

AN EXPERIMENTAL STUDY ON THE
MICROSTRUCTURE–MECHANICAL PROPERTY RELATIONSHIP
OF CRUMB RUBBER–POLYURETHANE FOAM COMPOSITES

By

ABHISEK BHADRA

Bachelor of Engineering in Mechanical Engineering
Jadavpur University
Kolkata, India
2006

Submitted to the Faculty of the
Graduate College of
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
July, 2010

COPYRIGHT ©

By

ABHISEK BHADRA

July, 2010

AN EXPERIMENTAL STUDY ON THE
MICROSTRUCTURE–MECHANICAL PROPERTY RELATIONSHIP
OF CRUMB RUBBER–POLYURETHANE FOAM COMPOSITES

Thesis Approved:

Dr. Raman P. Singh

Thesis Advisor

Dr. Kaan A. Kalkan

Dr. Sandip P. Harimkar

Dr. Mark E. Payton

Dean of the Graduate College

ACKNOWLEDGMENTS

It has been a fascinating experience for me to pursue my Master of Science degree at Oklahoma State University. From a learning point of view, it has never been easy, but nonetheless pleasant, as something great awaits for you after every disaster. There used to be time when I believed that I would never be able to construct a good research thesis because of numerous moments of failures I had undergone. But, eventually, the ray of hope came, as there was someone who had more belief on me than I had on myself. He is my advisor, Dr. Raman P. Singh. Probably, the only thing I never missed for a single day in the United States is his kindness towards me. I am very grateful to him for everything.

I would like to thank Dr. Kaan Kalkan and Dr. Sandip Harimkar for serving on my thesis committee. Dr. Kalkan has always been very helpful. I can still remember several instances of knocking the door of his lab with my bunch of questions but never came back without answer. I would also like to thank Dr. Harimkar from the bottom of my heart as I always received his generous support, whenever needed.

I shall be failing in my duties if I do not acknowledge the support of Dr. Gajendra Pandey. He has been such a wonderful and approachable mentor for me that after a point of time I started calling him “Gajju” shipping the title of ‘Dr’ in front of his name. Whenever I used to make samples in the laboratory with my vertical aluminum molds, I always remembered him, as this simplified design was by Dr. Pandey. It is not possible for me even to remember the number of simple questions I have asked him, but he always answered with a smile. Gajju, I will always be grateful to you from the bottom of my heart. God bless you Sirjee.

I am thankful to Dr. Abhishek Singh and Dr. Pranav Nawani for acting as my mentors.

Though I have not been fortunate enough to spend enough time with them, it has been a fantastic learning experience.

I would also like to thank the cutest couple I have ever met in my life. It was not possible for me to know how good human beings can be until and unless I met Leila and Masoud. I can never forget the help and kindness I have received from them throughout my two years of life at Oklahoma State University. I would like to wish them best of luck for their future. May God bless you both.

It has never been possible for me to consider MAML and Arif as two different entities. A perfect Ph.D student, and a devoted Chelsea fan of course, Arif has been a fantastic friend. Whenever, I faced any problem, I saw him coming with a determined and smiling face ahead of me with a widespread helping hand. I wish Arif all the best for his upcoming life.

Chirag and Dhivakar have been fantastic friends and lab mates throughout my two years of study at OSU. I have always seen them being available for help, keeping tons of personal work aside. I still remember my first day in the lab when I broke one mechanical stirrer and became very disappointed. It would never have been possible for me to be confident enough to break things again, until I got these two friends along with Arif beside me.

No one can forget his first pal in a different country. Mohammed and I joined MAML on the same day and became friends. We took 30 credit hours together and had several major fights regarding Manchester United and Liverpool. He has always been a brother to me.

The difference between chemistry and mystery became much less from the day Ms. Sesumani Vorrey joined MAML. She has been a very helpful friend and research associate throughout my last 6 months of study. I would like to give her a big thanks for all of her support and help I have received.

I am also thankful to Dr. Dale Teeters at the University of Tulsa, for allowing me use the FTIR and other facilities. I also acknowledge the support of R. T. Vanderbilt, Inc.,

(Norwalk, CT) and Lubrizol Inc., (Cleveland, OH) in donating surfactants for this research.

Heroes always come at the end of any commercial Indian movie and give a dazzling performance. Hence, this is the time for my three heroes of MAML. I have been fortunate enough to get three wonderful roommates whose presence made United States a home away from home. One shares the name with me and is not much different from Leonardo Di Caprio. He is Mr. Abhishek Jain, a cinema lover and an early to bed, early to rise person. Mr. Clint Eastwood would be much more happy if he was compared with Kunal Mishra as Mishra is the real Dirty Harry in our group. Last but not the least is Mr. Suman Dasgupta, aka Don Cheadle (proclaimed by me, Jain, and Kunal) aka Hrithwik Roshan (self-proclaimed). All of these are fantastic students and very good friends. I have always taken valuable suggestions from them and it made my life much easier. We have shared some good times together and those moments are really unforgettable. God bless them all.

I would like to express my gratitude towards my other friends and lab mates at MAML, Chaitanya, Balaji, Vasu, Austin, Phil, Sadia, and my only cigarette partner, Hamim.

TABLE OF CONTENTS

Chapter	Page
1 INTRODUCTION	1
2 LITERATURE SURVEY	15
3 MATERIALS AND EXPERIMENTAL CHARACTERIZATION	27
4 RESULTS AND DISCUSSION	45
5 CONCLUSIONS AND FUTURE WORK	79
BIBLIOGRAPHY	83

LIST OF TABLES

Table		Page
1.1	Rubber waste situation in early 90s [1]	5
2.1	Properties of different organic compounds for rubber surface treatment [1] .	16

LIST OF FIGURES

Figure	Page
1.1 Piling yard of waste tires, adapted from [13]	2
1.2 Different uses of scrap tires, adapted from [5]	3
1.3 Typical structure of surfactants and formation of a micelle, adapted from [14]	6
1.4 Typical crumb rubber particles recycled from waste tires, adapted from [15]	8
1.5 Chemical synthesis of polyurethane, adapted from [16]	10
1.6 Chemistry behind polyurethane foam formation, adapted from [16]	11
3.1 Sieve analysis data for crumb rubber having 40-99-mesh size, adapted from [80].	27
3.2 Optical micrograph showing crumb rubber particles inside foam	28
3.3 Basic concept of polyurethane foam formation by chemical blowing method, as used in this investigation, adapted from [16]	28
3.4 Chemical structure of PMDI (Part A), adapted from [82]	29
3.5 Chemical structure of HFC-245fa (Part B), adapted from [83]	30
3.6 Chemical structure of Darvan WAQ, adapted from [84]	31
3.7 Monomer of Vycar 660 × 14, adapted from [87].	31
3.8 Mold for preparing rubber-foam composites used in the present study . . .	33
3.9 Visible color change in rubber by the application of surfactant	33
3.10 Rubber–polyurethane foam composites generated in this present study . . .	34
3.11 Microscope picture of rubber-polyurethane foam composite showing pores inside structure	36

3.12	Cylindrical samples along the height of rubber–foam composites for characterization	37
3.13	Determination of physical properties by density determination set up	38
3.14	Vacuum infiltration chamber set up used in the present study	39
3.15	Helium ultrapycnometer 1000 used in the present study	40
3.16	Foam–rubber specimens subjected to compression test following ASTM C365/C365M	41
3.17	Force versus displacement curve of a material with Hookean region, adapted from ASTM standard C365 [90]	42
3.18	The notations for specimen dimensions and 3-point bending test configuration [92].	43
3.19	Failure of composite specimens subjected to 3 point bending test	43
4.1	XRF analysis for the virgin crumb rubber samples	46
4.2	Effect of surfactants on the bulk density of polyurethane matrix system without rubber	46
4.3	Effect of surfactants on the open porosity of polyurethane matrix system without rubber	47
4.4	Effect of surfactants on the closed porosity of polyurethane matrix system without rubber	48
4.5	Effect of surfactants on the skeleton density of the polyurethane matrix system without rubber	49
4.6	Effect of crumb rubber particles on bulk density of polyurethane foam system	50
4.7	Effect of crumb rubber particles on skeleton density of polyurethane foam system	51
4.8	Effect of rubber particles on the closed porosity of polyurethane foam system	51
4.9	Effect of rubber particles on the open porosity of polyurethane foam system	52

