

**POLYURETHANE FOAMS**  
**CONTAINING RENEWABLE CASTOR OIL REPLACEMENT**

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A Thesis

Presented to

The Faculty of the Graduate School

At the University of Missouri-Columbia

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In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

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By

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May 2014

The undersigned, appointed by the dean of the Graduate School,  
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**CONTAINING RENEWABLE CASTOR OIL REPLACEMENT**

Presented by Rui Xing

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Master of Science

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## ACKNOWLEDGEMENTS

I am willing to dedicate the most lofty respect and gratitude to my mentor, Prof. Fu-hung Hsieh, for his full guidance, unremitting support, and critical spur. It is Prof. Hsieh that make it possible for me to complete this thesis. What is more important, Prof. Hsieh's knowledge, wisdom, principles and personality charm are always encouraging me, and I believe all this will benefit me through my life.

I also deeply appreciate my committee members Profs. Galen J. Suppes and Kattesh V. Katti for their valuable time, nice patience, helpful suggestions and critical reviews of my thesis.

My appreciation especially goes to our lab's technician, Mr. Harold Huff, for his unique skills on equipment and irreplaceable contribution to this research.

My special thanks goes to Dr. Hongyu Fan, who guided me into the fantastic world of foams, and Ms. Carla Roberts, who offered me precious and practical advice on thesis writing.

My thanks also goes to my lab colleagues, Alif Razi, Chih-Ying Lin, Fei Cheng, and Yun Wang, for their helpful suggestions and contributions to this research.

My final appreciation goes to my parents: Yahui Lin and Haibin Xing, for their full trust, financial support, unconditional encouragement and the most significant love. This appreciation also goes to my dear beloved, Yuanyuan Xue.

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## ABSTRACT

Polyurethane foams have a wide variety of commercial applications in daily life due to their unique advantages. Traditionally, polyurethane foams are made from petroleum-based polyols and isocyanates. Due to the shortage of fossil resources, renewable biobased materials are studied as alternatives to petroleum. In this project, castor oil was chosen as a renewable biobased polyol in order to replace the nonrenewable petroleum-based polyols. Water-blown rigid foams were made from polyols with different levels of castor oil replacement. For foams without castor oil and with 25% castor oil replacement, the effects of water added content were studied. Another group of foams made from a castor oil/glycerol mixture were also prepared to investigate the effects of hydroxyl number. With the help of glycerol, rigid polyurethane foams with 80%-95% castor oil replacement were successfully prepared and showed competitive physical properties. Water-blown flexible foams were made from polyols using different levels of castor oil replacement. At the same time, the influence of cross-linker contents and isocyanate index on flexible foam was studied. Considering the low reaction rate of castor oil during the synthesis of polyurethane, a specific "heated mold" method was applied. Density, compression force deflection (CFD), 50% constant deflection compression (CDC), tear resistance (TR) and resilience were tested to identify the physical properties of flexible polyurethane foams. Results show that castor oil replacement often leads to a high cross-linking density. With 0.5% necessary cross-linker and low isocyanate index, flexible polyurethane

foams with 100% castor oil replacement showed a good recovery property and proved to be a suitable alternative to nonrenewable petroleum-based polyols.

# CHAPTER 1. INTRODUCTION

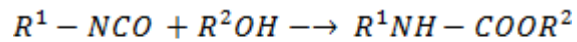
## 1.1 Background

Polyurethane is a kind of polymer formed by urethane linkage. It was first studied and developed by Dr. Otto Bayer and his colleagues in 1937. In the 1950s, with the introduction of blowing reaction, polyurethane foams were developed and soon became one of the most popular polymers.

As a widely applied material, polyurethane has many unique advantages. Due to different recipes and multiple production processes, the physical properties of polyurethane can be adjusted in a wide range. Due to the hardness, polyurethane products can be classified as flexible foams, semi-rigid foams, rigid foams, fibers, and hard plastics. Gas bubbles inside foams also give products more advantages such as low density, good heat insulation, excellent strength and weight ratio, and mechanical wave absorbing properties. Therefore, polyurethane foams can be easily found in both daily life and industry (Herrington and Hock, 1997). They are in shoes, packing materials, refrigerators, furniture, vehicles, water vessels, building materials , and even in the new iPad® Smart Covers.

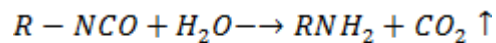
## 1.2 Chemistry

Basically, polyurethane is produced by the synthesis of polyols and isocyanates. A bond of urethane is formed when the isocyanate group reacts with the hydroxyl group as shown below (Herrington and Hock, 1997).

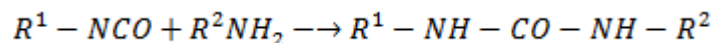


For polyols with two or more hydroxyl groups, the same reaction may repeat and thus form the polyurethane structure.

For water-blown polyurethane foams, due to the reactive –OH group in the molecule, water can also react with isocyanate and produce carbon dioxide. The blowing reaction in water-blown polyurethane preparation is shown as:



The product amine of blowing reaction can also react with isocyanate again to produce another urea linkage (Herrington and Hock, 1997).



## 1.3 Chemicals

Isocyanates and polyols are the two main parts of the chemical content in the synthesis of polyurethane foams. Blowing agents, catalysts, surfactant and other chemicals are also required to modify the processes and properties.

### 1.3.1 Isocyanates

Isocyanates are the most reactive components due to the “N=C=O” (NCO) groups in their chemistry structures and are usually kept separately as “A-side.” These NCO groups are the key to reactions within the hydroxyl groups in “B-sides” referred to the polyols. The major two types of isocyanates used to produce polyurethane are methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI).

Commercially, TDI contains two major isomers, which are 2,4-TDI and 2,6-TDI as shown in Figure 1.1. The raw material of TDI is toluene, a product of petroleum. Toluene reacts first with nitric acid to get two nitro groups in the position of 2,4 or 2,6. The next step is to transform the nitro groups into amino groups with the participation of hydrogen. The product of this step is called diaminomethylbenzene or diaminotoluene (TDA). The final step is to react TDA with phosgene ( $\text{COCl}_2$ ) to produce TDI and HCl (Six and Richter, 2000). TDI is very reactive but also volatile and dangerous. The permissible exposure limit (PEL) of TDI is 0.02 ppm ( $0.14 \text{ mg/m}^3$ ), according to the documents from the Occupational Safety and Health Administration (OSHA) in the United States. It is also defined as very toxic (T+) according to EU classification.

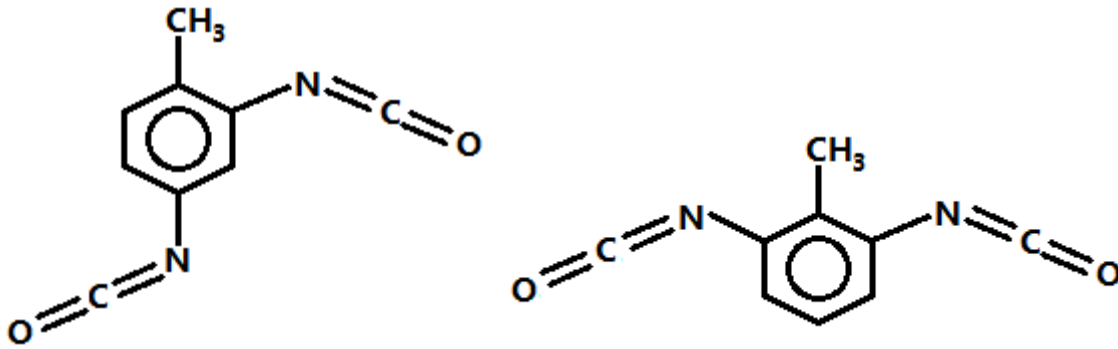


Figure 1.1 Chemical structures of TDI. (Left: 2,4-TDI; Right: 2,6-TDI)

The raw material of MDI is aniline. Before the amino groups are transformed into isocyanate, aniline first reacts with formaldehyde to produce diphenylmethane diamine. Then the diphenylmethane diamine is transformed into diisocyanate through a similar path as the production of TDI (Randall and Lee, 2003). Due to the structures of diamines, pure MDI mixture contains three major isomers: 4,4'-MDI, 2,4'-MDI, and 2,2'-MDI. During the distillation of the MDI, polymeric MDI can also be formed as a kind of polyisocyanate. Since the polymeric MDI mixture has lower vapor pressure and is less hazardous compared with other diisocyanates (such as TDI), polymeric MDI is more commonly used in the polyurethane industry.

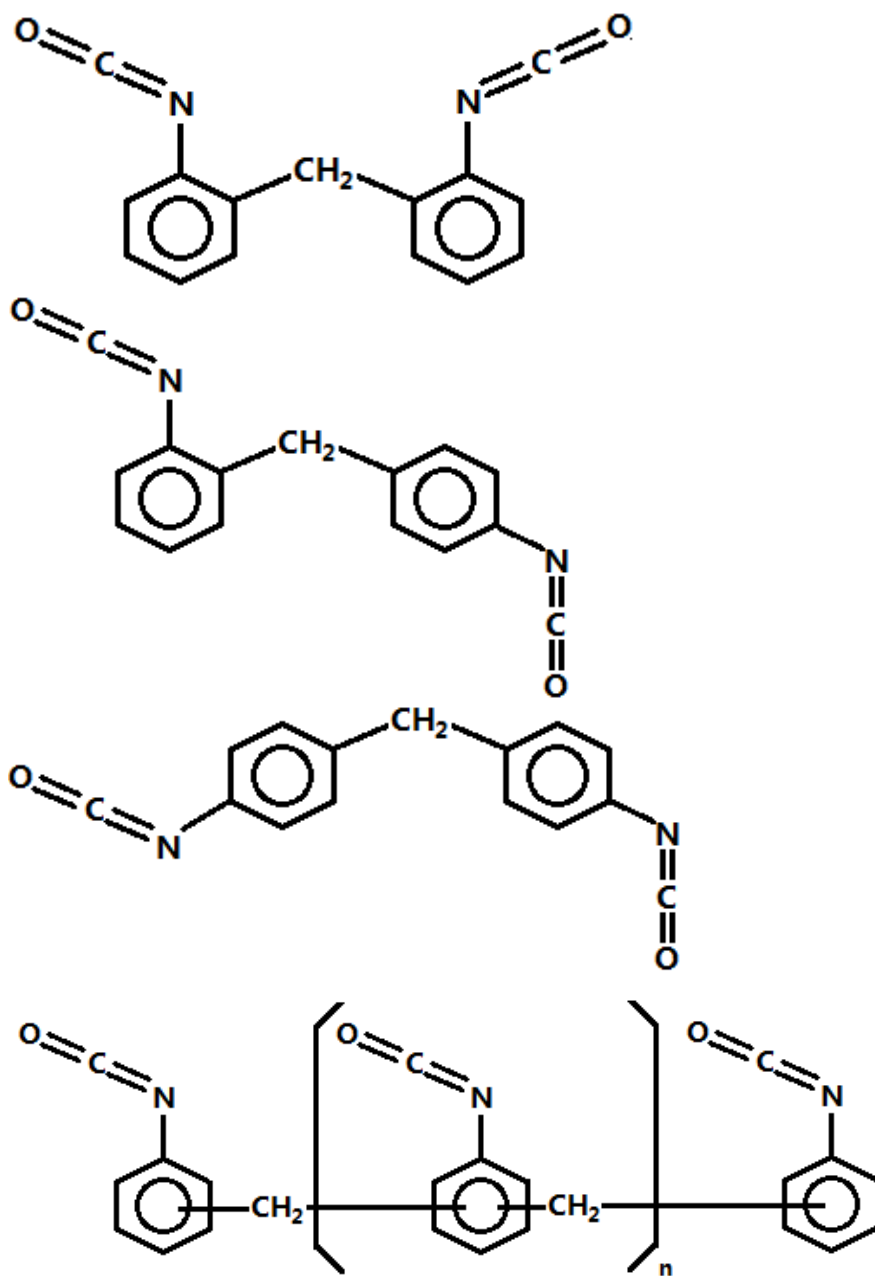


Figure 1.2 Chemical structures of MDI (from upper to lower: 2,2'-MDI; 2,4'-MDI; 4,4'-MDI; polymeric MDI)

Isocyanate index is a significant parameter that affects the properties of polyurethane foams directly. It is usually defined as the actual amount of isocyanate consumed relative to the amount that is theoretically required. Usually

higher isocyanate index leads to more hardness. For rigid polyurethane foams, the isocyanate index is usually over 100. But there is still a limitation to the isocyanate index over which the stiffness of foams can hardly increase; Herrington and Hock (1997) claimed that value should be 140. To produce flexible polyurethane foams, the isocyanate index is usually less than 100 (Klempner and Senijarevic 2004).

### 1.3.2 Polyols

In polymer chemistry, polyols are usually defined as compounds containing multiple hydroxyl groups. Hydroxyl groups are the functional groups that react with isocyanate to produce polyurethane. Functionality of a polyol is defined by the number of reactive hydroxyl groups on a single polyol molecule. Equivalent weight is based on the molecular weight of the polyol and its functionality as follows (Herrington and Hock, 1997):

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{Functionality}} \quad \text{Eq. 1.1}$$

The hydroxyl number is also a parameter to characterize a polyol. It is defined as the equivalent amount in milligrams of KOH per gram of the polyol (mg KOH/g). Hydroxyl number can be tested through the methods according to ASTM Designation E222-10 and the relation of the hydroxyl number and the equivalent weight of the same polyol can be described as follows:



$$\text{Hydroxyl Number (mg KOH/g)} = \frac{56100}{\text{Equivalent weight}} \quad \text{Eq. 1.2}$$

Besides the –OH amount of a polyol, the types of hydroxyl groups are also very important. According to Herrington and Hock (1997), primary hydroxyl groups are very reactive in the synthesis of polyurethane and almost 3.3 times faster than secondary hydroxyl groups in polyurethane reaction rate, while the tertiary hydroxyl groups can hardly react with isocyanate. Most of the petroleum-based polyols such as polyester polyols and polyether polyols contain primary hydroxyl groups. But most of the biobased polyols have only secondary hydroxyl groups.

### 1.3.3 Blowing agents

Blowing agents are another significant content of product polyurethane foams, which can produce gas bubble inside the structure. Water is a widely used blowing agent because it costs little and it is environmental friendly. The carbon dioxide produced from water is also nontoxic and can contribute to the improvement of many properties such as density and thermal conductivity.

Besides water, there are also other types of blowing agents, such as chlorofluorocarbons, which are liquid in standard state and then vaporize after absorbing enough heat produced from the synthesis of polyurethane. However, since chlorofluorocarbons are considered a major cause of stratospheric ozone

depletion (Drake, 1995), the application and production of chlorofluorocarbons have been strictly limited.

#### **1.3.4 Other chemicals**

Catalysts, mainly including gelling catalysts and blowing catalysts, are vital to the foaming reaction. The ratio between the gelling catalysts and blowing catalysts directly affects the chemical balance needed to form a stable foam structure.

Surfactant is also needed in the system, which plays two important roles: 1) A surfactant can help mix the raw chemicals uniformly, and 2) a surfactant can help control the size of gas bubbles in the foam and adjust the status of these gas cells. For rigid foams, the surfactant is selected to strengthen the cell walls and protect the cells from breaking, which is beneficial to secure a low thermal conductivity. For flexible foams, which is just the opposite, the surfactant is designed to break the cell by dissolving the urea in silicone oil.

To reduce the consumption of petroleum resources, researchers have been experimenting with renewable biobased materials to replace petro-based chemicals since Rheineck and others started making urethane coatings from biobased aldehyde oils (1969). Since isocyanates and polyols are two main components of the polyurethane synthesis system, biobased isocyanates and polyols have been widely studied and developed.

## 1.4 Biobased content replacement

### 1.4.1 Biobased polyols

Many biobased products, such as animal fat or vegetable oil, have fatty acid glyceride. Most of the fatty acids have or have the potential to add/replace at least 1 hydroxyl group on its carbon chain. This means biobased triglyceride can be considered as a wonderful alternative to replace the current petroleum-based polyols.

#### 1.4.1.1 Castor oil

Castor oil is a renewable bio-based resource. The hydroxyl group on the 12th carbon atom of ricinoleic acid, the main fatty acid in castor oil, reacts with isocyanates to form a crosslinking structure (Figure 1.3). Therefore, it is possible for castor oil to form polyurethane without any pretreatment.

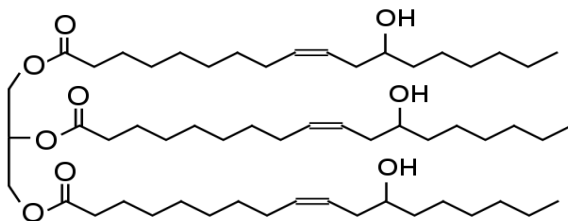


Figure 1.3 Structure of ricinoleic triglyceride

Long fatty chains on the ricinoleic acid make castor oil fit for preparing flexible polyurethane foams, which is supported by Beneš and others (2012).

However, castor oil cannot be used in rigid polyurethane foams. With the help of the cross-linker, a small molecule with three or more hydroxyl groups, foams can be modified with properties near to the control (Veronese, 2012). Also, Ristić and others (2012) tried to introduce Ti nanoparticles into the system and found that these novel castor-oil-based polyurethane foams have excellent damping properties, which have the potential to create a new type of vehicle body that can lessen damage on impact during accidents.

#### **1.4.1.2 Soybean oil**

Soybean oil does not have any natural hydroxyl group on its structure. However, it contains many functional or active groups, including double bonds, allylic compounds, and ester groups. These help to introduce the hydroxyl groups through chemical methods. Through using organic peroxy acid, the double bonds on the triglyceride can be epoxidized and the epoxy groups can then be transformed into a hydroxyl group that react with organic acid (Casper and Newbold, 2006). Lubguban and others in Dr. Suppes' lab from the University of Missouri-Columbia developed a novel polyol called soy-phosphate polyol (2009). Fully epoxidized soy-bean oil is prepared and phosphoric acid is added to decompose and then recollect the polyols. Soy-bean-based polyols can now replace as much as 50% of petroleum-based polyols in rigid polyurethane foams without obvious property changes (Tu and others, 2008).

### **1.4.1.3 Other biobased polyols**

There are also other research groups focusing on many other biobased polyols. Due to the multiple hydroxyl groups on starch molecules, corn stover can also be prepared as liquid polyols after microwave and heat treatment (Wu. and others, 2009). Fish-oil-based polyols also have the potential to make rigid polyurethane foam, which perform well in compressive strength. Molasses, a by-product from the sugar industry, can also take part in polyols and adjust the properties of polyurethane foams together with castor oil (Hatakeyama and others, 2012). In a word, almost all biobased triglyceride and starch products have the potential to prepare polyols for synthesis polyurethane. But researchers still need to consider the cost of raw material and pretreatment, and also the effect of the replacement.

### **1.4.2 Biobased isocyanates**

Isocyanates are very active chemicals, which cannot be easily found or collected directly from biological products. Chemical methods are used to add Br on the double bond of oil and then AgNCO are introduced to the triglycerides with Br replacing the functional groups to produce biobased isocyanates. Although AgNCO is costly, the byproduct, AgBr, can be easily recycled to reproduce AgNCO again. (Çayli and Küsefoğlu, 2008)

According to the literature above, both isocyanates and polyols can be prepared by biobased materials, theoretically making it possible to produce polyurethane with both biobased polyols and renewable isocyanates. However, products with almost totally biobased content do not have the mechanical

properties needed to perform well. In this study, raw castor oil was applied to synthesize both flexible and rigid polyurethane foams. Their physical and thermal properties were also tested and studied. Many foam samples produced in this research contained nearly 100% biobased polyols, which is a new product not previously considered possible in previous research.

## **CHAPTER 2. LITERATURE REVIEW**

### **2.1 Introduction of castor oil**

Castor oil is a kind of plant seed oil refined or pressed from the seed of castor plant. Castor plant exists widely and mostly in tropical regions, such as Southern Asia, South America and Africa (Phillips and Rix, 2002). The seed of castor plant is useful but toxic. The main toxin in castor seed is ricin, a toxic protein which can be effectively denatured and inactivated when the temperature is over 80 centigrade degrees (Audi and others, 2005).

