IMPROVING THE MECHANICAL PERFORMANCE OF WOOD FIBER REINFORCED BIO-BASED POLYURETHANE FOAM

by

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Abstract

Because of the environmental impact of fossil fuel consumption, soybean-based polyurethane (PU) foam has been developed as an alternative to be used as the core in structural insulated panels (SIPs). Wood fibers can be added to enhance the resistance of foam against bending and buckling in compression. The goal of this work is to study the effect of three modifications: fiber surface treatment, catalyst choice, and mixing method on the compression performance of wood fiber-reinforced PU foam. Foams were made with a free-rising process. The compression performance of the foams was measured and the foams were characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray computed tomography (CT). The foam reinforced with alkali-treated fibers had improved compression performance. The foams made with various catalysts shared similar performance. The foam made using a mechanical stirrer contained well-dispersed fibers but the reinforcing capability of the fibers was reduced.

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List of Nomenclature

C_1		Geometric constant of proportionality
D	μm	Diameter of fiber
E_c	MPa	Experimental modulus of foam sample
E_o	MPa	Elastic modulus of the foam with no fibers
E_{PU}	MPa	Elastic modulus of cell wall material (PU)
E_x	MPa	Modulus of the matrix for composite foam with the removal of fibers
L	mm	Length of fiber
m_{fibers}	g	Mass of fibers
m_{foam}	g	Mass of the entire foam sample
m_{solid}	g	Mass of cell struts
V_{foam}	cm^3	Volume of the entire foam sample
V_{solid}	cm^3	Volume of cell struts
ρ_o	g/cm^3	Density of the foam without fibers
ρ_{PU}	g/cm^3	Density of cell wall material (PU)
ρ_x	g/cm^3	Density of the matrix for composite foam with the removal of fibers

1. Introduction

Polyurethane foam is a synthesized cellular plastic and has been used in a number of diverse fields, such as cushioning, packaging, automotive, and structural applications. In the field of structural applications, polyurethane foam is an insulating core material placed in structural insulated panels (SIPs); SIPs consist of two sheathing layers with an insulating core. Polyurethane foam being used as a core material needs to have the ability to withstand compressive and shear loading.

In order to enhance the mechanical properties of foam without an increase in petrochemical feedstock, polyurethane foams reinforced with wood fibers have been developed. The thermal stability, energy absorption, physical and mechanical properties of wood fiber-reinforced polyurethane foam have been studied in the literature. Although considerable effort has been spent in studying wood fiber-reinforced polyurethane foams, one problem is still unsolved: compressive strength and modulus of foam either decreases or stays constant with increasing fiber content. This study was carried out to understand and enhance the compression performance of wood fiber-reinforced polyurethane foam. The results showed that the application of alkaline treatment and the use of a mechanical stirrer enhanced the compression performance of fiber-reinforced foam.

The main objective of this study is to try several methods to enhance the compression performance of wood fiber-reinforced polyurethane foam. In order to achieve the objective, approaches centering on the surface modification of fiber and manufacturing process of foam were implemented. In the thesis, three aspects of foam performance were investigated: (1)

the effect of fiber surface treatment, (2) the effect of catalyst, and (3) the effect of mixing method.

There are five chapters in the thesis. Chapter 1 gives an overview of the thesis and Chapter 2 provides an introduction to polyurethane foam and other plastic foams and covers related works reported in the literature. Chapter 3 describes the experimental methods, and materials used during the experiments. Chapter 4 presents experimental results along with the discussion of the results. Lastly, in Chapter 5, the results are summarized and recommendations proposed for future work.

2. Literature Review

2.1 Introduction

Foam is a three-dimensional cellular solid containing pore space and a skeletal frame. Foam is found widely in nature and is used extensively by humans; it is primarily found in structural applications. The mechanical behaviors of foam depend on cellular structure. The reduction of weight and increase in load-carrying capability under bending are advantages of the cellular structure. Wood and cancellous bone are two examples of natural cellular materials taking advantage of this.

Wood is composed of lattices of cells, basic units of wood structure. These cells act as vessels for fluid conduction and provide structural support; cell vessels facilitate the transportation of water and the foam-like structure of wood allows it to resist bending in order to maximize the growing efficiency of tree [1].

Skull bone is a sandwich structure composed of layers of compact bone with internal cancellous bone as a core. Cancellous bone is a porous solid composed of interconnected cells. The cellular structure of the cancellous bone is responsible for separating layers of dense bone and increasing the moment of inertia [13].

Cellular materials with low weight and high rigidity have been exploited in many applications and served human for millennia. Wood, for example, has been used extensively as construction materials due to its light weight and high stiffness. For its application in structural engineering, low density wood has been used in sandwich panels as core material which was replaced by other materials such as honeycombs and plastic foams after World War II and high density wood is used as external layer material. The need of alternative lightweight and rigid foamed materials has grown and leads to the development of synthetic foams.

Foams also can be made artificially. Many materials can be foamed, for instance, glasses, ceramics and metals. In particular, plastic foam is of academic and industrial interest. Plastic foam consists of a polymer matrix filled with numerous pores. Plastic foams such as polyurethane (PU) foam, polyolefin foam and polystyrene (PS) foam are commonly found in daily use and industry.

The first man-made cellular polymer, sponge rubber, was made in 1914 [3]. The first synthetic plastic foam, extruded PS foam, was developed in 1931[4, 5]. In 1937, Otto Bayer synthesized the first PU foam [6]. After the war, the increase in demand of foam from industry caused the widespread use of rigid PU foams [7-10]. Flexible PU foam was introduced into market in the early 1960s [11].

Foaming is a process of generating and stabilizing gas bubbles in polymeric solid. Foaming mechanisms can be divided into two categories: soluble foaming and reaction foaming. In soluble foaming, blowing agents are mixed with polymer and release of gas is controlled by either the decrease in pressure or increase in temperature. Examples of this category include polyethylene (PE) foam, polypropylene (PP) foam, polyvinyl chloride (PVC) foam and PS foam made by extrusion and injection molding. In reaction foaming, the release of gas is governed by the reaction of the blowing agent with other chemicals or thermal decomposition of blowing agent. Generally, PU foam, polyisocyanurate (PIR) foam, and phenolic foam are fabricated through reaction foaming [12].

Different formulations and processing variables in foam fabrication result in different cell shape distributions and cellular structures. The change in structure affects physical, thermal, and mechanical properties of the foam.

Plastic foams are classified according to thermo-reversibility of a polymer and the cellular structure of foam. Plastic foams can be classified into thermoplastic foam and thermosetting foam according to the thermo-reversibility or be divided into closed-cell foam and open-cell foam according to the cell structure of foam [12].

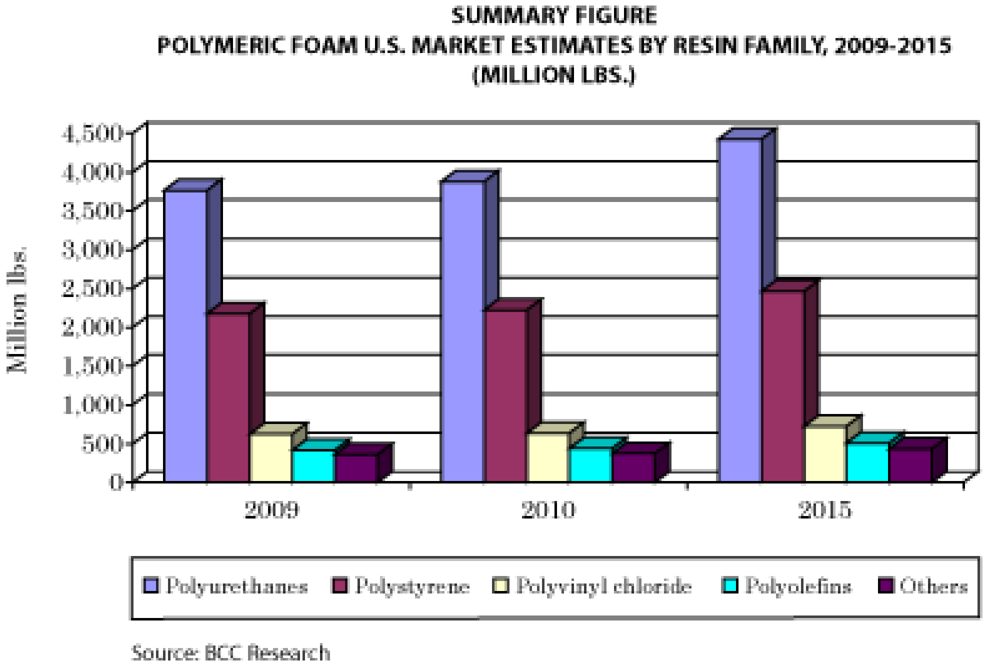
For open-cell foam, the cell walls are ruptured and air fills the hollow cells. In contrast, cell walls of closed-cell foam are essentially intact and cells are filled with gas. The gas is either remaining gas from those used to saturate polymer or gas released by blowing agent during the formation of foam [13]. Open-cell foam has less inherent resistance under external force due to ruptured cell wall and a lower R-value because of the interconnected pores. On the other hand, the high rigidity and R-value of closed-cell foam are attributed to the support of cell walls and insulation of gas enclosed in foam cells, respectively; however, disadvantages of closed-cell foam are high cost and density compared with those of open-cell foam. The choice between open-cell and closed-cell foams depends on the application. Generally, open-cell foams have been used to develop products in shock absorption and cushioning package while closed-cell foams are applied for insulation purposes in building construction.

Thermoplastic foams including PE foam, PP foam, PS foam, and PVC foam are used in many applications. PE foams are used in agriculture, automotive, packaging and building industry. PE foams are also found in the insulation of heating pipe and enhancing the resilience of sport protector [14, 15]. PP foam has high abrasion resistance and substitutes other thermoplastic foams in a lot of application domains [16]; PP foams are commonly used in food manufacturing and automotive industry. It is because PP foams have higher stiffness compared with PE foam and larger impact strength with respect to PS foam. Most importantly, production cost of PE and PP foams is lower than that of PS foam. In addition, expanded PP foam developed by JSP Corporation [17] is considered as a suitable material for flotation devices, such as life jacket and buoyancy aid [18]. PVC foam is another cellular material commonly used in flotation applications. It is used in the marine and shipbuilding industry for its high tolerance to dynamic loading in the marine environment [19, 20]. PS foam is used in packaging and building construction [21]. In construction, open-cell PS foam is used as a major core material in vacuum insulated panel (VIP) for thermal insulation [22-24].

Thermosetting foams are also suitable materials for construction application. For instance, PIR foam has been used not only in domestic hot water storage tanks but also in construction [25]. It was reported that PIR foam has better fire resistance than other plastic foams, making it a desirable material to be applied in construction; this is because urethane linkages in PU foam are replaced by imide or amide linkages [26] resulting in improved thermal stability but with high surface friability [27, 28]. In addition to the high friability causing failure at the foam/sheathing interface, PIR foams have another drawback, a high content of isocyanate used for the synthesis of foam. Without these disadvantages and with excellent thermal insulating characteristics, PU foams have been used for insulation in building; they are well known core materials for structural insulated panels (SIPs) in construction.

The market for plastic foam is expanding rapidly. According to a BCC research report [29] focusing on the U.S. market, 7.5 billion pounds of plastic foams were produced 2010. The report predicted that this amount will increase to 8.6 billion pounds with an annual growth rate of 2.9 %. 443 million pounds of polyolefin foams, including PE foam and PP foam, was produced in 2010 and the amount of polyolefin foams is expected to grow by 15 % from its 2010 level to 509 million pounds by 2015.

The largest market share in plastic foam industry belongs to PU foam. 3.9 billion pounds of PU foam was produced in 2010 and the amount of PU foam is forecast to be 4.4 billion pounds in 2015 with an annual growth rate of 2.6%. Figure 2-1 shows the past and estimated market for plastic foams. Another report done by Freedonia group (Cleveland) described U.S. foam demand in 2007 (Table 2-1). The demand analysis predicted an expanding market for PU foam [30].


SUMMARY FIGURE
POLYMERIC FOAM U.S. MARKET ESTIMATES BY RESIN FAMILY, 2009-2015
(MILLION LBS.)

Source: BCC Research

Figure 2-1 U.S. market of polymeric foams [29]

Materials	Percentage (%)
Polyurethane Foams	33
Engineering Plastic Foams	20
Non-plastic Foams	17
Polyolefin Foams	10
Others (Metal and Ceramic foams)	20

Table 2-1 U.S. foam demand (total: 1.3 billion dollar) in 2007 [30]

2.2 Polyurethane Foams

2.2.1 Introduction

PU is a synthetic polymer where organic units are formed by connecting molecules with urethane linkages [31]. The synthesis of PU is mainly based on the reaction between isocyanate group of di-isocyanate and hydroxyl group of polyol (Figure 2-2 shows this reaction). End groups of the polymer chain are determined by dominant species among reactants; an excess of di-isocyanate results in the polymer chain being end capped with isocyanate groups.

$$\mathrm{O{=}C{=}N\text{-}R_{(isocyanate)}\text{-}N{=}C{=}O + HO\text{-}R_{(polyol)}\text{-}OH \rightarrow O{=}C{=}N\text{-}R_{(isocyanate)}\text{-}NH\text{-}C(O)\text{-}O\text{-}R_{(polyol)}\text{-}O\text{-}C(O)\text{-}NH\text{-}R_{(isocyanate)}\text{-}N{=}C{=}O}$$

Figure 2-2 PU synthesis reaction (elements parenthesized mean double bond of element at branch point in a polymer)

Other reactions may accompany the formation of PU. For instance, isocyanate groups, in addition to reacting with the hydroxyl groups of the polyol, can react with the urethane linkages of PU to form allophanate. In addition, the isocyanate group can react with other isocyanate groups to form dimers or trimers. With the presence of water, the isocyanate group can react with urea to form biuret, where urea is a product of the reaction between water and isocyanate. Although these side reactions lower the stability of PU, at the same time they can increase the degree of crosslinking between molecules, increasing the stiffness of the PU [32].

Based on the degree of crosslinking, PU foams are divided into three groups: flexible foam, semi-rigid foam, and rigid foam. They are made from different formulations and with different compositions. In general, flexible foams are used for packaging and cushioning, while rigid foams are for building insulation. Table 2-2 lists common application of different types of PU foams.

PU has been developed for versatile applications, such as paints, coatings, adhesives, elastomers, and foams. The high degree of vapor permeability and water resistance of PU film enables it to be used for flexible surface coating. PU adhesives have been extensively used for bonding between core material and sheathing in structural panels as well as between interiors in automotive vehicles [33, 34]. For implanting medical devices, PU elastomer outperforms silicon elastomer with regards to its high abrasion and fatigue resistance under dynamic loading [35]. Insulation is one of them. PU foams have advantages of lightweight, low cost, and especially good adherence toward the surface of sheathing layer. More importantly, they are popular insulating materials with excellent insulating properties for their lowest thermal conductivity over other cellular materials (shown in Figure 2-3). Hence, PU foams take up a considerable fraction of PU production (almost a quarter) [36].

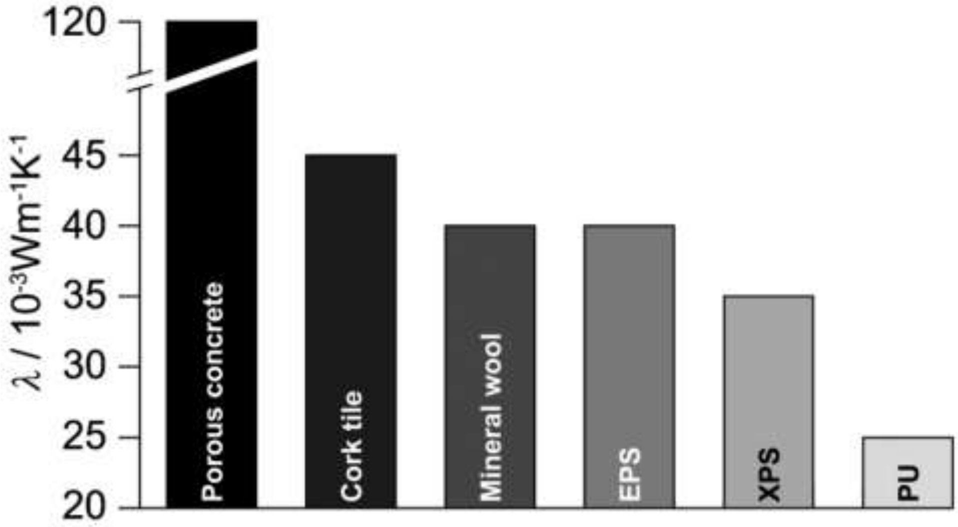


Figure 2-3 Thermal conductivity (λ) of cellular materials [34]

Foams	Markets	Applications
Flexible PU	Transportation	Seating, pads, liners, dampening, carpet backing, filters, flooring, armrests, trim
	Furniture	Bedding, padding, flooring
	Recreation	Sport mats, toys, helmet liner, chest protection
	Packaging	Electronic, computer, china, equipments
Semi-rigid PU	Automotive	Dash panel, liner, viser
	Footwear	Soles
Rigid PU	Construction	Insulation, flooring, siding
	Appliance	Refrigerator frame, door, dishwasher door

Table 2-2 General applications of PU foams [37]

2.2.2 Natural Resources for Foam Development

Polyol, which is a main reactant for commercially PU production, is based on polyethers obtained from the reaction between initiators and propylene oxide or ethylene oxide, both of which are derived from petrochemical sources [38].

Because of environmental concerns and unstable petroleum price profiles, there is a trend toward substituting petroleum-based polyol with renewable resources. The use of natural oils in the synthesis of polyol for PU foam preparation has been reported in the literature. For example, canola oil [39], castor oil [40], lesquerella oil [41], rape seed oil [42], palm oil [43], and soybean oil [44] have all been used for this purpose. Furthermore, the fabrication of PU foam using bio-wastes recycled from pulp and paper mill was studied [45, 46], in an attempt to solve the problem of increasing paper wastes and reduce the energy consumption of PU foam production. Another way of producing environmentally friendly PU foam is to leverage the abundance of agricultural resources. Liquefaction of agricultural materials containing cornstalk [47], bamboo [48], sugar cane [49], bark [50], wood and starch [51] were conducted and reported for the preparation of PU foams in the literature. In addition, PU foams can also be made from lignin through oxypropylation [52, 53].

2.2.3 Soybean oil-based Polyol

Soybean oil-based polyol is derived from soybean oil through a continuous two-step process. Unlike caster and lesquerella oils, soybean oil lacks a hydroxyl group on the chain. Thus, the first step is to add the hydroxyl group to the side chain of soybean oil; in the synthesis of polyol, performic acid is added to form epoxidized soybean oil. Then epoxidized oil then undergoes ring opening and hydroxylation to form polyol. Figure 2-4 shows the chemical structure of soybean oil-based polyol [54].

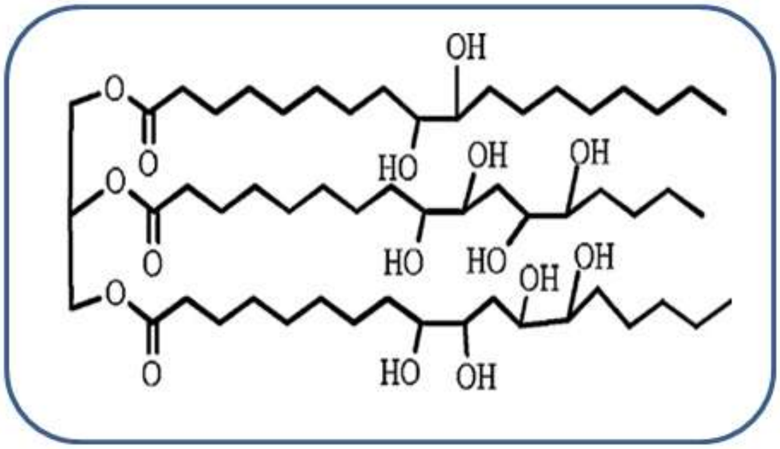


Figure 2-4 Chemical structure of soybean oil-based polyol

Tan *et al.* compared the properties of foam made from soybean oil-derived polyol with those of foam made using petrochemical-based polyol. The results showed that the foam made from soybean oil-based polyol can reach comparable thermal conductivity and even have better compressive performance than that of the petrochemical counterpart. However, the thermal conductivity of soybean oil-based foam increases faster than that of petroleum-based foam under humid conditions [36].

Life cycle assessments have been implemented in order to estimate whether soybean oil-based polyol is a potential substitute for petrochemical-based polyol. One study [55] assessed the production systems of soybean oil and petrochemical polyols regarding their input, output and environmental impact. Figure 2-5 shows the composition of energy sources consumed by each system. For the productions of castor oil and soybean oil-based polyols, 35 % of energy is attributed to fossil fuel-related source while for the production of petrochemical-based polyol over 90 % of energy consumed comes from fossil fuel. When acid gas emissions of the production of polyol were taken into account, the production of natural oil-based polyol emitted only one fifth of the amount that the production of petrochemical-based polyol did (Figure 2-6). Another important and beneficial aspect of using polyols derived from natural oils is on environmental impact; in Figure 2-7, both the polyols made from castor and soybean oils have essentially zero carbon dioxide emissions. These data confirmed that natural oil provides a valuable and renewable route with minor environmental impact for the synthesis of polyol.