4.10	Effect of Darvan on the bulk density of rubber and polyurethane foam composites	53
4.11	Effect of Darvan on the skeleton density of rubber and polyurethane foam composites	54
4.12	Effect of Darvan on the closed porosity of rubber and polyurethane foam composites	55
4.13	Effect of Darvan on the open porosity of rubber and polyurethane foam composites	56
4.14	Effect of rubber on the physical properties of polyurethane foam composites	56
4.15	Agglomeration of rubber particles inside polyurethane foam	57
4.16	Effect of rubber on the physical properties of polyurethane foam composites	58
4.17	Effect of rubber particles on the porosity ratio of polyurethane foam system	59
4.18	Effect of rubber particles and surfactants on the porosity ratio of polyurethane foam System	60
4.19	Compressive stress-strain curve of rubber-polyurethane composites at different strain level	61
4.20	Compressive modulus of rubber-foam composites	62
4.21	Compressive strength of rubber-foam composites	63
4.22	Load-deflection curve of rubber-foam composites	64
4.23	Flexural modulus of rubber-foam composites	65
4.24	Flexural strength of rubber-foam composites	65
4.25	Specific compressive strength of rubber-foam composites as a function of rubber content	66
4.26	Specific compressive modulus of rubber-foam composites as a function of rubber content	67
4.27	Specific flexural strength of rubber-foam composites as a function of rubber content	69

4.28	Specific flexural modulus of rubber-foam composites as a function of rubber content	71
4.29	Cubic cell model of a closed cell foam [94]	72
4.30	Comparison of experimental relative elastic modulus with different models	74
4.31	SEM images showing tearing of rubber particles in the tension side of test specimens	75
4.32	SEM images showing defects inside blend composites with highest rubber content	75
4.33	SEM images of fractured surfaces of composite samples with 30 weight % of rubber	76
4.34	FTIR spectra of only Darvan and blend composites made with Darvan . . .	78
4.35	FTIR spectra of only Vycar and blend composites made with Vycar	78

CHAPTER 1

INTRODUCTION

Problem Statement and Motivation

The disposal of waste materials is a serious concern for humankind. Certain polymeric materials are specially problematic as they can be hard to decompose. One such example is rubber. Probably, the most common use of rubber all over the world is as tires in automobiles and other transport vehicles. While the unique structure and property of both vulcanized natural rubber and synthetic rubber provides stability for use in tires, it also makes recycling challenging. As a result, very little raw chemical precursor material (less than 1%) can be reclaimed for reuse from these waste tires. The chemistry of rubber in these disposed tires also plays a major role in the associated environmental pollution. Due to its cross-linked structure, rubber needs a long time for natural degradation. In addition, the presence of stabilizers and additives in rubber further delays the process [1].

In United States of America, more than 270 million of tires are scrapped every year. In addition, almost 300 million tires are stockpiled in different landfills [2]. This has a detrimental effect on the environment as well as reducing the number of available disposal sites. Tire piling yards, as shown in Fig. 1.1, become the inhabitation of animals and insects resulting in further environmental damage [3]. It has been found that the two species of mosquitoes, *Aedes aegypti* and *Aedes albopictus*, that are mainly responsible for yellow fever and dengue, prefer scrap tires as their main habitat [4].

The most convenient way of decomposing waste tires is to burn them. Probably this is the reason why the Scrap Tire Management Council reports almost 57% of recycled tires are used as fuel [5]. But this is not a very sophisticated methodology and suspect from an

environmental viewpoint. In some countries, the stockpiling of tires is strictly prohibited as this can create a possible fire hazard. Several investigators have pursued methods to recycle rubber from used tires [1, 2, 5–12]. However, the primary challenge has been the three-dimensionally cross-linked chemical structure, and consequently, no recycling technology has been found to be very appropriate or effective [1].



Figure 1.1: Piling yard of waste tires, adapted from [13]

Objective

The basic aim of this current work is to reinforce polyurethane foam using crumb-rubber to enhance mechanical properties of the foam without affecting the thermal insulation or acoustic absorption properties. This effort employs direct incorporation of rubber particles into rigid polyurethane foam. The hope is that this resulting material can be used in place of traditional application of polyurethane foam, but offer greater mechanical properties in terms of specific strength, modulus, and toughness, and can definitely be seen as a means of utilizing post-consumer waste tires. The more resilient rubber particles are supposed to be effective in resisting impact damage. Initial studies showed that materials can be easily fabricated using various volume fractions of crumb rubber with promising mechanical properties, which has served as the basis for this current research work. Polyurethane

foams are selected as they are widely used in the industry. We believe that if small rubber particles can be successfully incorporated inside polyurethane foam matrix with enhanced properties of the end products, this approach will yield a good avenue for recycling of rubber from used tires.

Overview of Waste Tire Recycling

The recycling and reclaiming of rubber particle has been a subject of serious concern for humankind, as with the decrease of available landfill sites that accept tires, the disposal of waste rubber is becoming more difficult. The process of rubber compounding always involves the mixing of various ingredients like stabilizers, plasticizers, flame-retardants, and colorants. These chemicals leach from the bulk to the surface and ultimately to the landfill. Consequently, they kill the advantageous bacteria of soil [1]. Fig. 1.2 shows different uses of scrap tires.

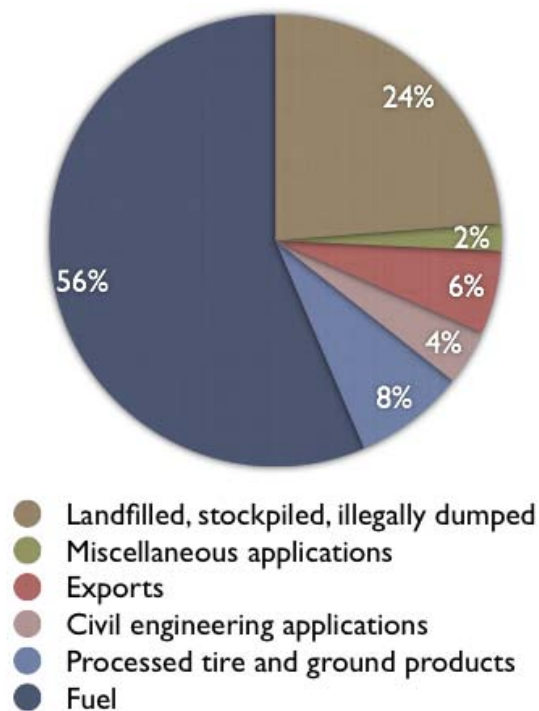


Figure 1.2: Different uses of scrap tires, adapted from [5]

As we can see from the Fig. 1.2, the biggest market for the recycled rubber technology

is the tire derived fuel industry. This is simply the burning of tires in cement kilns, and a method suspect from environmental considerations. Almost 4% of scrap tires are used in the civil and infrastructural applications where novel products are made mixing recycled rubber particles with concrete [5]. Another major reuse application is the production of crumb rubber which is mostly related to the present work.

Recycling technologies have either focused on chemical reclamation, or shredding as use as secondary material. Reclamation technologies have not been found to be highly effective due to the three-dimensionally cross-linked structure of rubber. Recycling by reuse of shredded tires has been limited by end-use application.