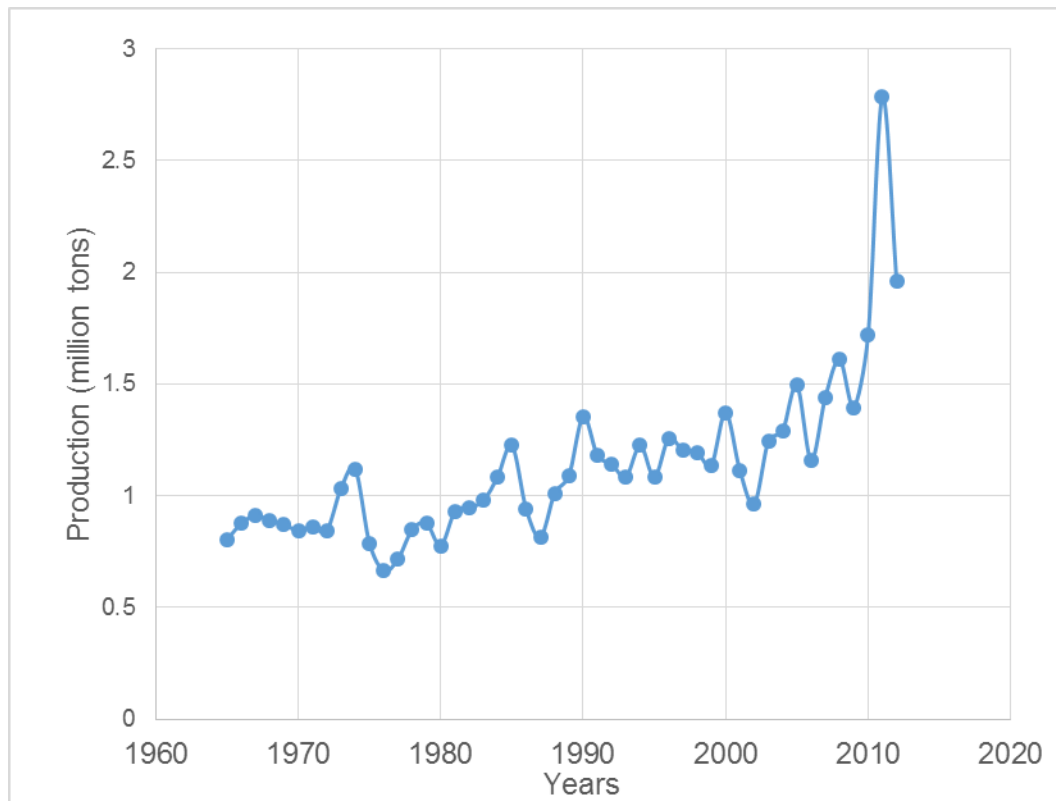


Figure 2.1 The annual worldwide production of castor oil seeds from 1965 to 2012 according to faostat.fao.org.



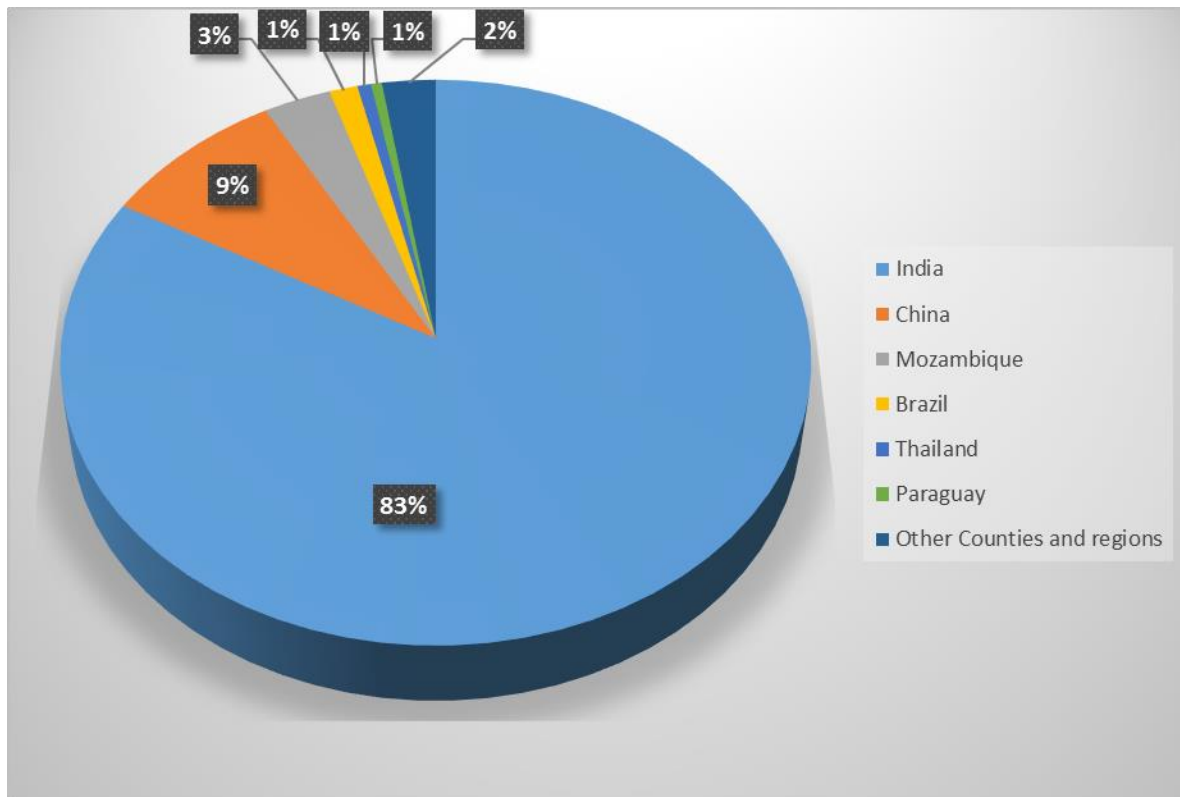


Figure 2.2 The production of castor oil seeds among major countries in 2012 according to faostat.fao.org.

Castor oil is a biological based oil refined from the castor oil seeds. It is a light yellow liquid with a unique smell. Its density is 961 kg/m<sup>3</sup>. The boiling point of castor oil is 313°C, and its melting point is between -10 to -18°C (according to National Institute for Occupational Safety and Health). The chemical formulation of castor oil is a triglyceride containing three fatty acids and 90% of its fatty acids are ricinoleic acid, a hydroxyl fatty acid with a hydroxyl group on its 12th carbon atom. Therefore, castor oil is highly valued in industry processing.

## **2.2 Uses of castor oil**

Castor oil is commonly used in the food processing, medicine, fuels and chemical industry.

### **2.2.1 Uses of castor oil in food processing**

Although castor oil seed contains toxic ricin proteins, food-grade castor oil is still available due to the development of methods to detoxify castor seed. The half-life of ricin at 80 °C is 9 minutes (Wang, 2010). So heating or steaming is very effective to detoxify ricin.

Food-grade castor oil is commonly applied as food additives. In South Asia, castor oil is directly used to coat on grains, such as rice and wheat, to keep them from rotting (Gana and others, 2013). Another successful example is the use of polyglycerol polyricinoleate (PGPR). PGPR is prepared through the esterification of ricinoleic acids with polyglycerol. It is a good water-in-oil emulsifying agent, and it proved to be safely edible when used in tin-greasing emulsions and in chocolate couverture. (Wilson R and others, 1998) In addition, castor cake, the byproduct of castor oil extraction, is also widely used as cattle feed after fully steamed (Ogunniyi, 2005).



Figure 2.3 The derivative of castor oil (PGPR) applied in candy bars.

## 2.2.2 Uses of castor oil in medicine

According to the United States Food and Drug Administration (FDA), castor oil is generally recognized as safe and effective (GRASE) as a stimulant laxative. When in the small intestine, castor oil can be digested into ricinoleic acid and stimulate the small intestine. Castor oil is also used for external application as a skin protectant or wart remover (FDA OTC Ingredient List, 2006).

Castor oil is used to produce polyethoxylated castor oil, which is also known as Kolliphor EL or Cremophor EL. Kolliphor EL is a nonionic surfactant commonly applied in both liquid drugs and capsules (Zhang and others, 2001).

## 2.2.3 Castor oil as a biodiesel

Castor oil contains medium length (C18) fatty acids and is possible to be regarded as a biodiesel. Compared with other vegetable oil, castor oil can show a distinguish cold flow property. The 10% castor methyl ester blend with petro diesel can achieve all the standard limits in ASTM D6751 and D7467, while

100% castor methyl esters failed only two of the properties (Berman and others, 2011), which shows a considerable potential as alternative fuel.

## **2.3 Uses of castor oil in chemical industry**

Castor oil has multiple applications in chemical industry, such as soap manufactory, lubrication, paints, adhesives, inks, nylon, and many other useful derivatives.

### **2.3.1 Castor oil for cosmetics**

As a non-comedogenic bio-based oil, castor oil is a most vital ingredient in cosmetics. For soap manufactory, castor oil can be a wonderful bubble booster. Due to the unique hydroxyl group on ricinoleic acid, castor oil can also act as a humectant in soaps, washing powders, shampoos, and hair waxes. Cosmetics with castor oil can provide a special silky, but not oily feel on skin or hair. (Nagaraj, 2009)

One of the distinguished castor oil product is known as Turkey red oil. Turkey red oil is actually sulfated castor oil, which is prepared from castor oil and concentrated sulfuric acid. The product is then neutralized with sodium hydroxide solution. Sulfated castor oil is a powerful moistening agent and helps pigments and dyes. Therefore, turkey red oil is often used in hair coloring. (Ogunniyi, 2005)

### **2.3.2 Castor oil for lubrication**

Castor oil has not only a wonderful cold flow property, but also high temperature lubrication. At 10°C, the viscosity of castor oil is 2420 centipoise. (Brady G and others, 1986) Some lubricants companies, such as Castrol, developed castor oil as an attractive vegetable-based alternative to petroleum-

based lubricants in jet, diesel, and race car engines. Unlike ordinary chemical oils, castor oil will not dissolve natural rubbers. Thus, castor oil is also considered as a wonderful lubricant for bicycle (Older, 2000).

### **2.3.3 Castor oil for inks, paints, and adhesives**

As a fatty alcohol, castor oil has specific pigment-wetting properties and is a significant component in printing or duplicating inks (Abraham T, 2012). For paints and adhesives, castor oil and ricinoleate are also used to adjust the viscosity. In non-polar solvent, the long carbon chains in castor oil will wind each other to form thixotropic structures and contribute to a higher viscosity, which prevents dyes from precipitating. When shear force happens, thixotropic structures are unwound to offer less viscosity, which helps dyes disperse uniformly. (Shareef and others, 1985)

Castor oil is non-drying liquid. However, dehydrated castor oil is commonly used in semi-drying or drying paints and adhesives. By removing the hydroxyl group on the ricinoleic acid, dehydrated castor oil contains conjugated double bonds. Therefore, dehydrated castor oil is converted into a drying oil (Ogunniyi, 2005).

### **2.3.4 Undecylenic acid, nylons, and other derivatives of castor oil**

Undecylenic acid is prepared through the pyrolysis of ricinoleate (Ereaux and Craig, 1949). According to FDA, undecylenic acid is approved to use for skin infections (FDA OTC Ingredient List, 2006). It is also a wonderful antifungal

ingredient for skin care product. In addition, some perfume contains undecylenic acid as well (Kula J and others, 1994).

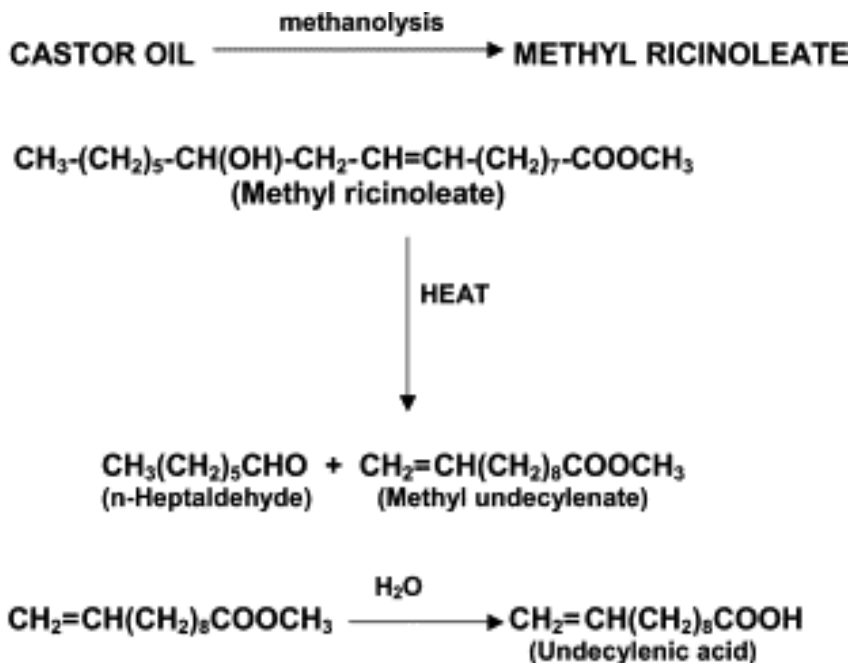


Figure 2.4 Production of undecylenic acid from castor oil (Ogunniyi, 2005)

Sebacic acid is another pyrolysis product of castor oil. It can be applied in plasticizers and lubricants. Plastic made from sebacic acid is approved with good thermo stability and low toxic. (Daintith, 2008)

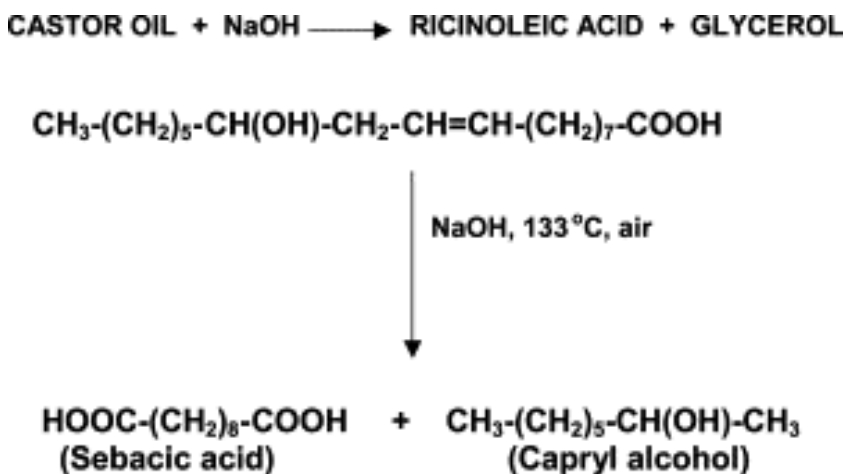


Figure 2.5 Production of sebacic acid from castor oil (Ogunniyi, 2005)

Sebacic acid and undecylenic acid are the raw material for making nylon-11. (Kovaly K, 1982) Nylon-11 is a castor-oil-based polyamide with good molding properties and resilient. It is widely applied as flexible fiber, powder coating, and engineering plastic. (Nagaraj, 2009)



## **2.4 Uses of castor oil in polyurethane**

Castor oil is a triglyceride with multiple hydroxyl groups. Such a structure enables castor oil to make polyurethane through the reaction with isocyanate. Castor-oil-based polyurethane have been widely researched to produce plastics, elastomers, nanoparticles, and foams.

### **2.4.1 Interpenetrating polymer network with castor-oil-based polyurethane**

Yenwo and others (1977) were the first to set up interpenetrating polymer network with castor-oil-based polyurethane and polystyrene. Devia and others (1979) developed the similar systems and produced tougher plastics, and elastomers. The elastomers can be extended to 125% at maximum. Later, Kumar V and others (1987) found out a marginal increase in tensile strength and crosslink density from pure castor oil polyurethane to 60% polyurethane with 40% polystyrene. Further studies indicated the effects of polyurethane and polystyrene in tensile modulus (Siddaramaiah and others, 2003), percentage elongation (Bai and others, 1997), and other morphological and mechanical properties (Suthar and others, 1994; Siddaramaiah and others, 2003).

Besides polystyrene, researchers also developed polyurethane interpenetrating polymer network with other polymers, such as polymethacrylate (Patel and Suthar, 1989), polyethyl-methacrylate (Patel and Suthar, 1990), and acrylonitrile (Xie and Guo, 2002). Especially, Guo and others (2011) have successfully introduced the *Eucalyptus globulus* cellulose nanocrystals into waterborne polyurethane based on castor oil/polyethylene glycol, which shows

promising potential of interpenetrating polymer network containing castor oil replacement.

#### **2.4.2 Polyurethane nanoparticles based on castor oil**

In recent years, polyurethane nanoparticles were widely developed and studied because of their good stability, biocompatibility, and mechanical properties (Page and others, 2012). So they are suitable for drug coating and delivery. Since Cremophor, the hydrogenated castor oil, has been commonly applied in medicine, it becomes an ideal material to form polyurethane nanoparticles. Morral-Ruiz's research (2014) indicated polyurethane network can help minimize the risk of acute hypersensitivity reactions and improve the biocompatibility of some drugs. Also, castor-oil based polyurethane can be applied on tissue engineering without a strong inflammatory reaction (Laschke, 2009).

#### **2.4.3 Polyurethane foams based on castor oil**

The functionality of raw castor oil is 2.7, thus, castor oil is commonly applied to produce rigid polyurethane foams. Lyon, Garrett and Frankel have already developed rigid urethane foams from hydroxymethylated castor oil with large amount (20–65%) of crosslinkers to strengthen the structure and prevent foams from shrinking (1974). The thermal properties of rigid polyurethane foams containing castor oil have been tested in roof systems (Cardoso and others, 2008). Recently, Zhang and others (2013) have developed epoxidized glycerolysis castor oil based flame-retardant polyols and introduced them into

rigid polyurethane foams. Such foams showed a high close-cell content and appear to be promising.

However, compared to rigid foams, castor-oil-based flexible polyurethane foams are much less studied. Directly using castor oil for flexible polyurethane foams leads to a low resiliency and a temperature dependent modulus (Nozawa and others, 2005). For flexible foam polyols, the range of two hydroxyl groups in castor oil is too short. Still, flexible polyurethane foams is a main part in polyurethane production (Zhang and others, 2007). Therefore, the study of castor-oil-based flexible polyurethane foams is meaningful.

## **2.5 Limitations of existing literature**

Castor oil is a natural polyol which can be directly used in polyurethane foaming. Many researchers have developed their castor-oil-based polyurethane products in order to select a biological resource as an alternative to petroleum. In most of the research, they used multiple petroleum-based chemicals to modify castor oil, and some of those treatments were not environmental friendly. In this study, raw castor oil was chosen as the only bio-based polyol to investigate its influence on both rigid and flexible polyurethane foams. Besides, other critical factors, such as average hydroxyl number, water content, and isocyanate index, were also adjusted to study their effects on physical and thermal properties of foams containing castor oil.

## CHAPTER 3. WATER-BLOWN RIGID POLYURETHANE FOAMS WITH CASTOR OIL REPLACEMENT

### 3.1 Background

Rigid polyurethane foams are very widely used in both industry and daily life due to their unique advantages which include low density and good heat insulation as well as excellent strength and weight ratio. Therefore, thermal insulation foam and structural foam are two of the main applications of polyurethane rigid foams.

The two main raw materials of polyurethane, polyol and isocyanate, are usually prepared from petroleum resources. Considering non-renewability of petroleum, researchers are studying bio-based resources such as corn stover and vegetable-based oils as alternatives for polyols. As one of the few vegetable resources which contain natural hydroxyl groups, castor oil can be directly applied to form polyurethane without any chemical modification . Narine and others (2007) produced polyurethane foams with different seed oils, and their results showed foams made with castor oil had the highest compressive strength over those foams made with soybean oil or canola seed oil.

Castor oil is a triglyceride containing three fatty acids and 90% of its fatty acids are ricinoleic acid, which has a hydroxyl group on the 12th carbon atom. Therefore, castor oil could be considered as a natural polyol with a functionality of 2.7 ( $= 0.9 \times 3$ ) and be used to prepare rigid polyurethane foams. The long fatty acid chains in castor oil, however, reduce the density of the hydroxyl group, and

also limit the degree of cross-linkage in polyurethane foams. Considering the application of the rigid polyurethane foams, more cross-linkages per volume are preferred to form a firmer and more stable structure (Seo and others, 2004), and also to trap the thermal-insulation gas more effectively (Klempner and Frisch, 1991).

Due to the active  $-OH$  group in the water molecule, it can react with isocyanate and produce carbon dioxide. So water can be used as the blowing agent making this isocyanate/castor oil/water combination a water-blown polyurethane system. The thermal conductivity of carbon dioxide is very low ( $0.0146 \text{ W/(m.K)}$ ), almost 50% lower than air ( $0.024 \text{ W/(m.K)}$ ). Therefore, water content can affect the thermal conductivity of the rigid foam product. Also, gas from the blowing agent will influence the shapes of the cells and the size of the whole foam (Tu, 2008 and Fan, 2011); hence, the blowing agent content also contributes to the density and some mechanical properties.

The aim of this study was to investigate the potential of castor oil to replace petroleum-based polyols in rigid polyurethane foams and study the effect of the blowing agent (water) in rigid foams containing castor oil.

## 3.2 Materials and methods

### 3.2.1 Raw materials

Raw materials of polyurethane foams are usually divided into two sides: A-side (referring to isocyanate) and B-side (referring to the polyol). In this research, PAPI® 27 from Dow Chemical Co. (Midland, MI) was used as the isocyanate in the A-side. VORANOL® 490 was used as the petroleum-based polyether polyol, which was also obtained from Dow Chemical Co. (Midland, MI). Castor oil was the bio-based polyol and it was obtained from Alnor Oil Company, Inc (Valley Stream, NY). Glycerol was obtained from Fisher Scientific (Fair Lawn, NJ). Distilled water was used as the blowing agent. Table 3.1 lists the properties of these chemicals.

Table 3.1 Properties of Raw Materials.

Raw Materials	Water Content	Average Molecular Weight	Functionality	Hydroxyl Number	Equivalent Weight
Castor oil	0	900	2.7	168	333.93
Voranol 490®	0.007	460	4.3	485	115.72
Glycerol	0	92.09	3	1828	30.7
Water	-	18.02	2	6233	9.01
Isocyanate	0	340	2.7	-	134

POLYCAT® 5 and POLYCAT® 8 were used as the blowing catalyst and gelling catalyst respectively. DABCO® DC-5357 was chosen as the surfactant. POLYCAT® 5, POLYCAT® 8, and DABCO® DC-5357 were obtained from Air Products & Chemicals (Allentown, PA).