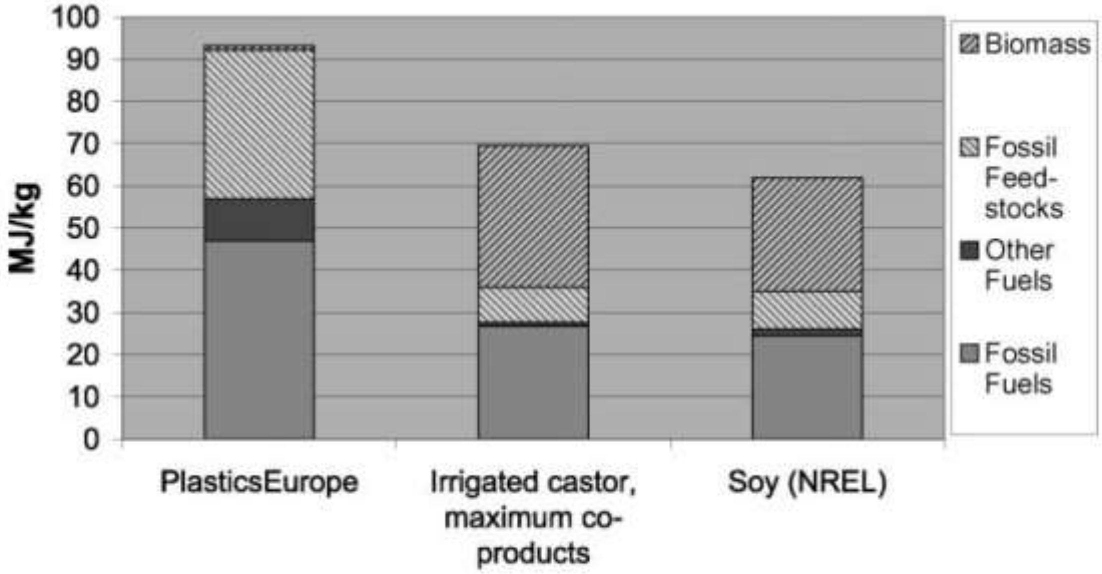


Figure 2-5 Energy sources for polyol productions [55]

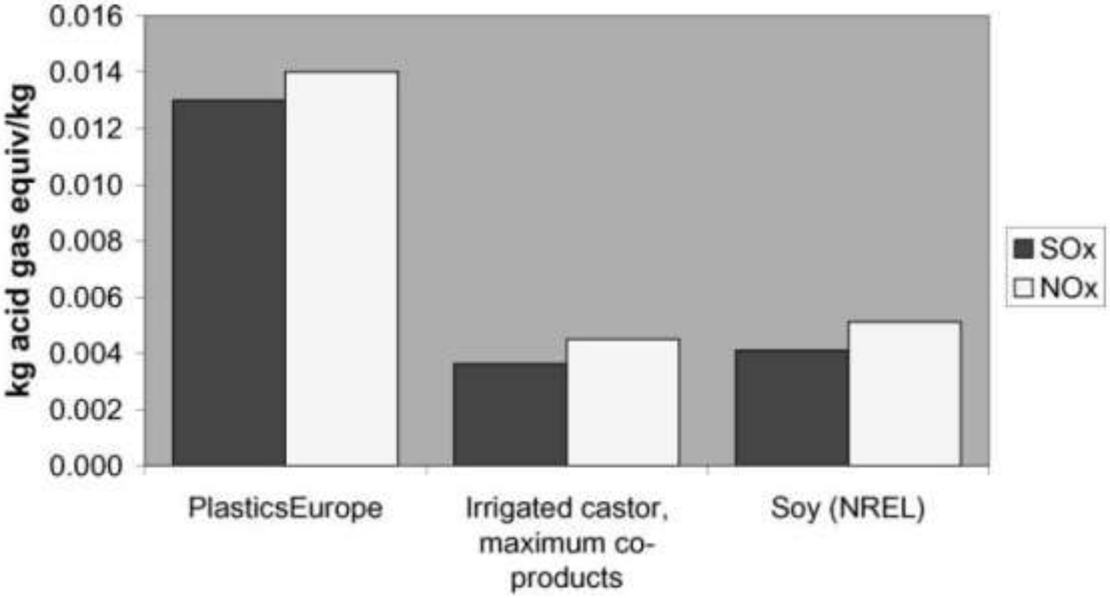


Figure 2-6 Acid gas emissions for polyol productions [55]

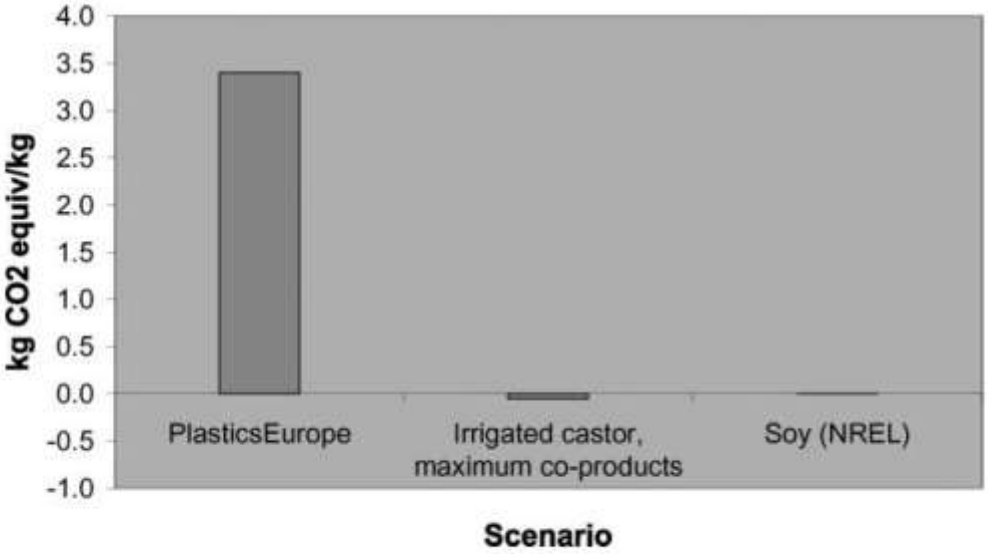


Figure 2-7 Greenhouse gas emissions for polyol productions [55]

2.3 Wood Fibers as Reinforcement in Composite Foams

Advanced composites are high-performance materials that benefit from high stiffness of fibrous materials embedded in polymeric matrix; fiber-reinforced resin composites and composite foam are examples. Fiber-reinforced composites are used in a wide range of applications such as aerospace, automobile, electronic, and marine industry [56]. Composite foams are mainly used as sandwich core materials for structural applications. The mechanical behavior of fiber-reinforced composites and composite foams depends not only on the properties of polymer matrix but also on those of fiber. In addition to increased stiffness, another advantage of adding fiber is to reduce the amount of material used in manufacturing and the weight of produced composites. Reduction of material usage can cause a decrease in feedstock cost and reduction in weight can lower carrying costs of composites in transit.

As environmental concerns become crucial in industry and ‘green’ products attract environmentally-conscious consumers, composites with natural fibers are displacing those with synthetic fibers. The application area and market of natural fiber-reinforced composites is expected to grow at a steady pace for future decade.

2.3.1 Composite Foams

Fiber-reinforced polymeric composites, a combination of fiber and polymer resin, has been commercialized and studied since 1916. In order to reduce processing and material costs, various kinds of fillers have been designed and added in thermoplastics. They are classified into two kinds: (1) inorganic fillers: glass fiber [57], calcium carbonate [58], talc and wollastonite [59], and (2) organic fillers: corn starch [60], rice hull [61], bamboo fiber [62], sisal fiber [63], kenaf fiber [64], wood flour and fiber [65].

Wood fibers in polymeric composites serve as fillers and reinforcing agents to achieve the desired characteristics of composites and thus are widely used in industry [66]. Wood fibers have high stiffness, low cost and natural fiber sources. However, wood fiber-reinforced composites have some limitations: reduced ductility, low resistance under impact and in moist conditions, increased brittleness, and high density compared with those of pure thermoplastics. In order to solve the above mentioned problems, composite foams were developed [67]. It was demonstrated that composite foams have enhanced fatigue life [120], impact strength, toughness, and most importantly, reduced density [121].

Wood fibers are added to composite foams as reinforcing fillers. The advantages of using the fibers are low cost, renewable sources, and small environmental burden. In addition, the density of the fibers is less than glass fibers and the fibers have better adhesive property between fibers and polymer matrix.

Yoon *et al.* made PE composite foams using injection molding with a physical blowing agent (PBA), nitrogen and compared PE solid composite and PE composite foam on the density, shrinkage, and mechanical properties. The results showed composite foams had reduced density and shrinkage, and enhanced mechanical properties [68]. Zhang *et al.* fabricated PE foam with wood fiber reinforcement using tandem extrusion method with carbon dioxide as a PBA. Comparing with the results of foam made by single extruder system, the authors described that fine-celled structure was observed of the foam made using tandem extrusion method; the fine structure of foam cells was attributed to the uniform mixing achieved by using tandem extrusion [69].

Bledzki *et al.* prepared wood fiber-reinforced PP foams by injection molding, compression molding, and extrusion with a chemical blowing agent (CBA) [70]. The effects of the CBA and flame retardant on mechanical properties of wood fiber-reinforced PP foam were studied by Bledzki *et al.* [71] and Zhang *et al.* [72], respectively. Furthermore, composite foams made by blending PE and PP with wood fibers were produced. It was observed that the foam made by blending PE and PP had uniform cell structure, while the individual cell morphology of PE foam and that of PP foam were unfavorable [73].

PVC composites with wood fibers for reinforcement have also been foamed and the dependence of cell morphology on the processing parameters was investigated [74, 75]. The relationship between mechanical properties and cell morphology was also studied. It was found that the impact strength of PVC/wood fiber foam increased with the increase of void fraction [76].

Wood fiber-reinforced PS foams were produced through extrusion and moisture in wood fibers was used as a blowing agent. One advantage of using wood fiber as a carrier of blowing agent is that moisture can be gradually released from fiber generating well-dispersed bubbles in polymer solid during the foaming process [77]. The concept of using moisture as a blowing agent has been extended to polypropylene carbonate (PPC) foam system [78].

Since the wastes of the foams described above (PE, PP, PVC and PS foams) are not biodegradable and become sources of pollution from disposal, foams based on biodegradable polylactic acid (PLA) have been investigated. Wood fiber-reinforced PLA composite foams have been developed using a batch process with supercritical carbon dioxide and improved stiffness of foams was reported [79]. It was shown that foam density, fiber-fiber interaction, and fiber-matrix interface are factors that can affect the mechanical behavior of fiber-reinforced composite foams.

In order to analyze the behavior of wood fiber-reinforced foams, not only the properties of polymeric matrix but also the dimensions of fiber needs to be taken into account. This is because the size of fiber affects the surface area that is exposed to the matrix, and also affects the viscosity of the fiber-polymer blend and cell expansion mechanism. For example, in the manufacturing of PE foam containing different lengths of wood fibers but the same content of the fibers, a larger viscosity was observed in the foam reinforced with shorter fibers due to larger surface areas compared with longer ones. As the surface area increased, more sites were available for cell nucleation. Therefore, small cell size and fine cell morphology were obtained [80].

2.3.2 Polyurethane Composite Foams

There have been many studies of PU foams containing wood fibers as reinforcing agents. Khazabi *et al.* investigated the effect of the amount of fiber added on the cell morphology of PU foam; the cell structure became irregular as the volume fraction of fibers increased [81]. Gu *et al.* further investigated the effects of fiber on thermal stability and mechanical properties of fiber-reinforced PU foam. The presence of fibers in the strut was observed under scanning electron microscope (SEM) where fibers located in cell struts support foam structure resulting in improved compressive strength of foam [82]. Nonetheless, the presence of fiber is not beneficial for all types of foams. Gu *et al.* found that while the addition of fiber increased the tensile and compressive strengths of semi-rigid foam and the compressive strength of rigid foam, adding fiber decreased the tensile and compressive strengths of flexible foam and tensile strength of rigid foam [83].

Fillers other than wood fibers have been used to enhance the mechanical properties of foams. Silva *et al.* made PU foam with the reinforcement of cellulose fiber residue. For cellulose fiber residue-modified PU foam, the compressive strength and modulus of foams first decreased and then increased as fiber content increased, but differences were minor [84]. Yuan *et al.* prepared PU foams with the incorporation of wood flour. However, the addition of wood flour caused reduced flexural and tensile strengths because of the poor interface compatibility between wood flour and PU [85]. Zhu *et al.* investigated the effects of cellulose microfibers and nanoclays on the mechanical properties and cell morphology. The addition of microfibers or nanoclays decreased the cell size and increased the compressive strength of foam [87], but in another study on nanoclay-modified foam, the compressive strength and modulus decreased after nanoclay content reached a certain amount [87]. There are other fillers with which PU foams are filled: hardwood pulp [88], hay straw [89], paper fiber [90], vegetable fiber [91], glass fiber [92] and carbon fiber [93].

2.3.3 Fiber/Polymer Interface

In composites, the adhesion between fiber and polymer is of great importance; it determines whether the stress can completely transfer to the fiber under loading or stretching and is a crucial factor in terms of the mechanical performance of composites. Poor stress transfer at the fiber/polymer interface can be caused by: (1) poor compatibility between hydrophilic wood fiber and hydrophobic polymer chain, (2) weak interlocking between fiber and matrix and (3) a large proportion of aggregated and poor dispersed fibers. To address these problems a number of studies have centered on making wood fiber more hydrophobic and the melt blend more stable. The chemical compatibility between fiber and polymer can be improved by using coupling agent. Maleic anhydride-based and silane-based coupling agents are two commonly used ones. These coupling agents are used in preparing PE [94], PP [95], PVC [96], and PS [97] composites. Other chemical modifications used to make fiber more hydrophobic include isocyanate treatment [97], crosslinking, and acetylation [98]. An alkaline treatment is another broadly used approach. The goal of implementing this treatment is to break down the hydrogen bonding between fibers, increase surface roughness of fibers and thus expose more contact area between fiber and matrix [99]. In addition, a partial removal of non-cellulosic components through the alkaline treatment allows cellulose fibrils to rearrange along the direction of fiber axis resulting in a better stress transfer in the fiber [122]. The effects of adding fiber treated by alkaline treatment on mechanical properties of PP composites have been widely investigated. Gwon *et al.* found that the composite with treated fibers had higher tensile strength compared with that of composite with untreated fibers [100]. Also alkaline treatment is used to provide rough surface of other natural fibers embedded in polymer composites [101].

The interaction between fiber and matrix in the polymeric foams also deserves attention. Coupling agent has been used to modify the fiber-matrix interface. Lee *et al.* used silane-based coupling agent to treat wood fiber [102]. They found that when compared with untreated fiber-reinforced PE foam, treated fiber-reinforced PE foam had fine-celled structure. Bledzki *et al.* studied the effect of coupling agent on mechanical properties of PP foam. It was observed that fiber-reinforced PP foam made from compounds containing coupling agent showed improvement in cell morphology and tensile and flexural properties of foam [103].

The modification of fiber-matrix interface in PU foam has not been studied extensively. Since PU has a lower hydrophobicity than that of thermoplastic resin due to the presence of carbonyl group, the use of coupling agent may not be an effective way to improve the interface compatibility of fiber-reinforced PU foam. On the other hand, alkaline treatment is considered to be an acceptable route for improvement of the interlocking between fiber and matrix. It is reasonable to assume increase in roughness and surface area of fiber through alkaline treatment can enhance PU foam mechanical properties. In this study, the alkaline treatment of wood fibers was conducted and treated fibers were used for the reinforcement of PU foam.

2.3.4 Role of Catalyst

PU foam synthesis is composed of two chemical reactions: One reaction is for urethane formation, also named as gelling reaction as shown in Figure 2-2. It is known that the formation of the urethane linkages which act as cross-linking joints forms a cross-linking network that is crucial in determining the mechanical performance of the foam. The other reaction is blowing reaction in which isocyanate group reacts with water producing carbon dioxide to expand the volume and fill internal voids (Figure 2-8).

$$O=C=N\text{-}R_{(isocyanate)}\text{-}N=C=O + 2H_2O \rightarrow H_2N\text{-}R_{(isocyanate)}\text{-}NH_2 + CO_{2\ (gas)}$$

Figure 2-8 Blowing reaction of the synthesis of PU foam

The performance of PU foam is controlled by these two reactions. In the fabrication of PU foam, polyol, isocyanate, and other additives are mixed together. During the mixing, some air bubbles are entrained; these bubbles act as nucleation sites in the foaming process [116]. Once the blowing reaction is initiated, it releases carbon dioxide that expands the bubbles and foam starts rising. As the gelling reaction is initiated, the viscosity of the blend increases, which impedes the foam expansion. Therefore, a good control between blowing and gelling reaction leads to compact cell structure and uniform cell morphology [104].

The rate of blowing and gelling reaction depends on many factors, for instance, reaction temperature, and the type and content of catalyst. Sipaut *et al.* reported that open cell content, cell size and foam density are dependent on the reaction temperature [118]. The catalyst plays a crucial role in achieving a balance between the blowing and gelling reaction and is responsible for achieving a fine cell shape and enhanced mechanical properties [111, 117]. Campanella *et al.* prepared soybean oil-derived PU foams made with and without a catalyst, N, N-Dimethylbenzylamine. It was found that, for the foam made without the catalyst, the blowing reaction dominated over the gelling reaction causing the foam to collapse before curing. The addition of the catalyst allows foam to expand properly. Furthermore, the cellular structure of foam was found to be dependent on the amount of catalyst used [117]. Choe *et al.* studied the effects of the catalyst on kinetic rate of foaming, density and mechanical properties of foam [105]. The results showed that the cell size decreased as the amount of catalyst increased implying the kinetic rate is governed by the catalyst. However, the amount of catalyst had no significant effects on the density and compressive strength of foam [106].

An amine-based catalyst, compared with organotin and dibutyltin dilaurate (DBTDL), has less toxicity and has been broadly used in industry [107]. Recently, other catalysts such as metal-amine complex have been synthesized and discussed [108]. In this study, foams were prepared using different mono-amines as catalysts and the compressive properties and cell morphology of foams investigated.

2.3.5 Fiber Dispersion

The capability of added fiber to strengthen the cell structure and enhance the foam mechanical behavior depends not only on the stiffness of fibers and the adhesion at the fiber-matrix interface, but also on the dispersion of fibers. In a previous study, PP composite was prepared using a mixer for intensive mixing [109]. Mixing is considered as an important step for polymeric foam preparation, especially for the foam containing fibers. Table 2-3 lists previous studies in regard of mixing of polyol-fiber mixture involving different types of natural fibers in the fabrication of PU foam; most of these studies mix the polyol-fiber mixture by hand. However, it is accepted that high degree of fiber dispersion is hard to attain because the viscosity of mixture increases accompanied by the addition of fibers. In this study, a mechanical mixer was used for mixing in foam preparation and the differences between foam made using hand mixing and that made by mechanical mixing in the cell morphology and mechanical behavior of foam were compared.

Type of fiber	Maximum amount of fibers added (wt%)	Mixing method	Reference
Aspen fiber	1	Hand mixing	[83]
Cellulose fiber	4	Hand mixing	[90] [110]
Cellulose fiber residue	16	Hand mixing	[84]
Cellulose microfiber	1	Hand mixing	[86]
Maple fiber	5	Hand mixing	[88]
Maple fiber	20	Hand mixing	[81] [82]
Birch fiber	10	Mechanical mixing	This work

Table 2-3 PU foams with natural fiber made using different mixing methods

2.4 Problem Statement

Since wood fiber-reinforced PU composite foam has not been reported extensively in the literature, an understanding of the compression performance of the fiber-reinforced foam is required and covered in this study. The adhesion between fiber and polymeric matrix, reagents used in foam preparation, and the dispersion of fiber in the foam are factors controlling foam mechanical performance. In this study, the effect of fiber surface treatment, catalyst, and mixing method corresponding to each mentioned factor on the compressive performance of PU foam reinforced by fiber was investigated.

2.5 Conclusions

In summary, PU foam reinforced by fiber has been designed as a core material in SIPs. Since there is a growing concern for environmentally friendly production of the fiber-reinforced foam, natural fiber and polyol derived from renewable sources are of major interest.

The adhesion between wood fiber and polymeric matrix affects the mechanical properties of fiber-reinforced foam. It is hypothesized that alkaline treatment can increase fiber coarseness and improve the interlocking between fiber and matrix.

Catalyst and mixing condition are the key manufacturing parameters that affect the cell morphology and mechanical properties of foam. The catalyst controls the balance between gelling and blowing reaction influencing the cell structure of foam and the mixing enhances the dispersion of fibers. Polyol-fiber mixture is mixed by hand in the traditional fabrication of foam. However, for the preparation of foam with high fiber content, mechanical mixing is required due to an increase in the viscosity of the mixture making proper mixing by hand impossible.

3. Experimental Methods

This chapter is composed of two parts. The first part lists the materials used in the fabrication of PU foam and details the process for preparing the foam. The second part discusses how the compression performance of the foam was measured and introduces the characteristic analysis using Fourier transform infrared spectrometer (FTIR) and imaging acquisition of the foam using scanning electron microscopy (SEM), stereo microscopy, and computed X-ray tomography.

3.1 Fiber-reinforced Foam Preparation

3.1.1. Materials

Soybean oil-derived polyols (Soyol ® 2102) were purchased from Urethane Soy Systems (Volga, South Dakota, USA). The viscosity of the polyols is 2181 cps at 25°C and the hydroxyl number is 63 KOH/g according to ASTM-D4274. Polymeric diphenylmethane diisocyanate (PMDI) was obtained from Huntsman Corporation (West Point, Georgia, USA) with a specific gravity of 1.23 g/mL at 25°C, a NCO content of 31.2 % and a functionality of 2.7. Polysiloxane and pyrrolidone used as surfactants and a tertiary amine used as catalyst were donated by Air Products and Chemicals Incorporation (Allentown, Pennsylvania, USA). Ethanolamine was received from Sigma Aldrich (St. Louis, Missouri, USA) and used as catalyst. It was substituted by four other monoamines in the preparation of samples for studying the effect of catalyst: benzyldimethyl amine (CAT-1), 2-(2-aminoethoxy) ethanol (CAT-2), 2-(methylamino) ethanol, and 2-[2-(dimethylamino)ethoxy] ethanol (CAT-4), purchased from Tokyo Chemical Industry American (Portland, Oregon, USA). Deionized water (DI water) was employed as a blowing agent for making foams. Chemi-refiner mechanically pulped medium-density birch wood fibers (*Betula papyrifera* Marsh) were donated by FPInnovations Canada Corporation (Point-Claire, Quebec, Canada). The average length of the fibers is 1.6 mm. These fibers were sieved in 20-30 mesh (American Scale) with fiber lengths ranging between 0.60 and 0.85 mm.

3.1.2. Fiber Treatment

Alkali treatment was used to modify the surface of fibers to improve the interfacial bonding between the fibers and a polymeric matrix. Fibers were dried in an oven at 80°C for 24 hr with a moisture content kept below 5 %. Next, the fibers (10 wt%) were added in NaOH solutions of different concentrations, 2 wt%, 4 wt%, and 7 wt% to assess the effect of NaOH concentration on the fibers. After the NaOH solution treatment, the fibers were rinsed with DI water until a pH value of 7 was reached. Finally, the fibers were once again dried in the oven at 80°C for 24 hr.

Acridine orange dye (AO), purchased from Sigma Aldrich (St. Louis, MO, USA) was employed as a dye to stain fibers for observation under stereo microscope. First, a 6.7×10^{-3} M AO solution in DI water was prepared and then the fibers were immersed in the AO solution at room temperature for 6 hr. The stained fibers were dried in an oven at 80°C for 24 hr. Figure 3-1 (a) and Figure 3-1 (b) show photos and Figure 3-2 (a) and Figure 3-2 (b) show stereo microscopic images of unstained and stained fibers, respectively.

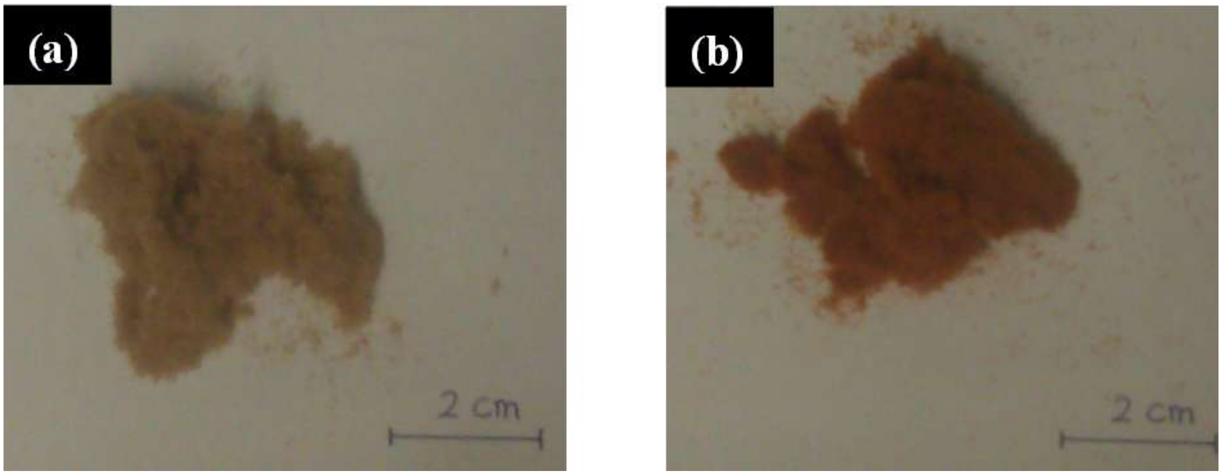


Figure 3-1 Photos of (a) unstained fibers and (b) stained fibers

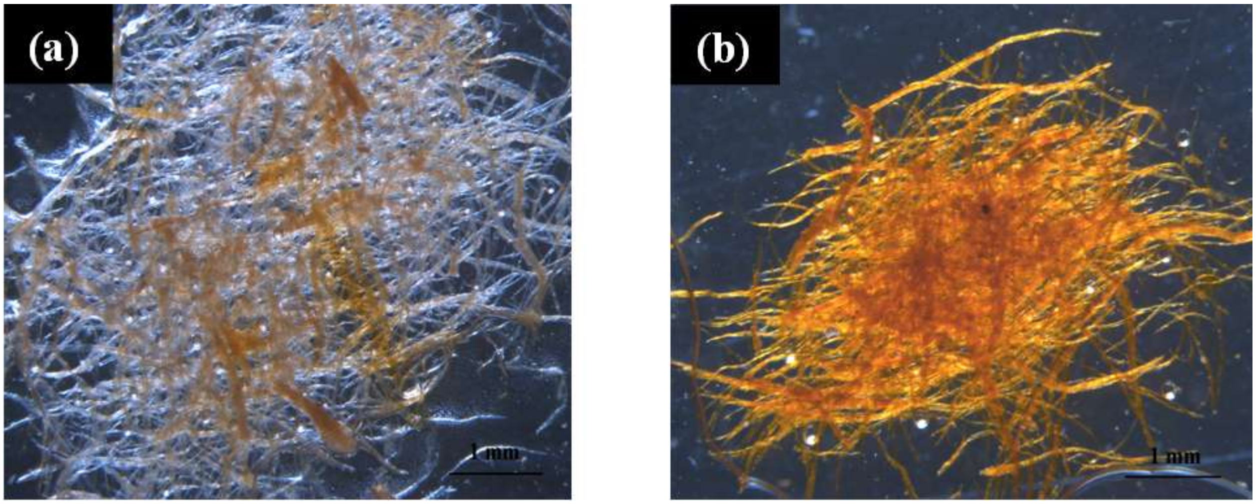


Figure 3-2 Stereo micrographic images of (a) unstained fibers and (b) stained fibers

3.1.3. Mixing

A mechanical stirrer purchased from Heidolph North American (Elk Grove Village, IL, USA) was used to mix fibers and polyol in the foaming process. The power of the stirrer was 37 W. An impeller, VISCO JET® with the diameter of 60 mm, was purchased from the same company.