The most primitive method of polymeric material recovery is reclamation. Reclamation is the chemical process where conversion of a three dimensionally interlinked and infusible thermoset polymer takes place into a two dimensional, soft, plastic low modulus product. In physical recycling, waste tires are processed into two main physical forms. The first type is shredded or chipped rubber tire that is produced through a two-step shredding–cutting process. After the first stage of shredding, rubber particles attain a length of 300–430 mm with a width of 100–230 mm. In the second stage, the shredded particles are cut down to dimensions of 100–150 mm. Continued shredding produces rubber particles having dimension of 13–76 mm. These shredded rubber particles are processed through subsequent steps of magnetic separation to remove the metallic inclusions from tires, grinding and screening. Ultimately, the particles are processed with a typical size of 0.075–9.5 mm, and this is called crumb rubber [6]. This study is focused on the use of crumb rubber, because the interest is in the use of small particles as reinforcing aids that can be easily incorporated inside a polyurethane foam matrix.

The rubber waste situation in early 90s is shown in Table. 1.1. It is very evident that in the early 90s, the rubber waste situation in the United States was quite environment-friendly in comparison to other countries as the percentage of landfill deposition was almost zero. But, this condition became worse with time. According to the Rubber Manufacturers Asso-

ciation, recent waste situation witnessed an annual deposition of almost 300 million waste tires to different landfills in United States [2] which is reducing the number of available disposal sites.

Treatment	France	Germany	Italy	USA
Retreading%	20	17.5	22	None
Recycled%	16	11.5	12	28
Energy%	15	46.5	23	72
Landfill%	45	4	40	None
Export%	4	16	2	None

Table 1.1: Rubber waste situation in early 90s [1]

Recycling of rubber tires necessitates the removal of metal wires from the same. This is a costly process. In addition, polymeric rubber compound requires some sort of surface treatment for its own stability and compatibility to other materials. It has been expected and seen that de-wiring and surface treatment of rubber would enhance its economic recycling and applicability to produce new generation materials [5].

Surface Treatment of Rubber Particles

The basic aim of surface treatment of rubber particles is to treat ground rubber to make it more reactive inside vulcanized material without breaking the bond. This is accomplished in several ways. One approach is to coat the rubber particles with a bonding agent to make it chemically reactive inside a new compound. The second approach is to activate the surface of the rubber particles by using some caustic gas. In the early 90s, researchers exposed ground rubber to oxidative gas mixtures containing small amount of fluorine and other reactive gases like oxygen or sulfur dioxide [5]. The resulting reactions form hydroxyl (OH^-) or carboxylic (COOH^-) reactive groups resulting in an enhancement of the surface energy of the material. Subsequently, the treated rubber particles formed strong chemical

bonds with other materials [5]. Smith *et al.* [10] also discussed the surface treatment of ground rubber particles by treating them with chlorine gas. This treatment improved the compatibility of rubber with other polymeric compounds, but is a hazardous procedure.

Some researchers have used surfactants to activate the rubber particles with an intention to enhance their bonding with different compounds. Our present work is based on the use of surfactants to avoid the exposure and hazards associated with caustic gases.

Surfactants are short chain fatty acids. They have a unique structure where one part has an affinity towards the polar media while the other part is attracted by the non polar media. Surfactant molecules generally form oriented monomers at interfaces and show surface reactivity. They do so by lowering the surface tension of the dissolving medium. An example of a commonly used surfactant in daily life is detergent. These are special kind of surfactants whose solutions provide cleaning properties. In other words, detergents change the interfacial properties and remove a phase from the solid surfaces [14]. Fig. 1.3 shows the typical structure of a surfactant.

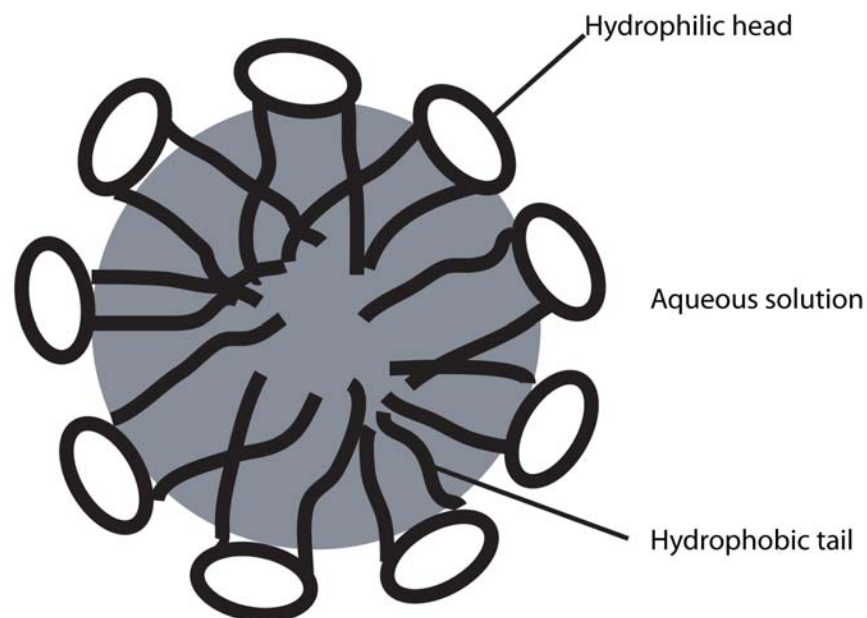


Figure 1.3: Typical structure of surfactants and formation of a micelle, adapted from [14]

The typical structure of a surfactant molecule is a combination of a hydrophilic head

group and hydrophobic chain group in the molecule. The polar or ionic group interacts with the aqueous environment through dipole-dipole or ion-dipole interactions. In aqueous solutions, surfactants work as an electrolyte. But they act differently at a higher concentration. They form organized aggregates of large number of molecules known as micelles. In a micelle, the lipophilic parts of the surfactants move towards the interior of the aggregate making hydrophilic parts to face the aqueous medium. The formation of a micelle can be seen as a compromise in between the desire for the alkyl chains to avoid the contacts with water and the tendency of the polar group to keep contact with water [14].

The physico-chemical properties of surfactants vary significantly above and below a particular surfactant concentration. This is known as the critical micelle concentration (CMC) of a surfactant. Below the CMC value, the properties of an ionic surfactant resemble the same of as that of an electrolyte. On the other hand, above the CMC value, these properties change markedly showing a cooperative process. At CMC, micelles are formed. Since the thermal and electrostatic forces directly oppose micellization, a low CMC value is always accompanied by increasing the lipophilic part of the molecule, lowering the temperature, and addition of electrolyte. Micellar models always consider micelles as a separate phase. According to pseudo-phase model, the critical micelle concentration of any monomer is defined as the concentration of maximum solubility of that monomer in that particular solvent. This is significant, as in any process the concentration of surfactants should be just near its CMC value or just a little bit higher. This is because the greatest effect of surfactant is always seen when it forms considerable micelle in the solution, whether it is the process of interfacial tension lowering or foam stability. Another significance of the CMC value is that it represents the solution concentration of surfactant where maximum adsorption takes place. Plotting the physico-chemical property against the concentration for a given surfactant-solvent system represents the importance of CMC value for each and every surfactant. This plot is called the Prestons classic graph, and it shows a considerable change in slope in a narrow concentration range of surfactant [14].

Crumb Rubber

Crumb rubber is usually defined as rubber having a particle size of 9.5 mm (3/8 inch) or less. They can be classified into four groups: coarse, 9.5 to 6.3 mm; mid range, 2 to 1 mm; fine, 0.4 to 0.2 mm; and superfine, 0.15 to 0.075 mm. The size of crumb rubber is designated by means of a mesh through which it is passed during its production. While only a small number of tires have been converted to crumb rubber historically, there is increasing interest in using this form of recycled tire rubber for creating reusable products [9, 12] because of the ease of material fabrication along with the probability of enhanced toughness in the end products. Based on available data, about 9 million tires were converted into crumb rubber in the year of 2001, and this number has been growing at an annual rate of 10–15% [12]. Also, as a point of reference, each tire produces about 10–12 pounds of crumb rubber [10].