### **3.2.2 Experimental design and foaming formulations**

There were two main parts in this study. Firstly, the influence of castor oil replacement (0, 25, 50 and 75%) was tested at a fixed water content of 3%. In addition, another group of foams made from castor oil and glycerol mixtures (80:20, 85:15, 90:10, and 95:5) were also prepared to investigate the effects of hydroxyl number. Secondly, according to the results from the first part, rigid foams with 25% castor oil replacement were chosen and the effect of blowing agent was investigated at different water contents (2, 3, 4 and 5%). Foams without castor oil replacement were also tested as controls at the same level of water content.

The isocyanate index for all rigid foams was fixed at 110%. Tables 3.2, 3.3, and 3.4 list the recipes of each test.



Table 3.2 Foaming formulation of rigid polyurethane foams with different castor oil replacement percentages.

Ingredients		Parts by Weight of Total Polyol			
		Control Foams	Castor Oil Foams		
B-side	VORANOL® 490	100	75	50	25
	Castor Oil	0	25	50	75
	Distilled Water	3.0	3.0		
	POLYCAT® 5	1.26	1.26		
	POLYCAT® 8	0.84	0.84		
	DABCO® DC-5357	2.5	2.5		
A-side	PAPI® 27 Index =110	176.6	155.8	134.9	114.1

Table 3.3 Foaming formulation of rigid polyurethane foams with different water content percentages.

Ingredients		Parts by Weight of Total Polyol							
		Control Foams				Castor Oil Foams			
B-side	VORANOL® 490	100				75			
	Castor Oil	0				25			
	Distilled Water	2.0	3.0	4.0	5.0	2.0	3.0	4.0	5.0
	POLYCAT® 5	1.26				1.26			
	POLYCAT® 8	0.84				0.84			
	DABCO® DC-5357	2.5				2.5			
A-side	PAPI® 27 Index =110	160.2	176.6	193.0	209.4	139.4	155.8	172.2	188.5

Table 3.4 Foaming formulation of castor-oil-based rigid polyurethane foams with different glycerol contents.

Ingredients		Parts by Weight of Total Polyol			
B-side	Glycerol	5	10	15	20
	Castor Oil	95	90	85	80
	Distilled Water	3.0			
	POLYCAT® 5	1.26			
	POLYCAT® 8	0.84			
	DABCO® DC-5357	2.5			
A-side	PAPI® 27 Index =110	115.1	136.9	158.7	180.5

### 3.2.3 Foam preparation

For B-side, both petroleum-based polyol (Voranol® 490), glycerol, and castor oil were weighed and mixed in a plastic container. Distilled water and two catalysts (POLYCAT® 5 & 8) followed. Finally, after surfactant (DABCO® DC-5357) was weighed and added, the mixture was taken to the electric mixer and mixed at 3450 rpm for 40 s. Then the mixture was set at quiescence and degased for 2 min. For A-side, the isocyanate was weighed in another plastic container. After adding to the B-side container, the whole mixture was mixed at 3450 rpm for 10 s. Then the mixture was put into a wooden mold covered with aluminum foil at once. The size of the mold was 11.4 × 11.4 × 21.6 cm. The reacting mixture in the mold grew freely and the foam would conform to the mold's shape in one to three minutes.

After foaming, the foams were cured at ambient conditions (around 298 K) for seven days, while their thermal conductivity was tested within 24 to 48 hours.

Figure 3.1 shows the procedures of the molded polyurethane foam's preparation in lab scale.

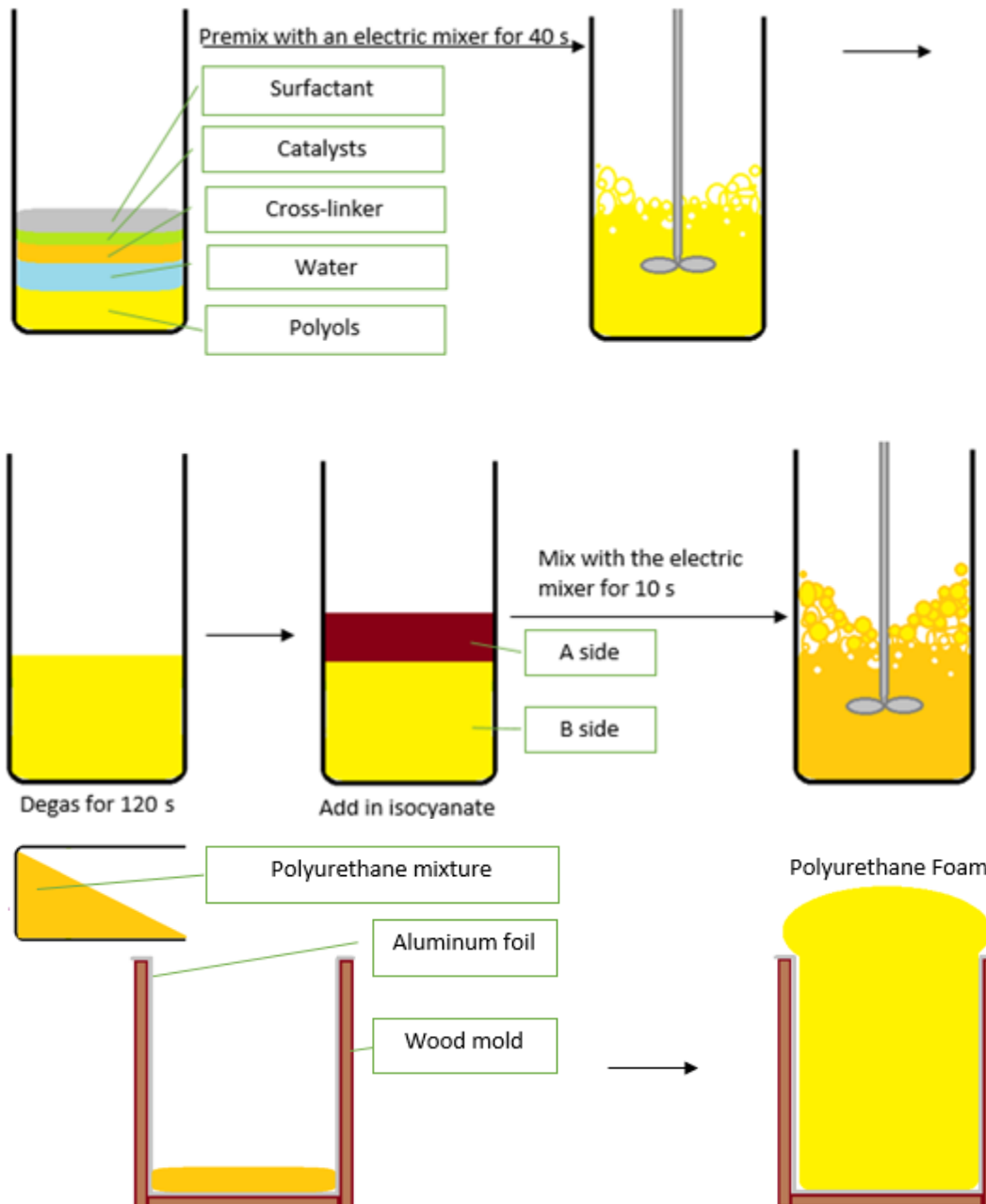


Figure 3.1 Procedures to make polyurethane foams.

### **3.2.4 Foam property measurements**

Thermal conductivity of foams were determined according to ASTM Designation C518–10 with modifications. Each foam sample was cut into 4 pieces (10.2 × 10.2 × 3.8 cm) within 24-48 h after foaming. They were assembled together to give a total size of 20.3 × 20.3 × 3.8 cm and tested using a Fox 200 heat flow meter instrument (LaserComp, Wakefield, MA).

For foam density, samples were cut to the size of 6.4 × 6.4 × 3.8 cm 7 days after preparation. Density was calculated by dividing sample mass by sample volume. There were four replicates from each treatment. The mean value was reported.

Compressive strength was determined after the density test using the same samples following ASTM Designation D1621–10 with modifications. A TA.HDi Texture Analyzer (Texture Technologies Corp., Scarsdale, NY) with XTRA Dimension software was used. The value obtained was shown as force. Compressive strength was then calculated as the force divided by the area of compression surface.

### 3.3 Results and discussion

#### 3.3.1 Influence of castor oil replacement

##### 3.3.1.1 Density

Density is a basic property of polyurethane foams. Usually a low density is preferred for saving ingredients.. Figure 3.2 illustrates the result of densities of foams with different levels of castor oil replacement.

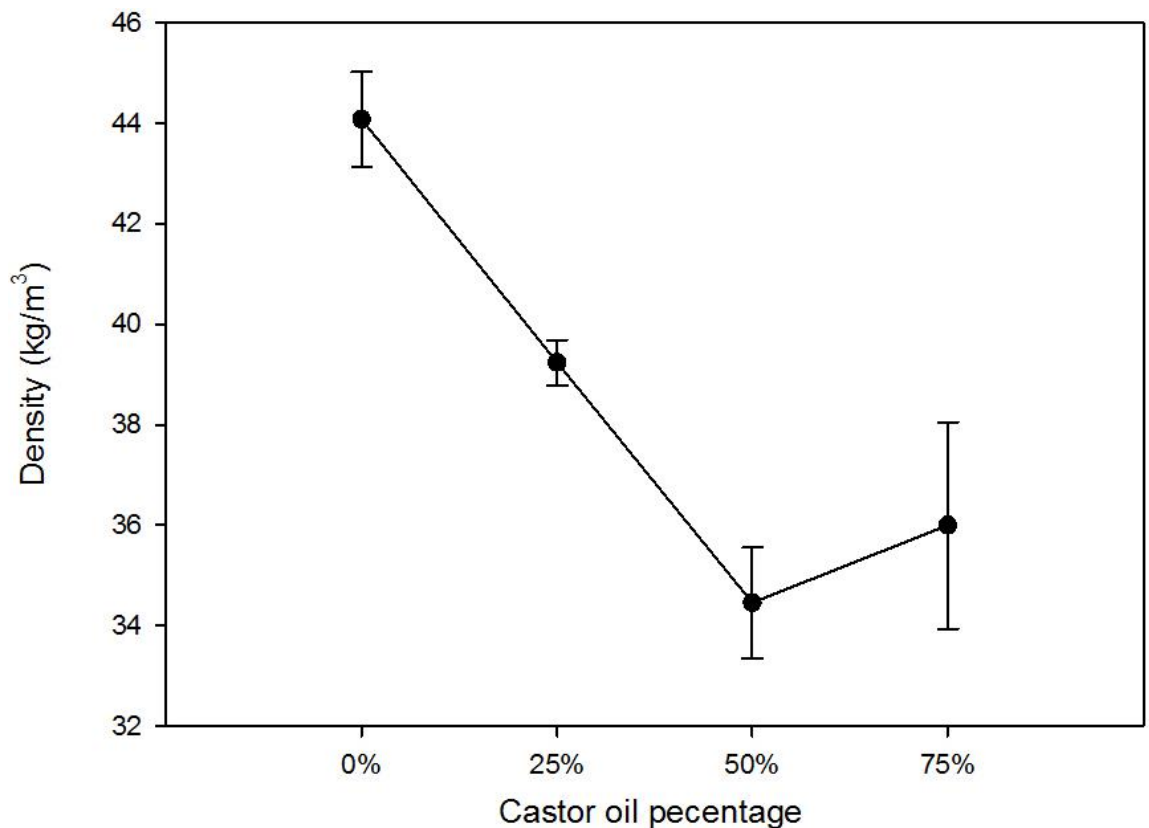


Figure 3.2 Effect of castor oil replacement on density of rigid polyurethane foams.

The density of the rigid foams decreased with the increase of castor oil replacement from 0 to 50%. This is mainly because of the molecular structure of the castor oil. One of the most significant characteristics of polyols is their hydroxyl number. It directly influences the equivalent weight and the amount of

the isocyanate for reaction. The hydroxyl number of castor oil (168) is much lower than that of VORANOL<sup>®</sup> 490 (490). Due to the lower hydroxyl number, castor oil requires less isocyanate. So the mass of the foam decreases with the increase of castor oil. Because the blowing agent was fixed at 3% and the isocyanate index was fixed at 110, which means there should be enough isocyanate to react with both polyols and blowing agent, the amount of carbon dioxide produced was similar among the foams with castor oil percentage from 0 to 50%. Because the CO<sub>2</sub> gas volume was the main factor of the foam volume, these foams had a similar volume. A linear relationship can be found between the density ( $y$  in kg/m<sup>3</sup>) and the castor oil percentage ( $x$ ) as shown by:

$$y = -19.25x + 44.071 \quad \text{Eq. 3.1}$$

However, the density of foam with 75% castor oil replacement was higher than that of foam containing 50% castor oil. This may have been due to the breakdown of the structure. A sample with 75% castor oil replacement and 3% blowing agent content challenged the foam's cross-linking structure and the cell walls inside the foams with 75% castor oil replacement were too fragile to maintain a volume as big as those of foams with 50% or less castor oil replacement. The reduction in volume with 75% castor oil replacement could be clearly observed during foaming.

### **3.3.1.2 Compressive strength**

Compressive strength reflects the hardness and compression behavior of rigid polyurethane foams. Rigid foams with higher compressive strength and

lower density are usually preferred. The compressive strength results of foams with different castor oil replacement are shown in Figure 3.3.

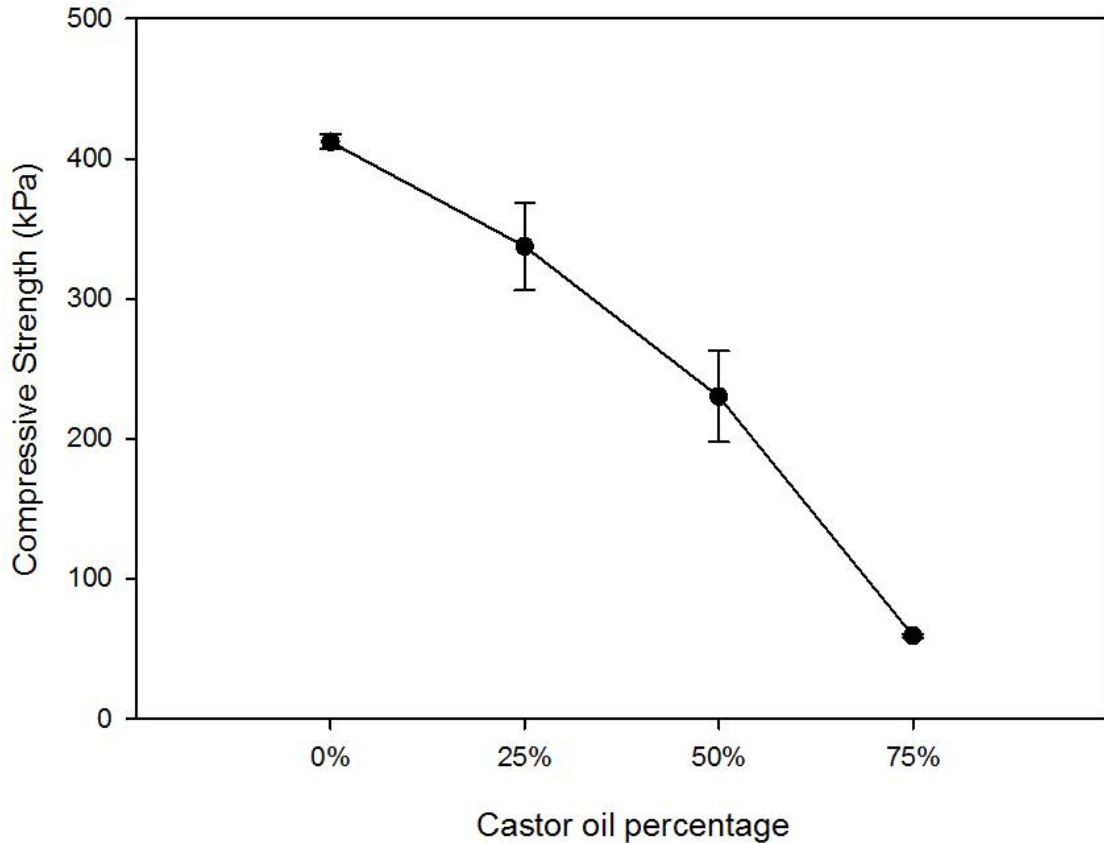


Figure 3.3 Effect of castor oil replacement on compressive strength of rigid polyurethane foams.

The compressive strength of foams decreased with an increased castor oil percentage. The rate of the decrease was higher at larger castor oil percentages. This may be due to the density of foam and the inner structure, especially cross-linkage in the foam. The density of foam decreased as shown in Figure 3.2 when the castor oil replacement increased, except for the foam with 75% castor oil. Due to the lower hydroxyl value of castor oil, when more castor oil was used, less isocyanate was involved in the gelling reaction, which led to the reduction of



cross-linkage in the foam. For rigid foams, a higher cross-linking degree was necessary to keep the strength of the structure. Therefore foams with 75% castor oil replacement in the test were too fragile to satisfy the hardness requirement.

### **3.3.1.3 Thermal conductivity**

Thermal conductivity is one of the most vital properties for rigid polyurethane foams. Higher thermal conductivity means the material can conduct heat more easily. Rigid polyurethane foams are often used for heat insulation. Therefore lower thermal conductivity is preferred. The result of thermal conductivity of foams with different castor oil replacement levels is shown in Figure 3.4.

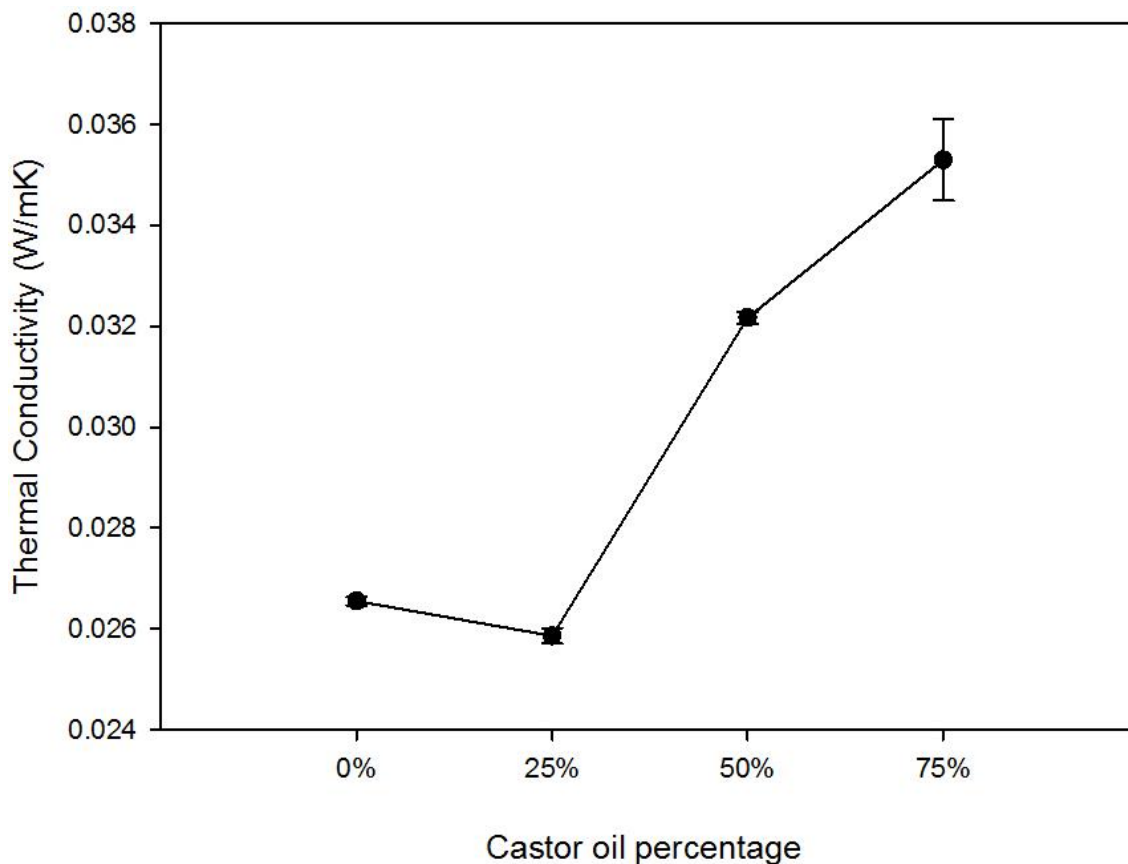


Figure 3.4 Effect of castor oil replacement on thermal conductivity of rigid polyurethane foams.

When the castor oil replacement was lower than 25%, the thermal conductivity remained at a lower level. When it was higher than 25%, the thermal conductivity rose rapidly. Thermal conductivity depends on the inner structure of the foams and the amount of carbon dioxide inside the foam.

According to its chemical structure, all hydroxyl groups in the castor oil triglyceride structure are secondary, while most of the hydroxyl groups in VORANOL® 490 are primary. Because the gelling reaction in polyurethane preparation is a nucleophilic addition, primary hydroxyl groups, as nucleophile,

are more active than secondary hydroxyl groups due to the steric effects. Thus the gelling reaction would be slower when the castor oil percentage was higher. Considering the speed of the blowing reaction, slower gelling reaction led to a weaker inner structure that cannot burden the pressure of the gas generated from the blowing reaction, which increased the thermal conductivity of foams.