3.1.4. Foaming Process

In the section, the preparation of samples was divided into two parts for clarity. The first part described the preparation of samples for the studies regarding the effect of alkaline treatment (Section 4.2) and catalyst (Section 4.3), and the second part for the study associated with the effect of mixing (Section 4.4).

Part I:

A free-rising foaming process was used to make PU foams. In the study of the effect of alkaline treatment, wood fibers were mixed with polyol for 20 min and then certain amounts of surfactants, catalysts, and blowing agent were added into the mixture. Table 3-1 lists the materials used. Then the mixture was mixed for another 5 min. Lastly, PMDI was added into the mixture and hand mixed for 15 s and then the mixture was poured in to a mold allowing the foam to rise and cure. A scheme for the preparation of the foam was shown in

Figure 3-3. Foams with various fiber contents (0, 2.5, 5, 7.5, and 10 wt %) of treated or untreated fibers were prepared. In the study of the effect of catalyst, foams were prepared using 100 parts of polyol, 2 parts of pyrrolidone, 3.3 parts of polysiloxane, 3 parts of tertiary amine, 6.7 parts of water and 135 parts of PMDI with different catalysts listed in Table 3-2. Different weights of catalysts were used to keep the same molar ratio with respect to polyol.

Materials		Parts by weight
Soybean oil based polyol	Soyol® 2102	100
Surfactant	Pyrrolidone	2.0
	Polysiloxane	3.3
Catalyst	Tertiary amine	3.0
	Ethanolamine	2.0
Blowing agent	De-ionized water	6.7
Birch wood fibre		0 to 10 wt%
NCO index*	PMDI	120

*The NCO index is defined as the ratio of the amount of used isocyanate over the theoretical amount of isocyanate.

Table 3-1 Materials used in the preparation of foam

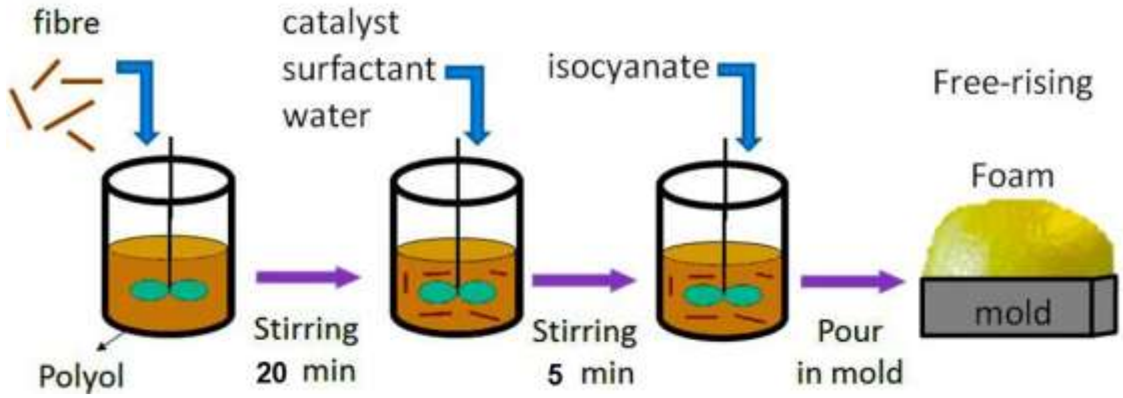


Figure 3-3 Schematic for the preparation of fiber-reinforced foam

Materials	Parts by weight based on 100 parts of polyol				
	CAT-0	CAT-1	CAT-2	CAT-3	CAT-4
Ethanolamine	2.0	-	-	-	-
Benzyldimethyl amine	-	3.04	-	-	-
2-(2-Aminoethoxy) ethanol	-	-	2.36	-	-
2-(Methylamion) ethanol	-	-	-	1.68	-
2-[2(Dimethylamion)ethoxy] ethanol	-	-	-	-	3.03

Table 3-2 Catalysts used in foam production

Part II:

PU foams were made using a free-rising method. Firstly, fibers were added into polyol and mixed using a mechanical stirrer. The mixture was mixed at designated stirring time and stirring rate. In the study of stirring time, stirring rate was set at 150 rpm and in the study of stirring rate, stirring time was set at 10 min. Then surfactants, catalysts, and blowing agent were added and mixed for another 5 min. The formulation was shown in Table 3-1. After PMDI was added the mixture was mixed for 20 s. A scheme for the preparation of the foam was shown in Figure 3-4.

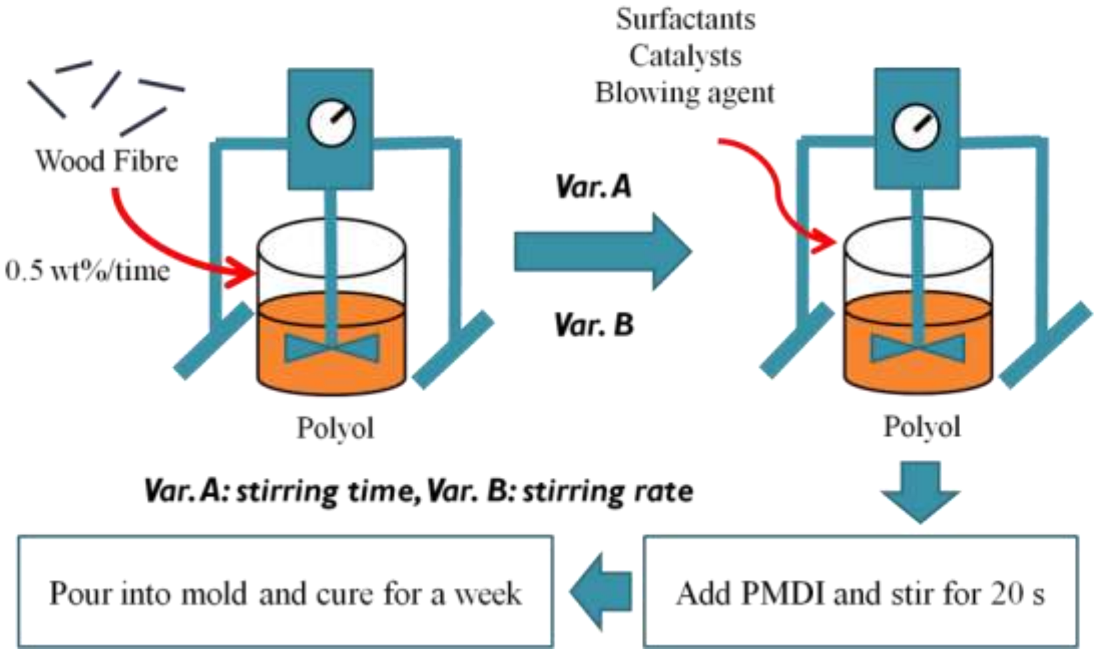


Figure 3-4 Schematic for the preparation of fiber-reinforced foam using a mixing stirrer

3.2 Fiber-reinforced Foam Characterization

3.2.1. Mechanical Testing

Specimens (5 cm × 5 cm × 3 cm) were cut using a bandsaw. The compressive modulus of the specimen was measured using a Sintech universal testing machine 20 with 1000 lb load cell according to ASTM-D 1621. The specimens were compressed at 15 % deformation and with the rate of crosshead movement set at 2.5 mm/min. A minimum of 5 specimens were tested for each condition, and the mean value and standard deviation recorded.

3.2.2. FQA and FTIR Characterization

The length distribution of wood fibers was measured using a Fiber Quality Analyzer (FQA), purchased from OpTest Equipment Inc. A FTIR TENSOR 27 spectrometer in conjunction with a FTIR attachment (Bruker Optics) was used to record the absorption spectra of wood fibers and PU foams. The sample of the fibers and foams was in pressed KBr pellets. The spectra were obtained over 4000-400 cm^{-1} at a resolution of 4 cm^{-1}.

3.2.3. Imaging Characterization

Scanning electron microscopy (SEM, Hitachi S-2500), was used to take the micrographs of the surface of wood fibers and the cell morphology of PU foams. The specimens were coated by sputtering a thin layer of Au in vacuum and then examined using SEM. The accelerating voltage was set as 10 kV. To analyze the data and measure the diameter of the fibers, image processing software, Image J in version 1.41 was used.

A high-resolution X-ray tomography (SkyScan 1172) was used to characterize the cell morphology of foams. Foam samples were scanned using a high resolution of 4000 × 2096 at a 45 kV and a current density 167 µA with pixel size of 1.5 micron. Software, NRecon developed by SkyScan, was used to reconstruct 2D cross-sectional images of the samples obtained from X-ray tomography.

A 3-D stereo microscope (Leica M165C) equipped with LED based illumination and digital camera was used to image the dispersion of fibers. A sample was cut by using a razor blade. Then the sample was positioned on the center of slide (75 mm × 25 mm). DI water was used as mounting agent. The slide was finally covered with a clean cover slip (25 mm × 25 mm).

4. Results and Discussion

4.1 Introduction

This study focuses on the manufacture of wood fiber-reinforced PU foam with enhanced mechanical performance. The goal is addressed in terms of three considerations: (1) fiber/matrix interface, (2) foam preparation and (3) mixing method, and these are factors that play pivotal roles in manufacturing high-performance PU foam.

The interface between wood fibers and a polymeric matrix affects the mechanical properties of PU foam: poor interfacial properties results in a low efficiency of stress transfer from the matrix to fibers under compression loading. The interfacial adhesion between the fibers and the matrix depends on the surface conditions of fibers. In this study, alkaline treatment was used to modify fiber surface in order to improve the interfacial bonding between fibers and the matrix.

The amount and type of catalyst used affect the cell morphology and mechanical properties of the foam. Since a catalytic reaction is sensitive to the chemical structure of the catalyst, in this study, foams were produced using five different mono-amines as catalysts and the characteristics and compression performance of these foams were observed.

Mixing is also a crucial step in the fabrication of foam. For the foam made using a mechanical stirrer, the behaviors of the foam depend on numerous processing factors, including stirring rate and stirring time. In addition, the dispersion of fibers embedded in and the mechanical performance of the foam made by mechanical mixing were compared with those of the foam made by hand mixing.

4.2 Alkali Treated Fiber-reinforced PU Foams

4.2.1 Characterization of Treated Fiber

The lengths of fibers before and after a treatment with sodium hydroxide (NaOH) solution were measured in order to assess the influence of alkaline treatment on wood fiber. Length distributions of untreated and treated fibers are shown in Figure 4-1 (a) and (b), respectively. Weight mean length of treated fibers was 1.14 mm, similar to that of untreated fibers, 1.15 mm. Fiber curl index of untreated fibers as measured by fiber quality analyzer (FQA) was 0.088 and that of treated fibers was 0.09. It is evident that the alkaline treatment had little impact on the length and curl index of fibers.

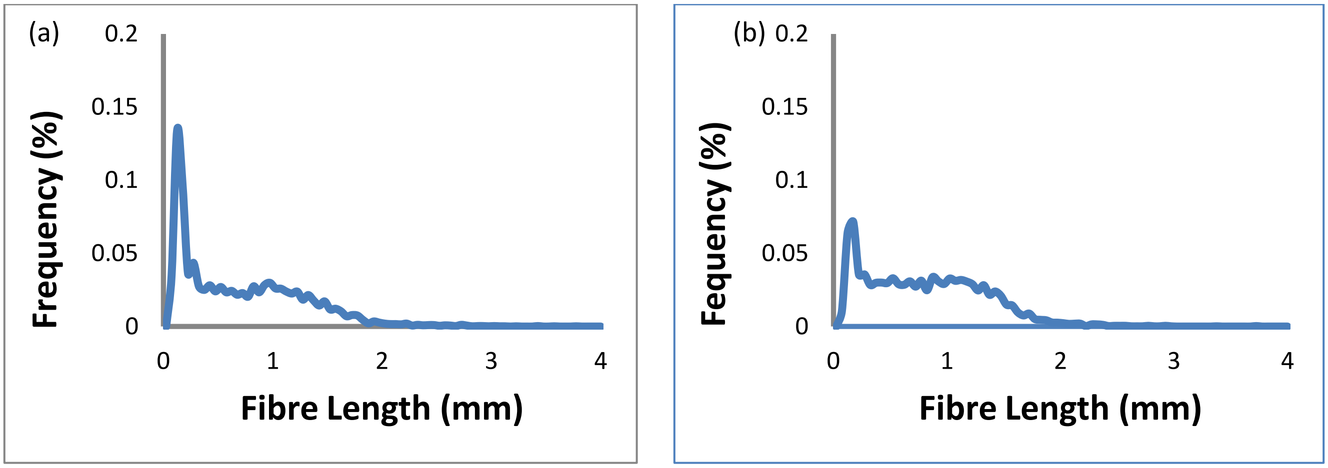


Figure 4-1 Distribution of length of (a) untreated and (b) treated fibers measured by FQA

The effect of alkaline treatment on fiber diameter was evaluated by measuring the width of fibers using SEM. The diameter distribution of untreated fibers and that of treated fibers are presented in Figure 4-2. As shown in Figure 4-2, the histogram of treated fiber shifted in the direction of decreasing fiber diameter. The reason for the decrease in fiber diameter is that parts of lignin and other extractives in fiber were removed during the alkaline treatment [2].

The aspect ratio (L/D) of a fiber is defined as the length (L) of the fiber divided by the diameter (D) of the fiber. As mentioned earlier, the length of treated fibers was similar to that of untreated fibers, but the diameter of treated fibers was less than that of untreated fibers. Therefore, treated fibers have higher aspect ratio than that of untreated fibers.

In order to investigate the effect of alkaline treatment on fiber surface, SEM images of untreated fiber and treated fibers were taken. The SEM image of the treated fibers (Figure

4-3 (b)) showed that the surface had become rougher compared with that of the untreated fibers, shown in Figure 4-3 (a); therefore, the surface area able to interact with polymer increased, and better fiber-polymer adhesion may be expected.

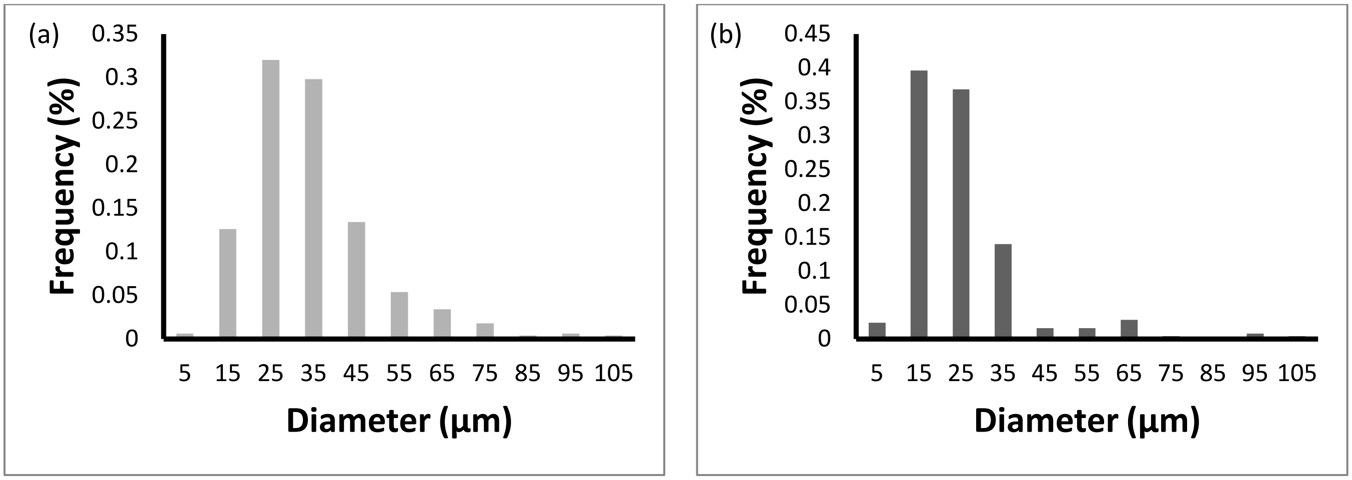


Figure 4-2 Distribution of diameters of (a) untreated and (b) treated fibers

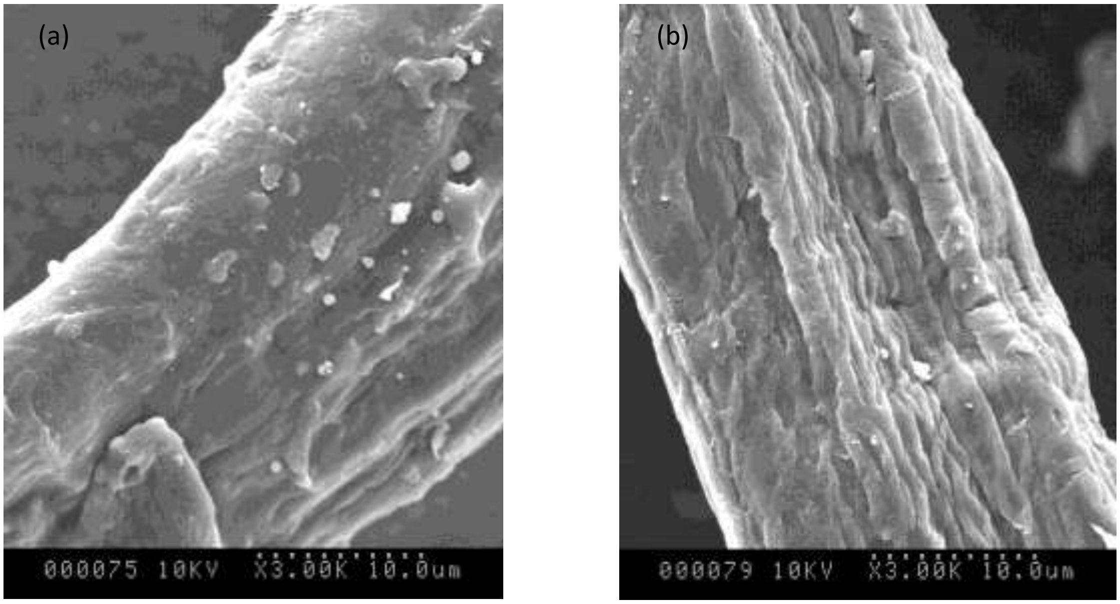


Figure 4-3 SEM images of fiber surface of (a) untreated and (b) treated fibers

The effect of different concentrations of NaOH solution used in alkaline treatment on the surface roughness and compressive performance of foam was investigated.

SEM images of fiber surface treated in different concentrations of NaOH solution: 0, 2, 4, and 7 wt% are shown in Figure 4-4; it can be seen that the surface of fibers became rougher as the concentration of NaOH solution increased. However, the number of defects and fractured fibers also increased with the increasing concentration of NaOH solution. This is an expectation at this point that the increase in concentration of NaOH solution reduced the stiffness and strength of the fibers.

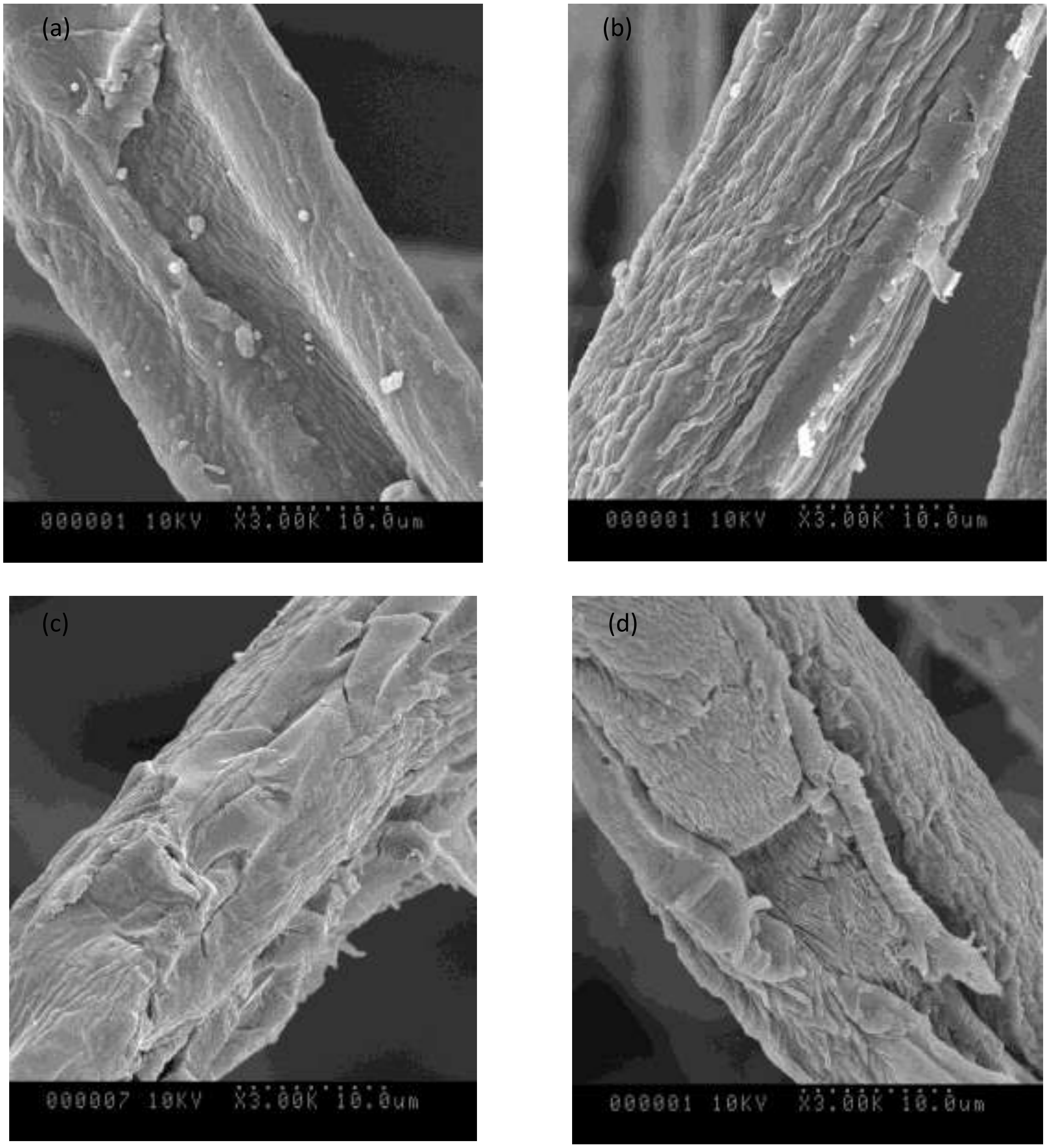


Figure 4-4 SEM micrographs of (a) untreated fibers and fibers treated in solutions of (b) 2, (c) 4, and (d) 7 wt% NaOH

Fourier transformation infrared (FTIR) spectroscopy has been used to investigate the components of alkali-treated fibers. Lignocellulosic fiber is mainly composed of cellulose, hemicelluloses, and lignin. EI-Shekeil *et al*. compared the FTIR spectra of kenaf fibers before and after the alkaline treatment. It was noted that the absorption peak at 1736 cm^{-1} in the spectrum of treated fibers disappeared attributed to the C=O stretching of hemicelluloses [123]. Cordeiro *et al*. studied the FTIR spectra of alkaline treatment modified eucalyptus, spruce, bagasse and wheat straw. The results indicated that lignin and hemicelluloses were partially removed in the fibers through alkaline treatment [124].