Figure 1.4: Typical crumb rubber particles recycled from waste tires, adapted from [15]

Out of all reuse options, crumb rubber is the most complex but least studied subject in terms of both production and market. In 1994, 2% of the total generated scrap tire was utilized into the production of crumb rubber. This had increased up to 12% by the year of 2001. The main advantage of crumb rubber market is the popularity and utilization of

all types of crumb rubber product. For example, different crumb rubber producers existing in the same industry always need different mesh size of rubber particles for their unique product. Consequently, it is not easy to generalize particle size requirement in crumb rubber market and to forecast the market demand and production planning of the same [9].

Polyurethane

Polyurethanes are polymers that have a chain of organic units joined by urethane or carbamate links. Their formation takes place through step-growth polymerization where a monomer having at least two isocyanate group forms bond with another monomer having at least two alcohol groups. The first work on polyurethane (or commonly urethane) polymers took place in Germany by Otto Bayers and his co-workers in the year of 1937 [16].

Polyurethanes are reaction polymers and they lie in the same group as epoxies, unsaturated polyesters, and phenolics. As mentioned, a urethane linkage is produced by the reaction of isocyanate group ($-N=C=O$) with hydroxyl ($-OH$) group. Similarly, the polyurethane linkage follows the same path having the urethane linkage ($-RNHCOOR$) in the resulting product, as shown in Fig. 1.5.

Commercially, polyurethanes are prepared by the reaction between liquid isocyanate with liquid blend of polyols. These two components together are termed as a polyurethane system [16]. But, sometimes, polyurethanes are produced by the reaction of diisocyanate with a blowing agent directly. This investigation employs the latter approach.

Polyurethane can be easily fabricated as foam. Different blowing agents can be incorporated inside the diisocyanate–polyol combination as an auxiliary system or into the poly side. Blowing agents react with isocyanate to produce carbon dioxide gas resulting in the expanding of cells during the mixing process. For example, water molecules react with isocyanate to produce carbamic acid, which is unstable and breaks down into carbon dioxide and an amine group. The amine group thus produced, reacts with more isocyanate to produce a substituted area. Water produce significant amount of urea. This is not very soluble

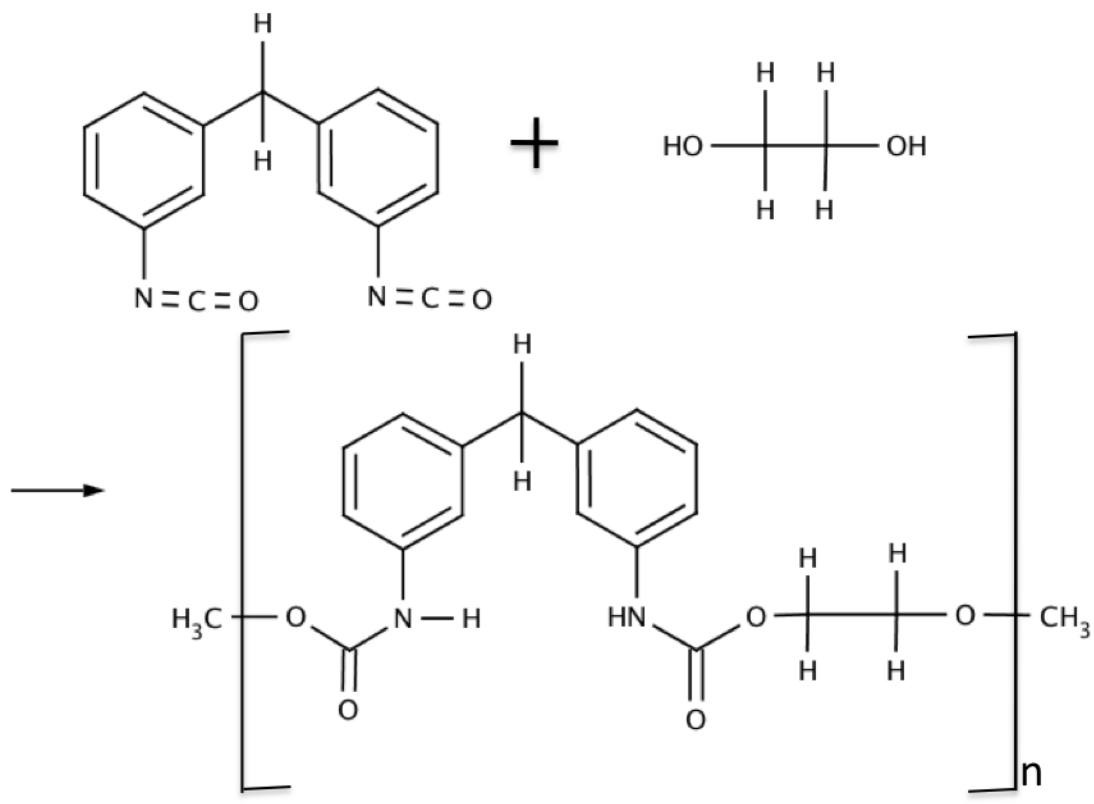


Figure 1.5: Chemical synthesis of polyurethane, adapted from [16]

ered highly versatile materials. The range of polyurethane type and the end products from them is high. They are available starting from rigid or flexible lightweight foams up to stiff and tough elastomers. This makes them widely used products in various industries. For example, rigid polyurethane foams are used mostly in thermal insulation of building, refrigerators, pipelines, and storage tanks, buoyancy and flotation device, packaging, furniture, and equipment housing. On the other hand, flexible foams find their applications in household furniture including bedding, automotive seating, textile laminates, and cushioning. Semi rigid and low-density structural foams are used in making sports goods, such as, skis and surfboards, steering wheels, and headrests. Elastomers have got wide applications in making shoe soles, vehicle body panels, rollers and gear wheels, conveyors, and sealants for automotive industry [19].

Effect of Particle Distribution on Foam Stability

Foams in liquid–liquid macro emulsions, where the droplet size varies between 1–100 micrometers, are thermodynamically unstable since their decay results in a decrease of the free energy of the system. Therefore, foams are considered as metastable for their applications because of their possible breakdown in the system. Primary processes of instability in foams are creaming, sedimentation, coalescence, and flocculation. The first two are gravity-induced movements caused by the density difference between phases. Since, gravity-induced movements are highly dependent on density, liquid drainage is significant in foams. This drainage is the basic force behind the formation of polyhedral structures in foam. Coalescence involves the binding of two bubbles where interfacial film drains and ruptures leading to the formation of one single large bubble. Flocculation involves interaction between emulsion droplets where, the interfacial film wall does not drain to rupture, and droplets are fastened to each other like a cluster. Another major foam instability is disproportionation. This is the process where air molecules diffuse between bubbles. As the pressure is increased inside smaller bubbles, diffusion flux generally results in shrinkage

of smaller bubbles and growth of the larger resulting in further drainage and coalescence. Therefore, a third component is required to stabilize the foams. This component can be a foaming or emulsifying agent. Such agents should satisfy the conditions of foaming as well as stabilizing it throughout required time periods. The most common emulsifiers are surfactants. They adsorb to the interface and reduce the free energy by producing high surface area interface resulting in a reduction in interfacial surface tension [20].

It is generally accepted that particles at an interface prefer to stay in any of the liquids, mainly the disperse phase. It is also known that the adsorption of particles at bubble interfaces is an important mechanism in the dynamic foaming processes. The association of particles to create a steric barrier to coalescence is the main reason for foam stabilization [20]. Smaller particle having high concentration form the most effective barrier. The effect of particles on the inter film, for example retardation of drainage and enhancement of maximum capillary pressure, is also important as the effect of drainage increases. Bridging of particles in between bubbles can also put forward important contribution because of the high force contact area in foam phases [20].