The carbon dioxide in foams contributes a lot to the decrease of thermal conductivity. At 25% castor oil replacement, the structure of PU foams was not obviously affected and the thermal conductivity remained low. However, when castor oil replacement was over 50%, the density of cross-linkage in the foams became too low to maintain the structure. When the structure traps less carbon dioxide, more CO<sub>2</sub> escaped from the foam and increased the thermal conductivity.

### 3.3.2 Influence of blowing agent content

#### 3.3.2.1 Density

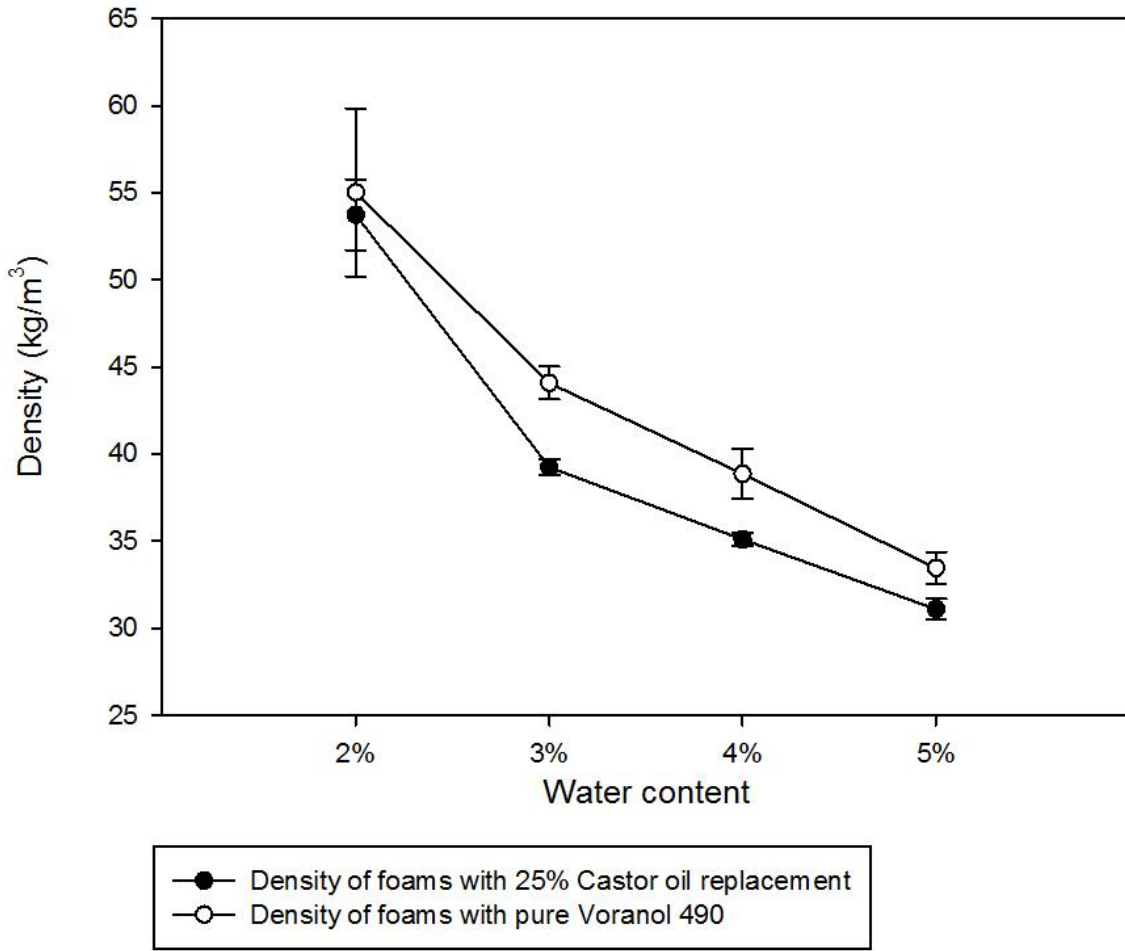


Figure 3.5 Effect of castor oil replacement on density of rigid polyurethane foams with different water content.

As shown in Figure 3.5, the density of foams with 25% castor oil was lower than control at 2-5% water (blowing agent) content, which is consistent with previous discussion. Furthermore, with the increase of water, the densities of foams decreased. More water in the foam formulation consumes more isocyanate which produces more carbon dioxide and more gas cells, which then

enlarged the volume of the foams. Because there was little change in foam weight the density of foam with higher water content was lower.

### 3.3.2.2 Compressive strength

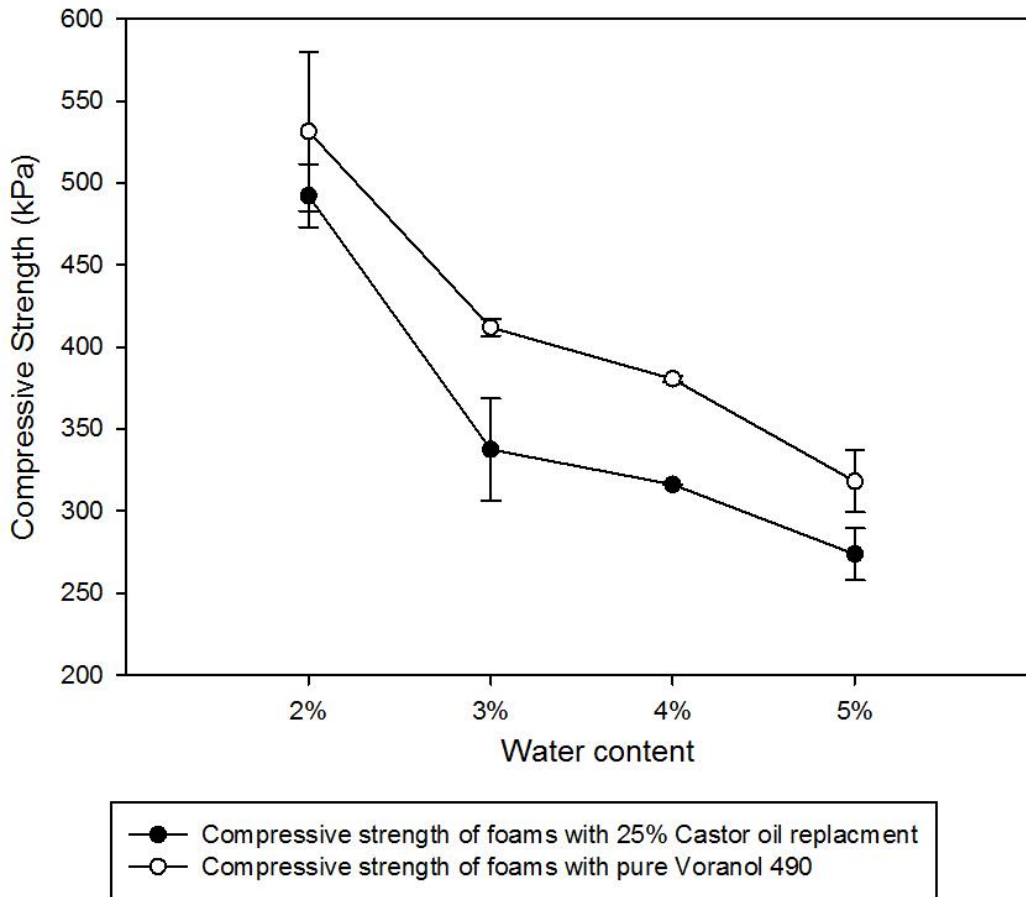


Figure 3.6 Effect of castor oil replacement on compressive strength of rigid polyurethane foams with different water content.

As shown in Figure 3.6, the compressive strength of foams with 25% castor oil was also lower than control at the same water content, respectively. For each

series, using more water (blowing agent) in the foam formulation reduced the compressive strength of polyurethane foams. In addition to the effect of water content on density, a higher water content boosted the blowing reaction and challenged the newly formed and unstable cross-linking structure. Therefore, the compressive strength of foams has the same order as the density of foams.

### 3.3.2.3 Thermal conductivity

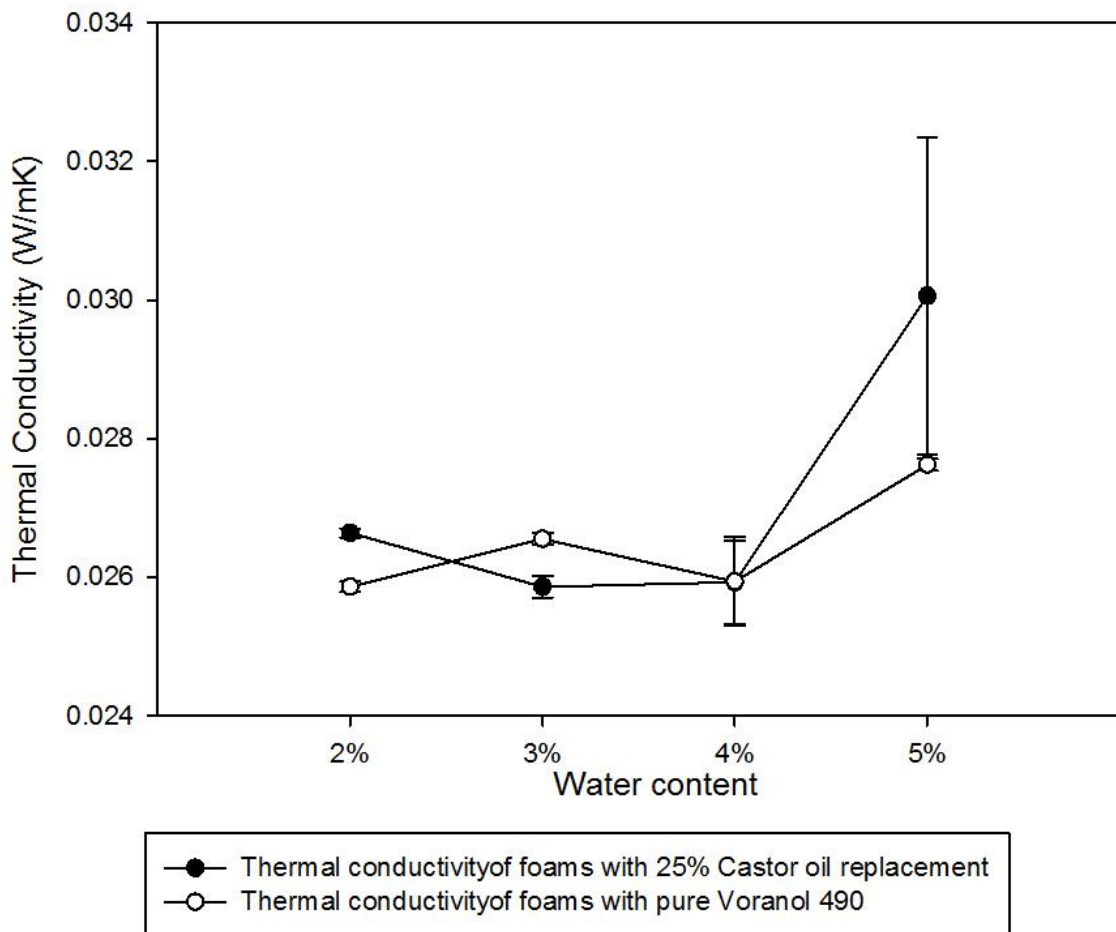


Figure 3.7 Effect of castor oil replacement on thermal conductivity of rigid polyurethane foams with different water content.

As shown in Figure 3.7, no obvious difference in thermal conductivity occurred due to increasing the water (blowing agent) content from 2~4%. But it became much higher at 5% water content. Principally, water helps produce carbon dioxide. However, the thermal conductivity did not decrease with increasing water content. In fact, it significantly increased at 5% water. This may be due to the weakening of the foam as the water content was increased. More water produced more carbon dioxide gas, and cell walls became thinner. More cells inside the foam were broken due to the high pressure from gas when foaming. Although the polyurethane structure at this point might be still stable, it cannot stop the gas flow from one cell to another or from inner structure to the outside. Although more CO<sub>2</sub> was produced, less was kept inside the foam. Then the space in the foam was overtaken by air in the environment, and thus the thermal conductivity increased (thermal conductivity of air, which was 0.0243 W/m.K at 0°C while CO<sub>2</sub> was 0.0105 W/m.K at 0°C).

### **3.3.3 Influence of hydroxyl number**

To investigate the effect of the hydroxyl number on the properties of rigid polyurethane foam, glycerol was introduced into the polyols' side to modify the overall hydroxyl number.

### 3.3.3.1 Density

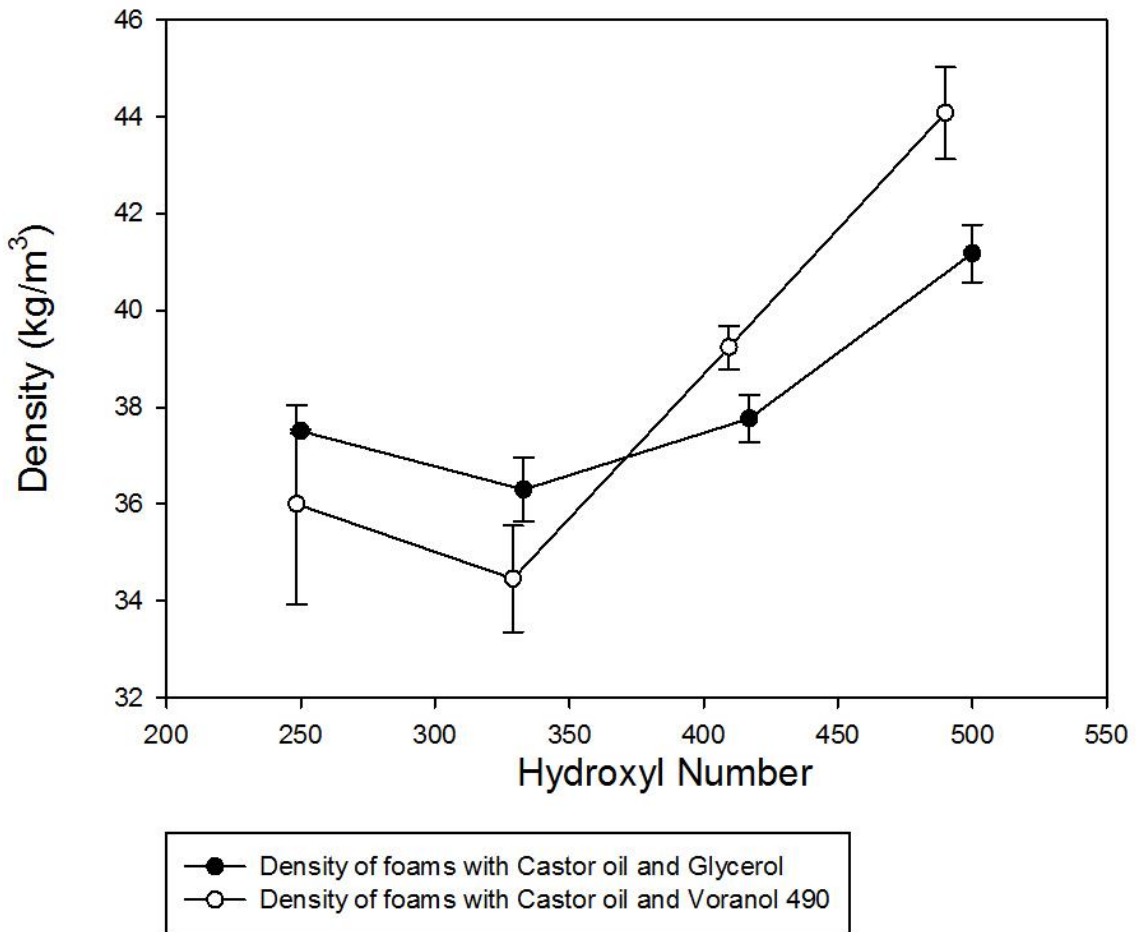


Figure 3.8 Effect of hydroxyl number on density of rigid polyurethane foams with castor oil and glycerol or Voranol 490.

Assuming that all the chemicals could be reacted to build the structure of polyurethane foams, water was the only blowing agent that defined the final volume of the product. Thus, due to the increasing hydroxyl number together with the isocyanate content, the total weight of the foams should also increase. Then the density would also increase with the increasing of hydroxyl number. However, this did not happen when the castor oil was added into the system. As



shown in Figure 3.8, when the hydroxyl number of polyol mixture was lower than 300, the density of foam was higher than that with a hydroxyl number of around 330. There are at least two factors resulting in the high density with a lower hydroxyl number. Firstly, too low a hydroxyl number contributed to a low cross-linking density foam. Foam structures with too low cross-linking density could not maintain their volumes, which led to the loss of volume. Also, foams with a lower hydroxyl number contained more castor oil. The hydroxyl groups of castor oil are all secondary, and their reaction rate with isocyanate was only 1/3 of the primary hydroxyl groups. During foaming, a fraction of gas produced from the blowing agent might have escaped from the system if the structure of castor oil had not been strengthened enough. Since the hydroxyl number of glycerol (1827.56) is much higher than that of Voranol 490, in order to achieve a similar average hydroxyl number level, the castor oil content with glycerol should be much higher than that with Voranol 490. Besides castor oil, glycerol also contains one secondary hydroxyl group out of the total three hydroxyl groups on each molecule. Thus even when the hydroxyl number is similar, foams with castor oil and glycerol combination contain more secondary hydroxyl groups than foams with castor oil and Voranol 490 combination. Therefore, when the hydroxyl number was lower than 350, the density of foam with castor oil and glycerol was higher than that with castor oil and Voranol 490. However, it is interesting to note that when the hydroxyl number was higher than 400, the density of foams with Voranol 490 was even higher than that with glycerol. One possibility for this phenomenon is that when the hydroxyl number was over 400, the main polyol in

the group of castor oil and Voranol 490 was Voranol 490 (with the percentage of 75 and 100). The structure was already finished and almost fixed when carbon dioxide was still involved in the blowing reaction. Such cases would not happen in foams with castor oil and glycerol because even when the hydroxyl number is over 400, castor oil remained as the main polyol (with the percentage of 85 and 80). With the help of glycerol as the cross-linker, the structure of polyurethane with castor oil could be pushed to its maximum possible volume during foaming. Therefore, the total volume of foams with castor oil and glycerol was larger than that with Voranol 490.

### **3.3.3.2 Compressive strength**

Figure 3.9 shows the relationship between the compressive strength and the overall hydroxyl number.

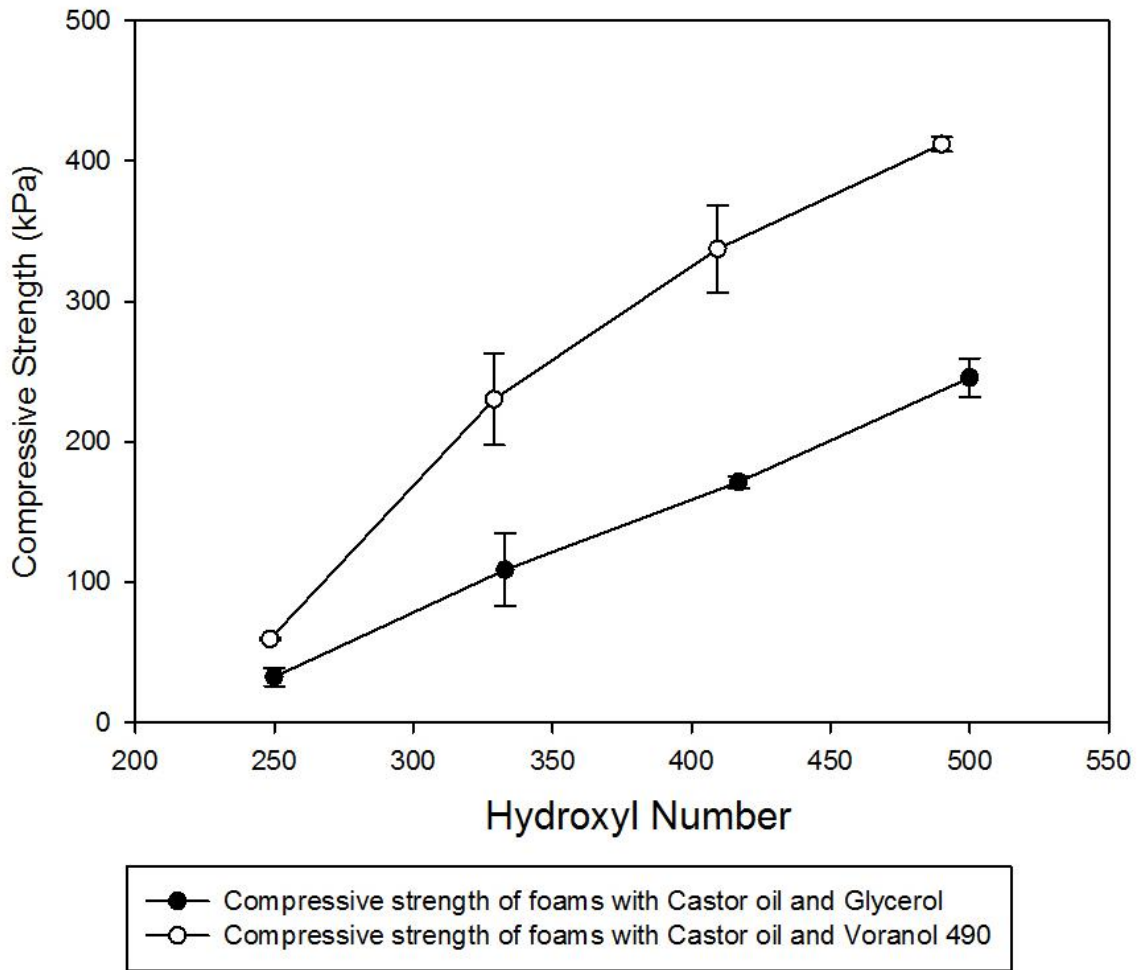


Figure 3.9 Effect of hydroxyl number on compressive strength of rigid polyurethane foams with castor oil and glycerol or Voranol 490.