The surface characteristics of fibers before and after alkaline treatment were studied using FTIR spectroscopy. The spectrum of untreated fibers (Figure 4-5 (a)) was compared with that of treated fibers (Figure 4-5 (b)). Peaks observed in both spectra are located at: 3402 cm^{-1}, 2911 cm^{-1}, 1612 cm^{-1}, 1043 cm^{-1}, and 895 cm^{-1}. The formation of an absorbance band at 3402 cm^{-1} is associated with the C-H stretching vibration of cellulose. An absorbance band at 2911 cm^{-1} is attributed to the O-H stretching vibration of cellulose. An absorbance band at 1043 cm^{-1} represents the lateral C-O bonds in cellulose. The presence of these three peaks indicates that cellulose remains in the fibers after alkaline treatment. On the spectra of untreated and treated fibers, the peak at 1612 cm^{-1} and the peak at 895 cm^{-1} correspond to the absorbance band of the aromatic vibration and the C=O stretching vibration of lignin and that of the aromatic C-H deformation of lignin, respectively. The results suggested that there was residual lignin in the treated fibers. The spectrum of untreated fibers had two additional characteristic absorbance bands: 1737 cm^{-1} and 1247 cm^{-1}. The absorbance band at 1737 cm^{-1} is attributed to the excitation of the C=O stretching of hemicelluloses and the absorbance band centered at 1247 cm^{-1} results from the excitation of the C-O-C stretching of ether linkages in lignin. It is evident from the presence of the absorbance bands at 1612 cm^{-1} and

895 cm^{-1} and absence of the bands at 1737 cm^{-1} and 1247 cm^{-1} that the alkaline treatment breaks down lignin molecules.

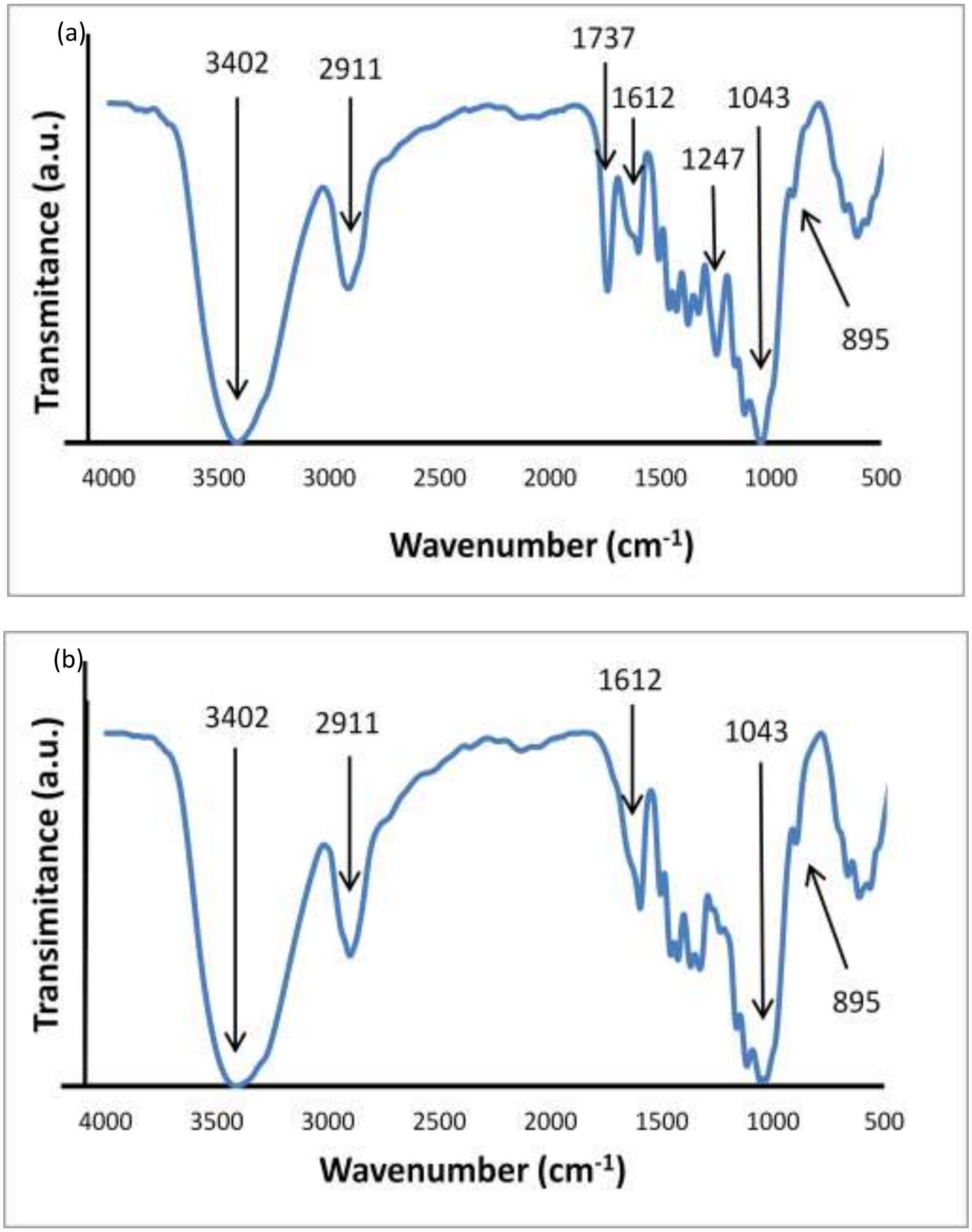


Figure 4-5 FTIR spectra of (a) untreated and (b) treated fibers

4.2.2 Compression Performance of Treated Fiber-reinforced PU Foam

It was expected that the concentration of NaOH solution with which fibers were treated could affect not only the dimension and surface topography of the fibers but also the compressive strength of the foam reinforced with the fibers. Compressive strengths of foams containing fibers treated in different concentrations of NaOH solution were measured and the results are shown in Figure 4-6. It was observed that the compressive strength of the foam containing fibers treated with 2 wt% NaOH solution was higher than that of the foam containing untreated fibers. However, for the foams containing fibers subjected to 4 and 7 wt% NaOH solutions, the compressive strengths were lower than that of the foam containing fibers treated with the NaOH solution of 2 wt%. The results imply that the alkaline treatment of fiber improves the performance of fiber-reinforced foam; however, high concentration of NaOH can lead to negative outcomes. The improved performance of the fiber-reinforced foam can be attributed to the increased roughness of fiber and the negative outcomes can be attributed to the increased number of defects and fractured fibers observed under SEM (see previous note). Now we have evidence that the fibers were affected and this affects performance.

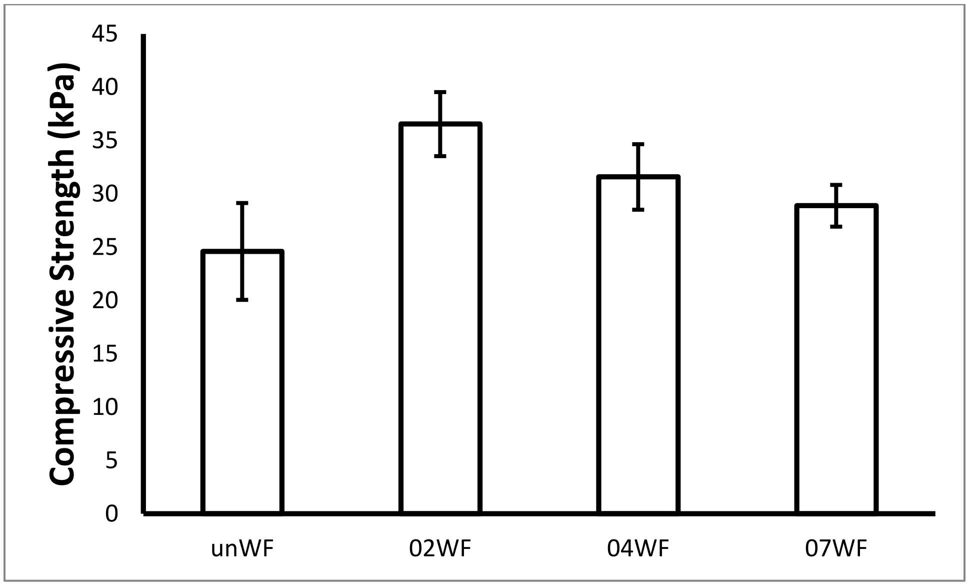


Figure 4-6 Compressive strengths of foams with the reinforcement of untreated fibers (unWF) and 2.5 wt % of fibers treated with 2 wt% (02WF), 4 wt% (04WF), and 7 wt% (07WF) NaOH solutions

Since the density of foams reinforced with fibers treated by various concentrations of NaOH solutions was not the same and the compressive strength varies as the density of foam, specific strength was calculated to normalize the compressive strength of foam by dividing the compressive strength by foam density and remove the effect of density [86]. Figure 4-7 shows the specific compressive strengths of foam containing the fibers.

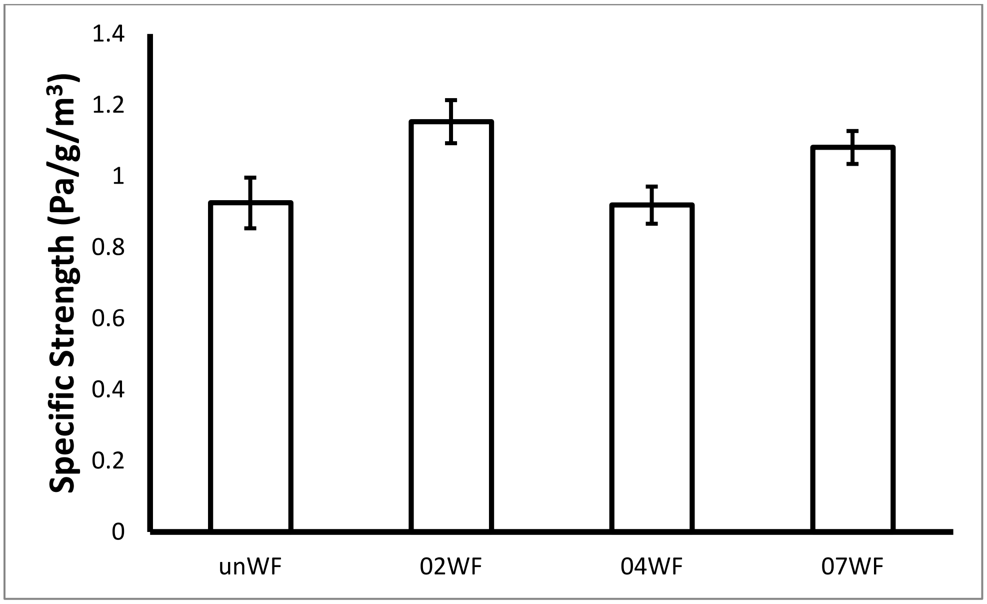


Figure 4-7 Specific strengths of foams with the reinforcement of untreated fibers (unWF) and 2.5 wt % of fibers treated with 2 wt% (02WF), 4 wt% (04WF), and 7 wt% (07WF) NaOH solutions

Compressive strengths of foams containing various amounts of untreated and treated fibers were measured and compared in order to estimate the effect of alkali-treated fiber on the mechanical performance of PU foam. The fibers were treated in 2 wt% NaOH solution. The results are shown in Figure 4-8. For untreated fiber-reinforced foam, the compressive strength decreased initially and then increased to a maximum value at a fiber content of 5 wt%. After exceeding the fiber content of 5 wt%, the strength started to decrease with increasing fiber content. For treated fiber-reinforced foam, in the same way, the compressive strength decreased initially, then increased as fiber content increased. Unlike the foam reinforced with untreated fibers, the compressive strength of the foam reinforced with treated fibers further increased with increasing fiber content. Specific strengths of foams reinforced with various amounts of untreated and treated fibers were computed and are shown in Figure 4-9.

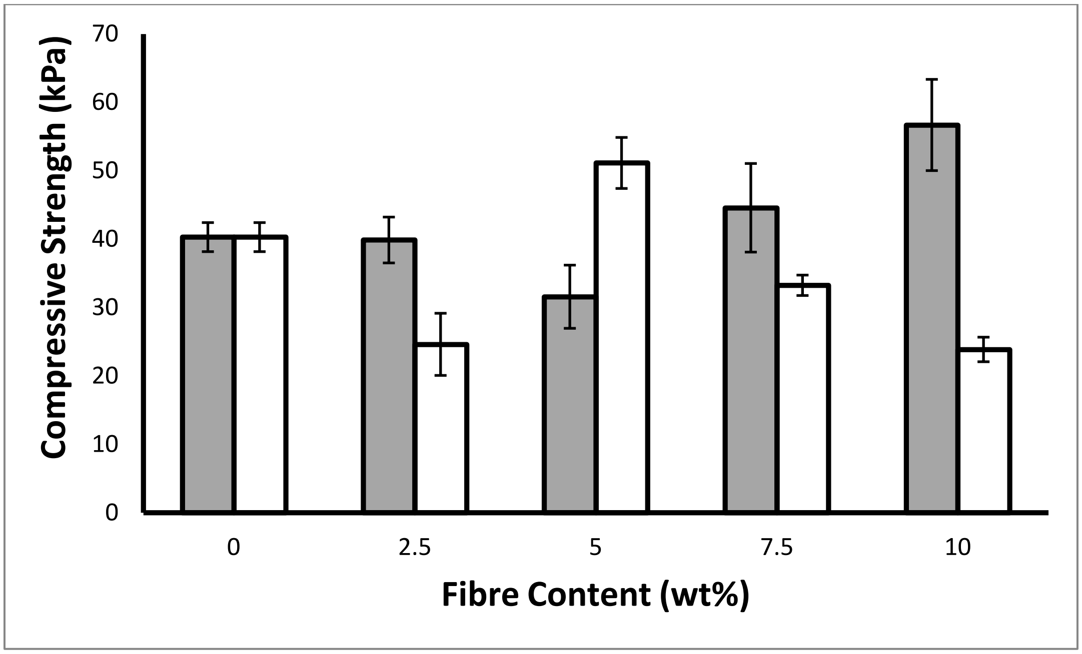


Figure 4-8 Compressive strengths of untreated fiber-reinforced (white) and treated fiber-reinforced (grey) foams with various fiber contents from 0 to 10 wt% with an interval of 2.5 wt%

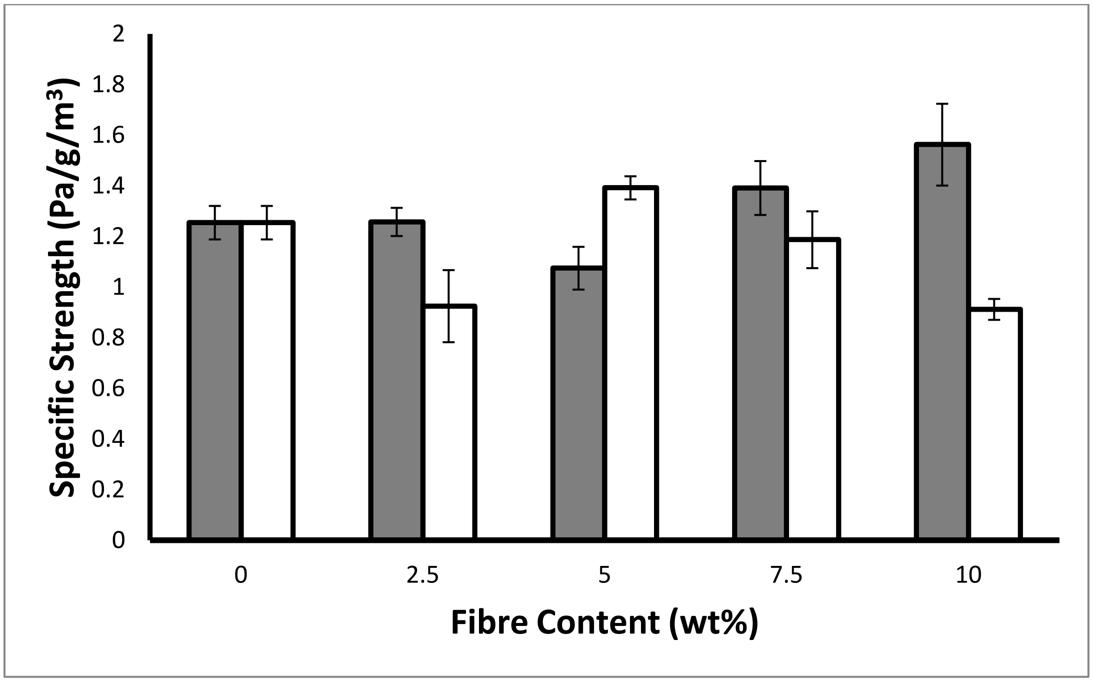


Figure 4-9 Specific compressive strengths of untreated fiber-reinforced (white) and treated fiber-reinforced (grey) foams with various fiber contents from 0 to 10 wt% with an interval of 2.5 wt%

The modulus of fiber-reinforced foam depends not only on the addition of fibers but also on the density of the foam. As fibers act as nucleation sites, foam density changes with the addition of fibers in an uncontrollable way which makes the fiber-reinforced foam a complicated system, and composite theory fails to predict the performance of the foam. Efforts have been made to isolate the effect of each factor. In order to evaluate the reinforcing effect of fiber on modulus, the modulus of pure foam matrix of the appropriate density was computed and compared with the measured modulus of the composite.

It has been reported in the literature that the modulus of neat foam (no fiber) varies with foam density in a predictable way. Gibson *et al*. used a cubic member to model the behavior of foam under compression where the modulus of foam is computed based on the linear deflection of beam and derived the equation [13]:

$$\frac{E_o}{E_{PU}} = C_1 (\frac{\rho_o}{\rho_{PU}})^2 \tag{1}$$

where E_o is the elastic modulus of foam with no fibers, E_{PU} is the elastic modulus of cell wall material (PU) , ρ_o is the density of the foam with no fibers, ρ_{PU} is the density of PU and C_1 is the geometric constant of proportionality.

For the modulus of the matrix of composite foam with the fibers removed, E_x, the Gibson Ashby eqation can be applied as below:

$$\frac{E_x}{E_{PU}} = C_1 (\frac{\rho_x}{\rho_{PU}})^2 \tag{2}$$

Although E_{PU} may change with the amount of added fibers due to the variation of the degree of crosslinking, it was assumed to remain constant in this case. In addition, the contribution of the fibers to the density of foam is negligible. E_x (fiber content, x = 2.5, 5, 7.5, or 10), was computed by dividing Eq. 2 by Eq. 1 and rearranging to get Eq. 3 as follows:

$$E_x = E_o \times (\frac{\rho_x}{\rho_o})^2 \tag{3}$$

where ρ_x is the density of the matrix for composite foam with the removal of fibers computed as below:

$$\rho_x = {(m_{foam} - m_{fibers})} \Big/ {V_{foam}} \tag{4}$$

The difference between the experimental modulus, E_c, and E_x represents the contribution of fiber reinforcement and the ratio was named reinforcing factor (RF):

$$RF = \left(\frac{E_c}{E_x}\right) \tag{5}$$

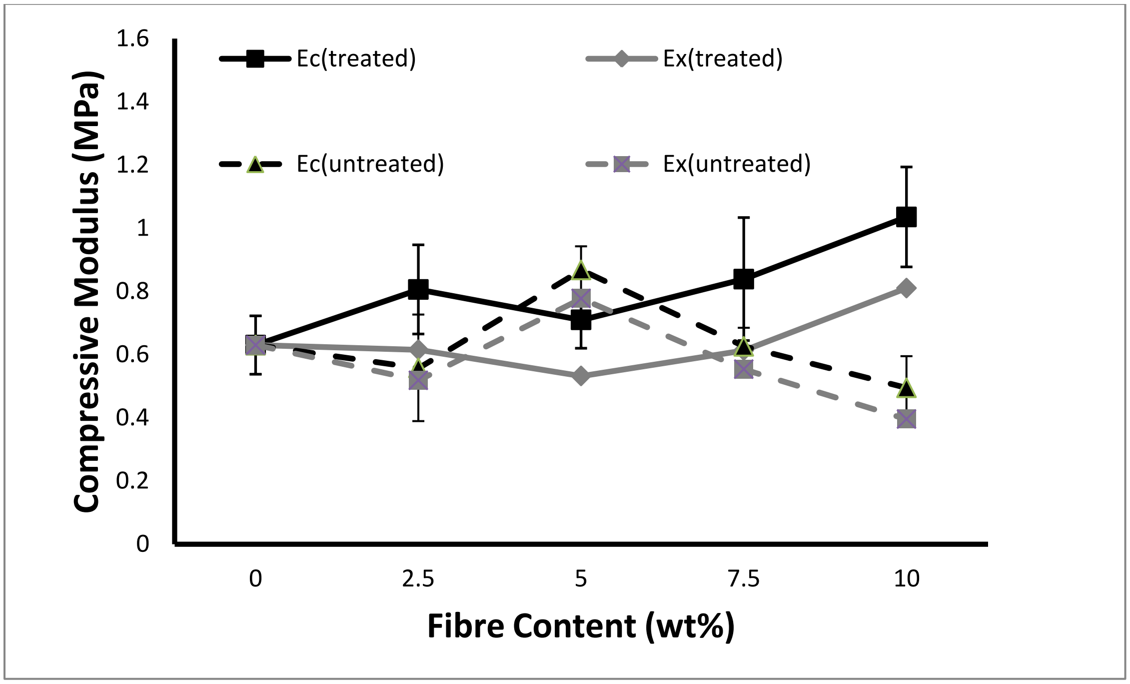


Figure 4-10 Experimental modulus of untreated ($E_{c(untreated)}$) and treated ($E_{c(treated)}$) fiber-reinforced foams and modulus of the matrix for composite foam of untreated ($E_{x(untreated)}$) and treated ($E_{x(treated)}$) fiber-reinforced foams with different fiber contents

Figure 4-10 shows E_c and E_x of foams reinforced with untreated and treated fibers. It can be seen that the difference between E_c and E_x of foam reinforced with untreated fibers was less than that of foam reinforced with treated fibers. The difference may be related to the nucleation of cells. Eq.1 can be expressed in the form:

$$E_o = C_1 \times (\frac{m_{foam}/V_{foam}}{m_{solid}/V_{solid}})^2 \times E_{PU} \cong C_1 \times E_{PU} \times (\frac{V_{solid}}{V_{foam}})^2 \qquad (6)$$

where m_{foam} and V_{foam} are the mass and volume of foam containing fibers, void, and solid PU, respectively, and m_{solid} and V_{solid} are the mass and volume of cell struts. Assume that m_{foam} equals m_{solid}, E_o is proportionate to the ratio, V_{solid}/V_{foam}, which is the fraction of solid in the foam. Since the surface of treated fiber is rougher, the increased roughness increases the number of nucleation sites and increases the porosity of foam. As the porosity increases, the fraction of solid in the foam decreases and, based on Eq. 7, the computed modulus of foam decreases. This could be the reason that the difference between E_c and E_x of foam reinforced with treated fiber was larger than that of untreated fiber.

Based on Eq. 1, the compressive modulus of foam is proportional to the square of the relative density of foam. Specific modulus was calculated by dividing the compressive modulus of foam by the square of the density of foam. The results of specific modulus are shown in Figure 4-11.