The wettability of particles also plays an important role. For example, particles do not contribute much as stabilizers in aqueous foaming system. They destabilize the foam from bridging drainage. Also, since, foams are deformable and delicate, they can be subjected to foam destruction by means of particle piercing in case of larger particles [20].

Focus of the Present Work

In this work, an attempt has been made to reinforce rigid polyurethane foam to enhance its specific strength, modulus, and toughness properties by incorporating particles of rubber recycled from scrap tires. In addition, the relationships between rubber content, surfactant, physical foam characteristics, and mechanical properties, are investigated in detail. These materials can definitely be seen as a means of utilizing post-consumer waste tires. Since, polyurethane is a widely used material in the industry, it is believed that the materials,

if developed successfully, will find wide applications and provide a high volume use of recycled rubber.

CHAPTER 2

LITERATURE SURVEY

Prior Research in Rubber Recycling

Investigations on the recycling of used rubber fall in to three broad categories: economic analysis; reclamation; and use of shredded or ground rubber. First, some studies discuss the engineering economics and feasibility analysis of recycled rubber products [5,9,10]. Amari *et al.* [5] analyzed how to maximize value recovery by calculating the life cycle energy budget considering both the energy consumed for tire production and energy recovered from their use as fuel. Their study put significant importance on the reuse of rubber products and showed that used tires represent 23 petajoules of embedded energy from raw materials annually, which is equivalent to four million barrels of oil. Sunthopagashit *et al.* [9] examined the engineering economics of crumb rubber facilities with a financial model of a nominal processing operation to aid the analysis of different market, crumb size, and production scenarios. Their study analyzed the complex interactions between the demand and production factors, and showed how pricing, quality, mesh size, and end-user markets could be deciding factors in the crumb rubber business. Smith *et al.* [10] proposed testing and evaluation of commercial applications of new surface treated rubber technology utilizing waste tires and proposed that recycled rubber particles without odor and low moisture content could be the keys to its successful commercial applications.

The common methods of reclamation have been achieved using various organic (diphenyl disulfide, dibenzyl disulfide, diamyl disulfide, alkoxy aryl disulfide, butyl mercaptan, thiophenols, xylene thiols and phenol sulfide etc), inorganic (toluene, naphtha, benzene, cyclohexane, iron oxide phenyl hydrazine based catalyst, copper chloride-tributyl amine catalyst,

diphenyl guanidine etc) and other chemical compounds (thiocarboxylic acid, thioacetic acid, 1,3,5-trimethyl benzene, 2-mercaptobenzothiazole etc) [1]. Some significant organic compounds used in the surface treatment of rubber during the process of reclaiming are shown Table. 2.1.

Name of the Chemical	Attacking Position of Cross-Link Bonds
Triphenylphosphine	Polysulfide links into monosulfide and to lesser extent disulfide
Sodium di-n-butyl phosphite	Di and polysulfide crosslinks
Propane-thiol/piperidine	Polysulfide linkages
Hexane-1-thiol	Both polysulfide and disulfide linkages
Dithiothreitol	Disulfide bonds into two thiol groups
Lithium Aluminum Hydride	Disulfide and polysulfide bonds
Phenol Lithium in Benzene	Polysulfide and disulfide bonds
Methyl Iodide	Monosulfide linkages

Table 2.1: Properties of different organic compounds for rubber surface treatment [1]

Several researchers have worked on the recycling and reclamation methodologies of waste rubber products to make them reusable for engineering applications [1, 8, 21]. Adhikari *et al.* [1] discussed the method to reduce the waste problem, recycling, reuse of used waste rubber and reclaiming of raw rubber materials. Their study discussed about several effective reclamation processes like cryo-mechanical, microwave, ultrasonic techniques, and mechanical means. The microwave methodology was found to be the most effective, as other methods cause undue degradation of rubber polymer chains. Romine *et al.* [21] discussed activation of the surface of ground rubber by using thiophilic microorganisms by selectively modifying sulfur cross-links to improve compounding properties. Final products showed increased reactivity of the particle surfaces and improved surface chemistry as a function of biooxidation of sulfur species and concentration of sulfoxide functionalities. Fukumori *et al.* [8] discussed devulcanization using high temperature and pressure.

The third class of studies have focussed on the use of shredded or ground rubber, without devulcanization, in secondary products. Significant amount of work have been done on the mixing of recycled rubber particles inside concrete, bitumen and asphalt to make products appropriate for structural applications. The brittle nature of concrete and its low loading toughness has initiated the use of rubber particles to remedy these drawbacks [7]. Several studies [2, 3, 6, 7, 11, 22–39] discussed the properties and performances of concrete mixed with high volume of crumb rubber from scrap tires. All of them demonstrated promising mechanical properties and enhanced performance by the use of crumb rubberized concrete. Another common trend investigated by all of the researchers was considerable deformation undergone by concrete before failure and its capability to withstand post-failure loads. All of these studies reveal a dependence of properties on the rubber particle size along with an increase in failure temperature. The biggest common advantage depicted by all of these studies had been the ease of fabricating crumb rubberized products for structural applications.

In spite of all these advantages, some drawbacks were also seen. Fattuhi *et al.* [40] analyzed the properties of cement-based materials containing shredded scrap truck tire rubber and got reduced compressive properties and densities of cement by the use of rubber. Fenner *et al.* [41] discussed the environmental and structural implications for the reuse of tires in fluvial and marine construction. They showed that leaching of different chemical compounds like zinc, cadmium and carbon black results in the degradation of rubber tires and limits their use for marine applications, especially in sea water and proposed one corrective measure for the same. In addition, researchers found increased water permeability in the concrete mixtures by the addition of rubber particles.

Rubber Particles in Polymeric Matrix

Rubber particles have been found to be usable in polymeric matrix as well. Elastic rubber particles are expected to absorb large impact energy through plastic deformation of the

particles. Rubber particles would also promote crack pinning and crack bridging. These mechanism should lead to higher toughness in rubber reinforced polymers [42].

Cawse *et al.* [43] proposed the use of rubber as a toughening agent in polyurethane networks and composite materials. They observed that the processing method, rubber particle size, and size distribution are important parameters in affecting rubber–matrix adhesion and material properties. Datta *et al.* [44] used waste rubber for filling cast urethane elastomers. Manoj *et al.* [45] studied the miscibility and fracture toughness of polyurethane–rubber composite blends and obtained enhanced values of fracture toughness by the incorporation of rubber particles. Pastor-Blas *et al.* [46] analyzed the failure behavior of surface treated unvulcanized rubber–polyurethane adhesive joints and found enhanced T-peel strength and improved surface adhesion. On the other hand, Tan *et al.* [47] studied abrasion resistance of thermoplastic polyurethane blended with rubber and found that the tensile strength, elongation at break, and abrasion resistance got increased with optimum rubber content. Danch *et al.* [48] made dynamic mechanical thermal analysis (DMTA) study of the urethane network in rubber waste–urethane composites and conducted thermal analysis of the end product. The reaction between rubber (disulfide bonds) and isocyanate free groups was observed using FTIR. Dhamodharan *et al.* [49] studied blends of ethylene propylene diene rubber and thermoplastic polyurethane and observed improved mechanical properties along with better solvent resistance and enhanced low temperature flexibility whereas, the glass transition temperature was found to increase. Ortiz-Morgan *et al.* [50] published their work on improved adhesion of RF plasma treated rubbers by isocyanate incorporation to polyurethane adhesive. They observed increase of rubber adhesion towards polyurethane adhesive. However, they mentioned the use of isocyanate as the cross-linker because of the presence of anti-adherent compound like zinc stearate. Pachpinyo *et al.* [51] made a preliminary study on the preparation of unsaturated polyester resin and rubber latex blends in the presence of dispersion aids like toluene and liquid ammonia, and obtained increased impact resistance. Sulkowski *et al.* [52] made thermogravimetric study of rubber waste–polyurethane

composites and concluded that no relationship can be drawn between material constitution and thermal or mechanical properties.