The compressive strength increased with the increase of the overall hydroxyl number. With a fixed total polyol content, foams with a higher hydroxyl number consumed more isocyanate to form denser cross-linkage inside the structure, and it also contributed to higher compressive strength. The figure also shows that the line of the glycerol series was always lower than that of the Voranol 490 series. The results reflect that the structure of foams with castor oil

and glycerol is not as firm as that with Voranol 490. As stated previously, foams with castor oil and glycerol contain much more secondary hydroxyl group content than that of Voranol 490. Thus the distribution of cross-linkage in the foams with castor oil and glycerol was not as uniform as that with Voranol 490, which could have contributed to the instability of the structure. In addition, Dr. Tu's (2008) and Dr. Fan's (2011) research also mentioned that the density of the foam had a positive influence on its compressive strength.

### 3.3.3.3 Thermal conductivity

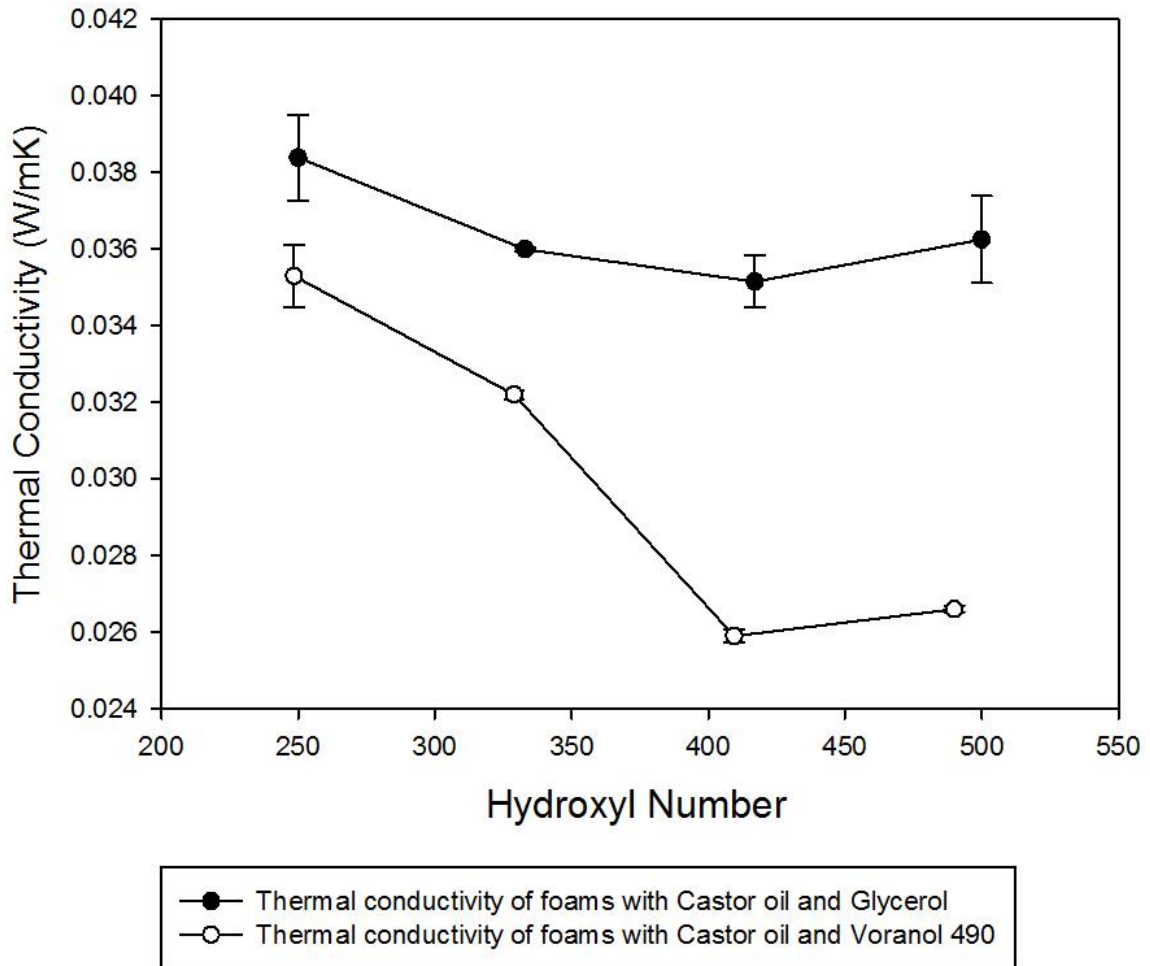


Figure 3.10 Effect of hydroxyl number on thermal conductivity of rigid polyurethane foams with castor oil and glycerol or Voranol 490.

As shown in Figure 3.10, the hydroxyl number itself is not a direct factor affecting the thermal conductivity of polyurethane foams. However, the huge difference between two series indicates that the type of hydroxyl groups is the main factor to the thermal insulation property. When the polyols have more secondary hydroxyl group (glycerol series and foams with 75% castor oil and 25% Voranol 490), the thermal conductivity is always above 0.034 W/m.K. While

the polyols have more primary hydroxyl group (75% or 100% Voranol 490 content), the thermal conductivity remains at a very low level. Due to the faster reaction rate, primary hydroxyl groups can help strengthen the foams' structure more effectively and trap more carbon dioxide. Also the series of foams with castor oil and glycerol have less uniform structures, which might also lead to the escape of carbon dioxide.

In summary, castor oil replacement influenced the physical and thermal properties of polyurethane foams. The product with more castor oil replacement tends to be lighter (from the changes in density) and more fragile (from compressive strength) due to the lower hydroxyl number. At the same time, the thermal conductivity increased when the castor oil percentage was over 50% due to the lack of cross-linkage. Therefore, the replacement of the castor oil should be limited.

The blowing agent also affects the properties of PU foams. Water helps produce more gas and enlarge the foam volume, which is reflected by the decreasing density. Water also weakens the foam structure. The decrease of the compressive strength shows water makes foams more fragile. Too much water will break cell walls, weaken the foam structure and increase the thermal conductivity of polyurethane foams.

Hydroxyl number is a key factor affecting many properties of polyurethane foams. It directly affects the cross-linking density. With the help of the cross-linker, glycerol, the overall hydroxyl number can be increased and part of the

mechanical properties can be modified. However, the type of hydroxyl group is still a limitation of castor-oil-based polyurethane foams.

### **3.4 Conclusion**

In this study, water-blown rigid polyurethane foams were prepared using four levels (0, 25, 50, and 75%) of castor oil to replace petroleum-based polyol and four levels (2, 3, 4, and 5%) of water content. The results indicate that both the castor oil replacement and the water content can affect the physical and thermal properties of rigid foam. Too much castor oil replacement makes foams light but fragile, and product can conduct heat more easily. Water has a similar effect on physical properties and has a complex influence on thermal conductivity. The overall hydroxyl number of castor-oil-based polyurethane foams can be modified by adding glycerol as a cross-linker and have potential to increase castor oil replacement level. Still the secondary hydroxyl group in castor oil is a limitation leading to foams with a higher thermal conductivity.



## CHAPTER 4. WATER-BLOWN FLEXIBLE POLYURETHANE FOAMS WITH CASTOR OIL REPLACEMENT

### 4.1 Background

Flexible polyurethane foams are polymers with low hardness but good properties in recovery and flexibility. The study of flexible polyurethane foams can be dated from the early research of polyurethane around World War II (Seymour and Kauffman, 1992). Usually, flexible polyurethane foams are applied as upholstery material in bedding, toys, footwear, packaging, and vehicles. In 1952, the global consumption of flexible foams was 1000 tons. In 2011, the consumption reached 5 million tons, representing an increase 5000 times of the 1952 estimate (Engels and others, 2013).

Flexible polyurethane foams, like other popular polymers, relied on petroleum resources as the major feedstock. Petroleum is a nonrenewable resource and the consumption of petroleum usually accompanies damage to the environment. Also, the cost of petroleum-based polyurethane is increasing annually along with the increase of petroleum prices. Therefore, both economic and environmental considerations mandate developing novel, renewable resources to take the place of petroleum resources (Molero and others, 2008).

Vegetable-based chemicals are regarded as the most significant renewable substitute for petroleum. Many plant-based raw materials contain unsaturated bonds and hydroxyl groups, which enable them to be used as or modified into polyols. Cinelli and others (2013) recently developed a method to prepare flexible

polyurethane foams from liquefied lignin. Meier and others (2007) investigated the properties of polyurethane foams with modified canola oil, sunflower oil, linseed oil and corn oil replacement. Tu (2008) and Fan (2011) have increased the soybean-oil-based polyols replacement ratio by as much as 50% and have investigated the influences of biobased polyol contents. Among those vegetable oils, castor oil is one of the most promising alternatives. Castor oil contains natural reactive hydroxyl groups on its ricinoleic acid branches, which is significant in the production of polyurethane structure. Also, castor oil plants can be cultivated in both acid and basic soil types. Thus, they are widely planted in southern Asia, South America and some areas in southern Africa. According to the Food and Agriculture Organization of the United Nations (FAO: <http://faostat.fao.org/>), India is the main producer of castor oil seeds. In 2012, the production of castor oil seeds in India was 5.05 million tons, which was about 90% of the global production. Large production and excellent adaptation ensure that castor oil can be a competitive renewable substitute for fuel oil or chemical feedstock.

Compared to rigid foams, flexible polyurethane foams usually have a lower degree of cross-linking. Thus, they require a lower Isocyanate index for foaming and polyols with lower hydroxyl value. However, as our preliminary tests showed - if we simply replace polyols by castor oil without any cross-linker, foams would soon fail due to serious collapse (Figure 4.1). The objective of this study is to investigate the potential and effect of castor oil replacement in flexible polyurethane foams.



Figure 4.1 Collapse of the flexible polyurethane foam with no cross-linker content but 100% castor oil replacement.

## **4.2 Materials and methods**

### **4.2.1 Raw materials**

Castor oil used in this study was obtained from Alnor Oil Company, Inc. (Valley Stream, NY) with a hydroxyl number of 168. Voranol<sup>®</sup> 4701, a petroleum-based polyol with a hydroxyl number of 34, was supplied by Dow Chemical Co. (Midland, MI). PAPI<sup>®</sup> 27 came from Dow Chemical Co. (Midland, MI) and is a polymeric diphenylmethane diisocyanate (MDI). Distilled water was the blowing agent. Diethanolamine was the cross-linker and supplied by Fisher Scientific (Hanover Park, IL). DABCO<sup>®</sup> 33-LV and DABCO<sup>®</sup> 8154 were the gelling catalysts and DABCO<sup>®</sup> BL-17, the blowing catalyst. Stannous octoate and DABCO<sup>®</sup> DC 2585 were a tin-catalyst and a surfactant, respectively. DABCO<sup>®</sup> 33-LV, DABCO<sup>®</sup> 8154, DABCO<sup>®</sup> BL-17, and DABCO<sup>®</sup> DC 2585 were supplied by Air Products & Chemicals (Allentown, PA). Table 4.1 lists the properties related to the chemicals used in this research.

Table 4.1 Properties of raw materials.

Raw Materials	Water Content	Average Molecular Weight	Functionality	Hydroxyl Number	Equivalent Weight
Castor oil	0	900	2.7	168	333.93
Voranol 4701	0.06	4900	2.97	34	1650
DABCO 33-LV	0	Not applicable	Not applicable	560	100.18
DABCO 8154	0	Not applicable	Not applicable	548	102.37
DABCO BL-17	0	Not applicable	Not applicable	476	117.86
DABCO 2585	0	Not applicable	Not applicable	60	935
Water	-	18.02	2	6233	9.01
Diethanolamine	0	105.14	3.00	1602	35.02
Isocyanate	0	340	2.7	-	134

#### 4.2.2 Experimental design and foaming formulations

This study was divided into three sections. Section 1 focused on the influence of different temperature conditions. Foaming formulations are shown in Table 4.2. Foams were prepared through three different treatments. The first group of polyurethane mixtures were allowed to foam in molds unheated, that is, at room temperature, and the foams were also cured at room temperature. Foams in the second group were prepared in molds that were preheated in the oven to 102°C and also cured at room temperature. The surface temperatures were recorded by a laser sensor during the foaming process. This method was called “hot-mold cold-cure” and it was applied for all the samples in Sections 2 and 3. Foams in the third group were prepared in preheated molds but cured in the 102°C oven for 1 hour. Tables 4.3 and 4.4 show foaming formulations for Section 1 and 2, respectively. The sample’s total height, foaming temperature,

density, compression force deflection (CFD), and constant deflection compression (CDC) were tested.

Table 4.2 Foaming formulation of flexible polyurethane foams with different temperature conditions.

Ingredients		Parts by Weight of total Polyol	
		Control Foams	Castor oil Foams
B-side	VORANOL <sup>®</sup> 4701	100	0
	Castor Oil	0	100
	Distilled Water	5.0	
	Diethanolamine	0.5	
	DABCO <sup>®</sup> BL-17	0.05	
	DABCO <sup>®</sup> 33-LV	0.3	
	DABCO <sup>®</sup> 8154	0.3	
	Stannous Octoate	0.4	
	DABCO <sup>®</sup> DC-2585	3	
A-side	PAPI <sup>®</sup> 27 Index =60	55.43	74.10

Table 4.3 Foaming formulation of flexible polyurethane foams with different cross-linker contents.

Ingredients		Parts by Weight of Total Polyol	
		Control Foams	Castor Oil Foams
B-side	VORANOL <sup>®</sup> 4701	100	0
	Castor Oil	0	100
	Distilled Water	5.0	
	Diethanolamine	0.25, 0.5, 1.0, 2.0	
	DABCO <sup>®</sup> BL-17	0.05	
	DABCO <sup>®</sup> 33-LV	0.3	
	DABCO <sup>®</sup> 8154	0.3	
	Stannous Octoate	0.4	
	DABCO <sup>®</sup> DC-2585	3	
A-side	PAPI <sup>®</sup> 27	Isocyanate Index = 60	

Table 4.4 Foaming formulation of flexible polyurethane foams with different castor oil replacements and isocyanate indices.

Ingredients		Parts by Weight of Total Polyol		
		Control Foams	Castor Oil Foams	Half Castor Oil Replacement
B-side	VORANOL® 4701	100	0	50
	Castor Oil	0	100	50
	Distilled Water	5.0		
	Diethanolamine	0.5		
	DABCO® BL-17	0.05		
	DABCO® 33-LV	0.3		
	DABCO® 8154	0.3		
	Stannous Octoate	0.4		
	DABCO® DC-2585	3		
A-side	PAPI 27	Isocyanate Index = 50, 60, 70, 80		

#### 4.2.3 Foam preparation

The process of flexible foam preparation in this study was similar to the procedures shown in Figure 3.1. Polyols, blowing agent (water), catalysts, cross-linker and surfactant were weighed and placed in a plastic container as B-side. The mixture was taken to the electric mixer and mixed uniformly at 3450 rpm for 40 s. Then the mixture was set at quiescence and degased for 2 min. For A-side, the isocyanate was weighed, placed in another plastic container, and then taken to the same electric mixer. After the isocyanate was added, the whole mixture was mixed at 3450 rpm for an additional 10 s. Then the mixture was poured into a wooden mold.

The wooden mold was preheated to 102°C except for foams in the first section. After foaming, foams were cured at either room temperature (Sections 1 and 2 foams) or at 102°C (Section 3 foams) for one hour. Then, they were pressed to their half thickness by an aluminum plate rapidly and relaxed. This

was repeated twice in order to break the inner gas cells and prevent foams from shrinking. All tests were conducted seven days after the foams were cured and pressed.

#### **4.2.4 Foam property measurements**

The properties of flexible foams were measured according to the ASTM D3574-11 (2011) with modifications, including density, compression force deflection, constant deflection compression, tear resistance, and resilience.

Density: Samples were cut according to a dimension of  $5.08 \times 5.08 \times 2.54$  cm<sup>3</sup>. Density was obtained through the mass and volume. There were at least 3 replicates for each set.

Compression force deflection (CFD): Samples were cut into  $5.08 \times 5.08 \times 2.54$  cm<sup>3</sup> blocks and tested using a TA.HDi Texture Analyzer. After placed on the TA machine's plate, each sample was pressed to 25% of its original height (about 0.7 cm and then released to assume its normal state, which is called "preflex". The preflex procedure was done twice before force measurement. After the second preflex the sample was allowed to relax for about 6 min. The sample was then compressed to 50% of its thickness and the final force was obtained 60 s after the maximum force occurred. The pressure value was reported as the final force divided by the sample area.



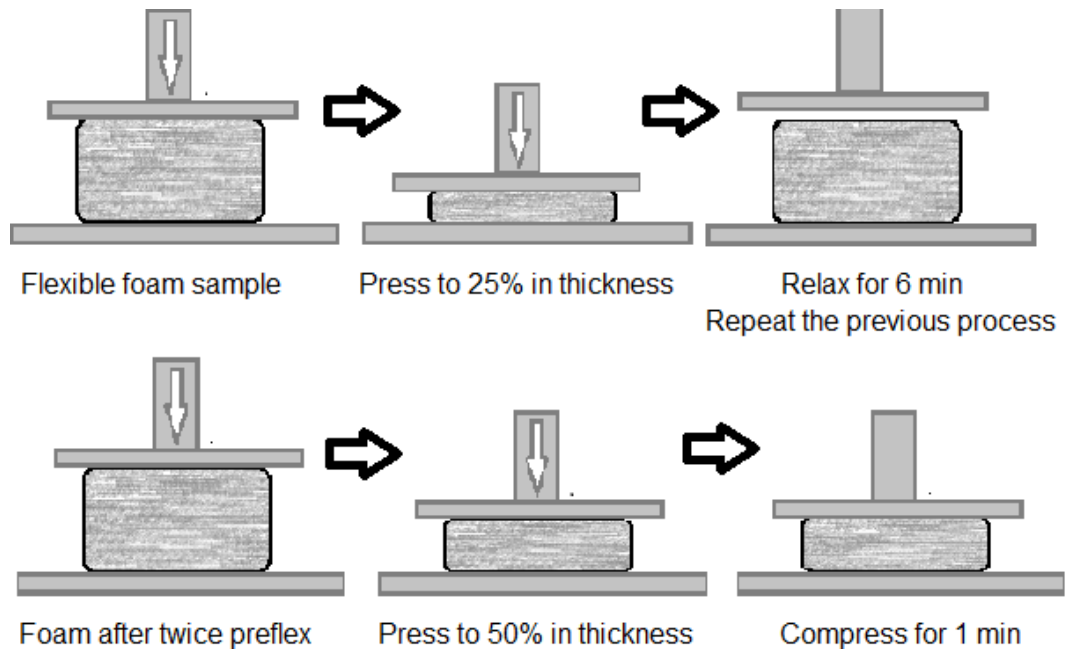


Figure 4.2 Procedures of compression force deflection test.

Constant deflection compression (CDC): Samples were cut into  $5.08 \times 5.08 \times 2.54 \text{ cm}^3$  squares and placed on the aluminum plate apparatus which was placed in an oven for the constant deflection process. The samples were compressed by two parallel aluminum plates. The distance of two plates was adjusted and fixed by bolts. The ratio of deflection was set as 50%. Constant deflection process was conducted in a  $70^\circ\text{C}$  oven for 22 h, and then the samples were taken out of the oven, removed from apparatus and recovered at room temperature for 30 min. Then the final thickness was obtained. The constant deflection compression set point was calculated as the difference between the original thickness and the final thickness divided by the original thickness.

Tear resistance test: Samples were cut into bars with a thickness of 2.54 cm and an incision of 10.16 cm length. Two parts from the incision were bonded

in the TA machine separately. Then the machine tore the sample with a speed of 8.5 mm/s. The tear resistance was reported as the maximum resistance force divided by the thickness.

Resilience test: Samples were cut into  $10.16 \times 10.16 \times 5.08 \text{ cm}^3$  squares. A transparent open tube (510 mm in length and 44.35 mm in diameter) was prepared marked from 0% to 100% from one side to the other along its length. The tube was placed vertically with its lower end 1.6 cm above the center of the sample. A steel ball with a diameter of 1.6 cm was released freely from the top inside the tube. The maximum rebound height was recorded by percentage as its resilience.

## **4.3 Results and discussion**

### **4.3.1 Influence of different temperature conditions**

Figure 4.3 describes the surface temperature history of the polyurethane foams during foaming. The treatments included the effect of composition (castor oil based or petroleum polyol based) and mold temperature (room temperature or heated to 102°C).