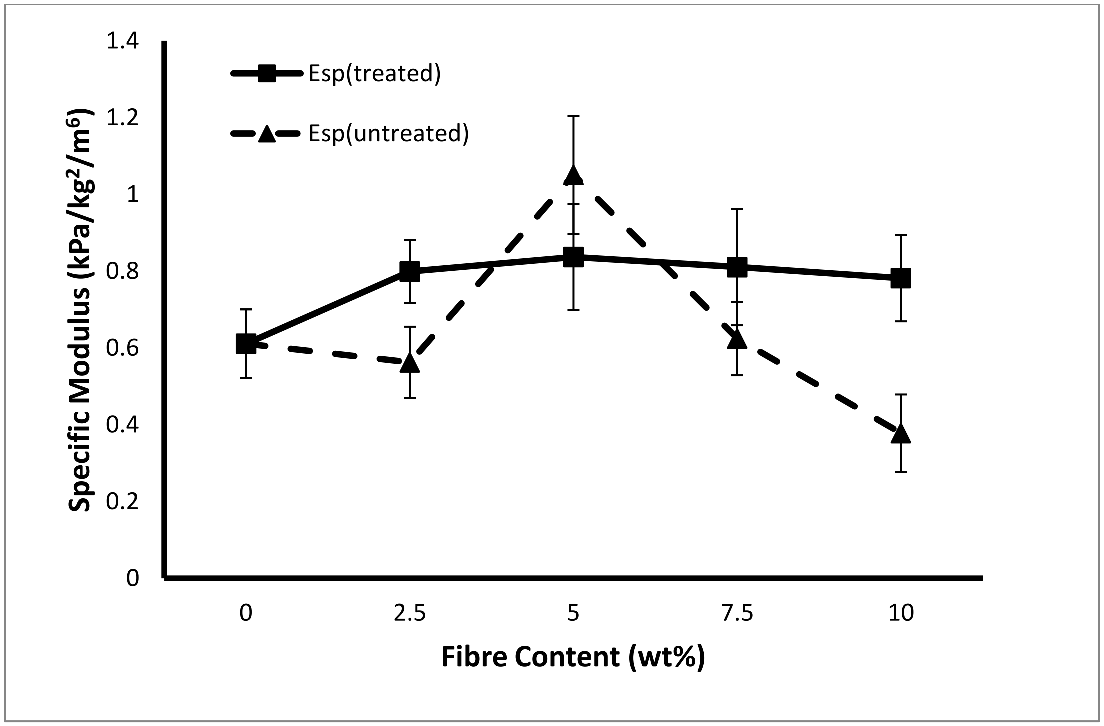


Figure 4-11 Specific modulus of untreated ($E_{sp(untreated)}$) and treated ($E_{sp(treated)}$) fiber-reinforced foams with different fiber contents

The relationship between fiber content and RF of foams reinforced with treated and untreated fibers is shown in Figure 4-12. For treated fiber-reinforced foam, there was a great increase in RF as fiber content increased; however, for untreated fiber-reinforced foam, RF increased gradually with increasing fiber content. The results suggested that alkaline treatment improved the fiber/matrix adhesion and increased the contribution of fibers on the compressive performance of foam. This can be attributed to an increase in aspect ratio and surface roughness of treated fibers implying higher degree of stress transfer at the fiber-matrix interface contributing to the improvement in the compressive performance of foam reinforced with the fibers.

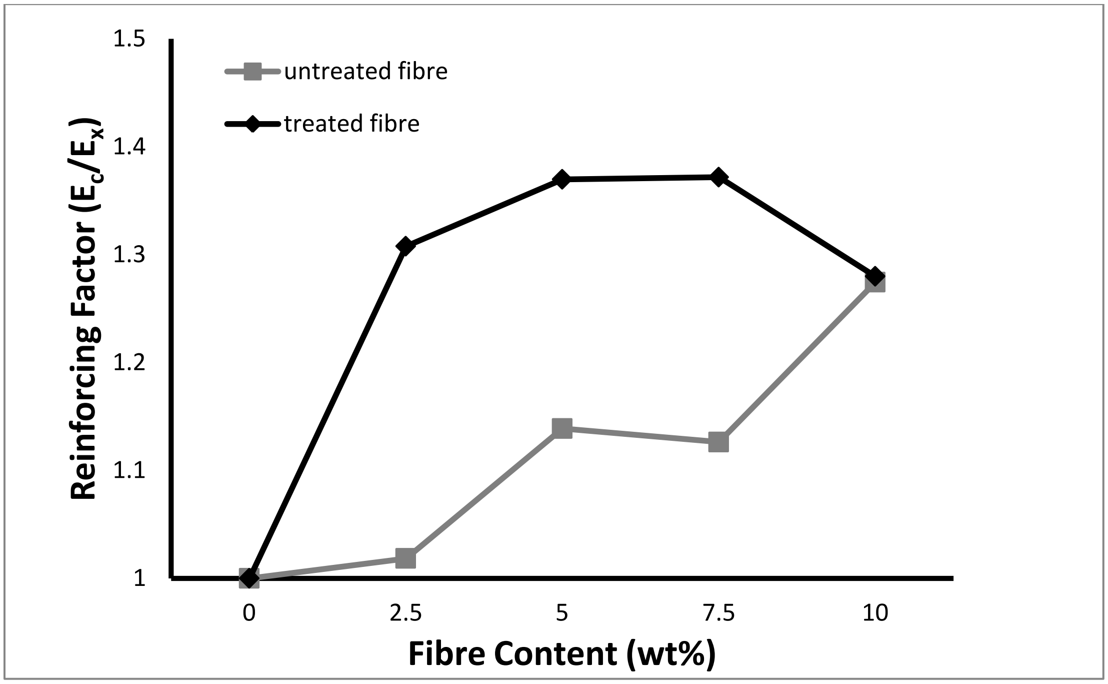


Figure 4-12 Reinforcing factors of untreated fiber-reinforced and treated fiber-reinforced foams as a function of fiber content

4.2.3 Cell Morphology

An imaging technique, X-ray computed tomography, was used to characterize three dimensional cell structure of fiber-reinforced foam. Figure 4-13 shows the tomographic image of neat foam. As shown in the figure, white area represents void volume of foam and black lines represent cell edges. Figure 4-14 shows tomographic images of fiber-reinforced foams with different fiber contents. In comparison with the image of foam with no fiber (Figure 4-13), darker parts in Figure 4-14 are considered to be the presence of wood fibers. These parts were located either in cell struts or spread around foam cells; the results support the observations of fibers embedded in foams under SEM reported by Khazabi *et al.* in the literature [81].

The effect of fibers on the cell morphology of foam was examined based on the tomographic results. It was found that the presence of fibers deformed the cell structure of foam. The deformation of the cell structure can be a reason for the decrease in compressive strength observed for foam reinforced with small amount of fibers (from 0 to 5 wt%) as shown in Figure 4-8. Based on the tomographic results, the foam reinforced with 10 wt% of fibers had the largest cell size. Cell size is considered to be a factor that affects the mechanical performance of foam; larger cell size leads to reduced mechanical properties of foam. However, the foam reinforced with 10 wt% of fibers had higher compressive strength and modulus than other foams with lower fiber contents. This is because the increase in the interfacial adhesion between fibers and a polymer matrix compensates for the undesirable effect of larger cell size. It is clear that the interaction between fibers and the polymer matrix plays a key role in enhancing the mechanical performance of fiber-reinforced foam.

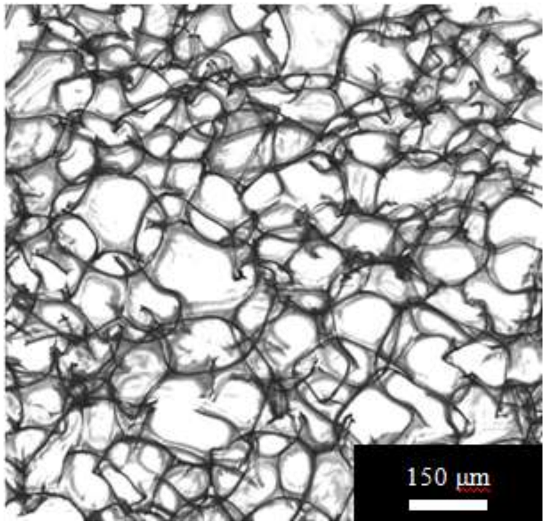
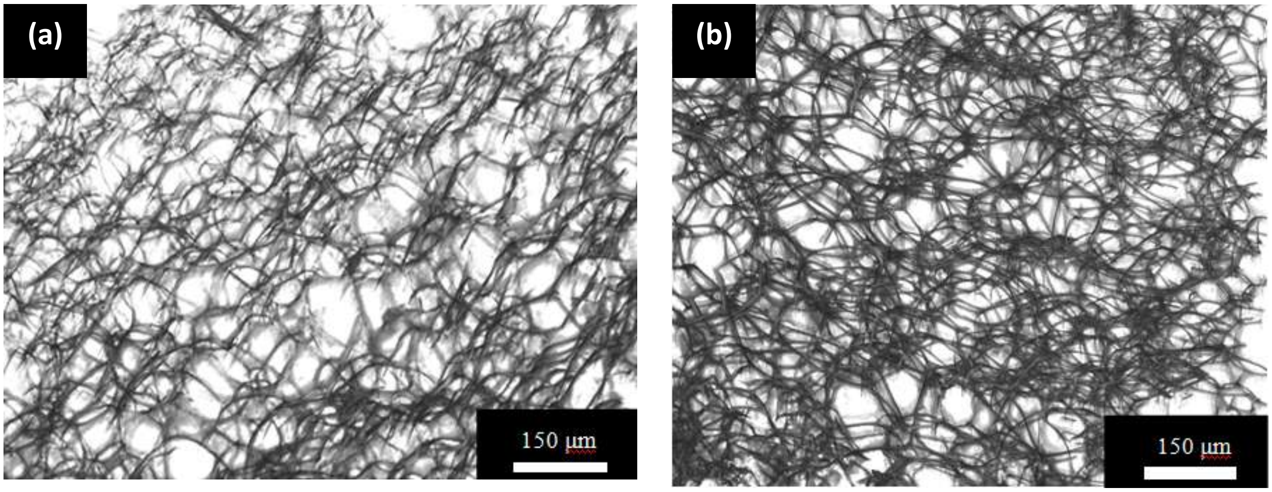


Figure 4-13 Reconstructed X-ray tomographic image of neat foam



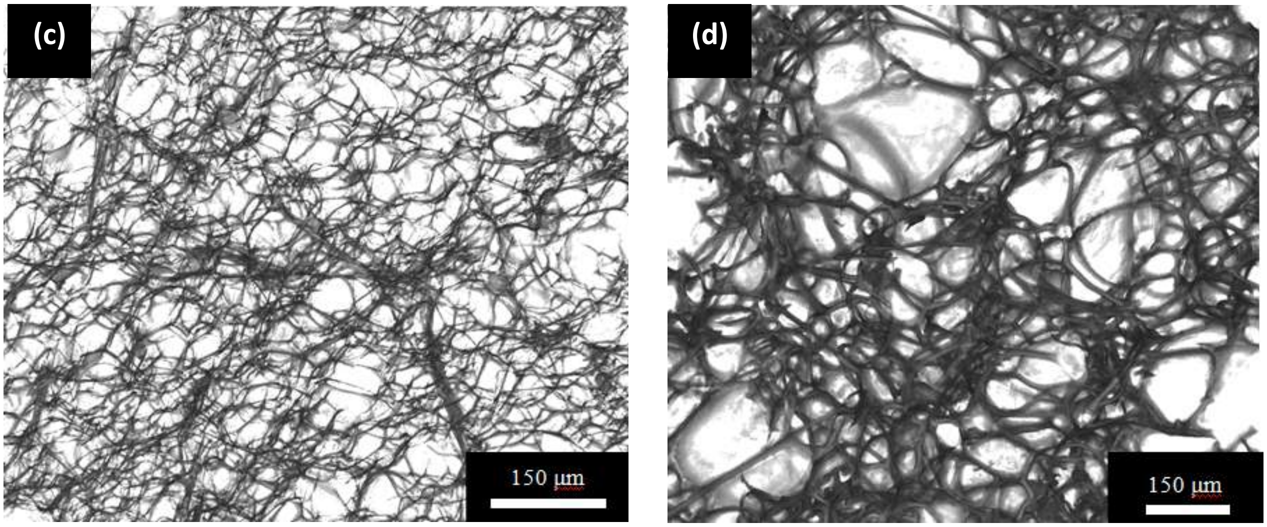


Figure 4-14 Reconstructed X-ray tomographic images of foams with (a) 2.5, (b) 5, (c) 7.5, and (d) 10 wt% treated fibers

4.2.4 Conclusions

Wood fibers were treated with NaOH solution to improve the interfacial bonding between fibers and a polymeric matrix. The concentration of the NaOH solution affects the surface of the fibers and further the compression performance of the foam reinforced with the fibers. Reinforcing factor was introduced to assess the reinforcing capability of the treated and untreated fibers embedded in the foam. It was concluded that an appropriate alkaline treatment can enhance the reinforcing capability of fibers and the compression performance of the foam reinforced with the fibers.

4.3 Effect of Catalyst on the Compression Performance of Foams

Foams were made using various mono-amines as catalysts and the compressive strength and cell morphology of the foams were measured in order to investigate the effect of the catalyst.

The preparation of PU foam consists of two reactions: blowing and gelling reaction. The catalyst plays a crucial role in achieving a balance between the blowing and gelling reaction and is responsible for achieving a fine cell shape and enhanced mechanical properties [111, 117]. In this study, five mono-amines were used as catalysts in the fabrication of PU foams. The chemical structures of these catalysts are displayed in Figure 4-15. Foams were made using each catalyst with other reagents (blowing agent and surfactants) and the kinetic rate of foam formation and the compression performance of the foams were measured.

4.3.1 Reaction Profile of PU Foams

The kinetic rate of reaction was estimated by measuring cream time, gel time and rise time during foam-forming process. Cream time is defined as the time counted from pouring a mixture into a mold to the initial point of rising at which the mixture is saturated with blowing gas. Gel time is the time counted from the same starting point to the formation of thin polymer string at which the cross-linking reaction between urethane and urea takes place.

Rise time is the time for the mixture to reach the maximum height. Cream time is related to the rate of blowing reaction while gel time associated with the rate of gelling reaction [106]. By comparing these kinetic times, the catalyst that favors blowing reaction or gelling reaction can be determined.

Kinetic times of foams made with different types of catalysts are listed in Table 4-1 for the assessment of the dynamics of foaming reactions.According to Table 4-1, foams made with catalysts, CAT-0, CAT-1, and CAT-4 had shorter cream time compared with those made with, CAT-2, and CAT-3. The results implied that these catalysts (CAT-0, CAT-1, and CAT-4) have relatively higher catalytic activity for the blowing reaction than other catalysts (CAT-2, and CAT-3).

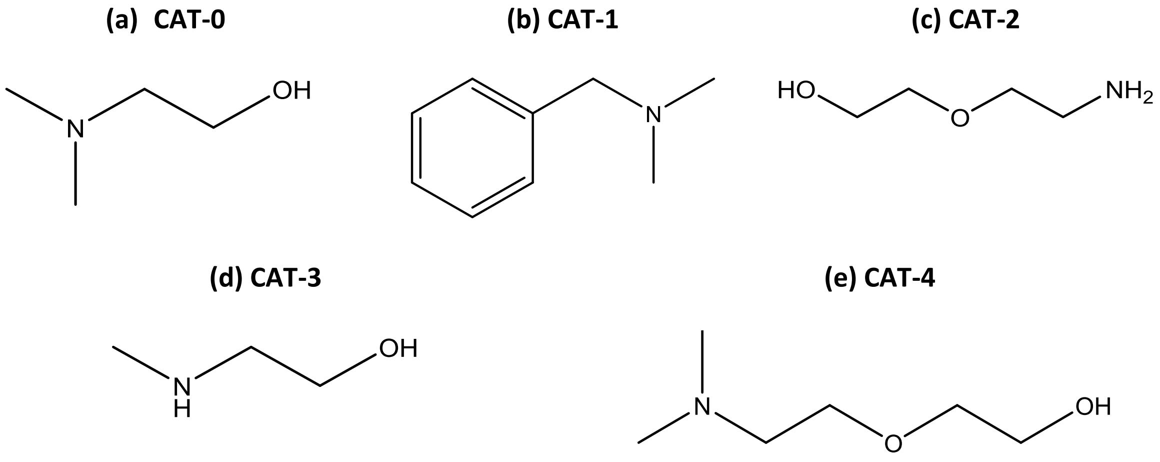


Figure 4-15 Chemical structures of (a) ethanolamine (CAT-0), (b) benzyldimethyl amine (CAT-1), (c) 2-(2-aminoethoxy) ethanol (CAT-2), (d) 2-(methylamino) ethanol (CAT-3), and (e) 2-[2-(dimethylamino)ethoxy] ethanol (CAT-4)

The relationship between rise height and time was examined in order to estimate the effect of catalyst on the kinetic rate of reaction in the preparation of foam. Figure 4-16 shows rising profiles of foams made using various catalysts. The results showed that catalyst type affected the slope of rise height versus time at the beginning of foaming. The slope represents the rising rate of foam. In Figure 4-16, there was a trend that foams made using catalysts, CAT-0, CAT-1, CAT-4 had a higher rising rate. This indicates that these catalysts have higher catalytic activity for the blowing reaction than CAT-2 and CAT-3.

Sample	Cream time (min:s)	Gel time (min:s)	Rise time (min:s)
CAT-0	0:32	0:37	1:31
CAT-1	0:37	0:52	1:42
CAT-2	0:51	1:02	2:38
CAT-3	0:45	1:12	2:16
CAT-4	0:22	0:33	0:54

Table 4-1 Cream time, gel time and rise time of PU foam prepared with catalyst: CAT-0, CAT-1, CAT-2, CAT-3, and CAT-4

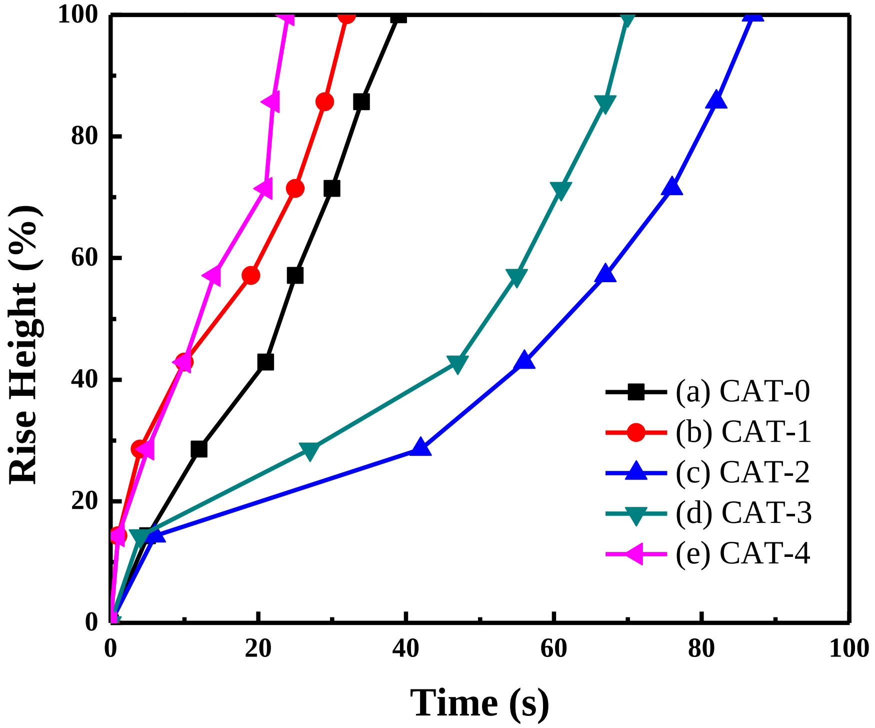


Figure 4-16 Rise height of PU foams prepared with catalyst: (a) CAT-0, (b) CAT-1, (c) CAT-2, (d) CAT-3, or (e) CAT-4 as a function of time

4.3.2 Effect of Catalyst on the Compression Behavior of Foam

The effect of catalysts (CAT-0, CAT-1, CAT-2, CAT-3, and CAT-4) on the compression performance of corresponding foams was investigated. In the literature, Choe *et al.* reported that the content of catalyst had an effect on the cell size, kinetic rate, and compressive strength of PU foam [105]. The compressive strength of the foam made using a physical blowing agent increased as the content of blowing catalyst increased due to the collapsed of foam cells while it was independent of the content of gelling catalyst. However, for the foam made using water as a blowing agent, the compressive strength was independent of the content of blowing and gelling catalysts [105]. The compressive strength and modulus of the foams made using various catalysts are shown in Figure 4-17 and Figure 4-18, respectively. In Figure 4-17, it can be seen that the foam made using CAT-1 had highest compressive strength. Similar results were observed in the results of compressive modulus while the foam made with CAT-3 had comparable value with that of the foam made using CAT-1 as shown in Figure 4-18.

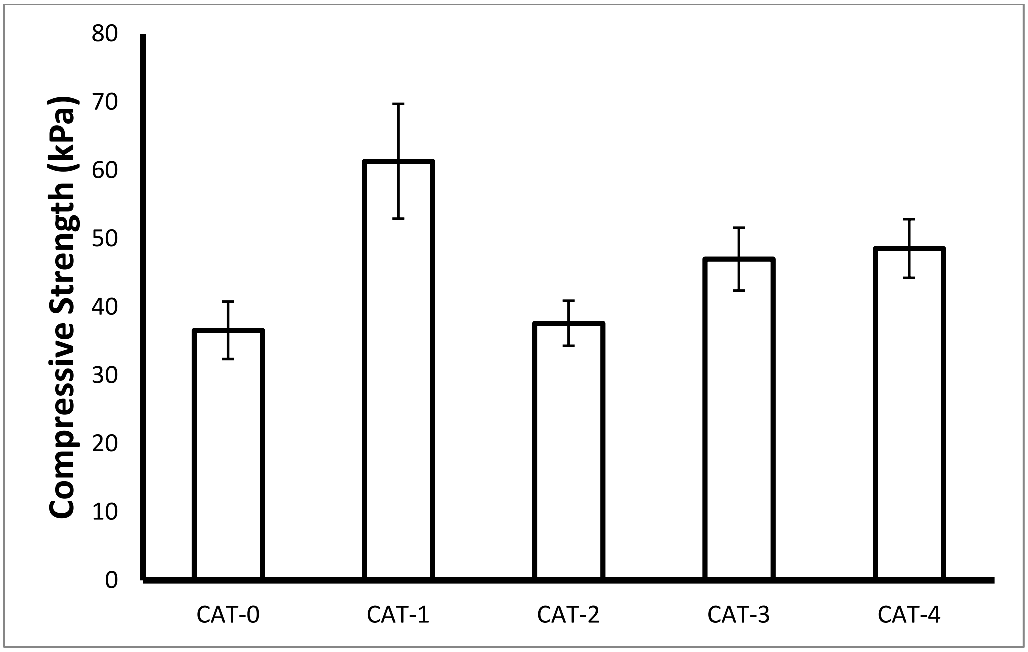


Figure 4-17 Measured compressive strengths of PU foams made with CAT-0, CAT-1, CAT-2, CAT-3, and CAT-4

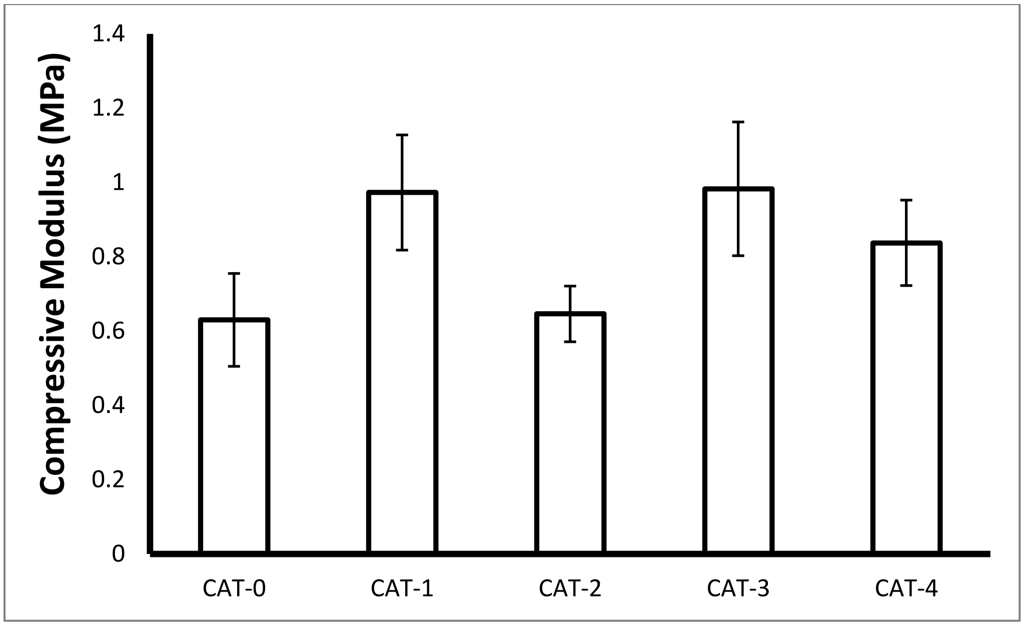


Figure 4-18 Measured compressive moduli of PU foams made with CAT-0, CAT-1, CAT-2, CAT-3, and CAT-4

The catalyst affects the density of foam and has effect on the results shown in Figure 4-17 and Figure 4-18. Densities of foams made with various catalysts were measured and are shown in Figure 4-19. As shown in Figure 4-19, the density of foam depended on the type of catalyst with which foams were made.