Studies on reinforced polymer foams have also been conducted. Li *et al.* [42, 53] synthesized and characterized rubberized syntactic foam. They concluded that the rubberized foam shows higher capability of absorbing impact energy at micro-length scales. This foam is also capable of preventing the micro-length scale damage from propagating into macro-length scale damage. El Lawindy *et al.* [54] studied the physical properties of foam-rubber composites with carbon black as the second binding agent. They concluded that a foaming agent promotes the dilution of carbon in the matrix. Mechanical parameters were found to decrease with an increase of both temperature and foaming agent content. Lin *et al.* [55] studied microstructure-mechanical property relationship of short fiber-rubber-foam composites. They showed that short fibers disperse uniformly in the composites irrespective of treatment, but treated fibers showed much better adhesion with the rubber matrix than untreated ones. The experimental results indicated the enhancement of most mechanical properties such as tensile modulus, hardness, and tear strength by the incorporation of short fibers in the rubber foam matrix. De Mello *et al.* [56] studied the effects of post-consumer PET (polyethylene terephthalate) on the performance of flexible polyurethane foams. They observed much more enhanced mechanical properties in terms of tensile resistance, strain at break, and tear resistance. The reinforced foam yielded better wear and compression resistance than the standard foam without changing the number of cells. Some more works on reinforced polymer foams have been discussed later in this chapter.

Surfactants in Polyurethane Foam System

The use of surfactants has become very popular in heterogeneous blend systems. Numerous surfactants have been tested in virgin polyurethane foams as well as crumb rubber-polyurethane system with specific purposes. Surfactants are expected to coat the rubber

particles resulting in their effective bonding in polyurethane matrix system. On the other hand, surfactants also help in stabilizing the foam matrix. Krupers *et al.* [17] studied the formation of rigid polyurethane foam with a mixture of commercially available siloxane L-6900 talc powder and several semi-fluorinated diblock copolymers as surfactants, and observed a reduction in cell size. Fluorinated surfactants helped in the stability of the foam system. Hawkins *et al.* [57] used the DC-193 surfactant in their study of the cell morphology and mechanical properties of a rigid polyurethane foam. They concluded that there is a relationship between the cell morphology and the compressive modulus and collapse stress in the final product, and also that the size of mold significantly affects the method of foaming. Morimoto *et al.* [58] used another silicon surfactant SH-193, having chemical formula $R(R_2SO)_y(C_nH_{2n}O)_xR$, in their work on rigid polyurethane foam. It was seen that the flexural modulus and the flexural strength increased and their temperature dependence reduced by the use of surfactant and longer fibers as reinforcing agent. Seo *et al.* [59, 60] used polysiloxane ether as a surfactant for the formation of water blown free rising polyurethane foam and saw that that the density and the compressive strength of the foam increased with an increase in the OH value and the functionality of the polyols along with the use of surfactants. Saint-Michael *et al.* [61] used a PDMS/POE copolymeric silicone surfactant to characterize the effect of filler particle size on high-density polyurethane foam. They found that the reinforcement of foam might not be effective if the filler are bigger than the bubble size. Thermal studies suggested that the fillers increase the crosslink density of the matrix. Some other studies can be mentioned in this connection. Singh *et al.* [62] used polysiloxane ether as a surfactant in their work on the reactivity of raw materials and studied its effects on the structure and properties of rigid polyurethane foam. They found increased cream time and gel time of foaming with larger cell size distribution, though, the effects of surfactants were found to be minimal. De Mello *et al.* [56] studied the effects of post-consumer PET (polyethylene terephthalate) on the performance of flexible polyurethane foams and used a silicone surfactant, polysiloxane-polyalkylene block copolymer. They

observed enhanced mechanical properties in terms of tensile resistance, strain at break, and tear resistance. The reinforced foam yielded better wear and compression resistance than the standard foam without changing the number of cells. Goods *et al.* [63] used silicone glycol copolymer surfactant DC-193 with an average hydroxyl number of 75 in their study on the mechanical properties of particle-strengthened polyurethane foam. They observed that the surfactant helped in dispersing the aluminum particles uniformly inside the foam resulting in higher values of modulus and collapse stresses. Lim *et al.* [64] studied the effect of silicone surfactant B 8404 on rigid polyurethane foam. They found the reduction of average foam density associated with the generation of finer cells and increase in closed cell porosity of the rigid foam and concluded that surfactants helped in the foaming process. In addition, the surfactant took part in stabilizing the foam system.

Surfactants in Rubber–Polyurethane Blend System

There is a significant number of studies on the use of surfactants on rubber–polyurethane blend systems. Datta *et al.* [44] used diazabicyclo[2.2.2]octane as a surfactant for characterizing cast urethane elastomers containing waste rubber particles. Lin *et al.* [55] used a new surfactant known as Accinox Tq (polymerized 1,2 dihydro 2,2,4-trimethyl quinoline) for studying the microstructure and mechanical property relationship of short fiber–rubber foam composites. The experimental results showed that the incorporation of short fibers into rubber foams is responsible for the enhancement of mechanical properties such as tensile modulus, hardness, and tear strength. The good interfacial adhesion of the short fibers with the matrix enables further improvement in the mechanical properties. Pastor-Blas *et al.* [46] analyzed the failure mode of unvulcanized rubber–polyurethane adhesive joints by treating the rubber by trichloroisocyanuric acid (TCI) to reactivate the surface and observed enhanced T-peel strength and improved surface adhesion. Danch *et al.* [48] conducted dynamic mechanical thermal analysis (DMTA) study of the urethane network in rubber waste-urethane composites by using Monothane A50 and Monothane A60 urethane

unary (one component) prepolymers as surfactant. FTIR analysis showed the reaction between rubber (disulfide bonds) and isocyanate free groups. Dhamodharan *et al.* [49] studied blends of ethylene propylene diene rubber and thermoplastic polyurethane and used dicumyl peroxide as surfactant. They found improved mechanical properties along with better solvent resistance and enhanced low temperature flexibility whereas, the glass transition temperature was found to increase. Ortiz-Morgan *et al.* [50] published on improved adhesion of RF plasma treated rubbers by isocyanate incorporation to polyurethane adhesive and enhanced the surface reactivity of rubber particles by the use of 4 weight % tris (p-isocyanatophenyl) thionophosphate surfactant. They observed increased rubber adhesion towards the polyurethane adhesive. However, they mentioned the use of isocyanate as cross-linker because of the presence of anti-adherent compound like zinc stearate. Pachpinyo *et al.* [51] studied the preparation of unsaturated polyester resin and rubber latex blends in the presence of dispersion aids like toluene and liquid ammonia and received enhanced impact properties by the use of dispersion aids. Sulkowski *et al.* [52] made thermogravimetric study of rubber waste-polyurethane composites and used one component polyurethane prepolymer surfactant Chemolan-M, Chemolan M-50 and Chemolan B-3 having hardness similar to that of fine rubber. Yang *et al.* [65] used simple silicon dioxide having a particle size of 30–50 micrometer as a surfactant. They concluded that the integrated mechanical properties of hybrid reinforced rigid polyurethane composite foam would achieve an optimal value by the incorporation of 7–8 % of rubber. Some other studies [66, 67] discussed the use of surfactants in polyurethane foam system. All of these works presented significant changes in properties by the use of surfactants.

It is to be noted that the discussion on the working principle of surfactants is mainly based on the application of surfactant in an aqueous medium. Most of the above mentioned studies have used water as a blowing agent in the foam system. Hence, corresponding surfactants were believed to work in the same principle. Though, our study does not directly involve water in the crumb rubber–polyurethane foam blend system, the working principle

of surfactants will be governed by the same basic principles.

