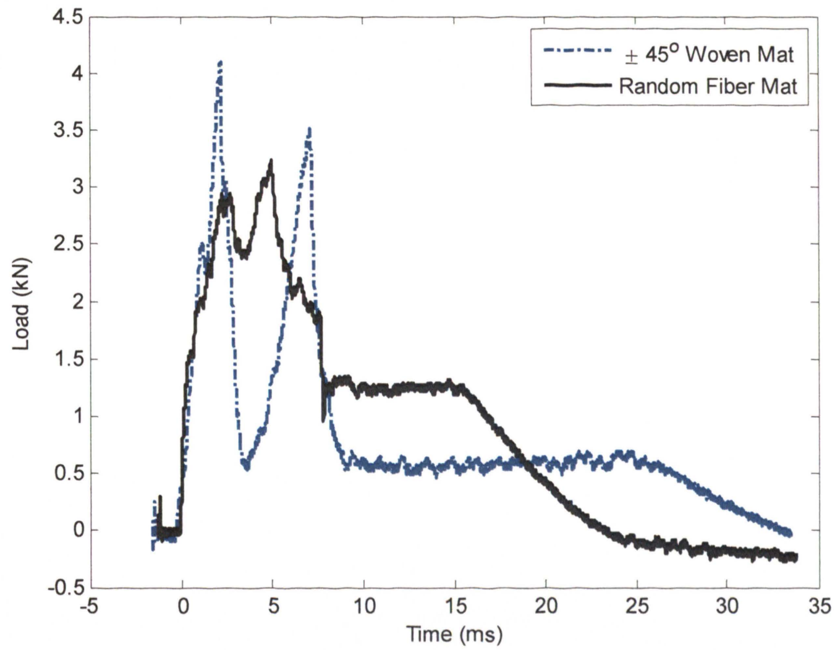


Figure 4.7. Contact Force as a Function of Time for In-Core Panels

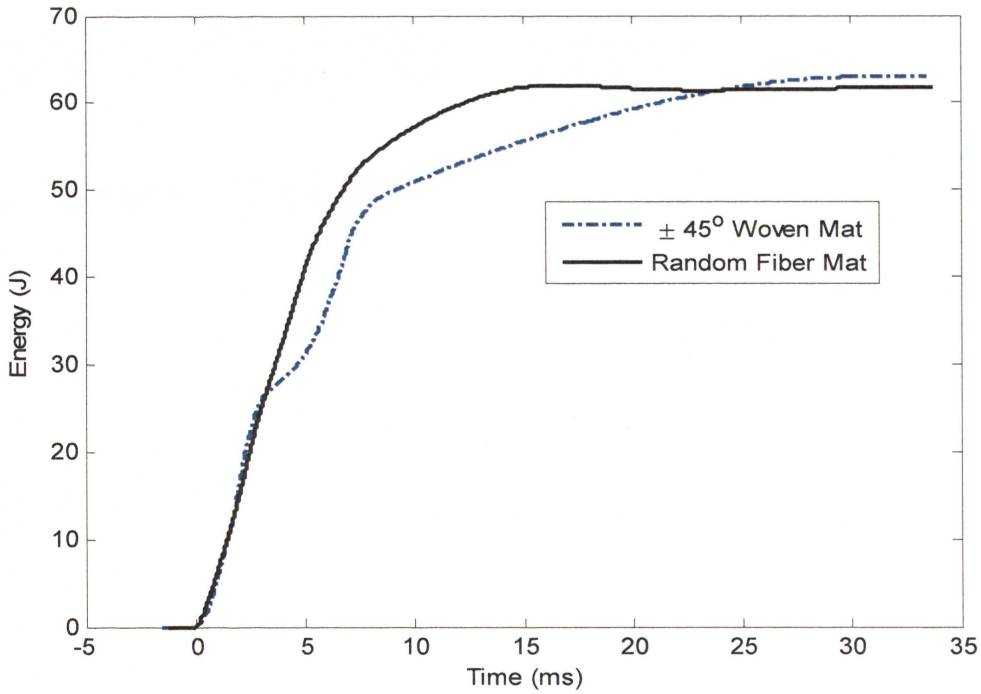
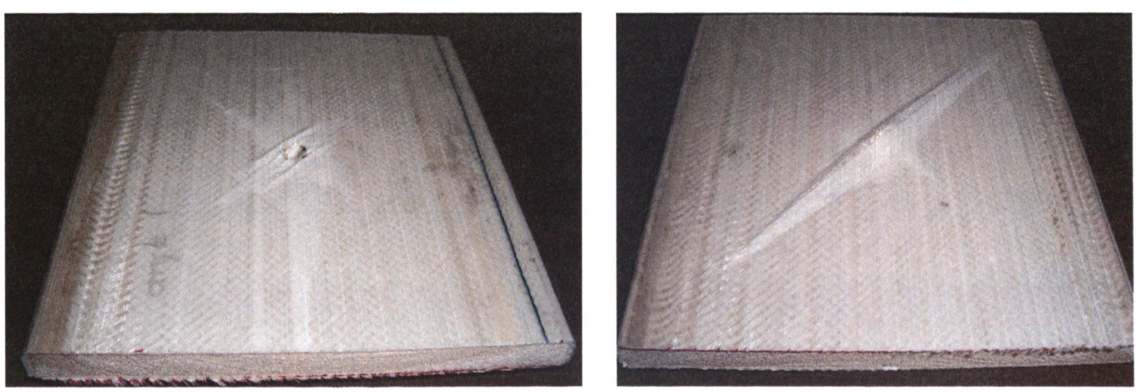


Figure 4.8. Energy as a Function of Time for In-core Pultruded Panels



(a) Front Surface **(b) Rear Surface**

Figure 4.9. Impact Damage of Pultruded Composite Panels with ±45° Woven Mat

(a) Front Surface

(b) Rear Surface

Figure 4.10. Impact Damage of In-core Pultruded Composite Panels with Random Fiber Mat

5 CONCLUSION

Pultruded parts were manufactured using the two blends of PU. Soy-based PU pultruded samples had higher flexural modulus and higher flexural strength when compared to that of base PU pultruded samples. The change in the impact properties was negligible when the manufacturing and testing errors are taken into consideration. Hence, soy-PU resin system can be considered to be a very good alternative to the conventional PU resin system. Use of soy-based PU helps in the increase in demand for the soybean thus helping the farming community and also decreases the dependence on fossil fuels.

Core-filled pultrusion setup has been successfully set up and pultruded parts have been manufactured using glass fiber and polyester resin system. Two different kinds of reinforcements were used for manufacturing the core-filled pultruded parts. These core-filled pultruded parts can be a viable alternative to conventional building materials both in terms of an ergonomic and commercial point of view.

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