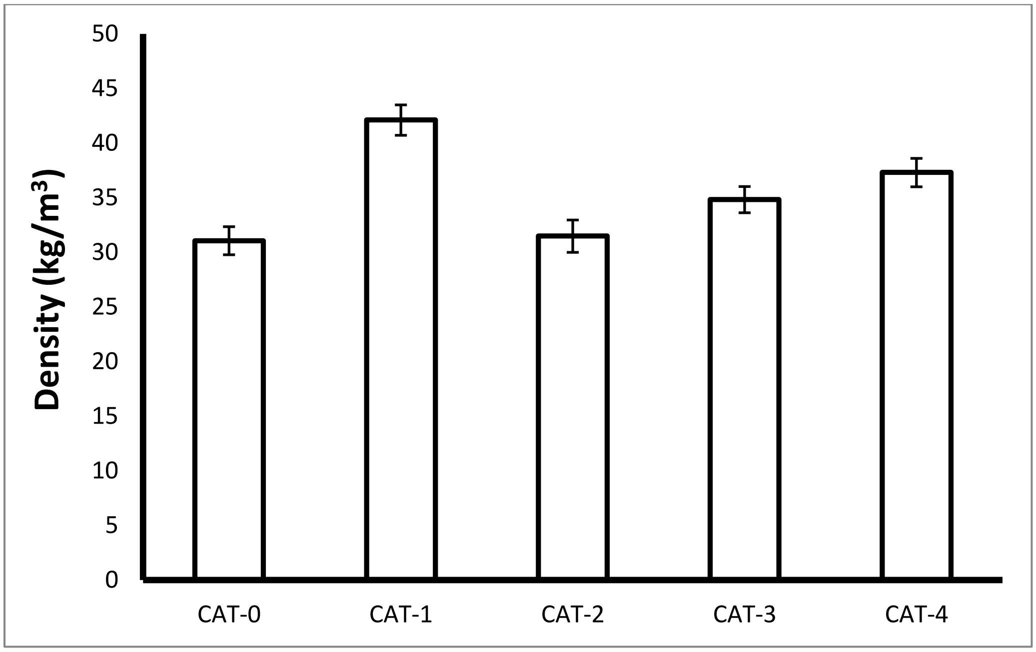


Figure 4-19 Densities of PU foams produced with various catalysts (CAT-0, CAT-1, CAT-2, CAT-3, and CAT-4)

Hence, in order to isolate the effect of catalyst on the compression performance of foam from any density changes, the compressive modulus of each sample was divided by the square of corresponding density (See Section 4.2.2). The calculated value was named as specific modulus as shown in Figure 4-20. From Figure 4-20, it is apparent that foams made using catalysts, CAT-0, CAT-2 and CAT-4 shared similar specific moduli while the specific modulus of foam made using CAT-3 was larger than that of foam made using CAT-1. The specific modulus results cannot be explained by considering the catalytic activity of the catalysts, toward blowing reaction or gelling reaction, since the materials formed by the blowing reaction and gelling reaction are urea and urethane, respectively. This is because urea and urethane can extend the cross-linking networks and increase the stiffness of polymer.

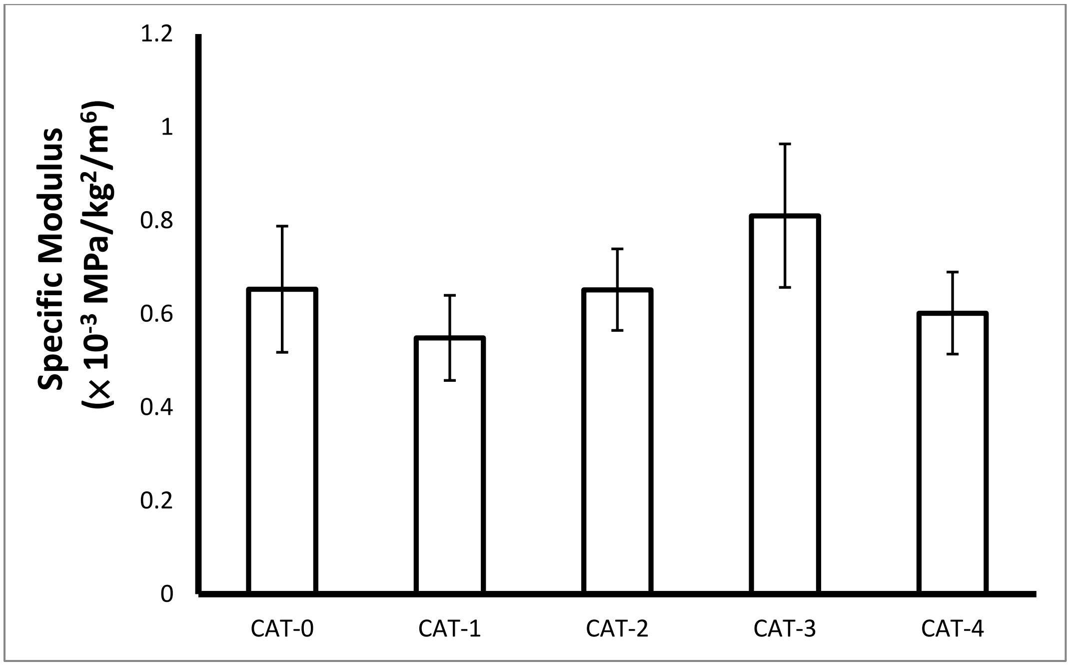


Figure 4-20 Specific compressive moduli of PU foams produced with catalysts: CAT-0, CAT-1, CAT-2, CAT-3, and CAT-4

An activation mechanism of catalyst in the gelling reaction proposed by Maris *et al.* [112] was used to interpret the results of specific modulus of foams made using catalysts with similar chemical structures but different chain lengths, CAT-2 and CAT-3. A schematic diagram of the mechanism is shown in Figure 4-21. The hydroxyl group on the polyol reacts with the catalyzed isocyanate group and forms an intermediate which then turns into a urethane linkage which connects polymer chains. As more urethane linkages are formed, the cross-linking degree and stiffness of polymer network increases. Based on the chemical structure of catalysts, it was hypothesized that CAT-3, with shorter chain length and smaller molecular size than CAT-2, has less steric hindrance which facilitates the formation of urethane linkages. Hence, it was expected that the specific modulus of foam made with CAT-3 is higher than that of foam made with CAT-2. However, the results of specific modulus (Figure 4-20) demonstrated that foams made using CAT-2 and CAT-3 had similar values. It was concluded that the steric hindrance of the chemical structure of catalyst is a factor that does not affect the formation of urethane linkages to a statistically significant extent.

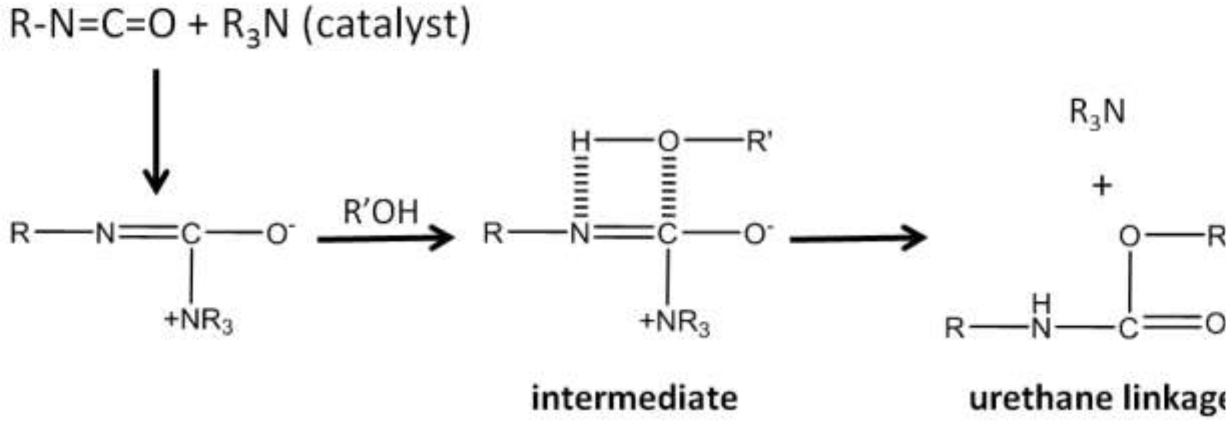


Figure 4-21 Schematic diagram of the activation mechanism of isocyanate-hydroxyl gelling reaction

4.3.3 FTIR Characterization of PU Foams

FTIR spectra of foams made with the different catalysts were measured to analyze the influence of the catalysts on functional groups in the foams. The FTIR spectra of foams are displayed in Figure 4-22. From Figure 4-22, foams made with all catalysts shared similar FTIR patterns. A broad absorption peak at 3320 cm^{-1} is attributed to the N-H stretching vibration of urethane linkages connected with hydrogen bonds [113]. An absorption peak around 2272 cm^{-1} represents the stretching of the NCO group of isocyanate which indicates that the incomplete conversion of isocyanate. Absorption peaks at 1224 cm^{-1} and 1513 cm^{-1} indicate the presence of N-H and N-C bond in urethane linkages, respectively. The absorption peak at 1725 cm^{-1} associated with the C=O stretching of urethane linkages [114] was observed in the spectra of foams made with CAT-0 and CAT-1, while the peak was hardly seen in the spectra of other foams. However, the reason for this has not yet been determined.

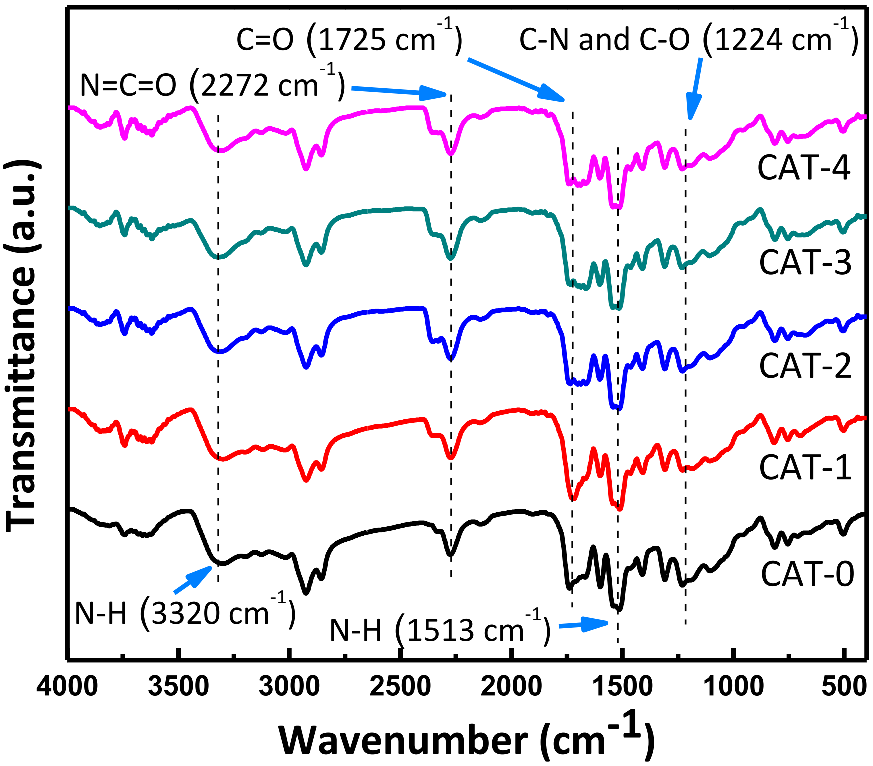


Figure 4-22 FTIR spectra of PU foams prepared with CAT-0, CAT-1, CAT-2, CAT-3, and CAT-4

FTIR spectra were used to estimate the concentration distribution of urethane and urea linkages of foam. The spectra were characterized using a curve-fitting analysis. Figure 4-23 shows the curve fitting results for the foam made using CAT-0. As shown in the Figure 4-23, the peaks can be determined by fitting the Gaussian distribution with the spectrum. Absorbance peaks around 1670 cm^{-1}, 1710 cm^{-1}, and 1730 cm^{-1} were observed. The peak at 1670 cm^{-1} is attributed to the carbonyl group of urea linkages. The absorbance peak at 1710 cm^{-1} and 1730 cm^{-1} indicates the presence of hydrogen bonded carbonyl group of urethane linkages and free urethane linkages, respectively. Table 4-2 shows the relative concentration of urea and urethane linkages of the foam made using catalysts (CAT-0, CAT-1, CAT-2, CAT-3, and CAT-4). It can be seen that the foam made using CAT-0, CAT-1, and CAT-4 had lower relative concentration of urea linkages than CAT-2, and CAT-3. Based on the kinetic time and rise height results, it was expected that the concentration of the urea linkages of the foam made using CAT-0, CAT-1, and CAT-4 would be higher than those of CAT-2, and CAT-3 due to the higher catalytic activity toward blowing reaction. However, the opposite results were observed in Table 4-2. Since the catalytic system for foaming is complex, there are factors in addition to the activity of catalyst that have an effect on the proportion of urethane and urea linkages formed in the foam. A more complete understanding is required to further investigate the catalytic system for making PU foam and the composition of the foam.

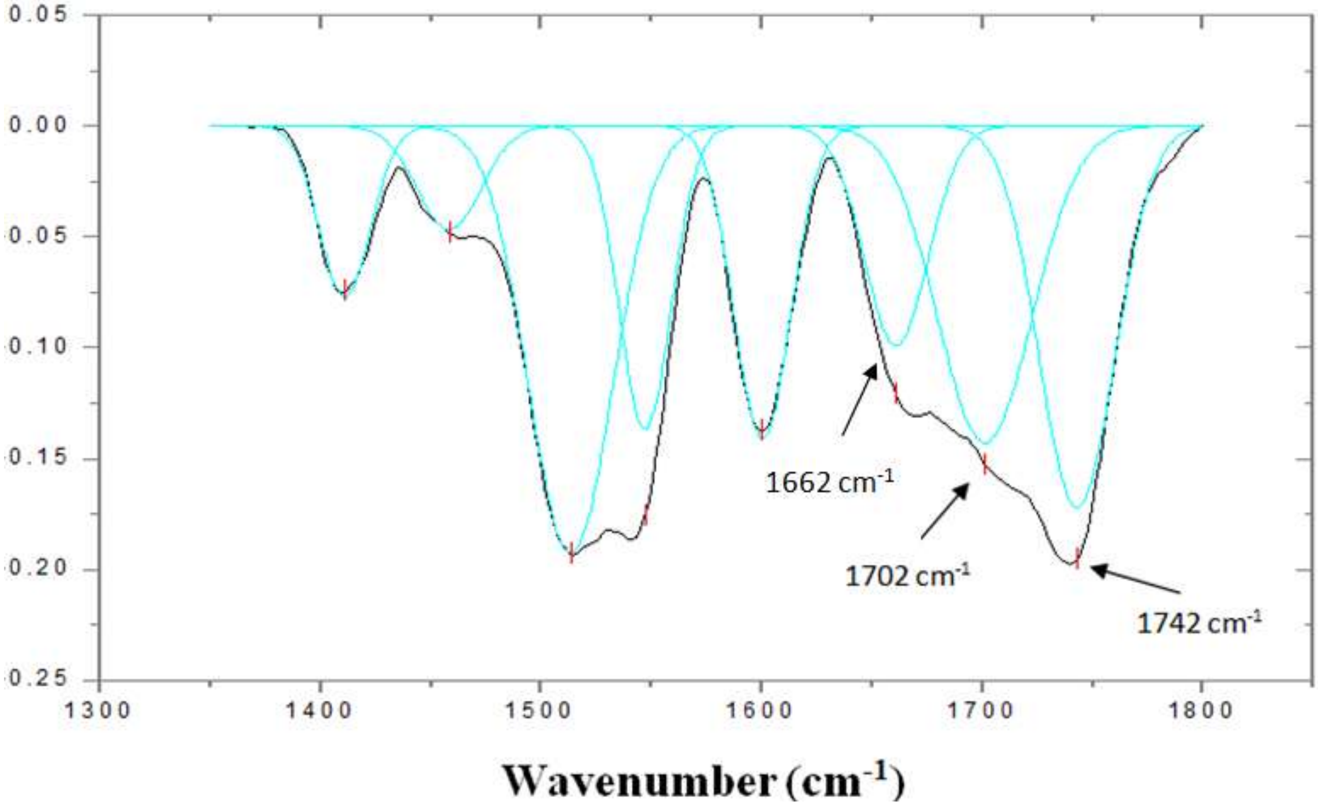


Figure 4-23 Curve-fitted FTIR spectrum of the foam made using CAT-0 as a catalyst in the 1350-1800 cm^{-1} region

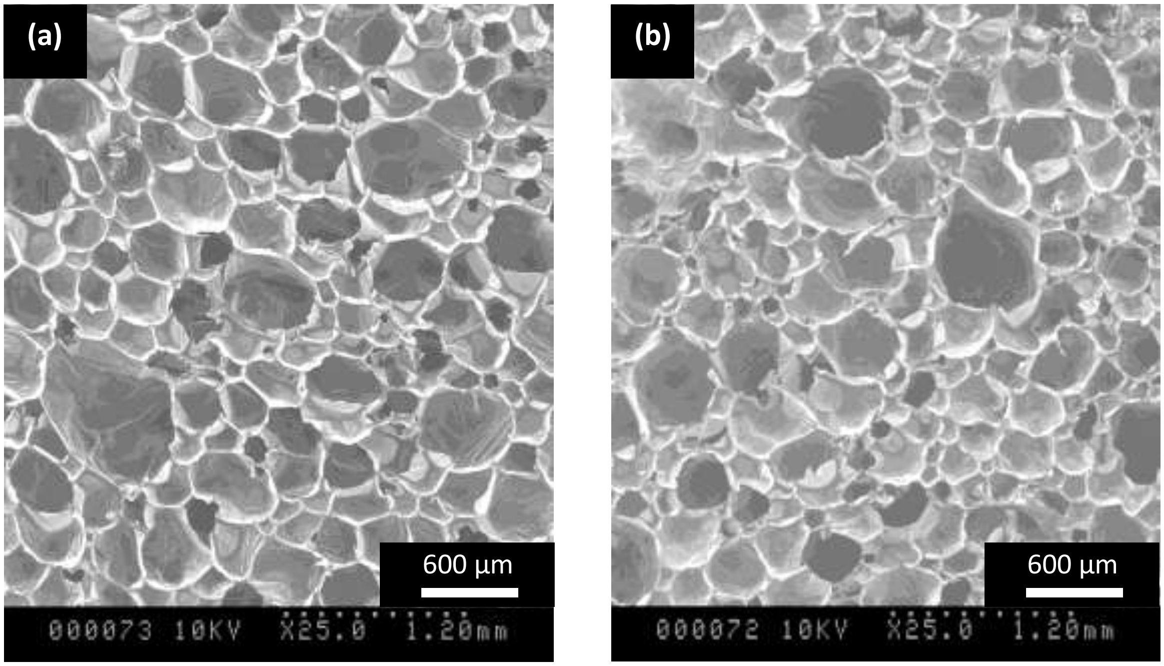
	Relative concentration (%)				
	CAT-0	CAT-1	CAT-2	CAT-3	CAT-4
Urethane linkage	80.0	81.6	69.6	61.7	85.6
Free Urethane	44.8	42.8	47.9	37.8	48.6
H-bond Urethane	35.2	38.8	21.7	23.9	37.0
Urea linkage	20.0	18.4	30.4	38.3	14.4

Table 4-2 Relative concentration of urea and urethane linkages of the foams made using catalysts, CAT-0, CAT-1, CAT-2, CAT-3, and CAT-4

4.3.4 Morphology of PU Foams

The mechanical properties of PU foam depend on the cell structure and cell distribution of foam. The presence of defects in the cell structure leads to poor mechanical performance of foam. It has been demonstrated that the cell structure is an important factor associated with the compressive strength of PU foam [115]. This section deals with the effect of different catalysts on the cell morphology.

Figure 4-24 shows SEM images of PU foams made using different catalysts. It can be seen that foams made using catalysts with the exception of CAT-3 had fine cell structure with foam cells in polygon shapes. The cell morphology of foams was similar to that obtained in the literature [86]. Irregular cell shape and uneven cell size distribution were observed in the foam prepared with CAT-3. In view of the cell morphology of foam, CAT-3 is less suitable for the preparation of PU foam, however, the selection of catalyst cannot be made based on the results of the compression performance or cell morphology of foam results alone.



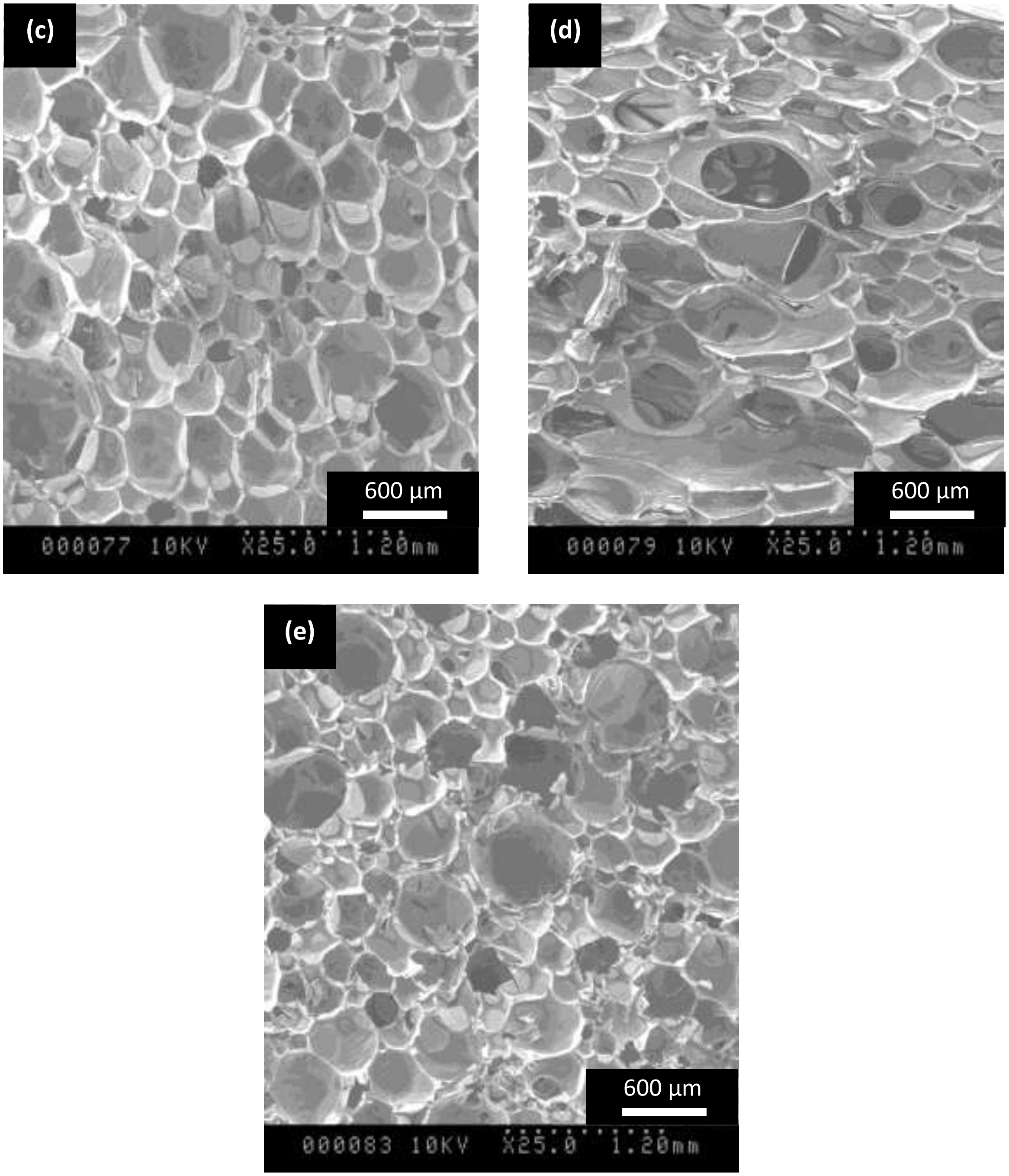


Figure 4-24 SEM micrographs of PU foams made with (a) CAT-0, (b) CAT-1, (c) CAT-2, (d) CAT-3, and (e) CAT-4 in the foam rising direction

4.3.5 Conclusions

In this section, foams were made using five different monoamines as catalysts in order to study their effect on the compression performance and cell morphology of the foams. The catalytic activity of amine catalysts was assessed by the kinetic time and rising profile results. The influence of the catalysts on functional groups in the foams was investigated by taking FTIR spectra. Based on the compression results, it was shown that foams made using different catalysts shared similar specific compressive moduli. An activation mechanism was used to interpret these results indicating that the steric hindrance of the chemical structure of catalyst is a factor that does not affect the compression performance of the foam to a statistically significant extent. From the SEM images of the foams, the cell morphology of the foams was similar except for the foam made using the catalyst, CAT-3.