Literature survey on Non-Reinforced Polyurethane Foam

There have been several studies on the properties of polyurethane foams. Most of the earlier investigations focussed on non-reinforced foams [57, 59, 60, 62, 68–74]. Mumford *et al.* [68] studied the component analysis of rigid polyurethane foam, and addressed suitable means for the elemental analysis of foams, for example by chemical ionization mass spectrometry and high pressure liquid chromatography. These methods were found to be effective. Hawkins *et al.* [57] studied the cell morphology and mechanical properties of rigid polyurethane foam. They concluded that cell morphology holds a relationship with compressive modulus and collapse stress in the foam. It was further concluded that the shape and orientation of the cells have significant effects on the mechanical properties if not explained by means of some different failure mechanism. Izakson *et al.* [69] published their work on the mechanical and thermo physical properties of polyurethane foam thermal insulation coatings for controlling the instability of deep quarry banks, where they obtained increased thermal and mechanical properties. Johlitz *et al.* [70] investigated experimental and theoretical properties of non-linear viscoelastic polyurethane systems by considering them as a material with zero plasticity and obtained proper agreement with the experimental results. Niyogi *et al.* [71] discussed the effect of blowing agent (water) on polyurethane foam. They concluded that with an increase in blowing agent concentration, more bubbles are formed and their average size decreases. In addition, the time of nucleation decreases, resulting in a narrower bubble size distribution. Seo *et al.* [59,60] studied mechanical, morphological, and thermal properties of water blown free rise rigid polyurethane foams. They concluded that the kinetic rate of polyurethane foam forming increases with an increase in water content by the reaction between water and foam component PMDI. They further concluded that that the density and the compressive strength of the polyurethane foam increase with an increase in the OH value and higher functionality group polyol. Singh *et*

al. [62] investigated reactivity of raw materials and their effects on structure and properties of rigid polyurethane foam. They found increased cream time, and gel time of foaming with larger cell size distribution. Sonneschein *et al.* [72] derived the relationship between polyurethane foam microstructure, and foam aging, and observed that foam aging is predicted by means of hard segments inside foam network. Subramani *et al.* [73] developed new polyurethane dispersion from blocked aromatic diisocyanate. These dispersions were found to be stable for more than six months and observed the possibility of using these anionically modified blocked-isocyanate adducts as potential crosslinkers. Tu *et al.* [74] discussed plastic deformation modes in rigid polyurethane foams under static loading. The mechanical properties of polyurethane foam were examined via compression in different directions. Results showed that the response is anisotropic. Further conclusion was the uniform distribution of foam by the effect of compression in the transverse direction.

Literature survey on reinforced polyurethane foam

Studies on reinforcements in polyurethane foam are more recent [42–47, 53–55, 58, 61, 75–79]. Haibach *et al.* [75] studied the mechanical properties of silica-particle reinforced polyurethane foams via emulsion templating and obtained enhanced elastic properties along with foam stability. Mahfuz *et al.* [76] studied the fabrication, synthesis, and mechanical properties of nanoparticle infused polyurethane system. They concluded that an optimum amount of nanoparticle enhanced the thermal as well as mechanical properties of polyurethane foams. Morimoto *et al.* [58] worked on the flexural properties of glass fiber reinforced rigid polyurethane foam. It was seen that flexural modulus and the flexural strength increased and their temperature dependences reduced by the use of surfactant and longer fibers as reinforcing agent. Saint-Michael *et al.* [61] worked on the mechanical properties of high-density polyurethane foam and the effect of filler size on their properties. They found that the reinforcement of foam might not be effective if the filler are bigger than the bubble size. Thermal studies suggested that the fillers increase the crosslink density of

the matrix. Rozman *et al.* [77] published on the mechanical and physical properties of polyurethane component based on rice husk and polyethylene glycol. They concluded that the introduction of rice husk as an OH groups provider in a polyurethane system enhances the properties. It was further concluded that properties of the composites also depend on the amount of homogeneous polyurethane matrix. Yosomiya *et al.* [78] reinforced rigid polyurethane foam with glass fibers and characterized the compressive properties. They concluded that out of different polymers, copolyimides show better resistance to swelling in solvents than the elastomers, but, they show worse performance in alkalis. It was further concluded that at low temperature, these copolyimides exhibit low stiffness, high deformation, and good elastic recovery. Cawse *et al.* [43] proposed the use of rubber as a toughening agent in polyurethane network and composite materials and observed that the processing method, rubber particle size, and size distribution are important parameters in affecting rubber-matrix adhesion, and material properties.. Datta *et al.* [44] used rubber wastes for filling the cast urethane elastomers. Li *et al.* [42, 53] synthesized and characterized novel rubberized syntactic foam. They concluded that the rubberized syntactic foam shows a higher capability of absorbing impact energy in micro-length scales. It is also capable of preventing the micro-length scale damage from propagating into macro-length scale damage. El Lawindy *et al.* [54] studied the physical properties of foam-rubber composites along with carbon black as the second reinforcing agent. They concluded that foaming agent promotes the dilution of carbon in the matrix. Mechanical parameters were found to decrease with an increase of both temperature and foaming agent. Lin *et al.* [55] studied microstructure-mechanical property relationship of short fiber-rubber-foam composites and showed that short fibers disperse uniformly in the composites irrespective of treatment, but treated fibers showed much better adhesion with the rubber matrix than untreated ones. The experimental results indicated the enhancement of most mechanical properties such as tensile modulus, hardness, and tear strength by the incorporation of short fibers in rubber foam matrix. Manoj *et al.* [45] published on the miscibility and fracture toughness

of polyurethane–rubber composite blends and got enhanced values of fracture toughness by the incorporation of rubber particles. These studies have helped in understanding the mechanism of polyurethane foam formation and served as the basis of future work.

Motivation

As of yet, however, no studies are present that provide a detailed discussion of the effects of the microstructure of rubber-polymer blend products on the mechanical properties. A few studies discuss the microstructure-property relationship of glass fiber and carbon black reinforced foam composites [55], no one has studied the same for crumb rubber particle reinforced polyurethane foam products. This provides a motivation for the current investigation.

CHAPTER 3

MATERIALS AND EXPERIMENTAL CHARACTERIZATION

This study investigates the fabrication and characterization of crumb rubber–polyurethane foam composites. Crumb rubber particles, 40–99 mesh size, were purchased from Entech, Inc. (White Pigeon, MI). Fig. 3.1 shows the particle size distribution of this particular size of crumb rubber. An optical micrograph of the crumb rubber particles is shown in Fig. 3.2.

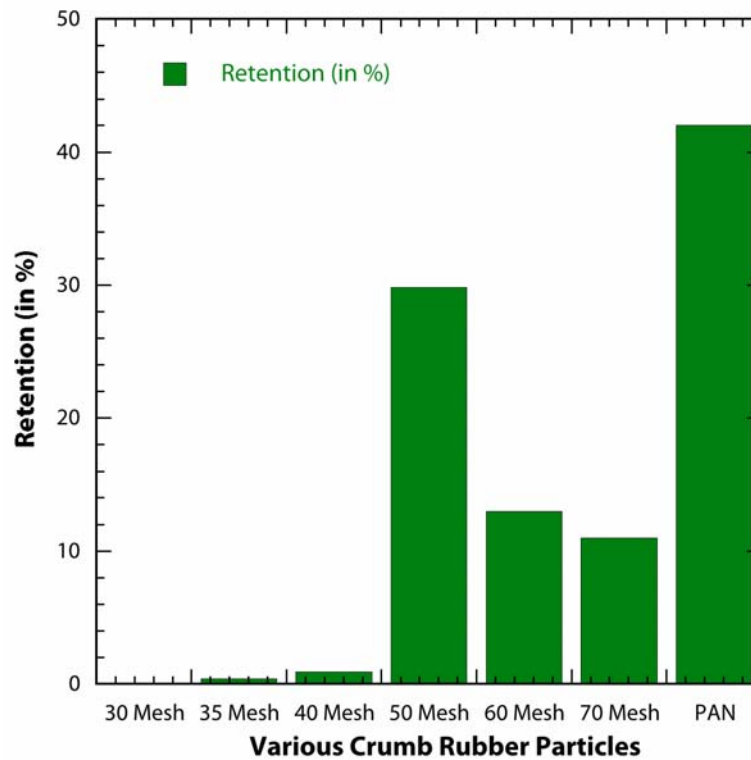


Figure 3.1: Sieve analysis data for crumb rubber having 40-99-mesh size, adapted from [80].