## Temperature change after pouring into molds

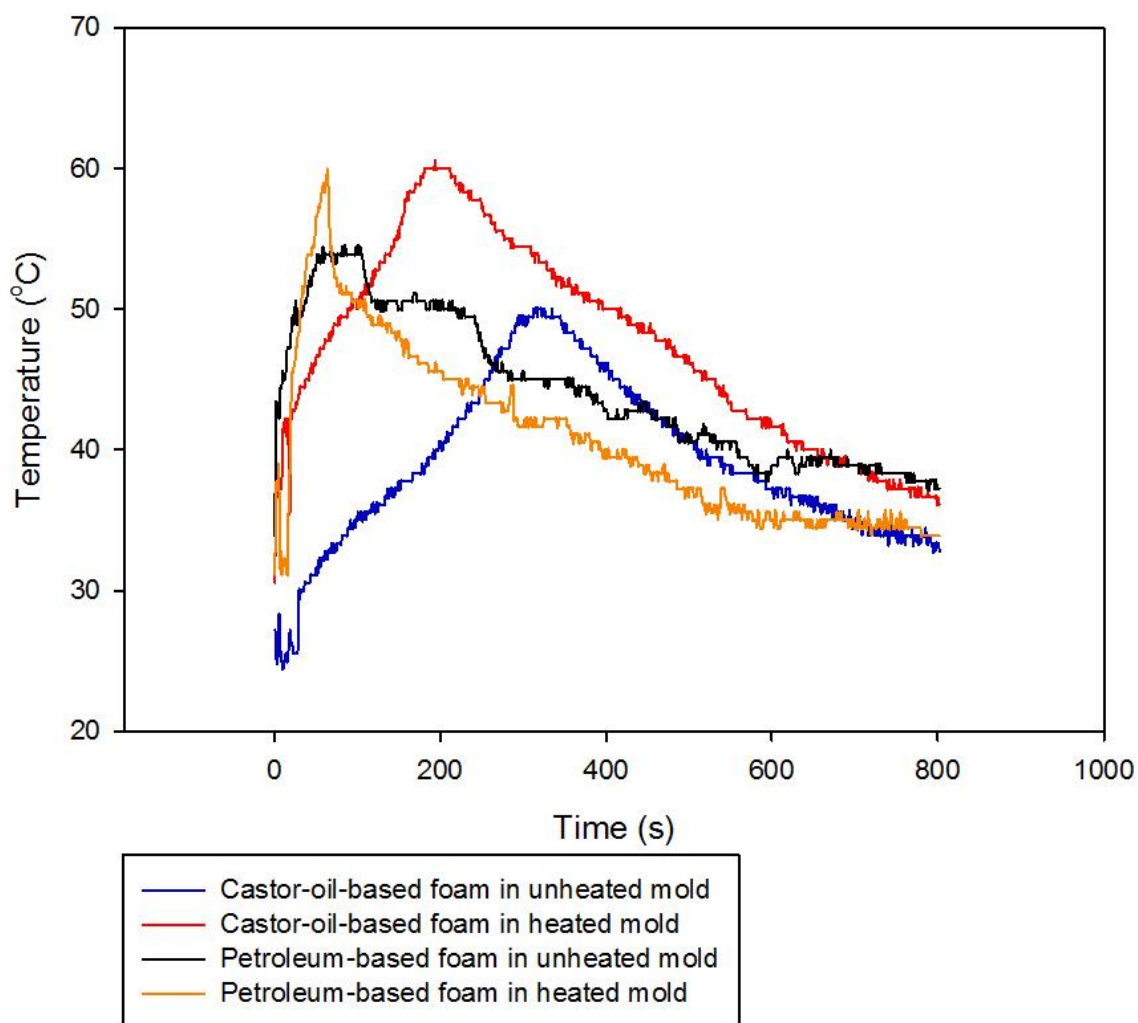


Figure 4.3 Surface temperature history of flexible polyurethane foams with different polyols (castor-oil based or petroleum-based foam) and mold temperatures (heated or unheated).

Due to the limitation of electronic laser sensor, the temperature of samples foaming in the oven could not be recorded and are not shown in Figure 4.3. We assume the temperatures of these foams were kept at 102°C. As shown in Figure 4.3, for petroleum-based polyurethane foams, the wooden mold

temperature did not influence the rapid temperature rise in the beginning of foaming. The only difference between the two methods was the peak value of surface temperature of petroleum-based foams in the heated mold was slightly higher than that of foams in unheated molds. The temperature rise of castor-oil-based polyurethane foams was much slower than that of petroleum-based polyurethane foams, which was due to the lower reaction rate of the secondary hydroxyl groups in castor oil molecules. The synthesis of polyurethane is an exothermic process. Lower reaction rate leads to slower heat generated. It required a longer time for castor-oil-based polyurethane mixtures to reach the maximum temperature. Under this testing method, the effect of a heated mold can be shown in the temperature curves. With higher initial mold temperature, castor-oil-based polyurethane was able to react faster at the beginning and accumulate more reaction heat from the synthesis of polyurethane to accelerate the foaming process. The peak foam surface temperature was about the same as the petroleum-based foam with heated mold.

#### **4.3.1.1 Density and height of foams**

Figures 4.4 and 4.5 show the height and density of flexible foams.

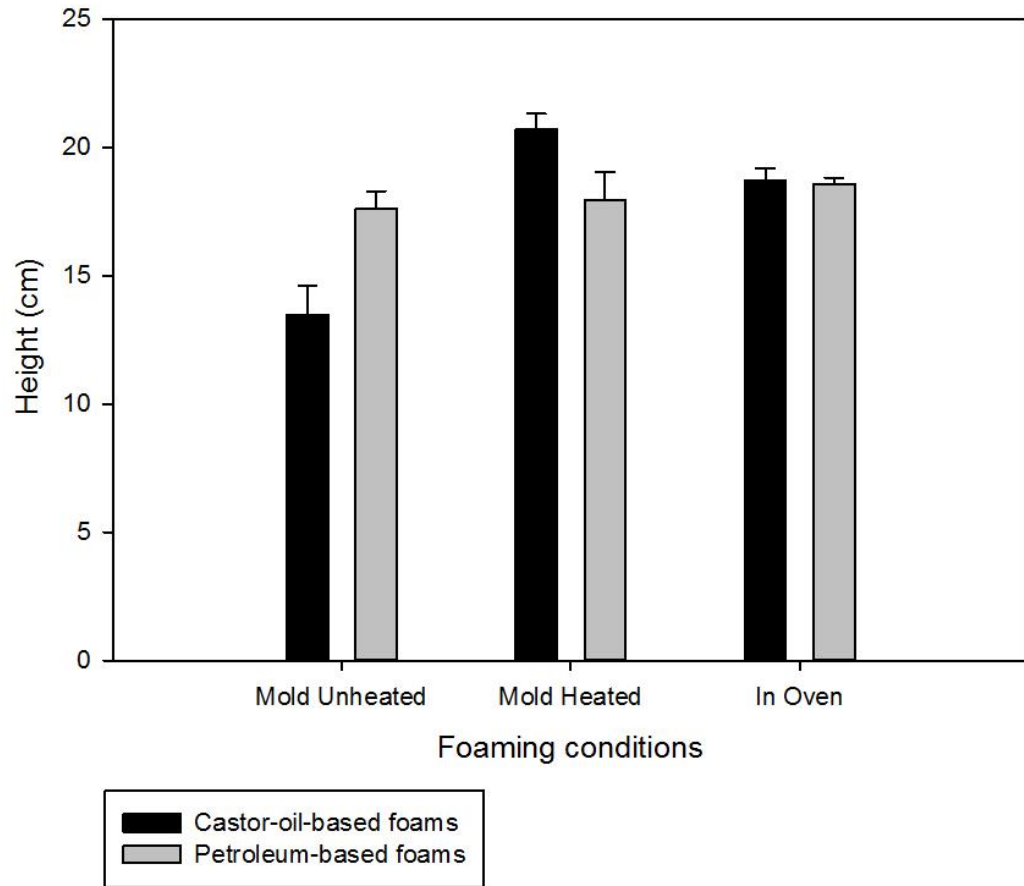


Figure 4.4 Height of flexible foams with different foaming conditions.

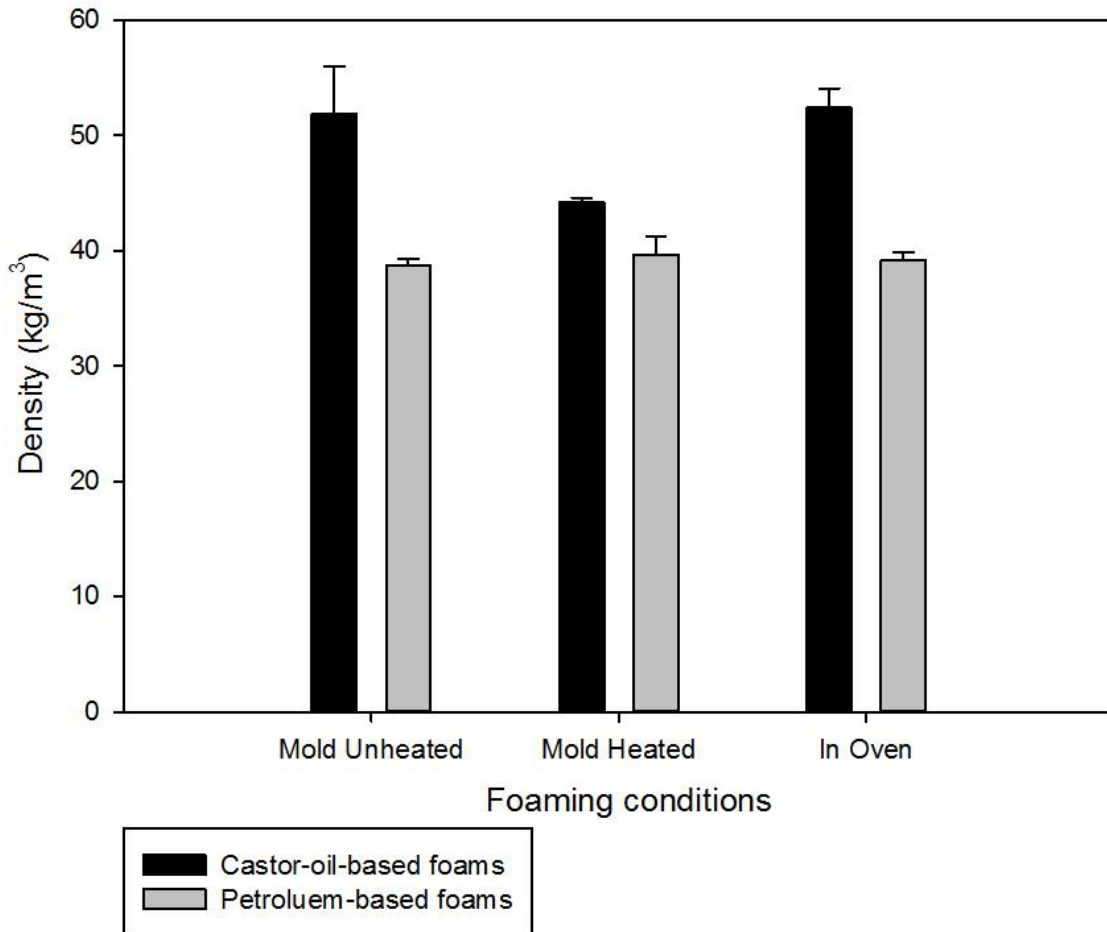


Figure 4.5 Density of flexible foams with different foaming conditions.

As shown, mold temperature did not have any significant effect on the height and density of petroleum-based polyurethane foams ( $p = 0.522$  for height and  $0.696$  for density according to single-factor ANOVA). However, the castor-oil-based flexible foams were higher and had lower density when mold was heated ( $p = 0.006$  for height and  $0.045$  for density). For castor-oil-based foams in unheated molds, the gelling reaction rate was too slow to fit the blowing reaction rate, even though the blowing catalyst BL-17, a delayed-action blowing catalyst, was applied. A large mass of carbon dioxide produced from blowing reaction

might have escaped from the mixture and could not contribute to the final volume. Therefore, the castor-oil-based foams in unheated molds had lower height and higher density. It was interesting that the castor-oil foams foaming in the oven had a higher density than those foams in unheated molds, but their actual height was still higher than the unheated foams. It was observed that these foams were not uniform in cell size and some spots showed signs of collapse which led to an increase in density. Due to the higher hydroxyl number, castor-oil-based foams required more isocyanate, but their volumes were limited due to the blowing agent content and their slower reaction rate. Therefore, the density of castor-oil-based foams were always higher than the density of petroleum-based foams.

### 4.3.1.2 Compression force deflection

Figure 4.6 shows the compression force deflection of foams at different foaming conditions.

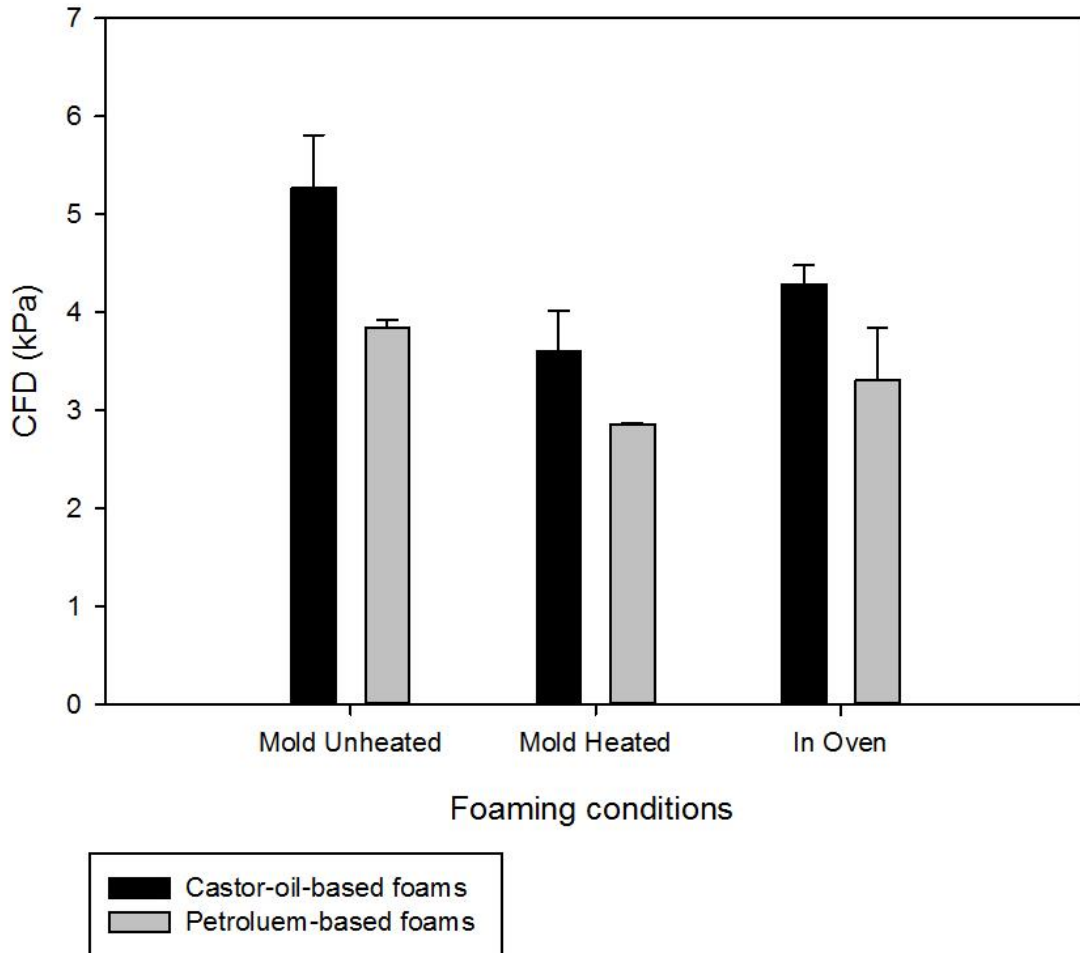


Figure 4.6 Compression force deflection of flexible foams with different foaming conditions.

For petroleum-based foams, the CFD of foams was affected by the mold temperature ( $p = 0.112$ ). Literature shows that the two main factors of CFD are the overall density and the cross-linking rate (Fan, 2011 and Tu, 2008). Since these foams had a similar density, there may have been a potential for high



temperature that reduced the cross-linking rate of polyurethane foams. Results of CFD for castor-oil-based foams verify this influence ( $p = 0.029$ ). The castor-oil foams foamed in the oven and the foams prepared in unheated molds had similar density but the latter samples had a larger value in CFD, which suggests the cross-linking rate of foams in unheated-molds was higher. The low CFD value of foams in heated molds can also be explained in the same manner. Under the same foaming conditions, the values of CFD for castor-oil-based foams were always higher than that for petroleum-based foams due to their higher density.

#### **4.3.1.3 Constant deflection compression**

Figure 4.7 shows the 50% constant deflection compression values of these foams.

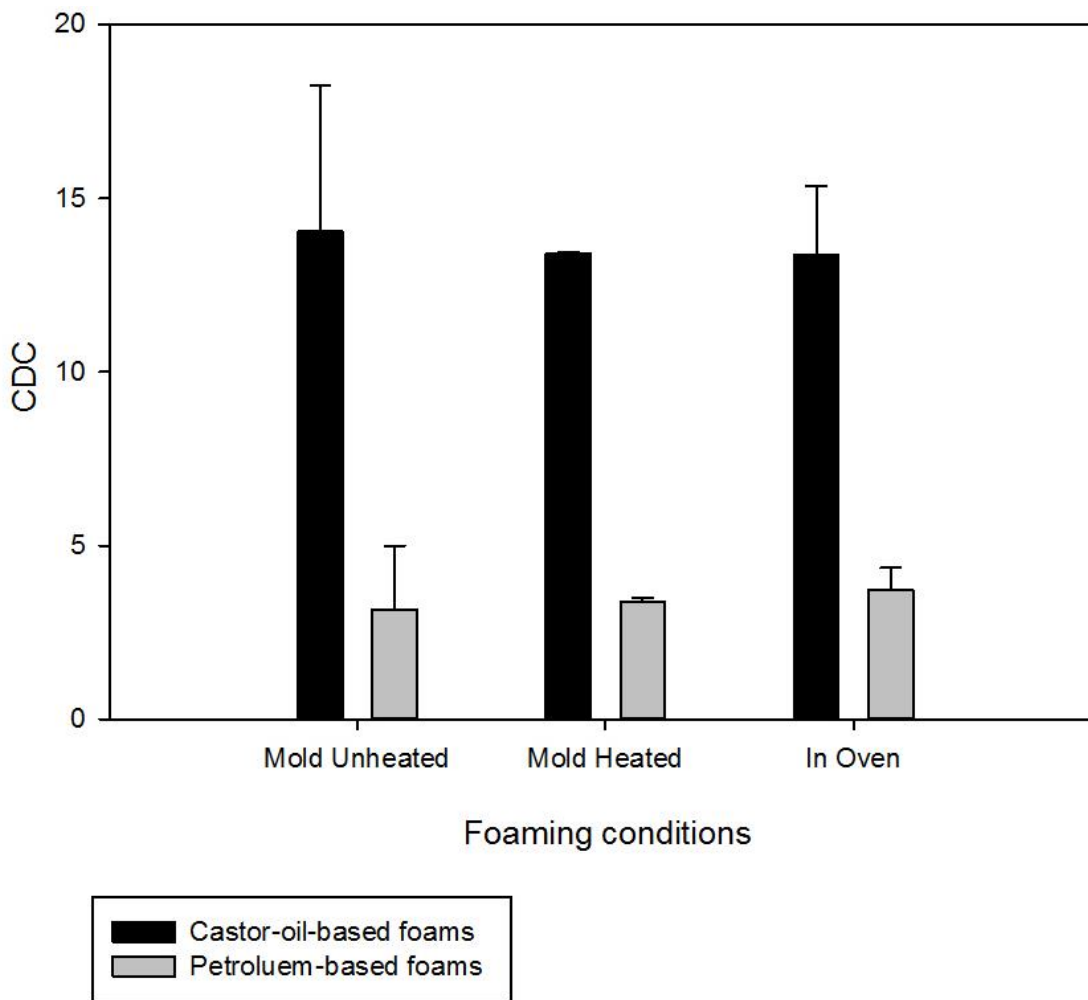


Figure 4.7 50% Constant deflection compression of flexible foams with different foaming conditions.

As shown, foaming conditions did not influence the properties of CDC ( $p = 0.888$  for petroleum-based foams and  $0.961$  for castor-oil-based foams). The value of 50% CDC reflects the flexibility of a foam. The lower the value is, the better its recovery to its original thickness. The difference in 50% CDC between castor-oil-based foams and petroleum-based foams was still evident. The key to a low CDC value and excellent recovery property lies in the soft segments of the foam. Usually longer polymer chains between the nearby reactive hydroxyl

groups can lead to more flexible foams. The hydroxyl number of Voranol 4701, the petroleum-based polyol in this study, is only 34 while castor oil has the hydroxyl number of 168, which means the degree of hydroxyl groups' density of castor oil is much higher than that of Voranol 4701. Thus, the distance between two hydroxyl groups in castor oil's structure is much shorter than that in Voranol 4701. Therefore, castor-oil-based foams had a higher value of 50% CDC than petroleum-based foams.