4.4 Characterization of Foams Made Using Different Mixing Methods

In fiber-reinforced polymer composite, fibers make polymer matrix mechanically stronger as the fibers are well dispersed. It is considered that the same is true in the fiber-reinforced foam system. In order to disperse the fibers uniformly in the PU matrix, a mechanical stirrer was used for mixing.

4.4.1 Effect of Stirring Time on the Compression Response of Foam

In order to investigate the effect of mixing on the mechanical properties of foam, foams were made under various mixing conditions and the effect of mixing conditions on the mechanical performance of foam was measured. Specified amounts of fiber and polyol were blended using either hand mixing or a mechanical stirrer. It was hypothesized that a truly thorough mixing can be achieved using the agitation force provided by the mechanical stirrer especially for longer stirring times and enhanced mechanical performance of foam can be achieved.

Stirring time and stirring rate are two important variables involved in the preparation of foam. In this section, the effect of stirring time on the compression performance of foam was examined. Foams made using the same formulation but under various stirring times were prepared and the compressive strength and modulus of foams were measured. The results are shown in Figure 4-25 and 4-26. Foams made with different stirring times shared the similar strength and modulus results except the foam mixed for 30 minutes, which had a decrease in both strength and modulus results.

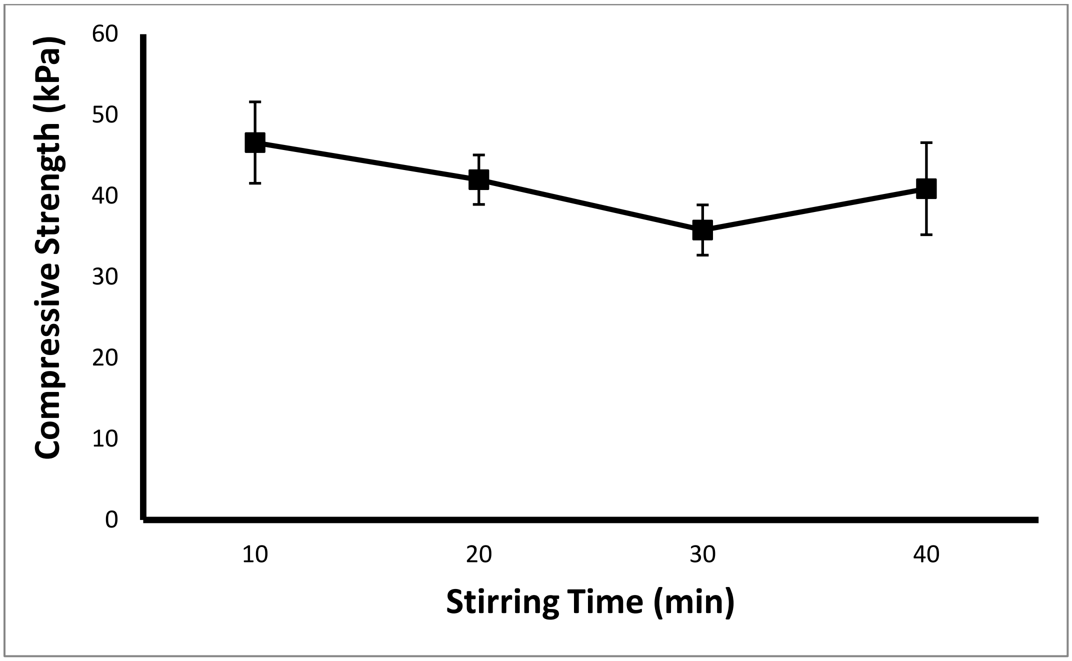


Figure 4-25 Compressive strength of fiber-reinforced foam as a function of stirring time

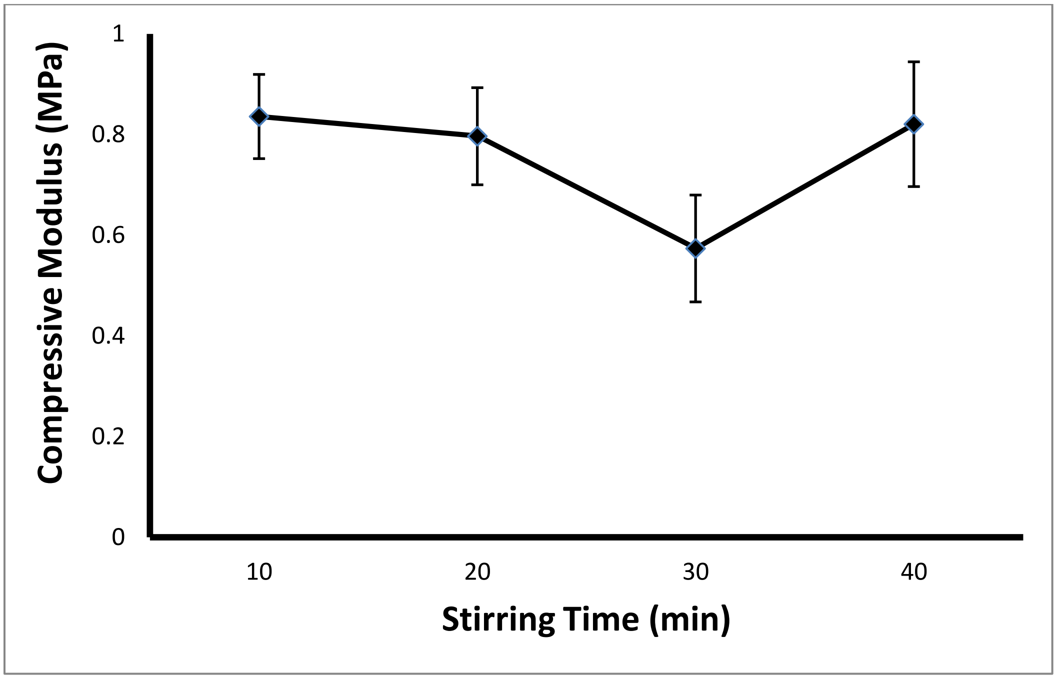


Figure 4-26 Compressive modulus of fiber-reinforced foam as a function of stirring time

RFs of foams made with different stirring times were computed and are shown in Figure 4-27 to isolate the effect of the fibers on the results. The results showed that no change of RF over stirring time was evident. This implies that the stirring time of 10 min was enough to disperse the fibers evenly. It was observed that the foams made using stirring time less than 10 min had large pores and collapsed easily.

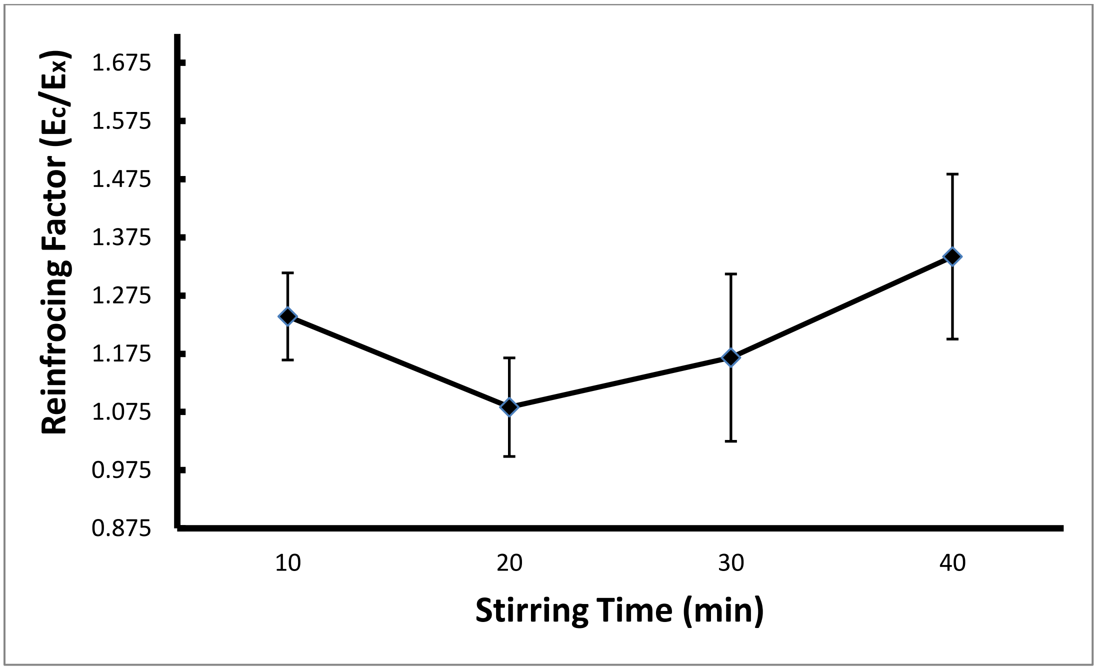


Figure 4-27 Reinforcing factor of fiber-reinforced foam as a function of stirring time

In order to examine the effect of stirring time on the cell morphology of foam, SEM images were acquired and are shown in Figure 4-28. As SEM image of foam made with 10 min stirring time (Figure 4-28 (a)) and that of foam made with 30 min stirring time (Figure 4-28 (b)) were compared, no significant difference was observed in terms of the cell morphology of foam. In addition, tomographic images were obtained in order to further study the effect of stirring time on the cell morphology of foam and are shown in Figure 4-29. It can be seen that the cell size of the foam made with 30 min stirring time (Figure 4-29 (b)) was a bit larger than that of the foam made with 10 min stirring time (Figure 4-29 (a)). Although SEM imaging is not a direct way of evaluating the degree of fiber dispersion, fiber aggregates and significant changes in the cellular structure observed under SEM may provide an evidence of poor dispersion of fibers. The results suggested that the increase in stirring time had no significant effect on the cell morphology of the foam since the fibers were already well dispersed after 10 min stirring.

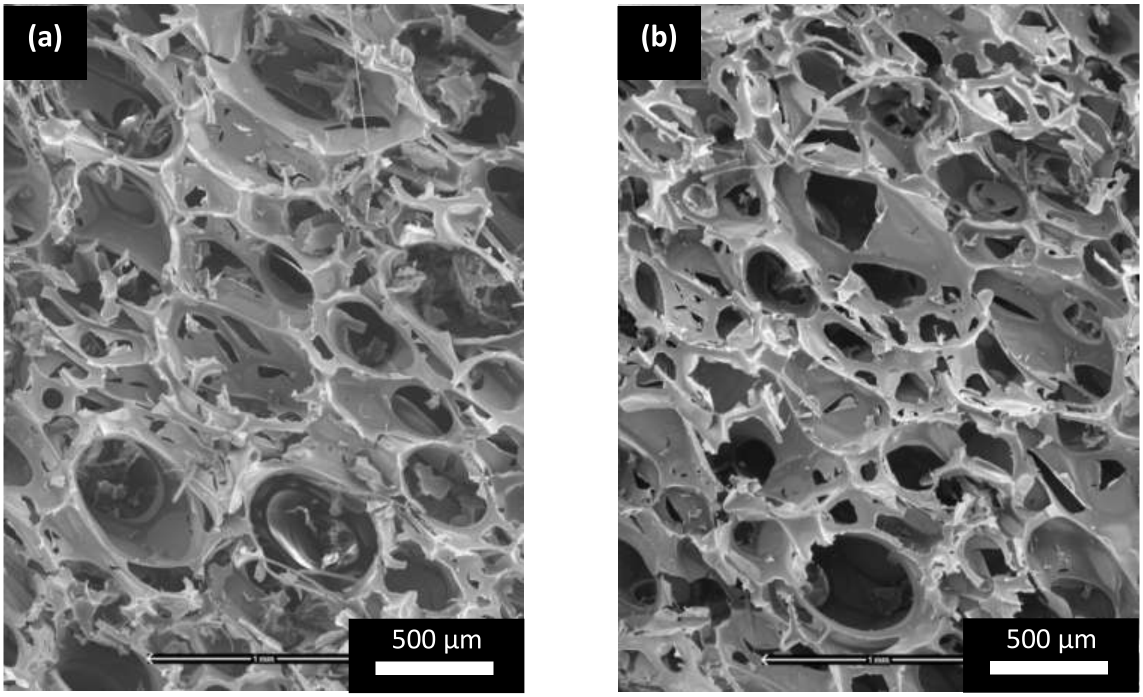


Figure 4-28 SEM micrographs of foams made with (a) 10 and (b) 30 min stirring times

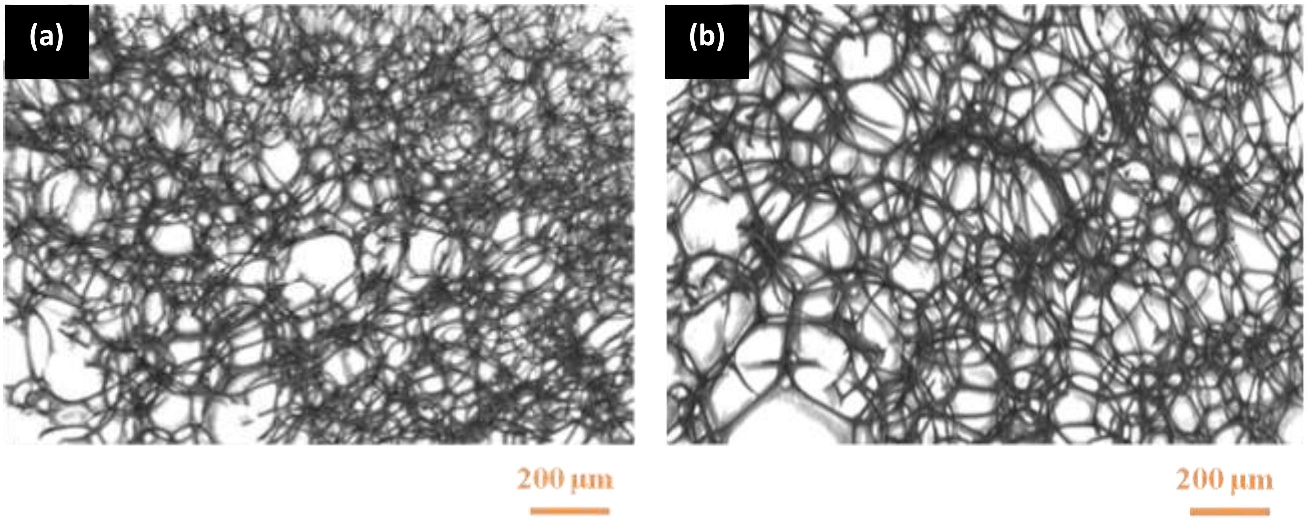


Figure 4-29 Reconstructed X-ray tomographic images of foams made with (a) 10 and (b) 30 min stirring times

4.4.2 Effect of Stirring Rate on the Compression Response of Foam

Section 4.4.1 discussed the effect of stirring time on the compression behavior and cell morphology of fiber-reinforced foam. This section sheds light on the effect of stirring rate on the above-mentioned properties. Foams were prepared with different stirring rates but at the same stirring time, 10 min, and the compression response of foams was measured in order to investigate the effect of stirring rate on the compression performance of foam. Figure 4-30 and Figure 4-31 show the compressive strength and modulus of foams made with different stirring rates, respectively. It can be noted that the strength and modulus of foam decreased as the stirring rate increased.

RFs of foams prepared with varying stirring rates were computed in order to isolate the effect of fiber and the results are shown in Figure 4-32. From Figure 4-32, it can be seen that RF decreased with increasing stirring rate. The decrease in RF can be attributed to the breakage of fibers during mixing. High stirring rate and force cause an increased number of fiber fractions and reduce the reinforcing capability of the fibers.

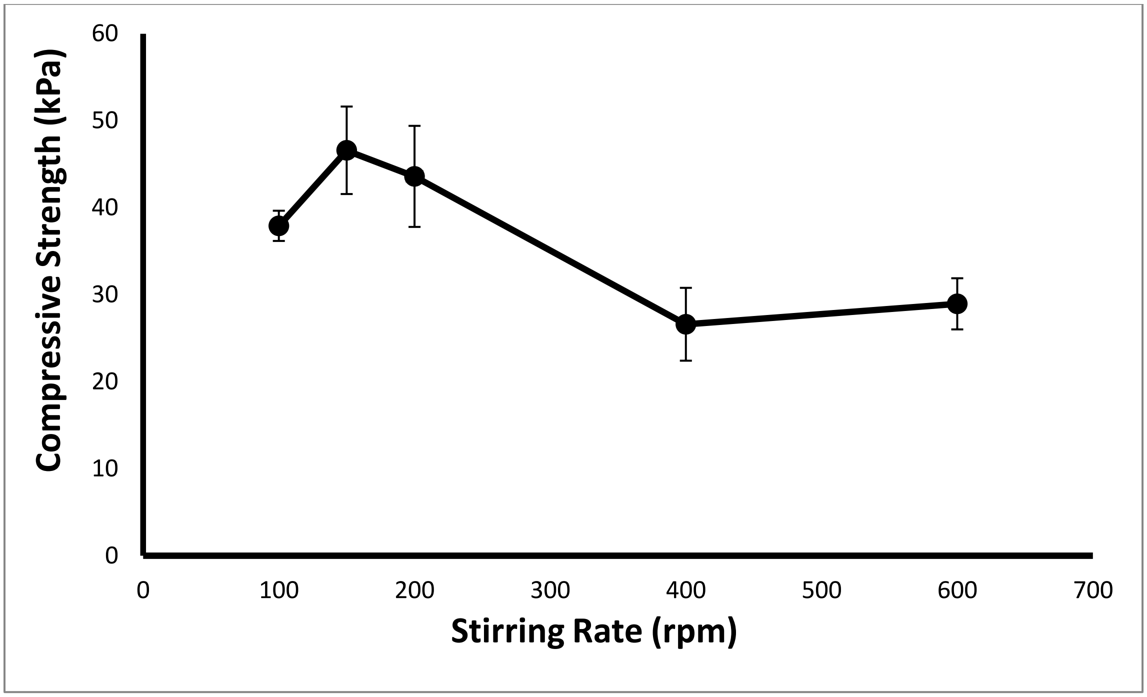


Figure 4-30 Compressive strength of fiber-reinforced foam as a function of stirring time

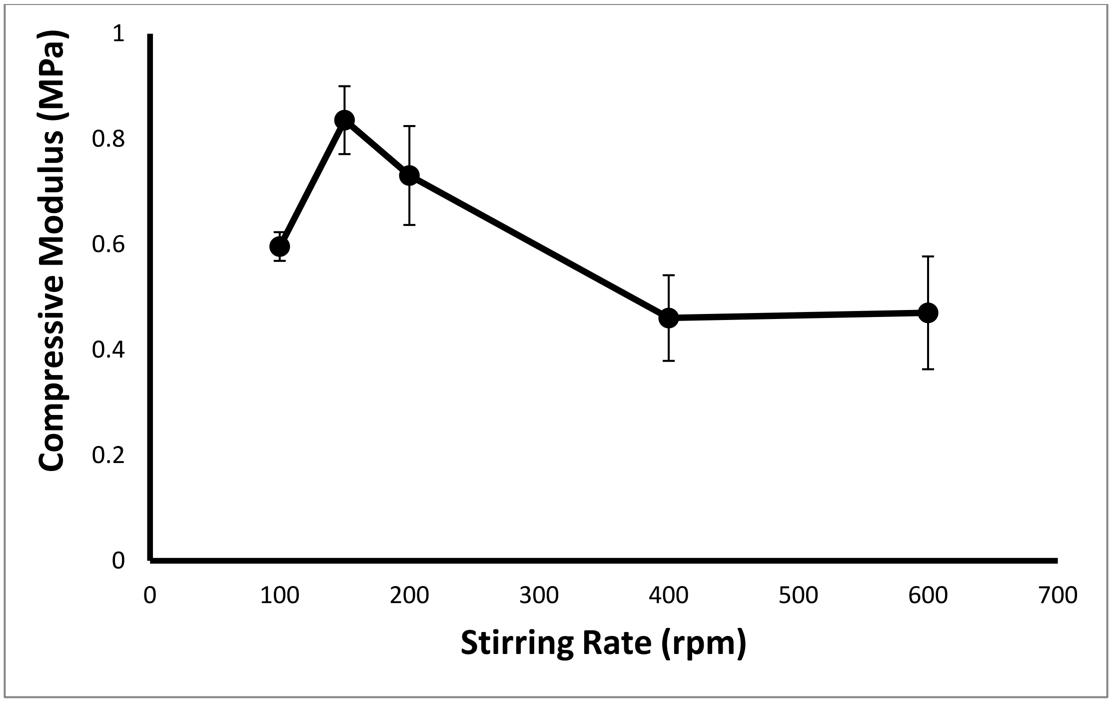


Figure 4-31 Compressive modulus of fiber-reinforced foam as a function of stirring rate

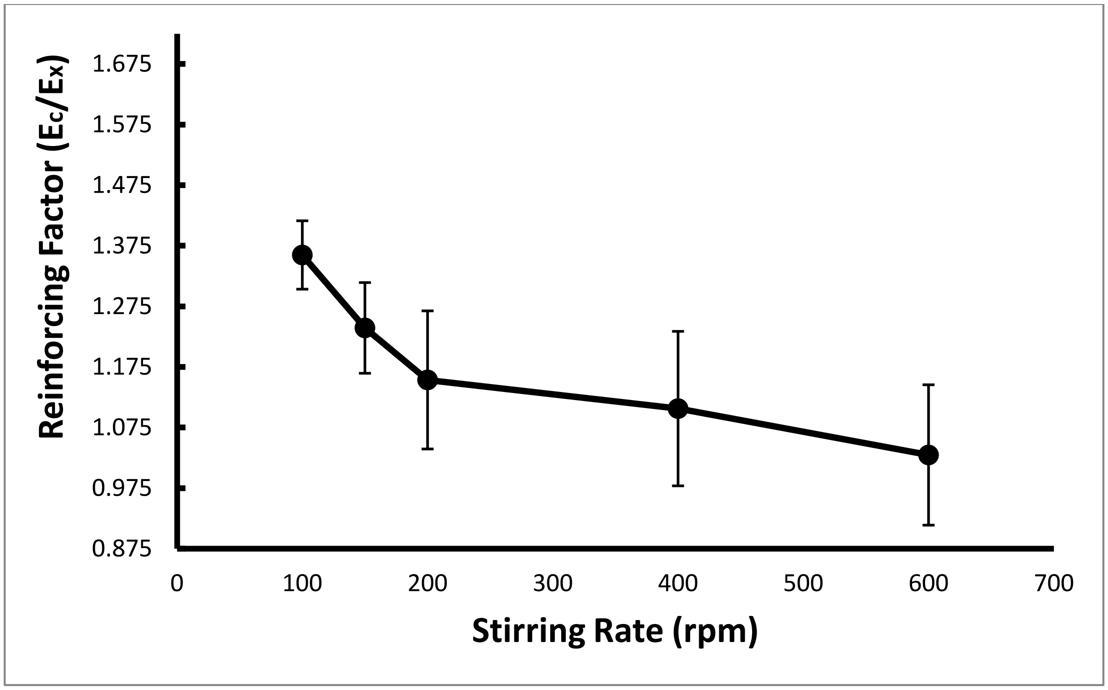


Figure 4-32 Reinforcing factor of fiber-reinforced foam as a function of stirring rate

SEM and tomographic images of foams made with various stirring rates were obtained in order to evaluate the effect of stirring rate on the cell morphology of foam. Figure 4-33 shows the SEM image of foam made with 600 rpm stirring rate. Compared with the SEM image of foam made with 150 rpm stirring rate (Figure 4-28 (a)), the foam made with 600 rpm stirring rate had irregular cell shapes and larger cell size. Figure 4-34 presents the tomographic image of the foam made with 600 rpm stirring rate. In Figure 4-34, cell edge of foam became less clear compared with that of foam made with 150 rpm stirring rate (Figure 4-29). This is due to a decreased amount of unbroken fibers. High stirring rate makes it possible to break down fibers into fractions. Since both the number of unbroken fibers spread over cells or collected in cell struts reduced, the cell edge of foam became less clear. It can be noted that high stirring rate in the preparation of foam led to increased amount of fractured fibers embedded in the foam.

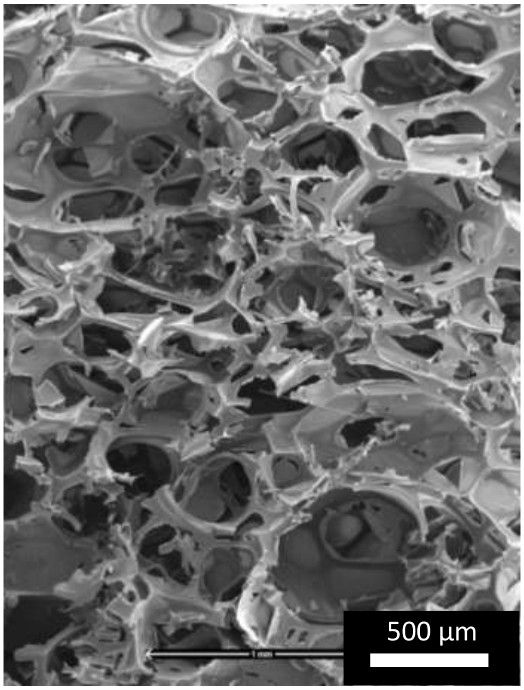


Figure 4-33 SEM micrographs of foam made with 600 rpm stirring rate

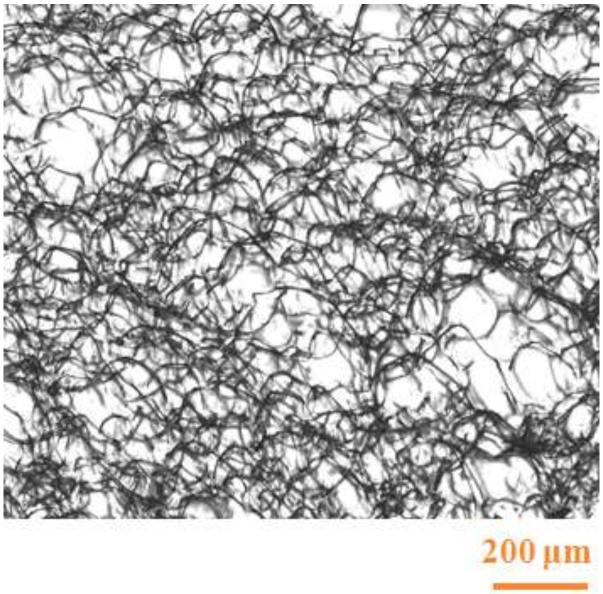


Figure 4-34 Reconstructed X-ray tomographic image of foam made with 600 rpm stirring rate

4.4.3 Mixing Method Comparison on the Compression Response of Foam

Foams were prepared using hand and mechanical mixing and their compressive strength and modulus were measured in order to examine the difference between the foam made by hand mixing and that made by mechanical stirring. For the foam prepared using the mechanical mixing, the stirring time was chosen to be 10 min, enough for good dispersion of fibers, and the stirring rate was 150 rpm, where fibers had highest reinforcing capability. The compressive strength of foams made using hand mixing and mechanical stirring is shown in Figure 4-35 and the modulus of these foams is shown in Figure 4-36. Figure 4-35 reveals that the compressive strengths of foams fabricated using hand mixing followed the same trend as those of foam using a mechanical stirrer for fiber contents less than 5 wt%. Above 5 wt%, there was a difference in compressive strength between the foam made by hand mixing and that made by mechanical mixing. Similar trends were seen in compressive modulus results of foams made using different mixing methods as shown in Figure 4-36.

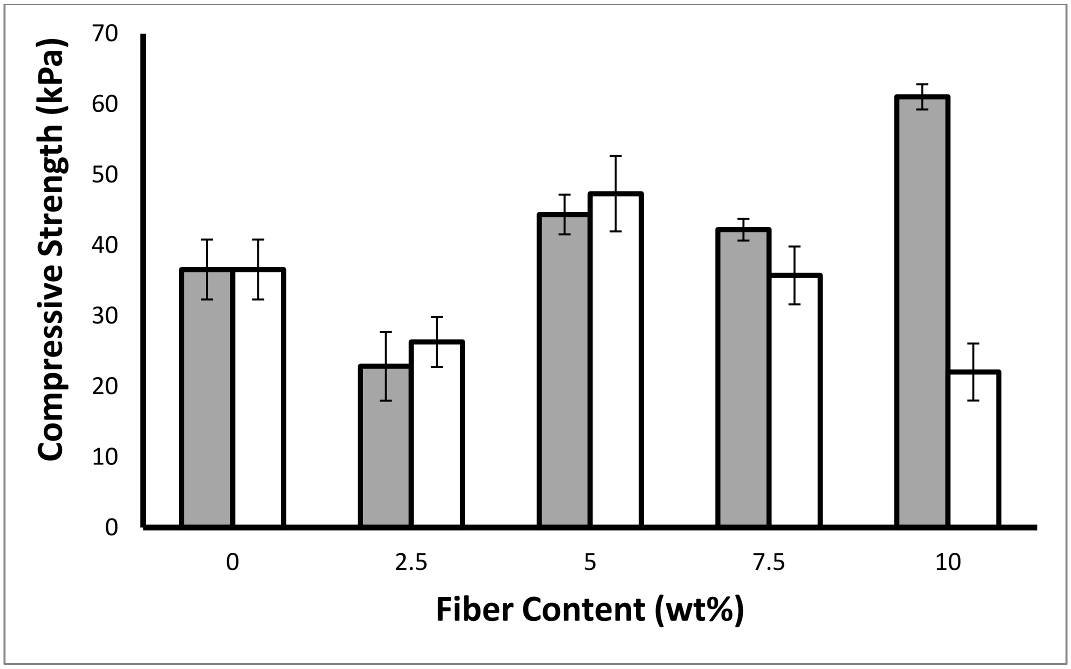


Figure 4-35 Compressive strengths of foams made using hand (white) and mechanical (grey) mixings

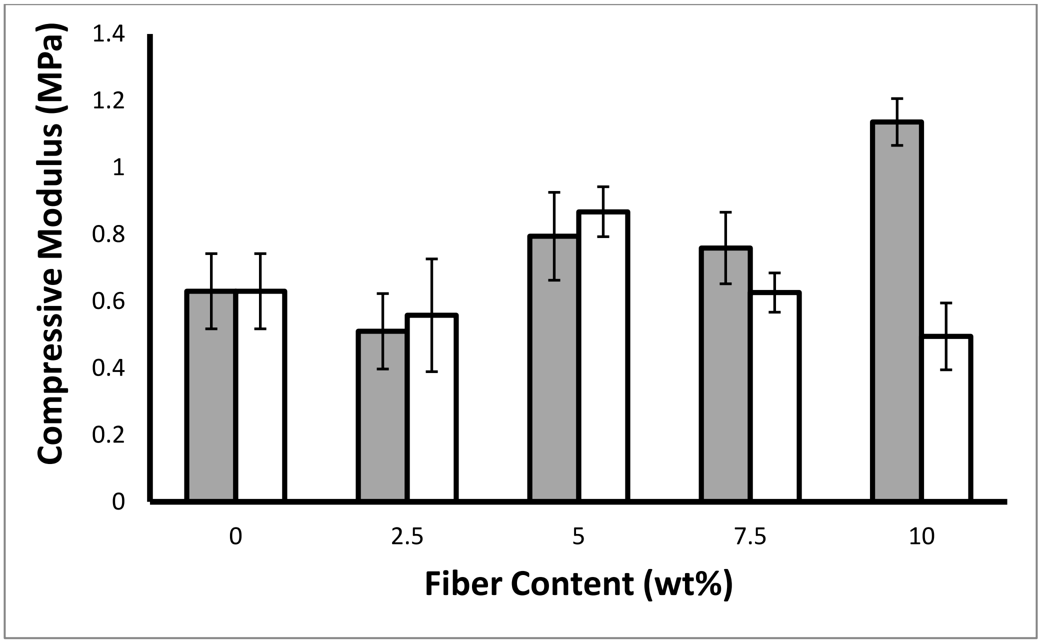


Figure 4-36 Compressive moduli of foams made using hand (white) and mechanical (grey) mixings

RFs of foams made using hand mixing and a mechanical stirrer were computed in order to evaluate the reinforcing capability of fibers. The results are shown in Figure 4-37. From Figure 4-37, it can be seen that the reinforcing capability of fibers embedded in the foam made using the mechanical stirrer decreased as fiber content increased while that of fibers in the foam made using hand mixing increased with increasing fiber content. This is because the stirring force breaks fibers into fractions during mixing. Thus broken fibers have reduced reinforcing capability and contribute less to the compressive strength and modulus of foam. Especially in the preparation of foam with high fiber content, this phenomenon became more significant as the viscosity of blend increased.

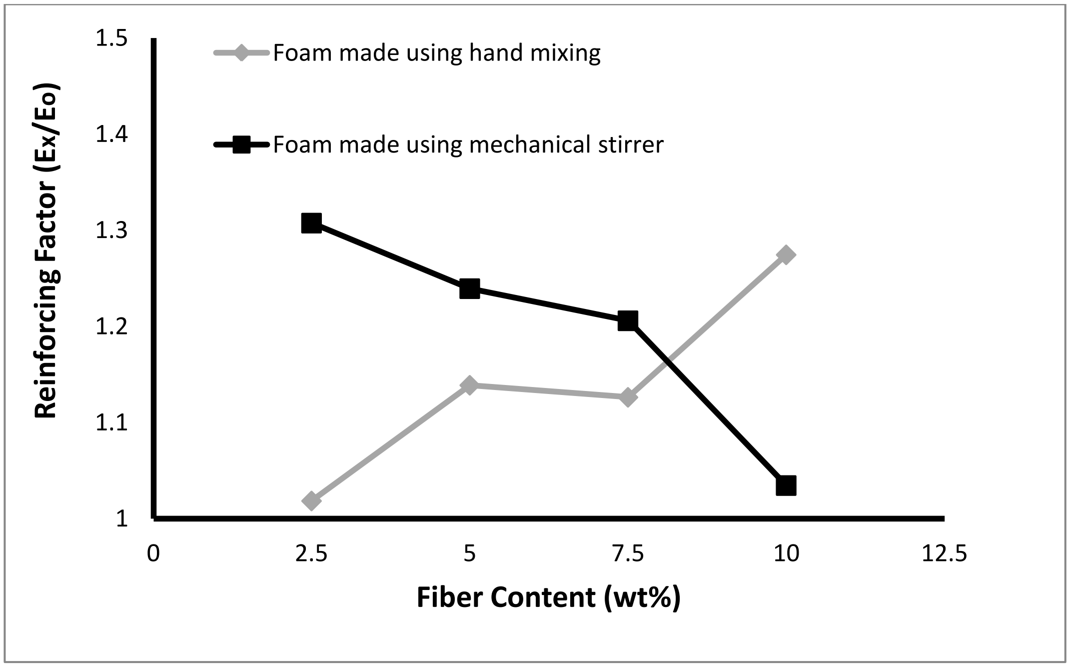


Figure 4-37 Reinforcing factors of foams made using hand and mechanical mixing as functions of fiber content

Morphological analysis techniques, SEM and tomography, were used to obtain the morphology of foams made using different mixing methods. SEM and tomographic images of foams made using hand mixing and a mechanical stirrer were recorded. Figure 4-38 shows SEM images of the foams made using hand mixing and the mechanical stirrer. It was observed that the cell morphology of the foam made using hand mixing was similar to that of the foam made using mechanical mixing. Tomographic images of the foam made using hand mixing and the foam made using mechanical stirrer were obtained and are shown in Figure 4-39. Tomographic results exhibited that fiber clusters were formed and observed in the foam made using hand mixing (Figure 4-39 (a)). The formation of fiber clusters indicated that fibers were less dispersed. The degree of fiber dispersion affects the cell morphology and mechanical performance of foam. The fibers well dispersed in the polymer matrix were assumed to have higher reinforcing capability. However, the results showed that the RF of fibers in the foam made using mechanical mixing decreased as the fiber content increased (Figure 4-37). It was concluded that the effect of fiber breakage outweighs the effect of fiber dispersion.

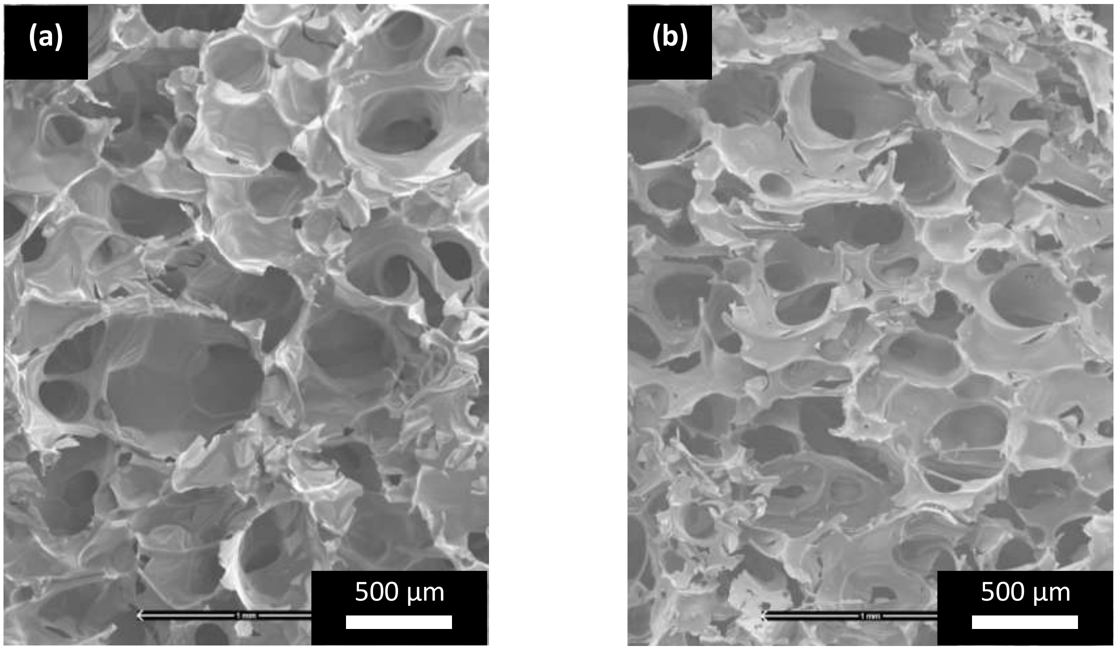


Figure 4-38 SEM micrographs of foams containing 10 wt% of fibers made using (a) hand and (b) mechanical mixing

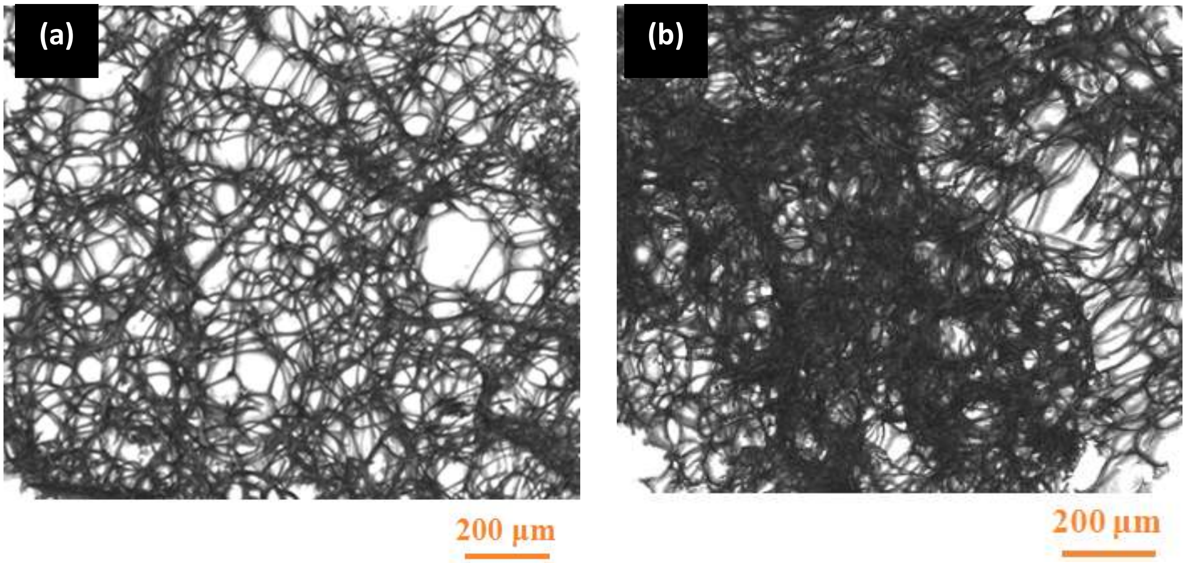


Figure 4-39 Reconstructed X-ray tomographic images of foam containing 10 wt% of fibers made using (a) hand and (b) mechanical mixing

The dispersion of fibers embedded in the foams made using hand and mechanical mixing was evaluated using a stereo microscope. Figure 4-40 shows microscopic images of foams made using hand mixing and mechanical mixing. It is evident that fiber clusters were observed in the foam made using hand mixing but not in the foam made using a mechanical stirrer. The results supported the argument that fibers tended to form fiber clusters in the foam made using hand mixing, consistent with the results observed using X-ray computed tomography.

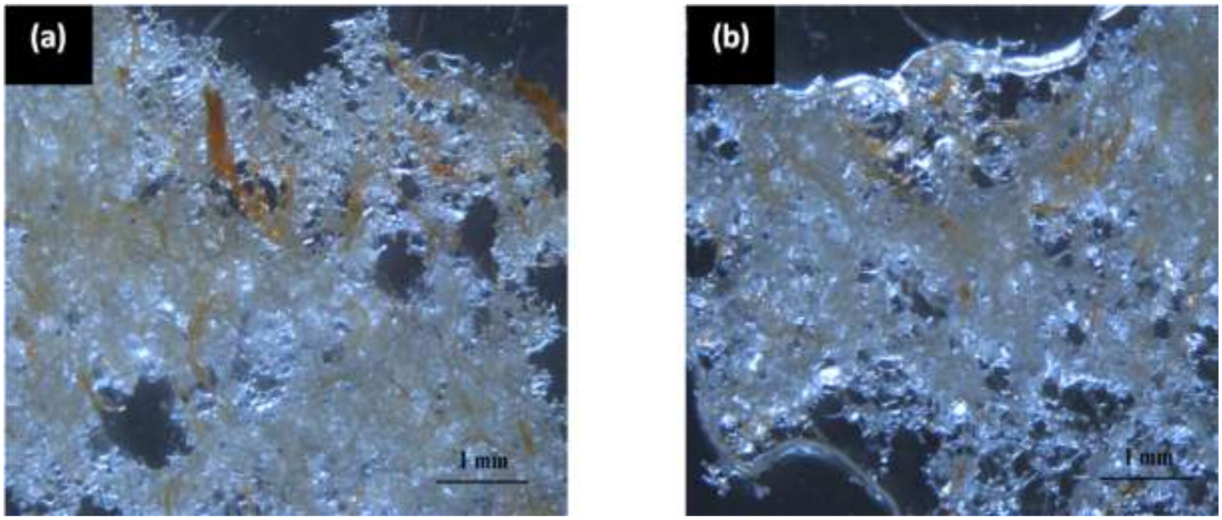


Figure 4-40 Stereo microscopic images of foams containing 5 wt% of fibers made using (a) hand and (b) mechanical mixing

4.4.4 Conclusions

Based on the investigated effect of mixing methods on the compression performance and cell morphology of fiber-reinforced foam, it can be concluded that, in the foam made using a mechanical stirrer, fibers were well dispersed but the reinforcing capability of the fibers was reduced. The reinforcing capability of the fibers in the foam made using the mechanical stirrer decreased as fiber content increased attributed to the breakdown of fibers during mixing, while the reinforcing capability of fibers in the foam made using hand mixing increased with increasing fiber content. Fiber clusters existed in the foam made using hand mixing but not in the foam made using mechanical mixing. In summary, the use of the mechanical stirrer provides a reproducible and controllable way for foam preparation and makes it possible to spread fibers evenly while the high shearing force of mechanical agitation breaks down the fibers and reduces the reinforcing ability of the fibers.

5. Conclusions and Recommendations

5.1 Conclusions

In this study, the effects of alkaline treatment, catalyst and mixing method on the cell morphology and compression behavior of wood fiber-reinforced PU foam were investigated. Conclusions that can be drawn from the experimental results are presented below:

1. Alkaline treatment improved the adhesion between fibers and polymeric matrix and increased the reinforcing capability of fibers and the compression performance of the foam reinforced with the fibers.
2. After the alkaline treatment, the length of fibers remains unchanged while the diameter of fibers decreased due to the removal of other extractives. A comparison of FTIR absorbance spectra of treated fiber and untreated fiber confirmed that the breakage of ether linkage in lignin.
3. The compression performance of treated fiber-reinforced foams depended on the concentration of NaOH solution in which fibers were processed. High concentrations of NaOH solution resulted in a rougher surface of fiber causing better adhesion at the fiber-matrix interface. However, the number of fractured fibers increases with increasing NaOH concentration, reducing the stiffness of fibers.
4. The effect of using different monoamines as catalysts on the cell morphology and compression behavior of foam was studied. It was observed that the type of the

catalyst has no significant effect on the compression performance of foam. SEM images showed that foams made using various catalysts have similar morphologies with the exception of foam made using catalyst, 2-(methylamino) ethanol.

5. The effects of stirring time and stirring rate on the compression performance of foam were investigated. It can be seen that the reinforcing capability of fibers embedded in foam is independent of the change in stirring time, indicating that 10 min stirring time was enough for good dispersion of fibers, while the reinforcing capability decreases with increasing stirring rate, due to increased number of fiber fractions.
6. As the foam made using hand mixing was compared with the foam made using a mechanical stirrer, it was observed that the reinforcing capability of fibers embedded in the foam made using the mechanical stirrer decreased as fiber content increased while the reinforcing capability of fibers in the foam made by hand mixing increased with increasing fiber content. About fiber dispersion, fibers in the foam made by mechanical mixing had lower chance of forming fiber clusters compared with fibers in the foam made by hand mixing.

5.2 Recommendations

This study reported that the compressive properties of wood fiber-reinforced PU foam can be enhanced through alkaline treatment of fibers and investigated the effect of catalyst and mixing method on the cell morphology and compression behavior of the foam. It is suggested that the use of alkali treatment can be extended to other natural fibers added in PU foams for reinforcing purpose. In the fabrication of PU foam, the effect of other amines used as catalysts on the mechanical properties of the foam should be studied. Moreover, further study on the type of propeller blade used in blending fiber-polyol mixture and the modulus development of the fiber-reinforced foam is recommended. In general, more efforts devoted to the exploration of the factors affecting the preparation of the wood fiber-reinforced foam and the way to enhance the mechanical properties of the foam are necessary.

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