In summary, the foaming temperature basically did not affect the properties of foams produced by petroleum based polyols. However, a higher mold temperature can boost the reaction between castor oil and isocyanate and help the polyurethane foams to grow faster and higher. However, higher temperature may also lead to the collapse of foams. Therefore a "hot-mold cold-cure" method is recommended in flexible polyurethane foams containing castor oil replacement.

### **4.3.2 Influence of cross-linker content**

#### **4.3.2.1 Density**

Figure 4.8 shows the effect of cross-linker content on the density of flexible polyurethane foams.

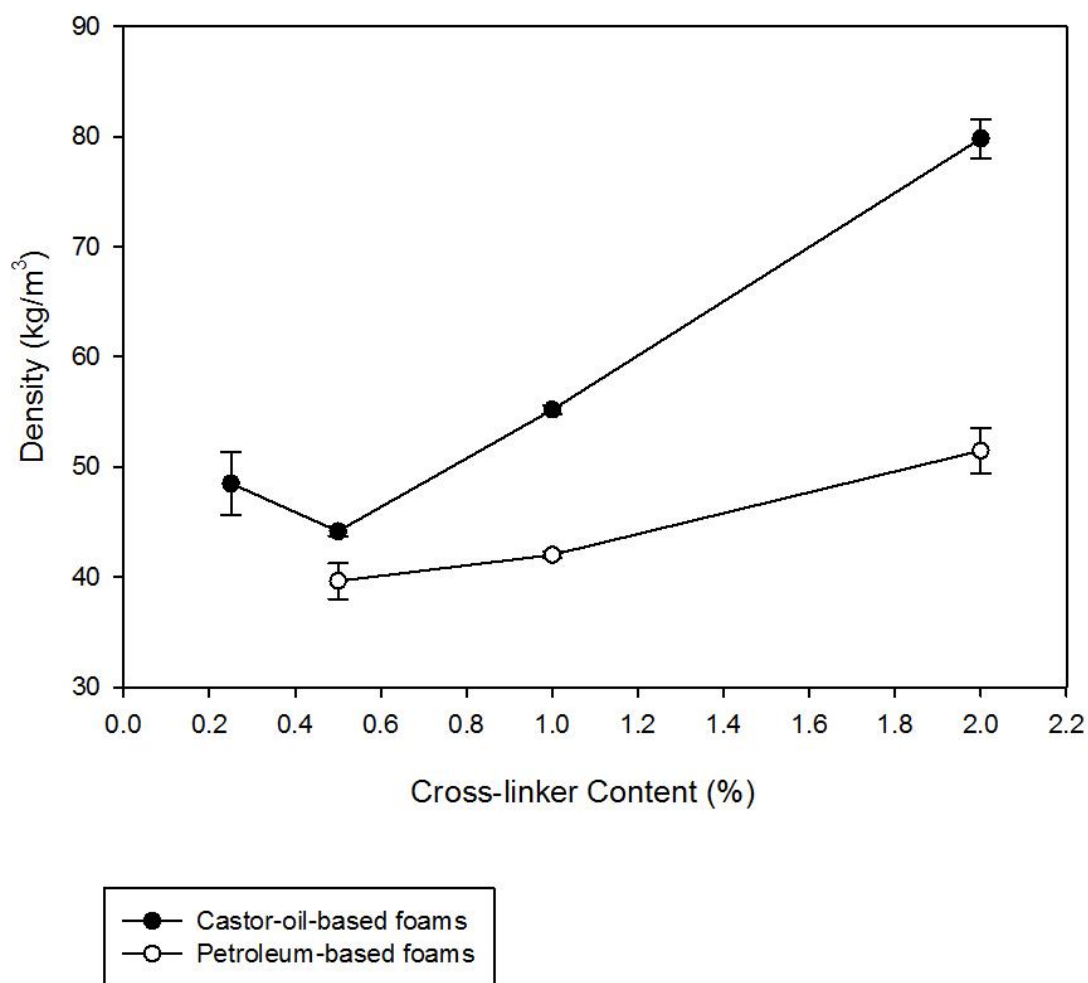


Figure 4.8 Density of flexible foams with different cross-linker content.

For both castor-oil-based flexible foams and petroleum-based foams, the density of foams generally increased with the increase of cross-linker content. Diethanolamine was the cross-linker applied in this study, which has a hydroxyl number as high as 1602. Thus more cross-linker content required more isocyanate to be added into the system, which led to an increase of total weight. Also, diethanolamine contains reactive primary hydroxyl groups on each of the two ends of its molecular structure, and its secondary amine structure can also

boost its reactivity 200-500 times higher than the reactivity of water (Herrington and Hock, 1997). Since the isocyanate index was set at 60, the cross-linker had the ability to capture the isocyanate from water and castor oil and less gas was produced in the foams. The increase of cross-linker content led to the decrease of foam volume. Thus the density of foams increased with the increase of the cross-linker content. However, the density of castor-oil-based foams with 0.25% cross-linker was higher than that of foams with 0.5% cross-linker content. This might be due to the partial structure collapse assuming that 0.25% cross-linker content was not enough to form the stable matrix before castor oil and isocyanate were reacted to produce polyurethane segments, which might lead to a loss of volume. On the other hand, the density of castor-oil-based foams had a higher density than that of petroleum-based foams due to the higher hydroxyl number as discussed previously.

#### **4.3.2.2 Compression force deflection**

Figure 4.9 represents the effect of cross-linker content on compression force deflection (CFD).

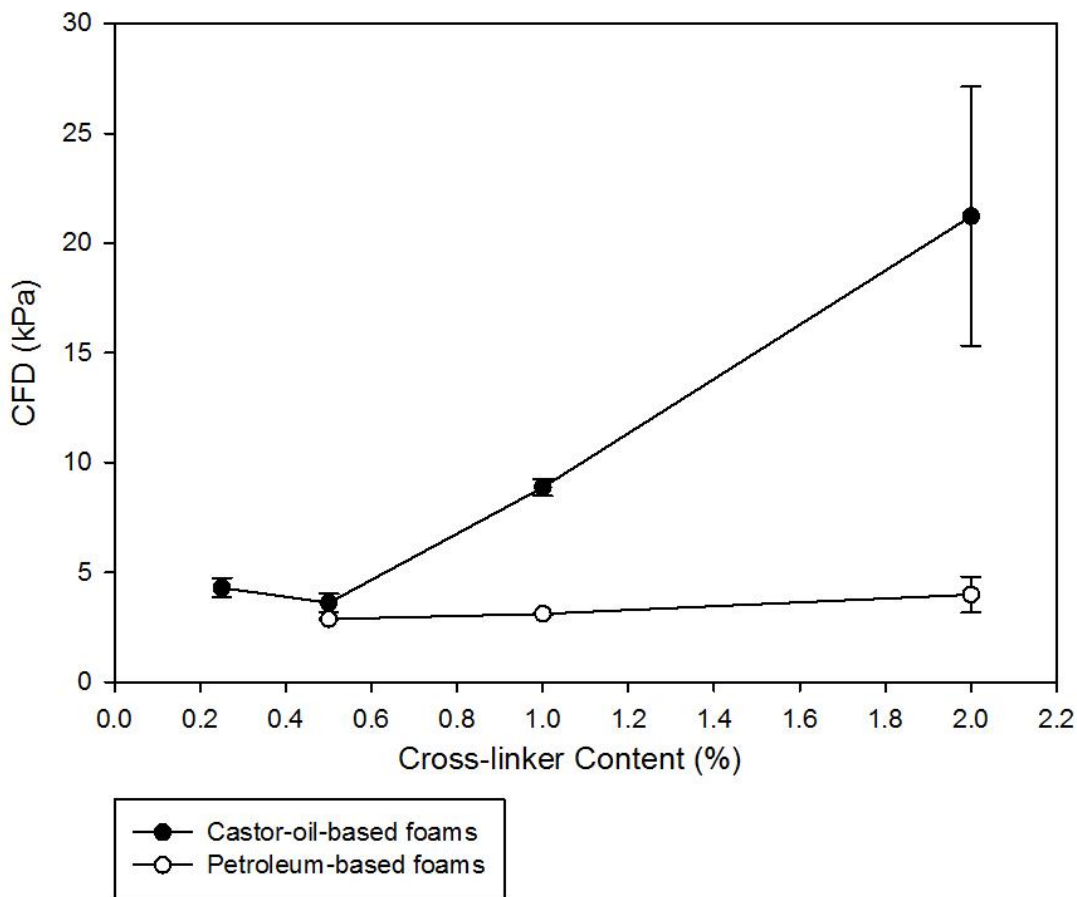


Figure 4.9 CFD of flexible foams with different cross-linker content percentages.

When the cross-linker content was higher than 0.5%, the value of CFD for castor-oil-based foams increased with the increase of cross-linker content while the value of CFD for petroleum-based foams only increased slightly following the same trend of density curves (Figure 4.8). Because of the reactive hydroxyl groups in the diethanolamine, the cross-linker generated hard urea segments rapidly. As the reactivity of primary hydroxyl groups on the molecular structure of Voranol 4701 was higher than that of secondary hydroxyl groups in the castor oil, the influence of cross-linker content on castor-oil-based polyurethane foams was much more profound than on petroleum-based foams.

### 4.3.2.3 Constant deflection compression

Figure 4.10 demonstrates the influence of cross-linker content on the values of 50% constant deflection compression tests.

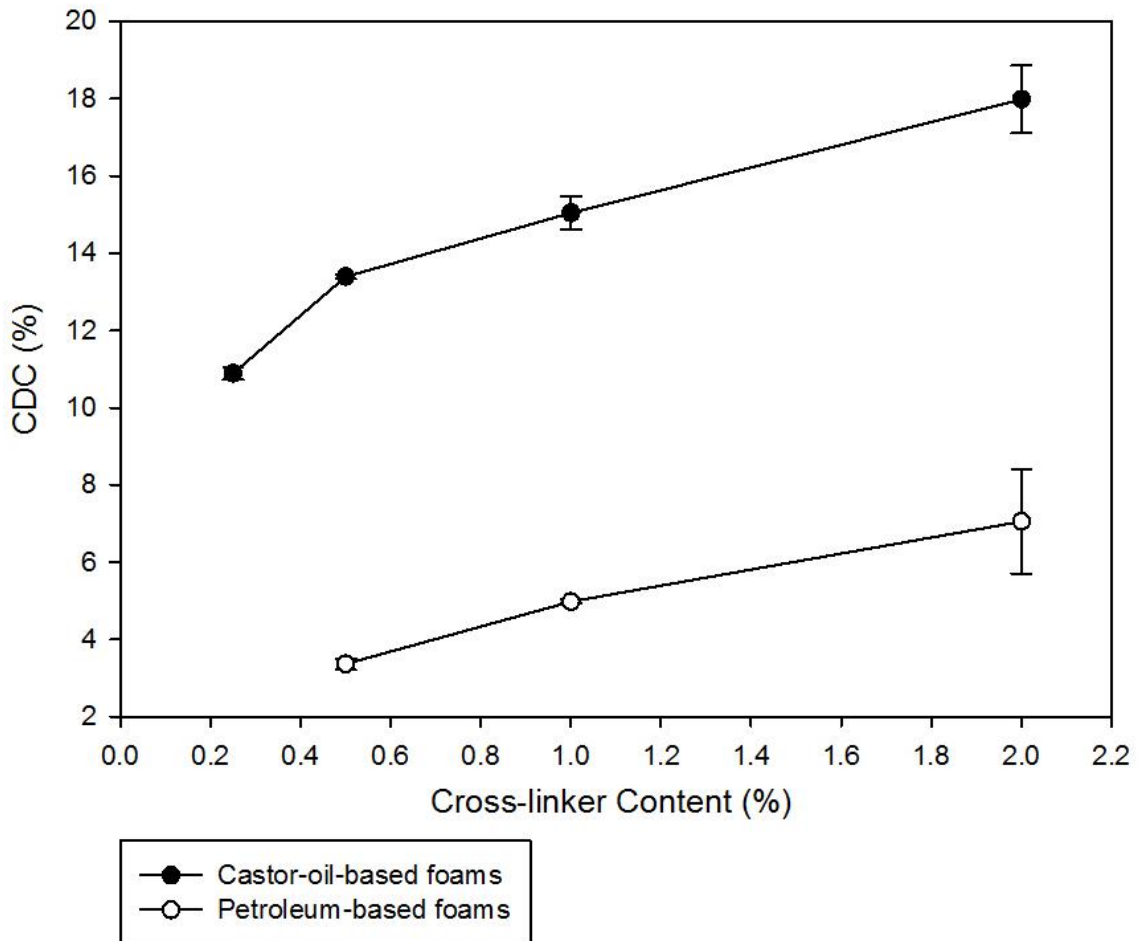


Figure 4.10 50% CDC of flexible foams with different cross-linker content.

As shown, petroleum-based foams had lower values of 50% CDC and better flexibility than the castor-oil-based foams because Voranol has a lower hydroxyl number and a longer carbon chains. For each series, the values of 50% CDC increased with the increase of the cross-linker content. This was because

more hard segments were produced from the cross-linker and less soft polyurethane segments were generated from polyols and isocyanate.

#### 4.3.2.4 Tear resistance

Figure 4.11 represents the influence of cross-linker content on tear resistance of flexible foams.

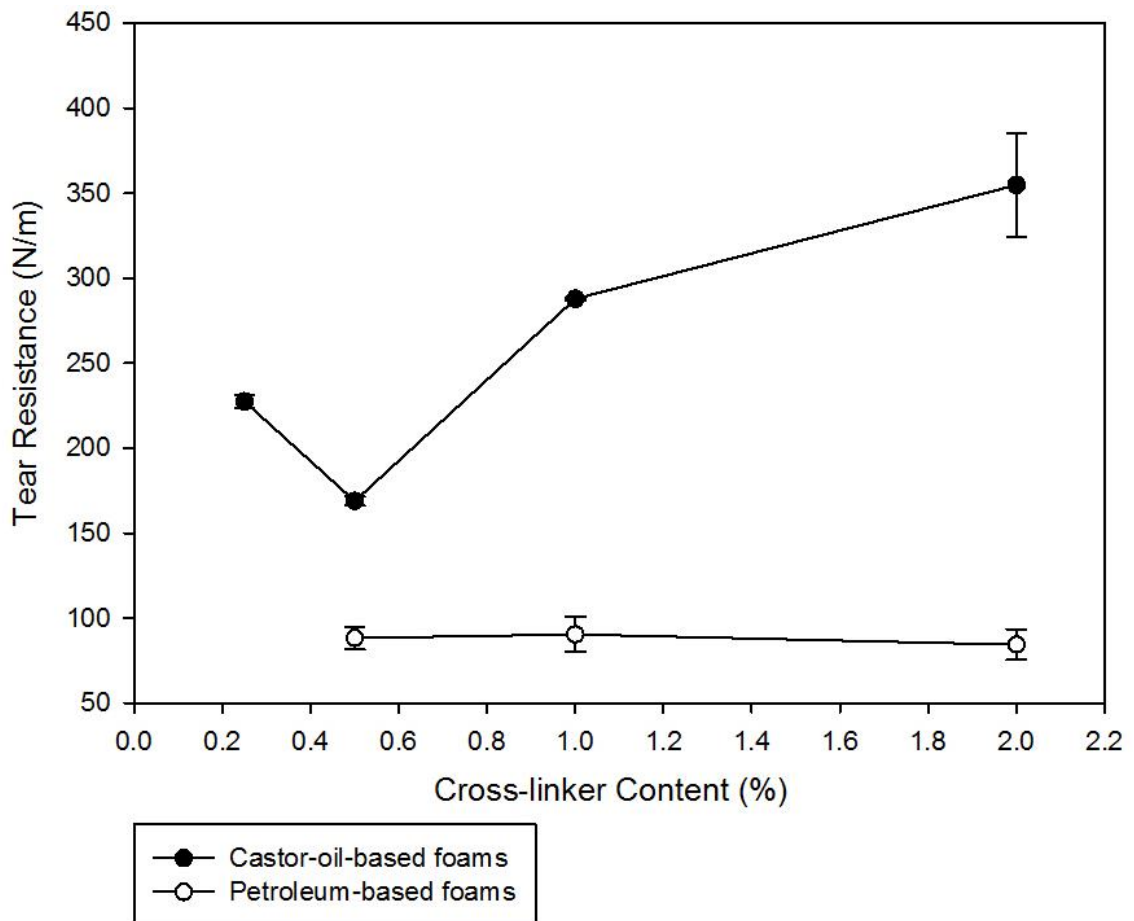


Figure 4.11 Tear resistance of flexible foams with different cross-linker content.

The test of tear resistance reflects the strength of the cross-linkage inside polyurethane foams. Several factors may contribute to the results of tear resistance tests, such as the degree of cross-linking, the contents of hard and



soft segments, and the structure of polyols. In Figure 4.11, the cross-linker content did not influence the tear resistance of petroleum-based foams. However, it increased the tear resistance of foams made from castor-oil-based polyols, similar to the trends shown in Figures 4.8 and 4.9. The results suggest that the cross-linker content might affect the tear resistance of flexible polyurethane foams through its influence on cross-linking density.

#### 4.3.2.5 Resilience

Figure 4.12 displays the effect of cross-linker content on resilience of polyurethane foams.

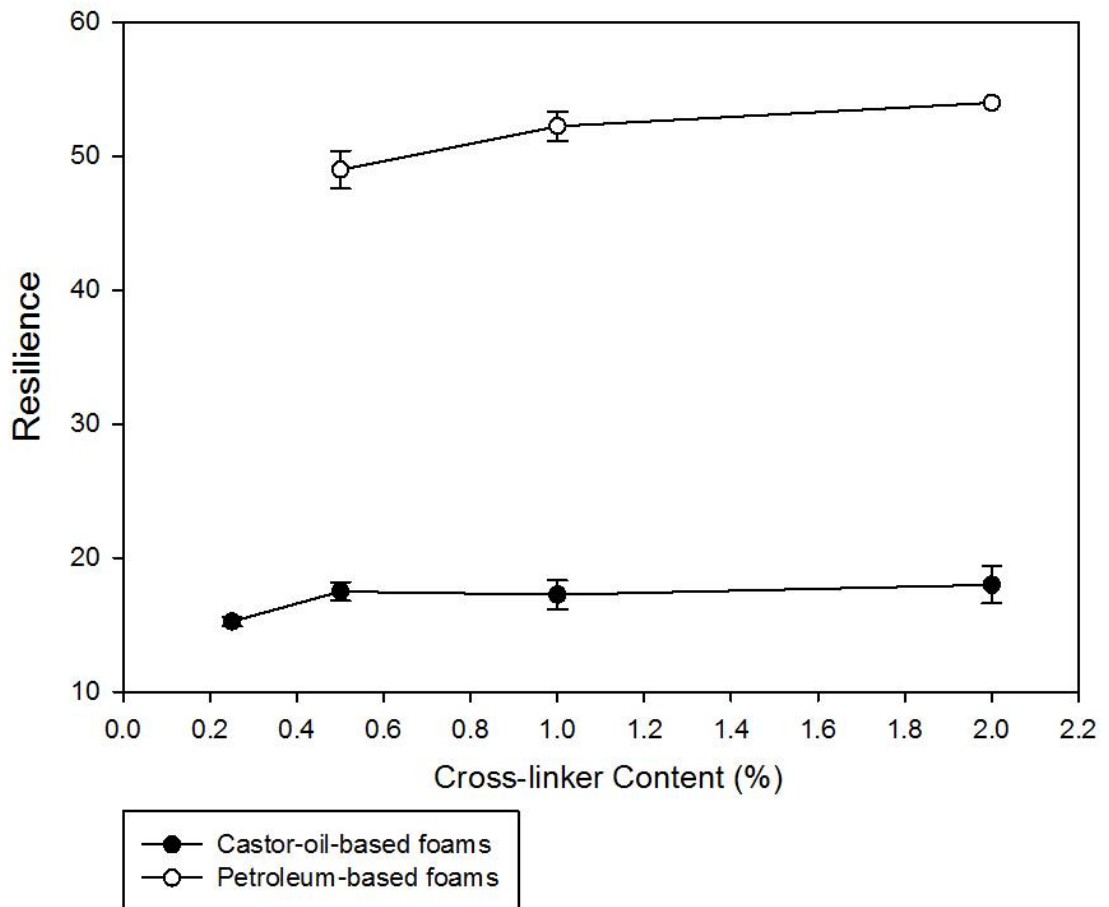


Figure 4.12 Resilience of flexible foams with different cross-linker content. \

Resilience mainly relies on the properties of soft polyurethane segments in flexible foams. Due to the disadvantage of the molecular structure of castor oil polyol, foams containing castor oil performed worse in resilience than foams made from petroleum based polyol. As shown in Figure 4.12, the effect of cross-linker content on resilience was not significant.

### 4.3.3 Influence of Isocyanate Index with different castor oil replacements

#### 4.3.3.1 Density

As shown in Figure 4.13, the density of each group of foams decreased with the increase of isocyanate index.

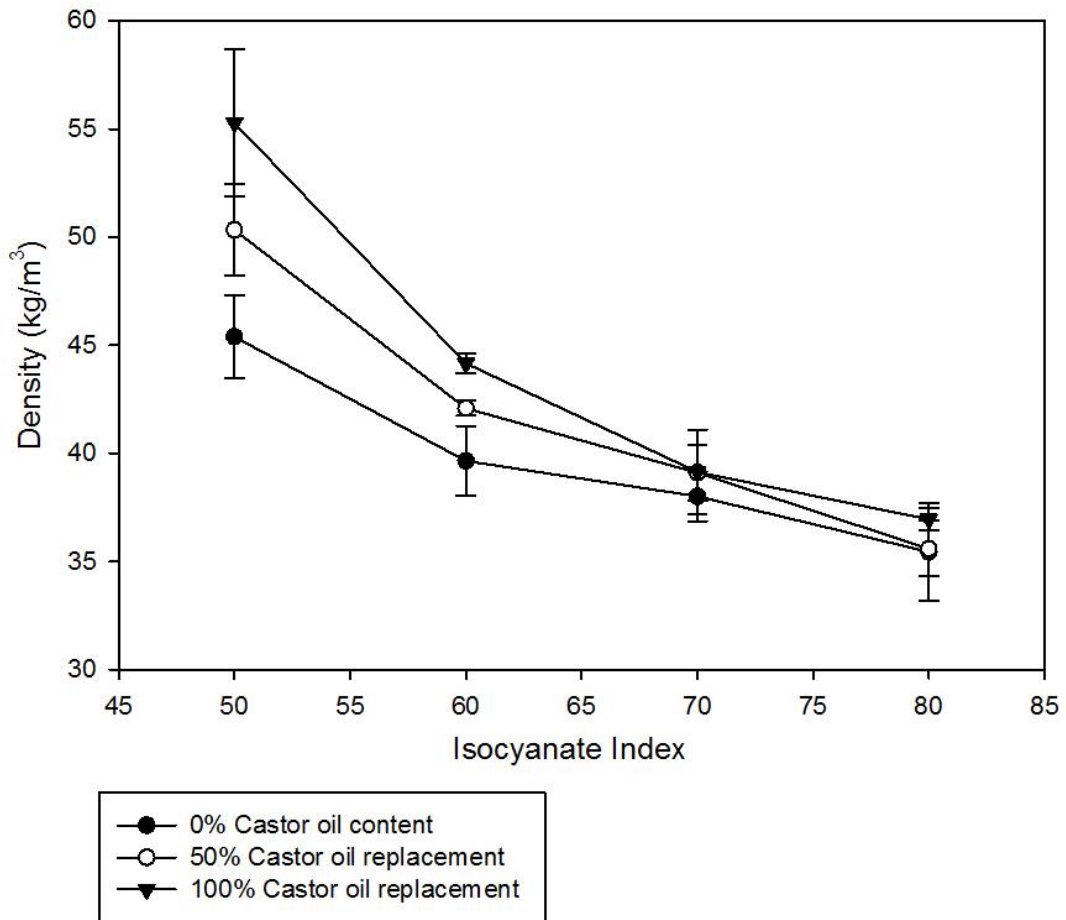


Figure 4.13 Density of flexible foams with different isocyanate indices.

Since the isocyanate index varied from 50 to 80 or less than 100 in this study, one may assume that part of the polyols did not react. Although the

increase of isocyanate index means more isocyanate was added and the total weight was increased, the added isocyanate could soon be consumed along with the rest of the polyols and water to form a larger volume of polyurethane foam. Compared with the increase of volume, the increase of weight was less significant. Therefore the increase of isocyanate index from 50 to 80 resulted in a decrease in foam density.

Additionally, the replacement of petroleum based polyol with castor oil based polyol contributed to the increase of density. This was because of the high hydroxyl number and low equivalent weight of castor oil. Therefore, compared with petroleum-based Voranol 4701, the same amount of castor oil required a larger amount of isocyanate to reach the same isocyanate index. Also as discussed above, the reactivity of secondary hydroxyl groups in castor oil was much lower than that of primary hydroxyl groups in petroleum-based polyols. During the process of foam blowing, castor oil cannot generate stable polyurethane matrix to trap carbon dioxide, which led to a smaller volume.

#### **4.3.2.2 Compression force deflection**

Figure 4.14 illustrates the effect of isocyanate index on compression force deflection with different levels of castor oil replacement.

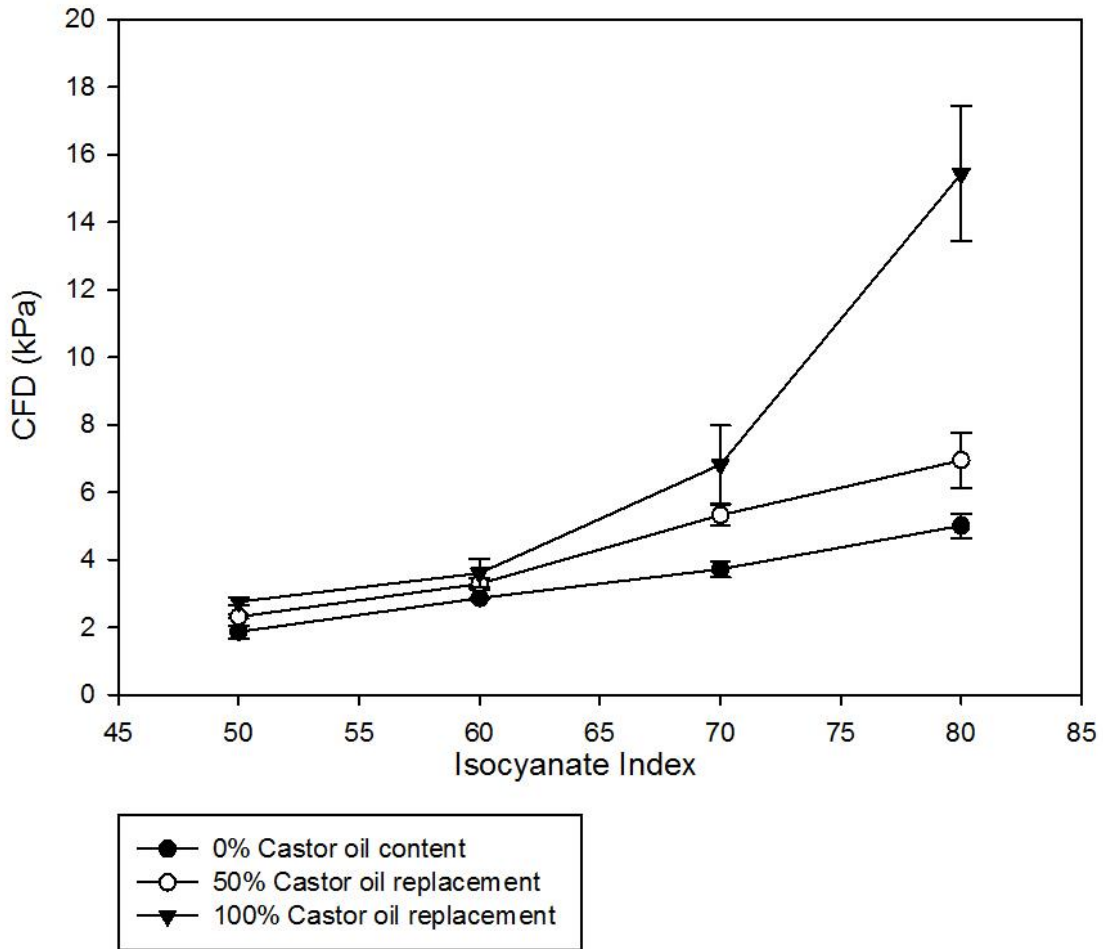


Figure 4.14 CFD of flexible foams with different isocyanate indices.

With the increase of isocyanate index, the compression force deflection of foams increased even though the foam density decreased at the same time (Figure 4.13). This was because a higher isocyanate index led to a higher cross-linking density which was beneficial to the increase of compression force deflection. Since the carbon chains of castor oil were much shorter compared to the petroleum-based Voranol 4701, the cross-linking density of castor oil was much higher and the influence of isocyanate index on CFD was much more significant for castor-oil-based foams.

#### 4.3.2.3 Constant deflection compression

Figure 4.15 demonstrates the influence of isocyanate index on 50% constant deflection compression.

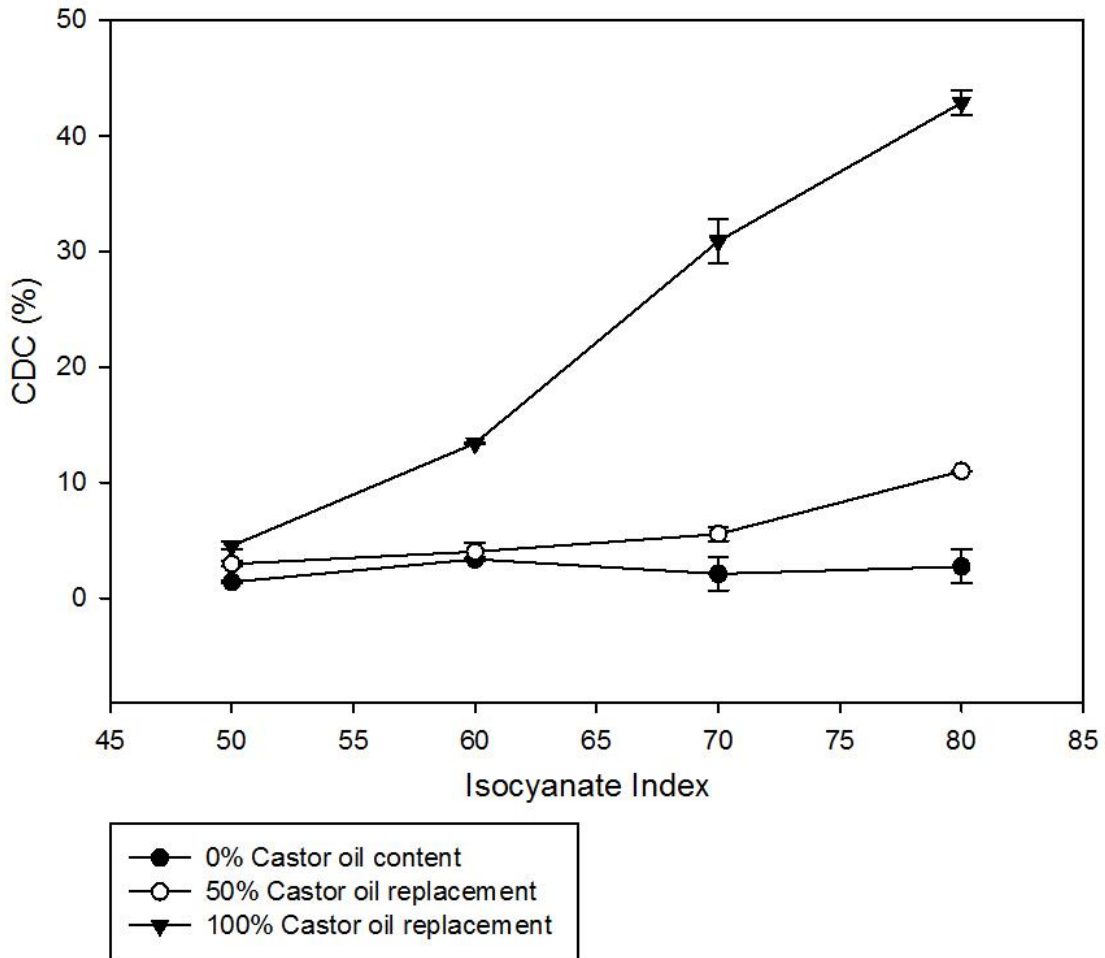


Figure 4.15 50% CDC of flexible foams with different isocyanate indices.

For petroleum-based polyurethane foams, Isocyanate index had no significant effect on the foam's CDC value. However, for the foams with 50 and 100% castor oil replacements, the value of CDC increased with the increase of

isocyanate index. Especially for foams with 100% castor oil replacement, the influence of isocyanate index was significant. Fifty percent CDC tests reflected the flexibility of a polyurethane foams, which depended on the polyurethane soft segments. Not all ricinoleic acid in castor oil was used after the depletion of isocyanate. The unreacted ricinoleic acid could form a part of soft segments. Increasing isocyanate index gradually consumed the unreacted hydroxyl groups from castor oil to form the cross-linkage structure. Thus, the flexibility of castor-oil-based foams was less leading to a higher value of 50% CDC. Due to the long carbon chains in the molecular structure of V4701, such influence was not present.

#### **4.3.2.4 Tear Resistance**

Figure 4.16 displays the positive relationship between tear resistance and isocyanate index.

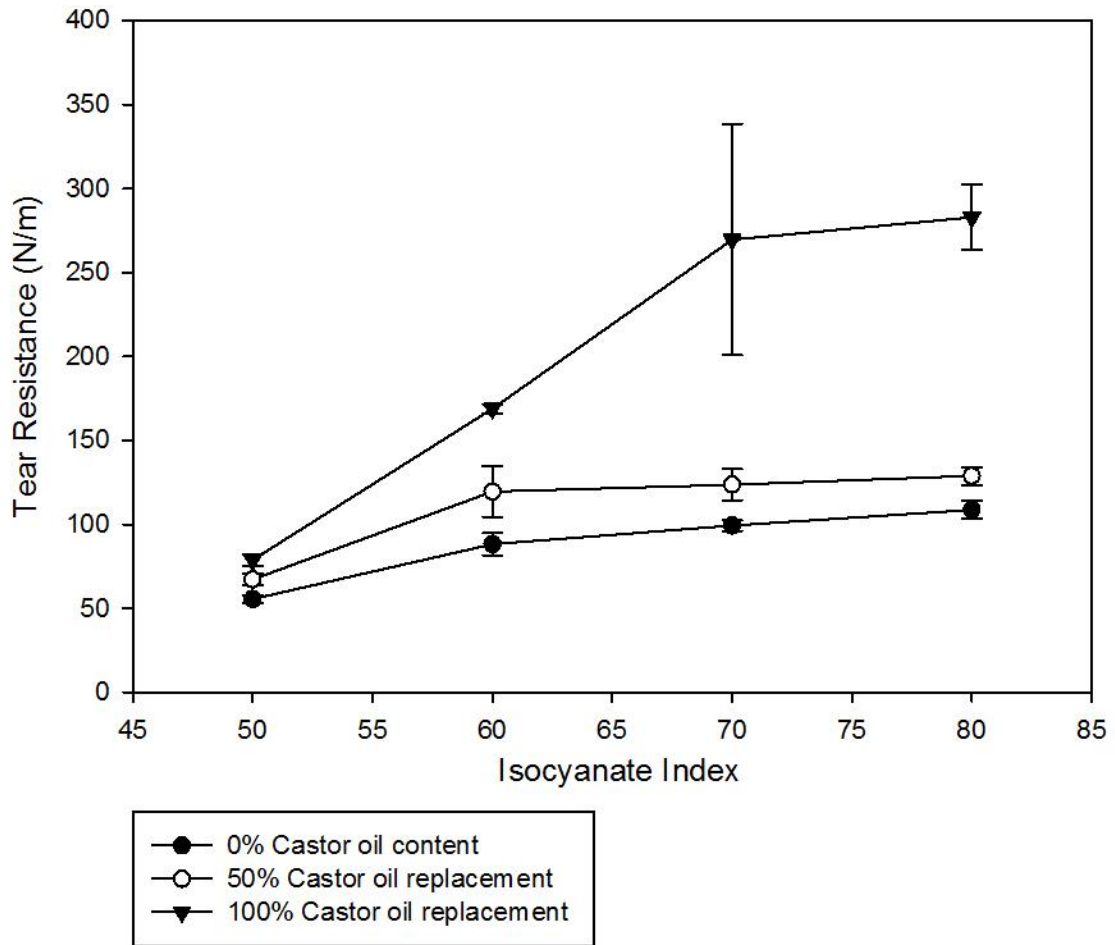


Figure 4.16 Tear resistance of flexible foams with different isocyanate indices.

As stated above, a higher isocyanate index resulted in a higher degree of cross-linkage. A larger force was then required to tear the foam into two pieces. For the same reason, the castor-oil-based foams with higher isocyanate index contained a denser cross-linking network and had a much higher tear resistance.

#### 4.3.2.5 Resilience

Figure 4.17 shows the relationship between resilience and the isocyanate index.



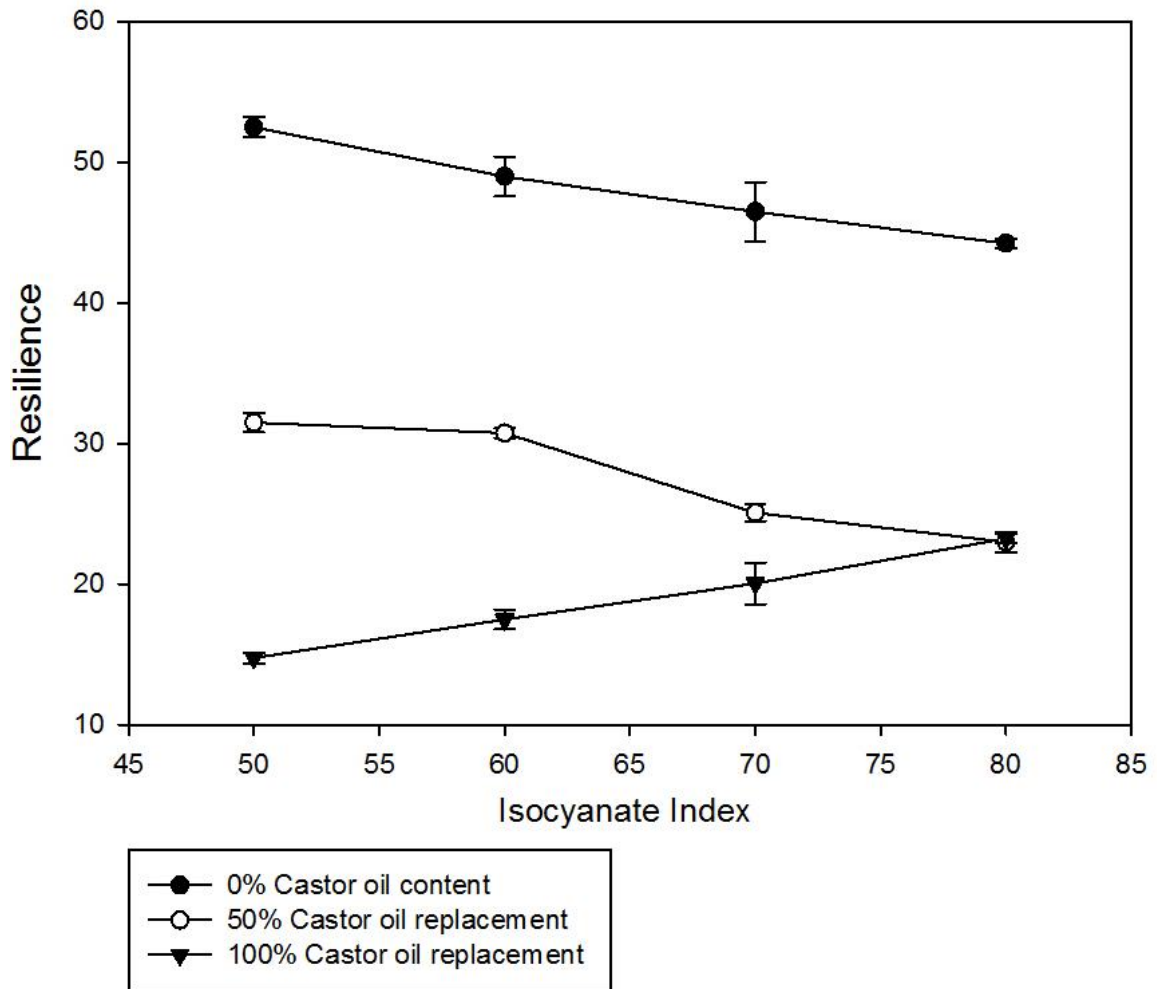


Figure 4.17 Resilience of flexible foams with different isocyanate indices.

For both petroleum-based foams and foams with 50% castor oil replacement, the resilience decreased with the increase of the isocyanate index. The increase of isocyanate index contributed to firmer cross-linking structures and thus increased the damping effect resulting in a low resilience.

However, foams with 100% castor oil replacement showed the opposite trend. The value of resilience test rose along with the isocyanate index.

According to the 50% CDC results in Figure 4.15, the flexibility of castor-oil-based foams decreased with the increase of the isocyanate index. Castor oil based foams with an isocyanate index of 80 could hardly recover after constant compression in the CDC test. It was not the property of foam resilience to rebound the iron ball, but the property of foam hardness. Just as when releasing a ball from above a rigid plate, the harder the plate is, the higher the ball would rebound. Therefore, in this instance, the ball rebound test did not reflect the resilience of these foams.

#### **4.4 Conclusion**

In this study, water-blown flexible polyurethane foams containing 50% and 100% castor oil replacement was prepared. The effect of foaming temperature was investigated and the “hot-mold cold-cure” method was applied in castor-oil-based flexible polyurethane foams. The effects of castor oil replacement, cross-linker content and isocyanate index were studied. Flexible foams with castor oil replacement had a higher density and higher cross-linking degree. Cross-linkers were necessary for foams with castor oil replacement to protect the structure from collapse. However, the cross-linker content also had a negative influence on density and flexibility. Isocyanate index influenced the density of cross-linking networks and hardness. Castor oil based foams with a lower isocyanate index had better flexibility properties, but improvement in the resilience of foams with 100% castor oil replacement needs further investigation.

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