The basic principle of polyurethane form formation is the reaction between an isocyanate with a polyol in presence of a blowing agent. This method is termed as physical

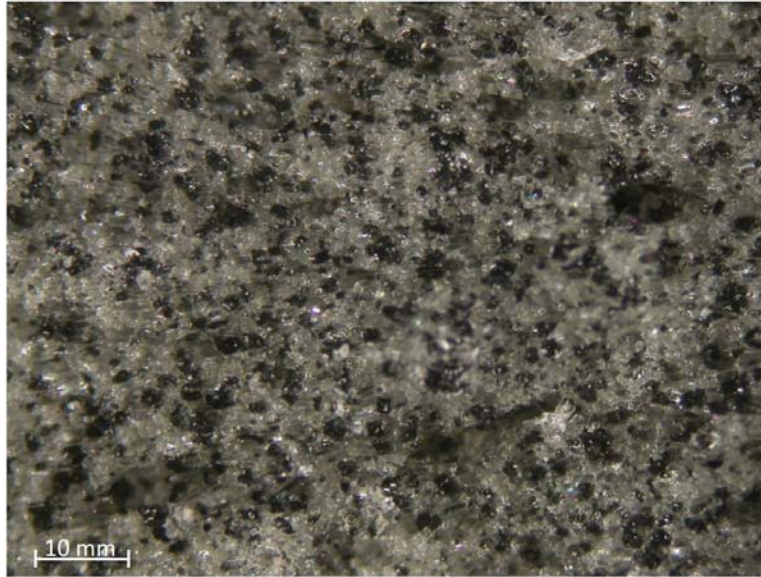


Figure 3.2: Optical micrograph showing crumb rubber particles inside foam

blowing or foaming. There is another method where blowing agents are directly reacted with the isocyanate and no polyol is involved. This is called chemical blowing or foaming and was used in this study. The approach involves the reaction of isocyanate with active hydrogen and the hydroxyl radicals of blowing agent to produce carbon dioxide gas for foaming and urea linkages to form polyurea, as shown in Fig. 3.3 [16].

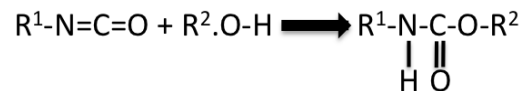


Figure 3.3: Basic concept of polyurethane foam formation by chemical blowing method, as used in this investigation, adapted from [16]

We selected an expanding, rigid, closed cell, pourable urethane foam to fabricate the composite, having a density of 0.03 g/cm^3 from US Composites (Palm Beach, FL). This foam has two parts (part A and part B), which are mixed in equal volume. Approximate ideal temperature for the foaming process varies between $24\text{--}27 \text{ }^\circ\text{C}$. When mixed, this system starts foaming in 45 seconds and completes expansion in 5 minutes. The total expanded volume is approximately 25 to 30 times the starting liquid volume.

Part A of this two-part foam system is polymethylene polyphenylisocyanate (polymeric MDI or PMDI), which is the polymeric form of diphenylmethane diisocyanate (MDI). This is a popular stable aromatic isocyanate and not considered to be carcinogenic. It is a brown liquid with slight aromatic odor having a boiling and flashing point of 329 °C and 199 °C respectively. It has a specific gravity of 1.24 and is insoluble in water. Above 204 °C, it can polymerize or decompose causing a pressure build-up in closed containers resulting in effective rupture of the same. Hence, it should be kept far from the presence of water, alcohols, glycols or other chemical materials having active hydrogens in their chemical structure. PMDI is highly incompatible with amines and strong bases. It is highly flammable in presence of carbon monoxide, carbon dioxide, benzene, toluene and traces of hydrocyanic acid [81]. Fig. 3.4 shows chemical structure of PMDI.

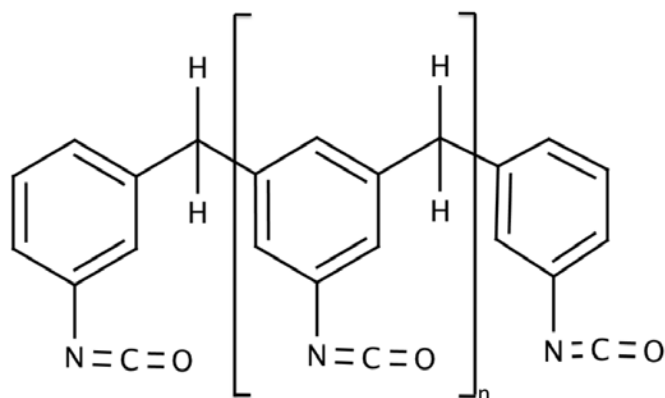


Figure 3.4: Chemical structure of PMDI (Part A), adapted from [82]

Part B of our two-part foam system acts as the polymerization blowing agent, and has the chemical name 1,1,1,3,3-pentafluoropropane. Commercially, this blowing agent is called HFC 245fa. Though, it belongs to polyol resin system, it is not a conventional polyol. Rather, it is a tertiary amine catalyst. This material is also stable and not carcinogenic. It has a boiling point and flashing point of 15.5 °C and 93 °C respectively. It is brown in color and 9% volatile by volume. HFC-245fa is slightly soluble in water with a specific gravity of 1.155. It should be kept below 29 °C and far from chemicals like carbon dioxide, carbon monoxide, halogens, and carbonyl halides [81]. It is essential to know

that blowing agents like HFC 245fa does not take part to create the cells of foam. Foam cells are created by the diffusion of blowing gases into bubbles that are nucleated during the time of mixing. Microcellular foams can rather be created without the use of blowing agents by the mechanism of frothing or nucleation [16]. Fig. 3.5 shows chemical structure of 1,1,1,3,3-pentafluoropropane.

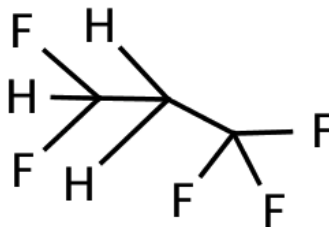


Figure 3.5: Chemical structure of HFC-245fa (Part B), adapted from [83]

As mentioned, because of the dissimilar chemical structure between the polyurethane foam and rubber particles, it was expected that the dispersion of rubber particles in the polyurethane matrix could be difficult. Surfactants or dispersion aids were therefore used to coat the rubber particles, to promote the uniform dispersion and enhance rubber–foam bonding [51]. This study employed two specific surfactants.

The first is soluble sodium lauryl sulfate (SLS) in water (Darvan WAQ, R. T. Vanderbilt Company Inc. ,Norwalk, CT), an important anionic surfactant. The most common use of SLS is as an emulsifier for emulsion polymerization of many polymers. It has both hydrophobic and hydrophilic structures that are supposed to react with rubber and polyurethane molecules. It is expected that hydrophobic sites would interact with rubber molecules, while hydrophilic sites would interact with the polyurethane molecule [51]. SLS is synthesized by the reaction between lauryl alcohol and sulfuric acid to produce hydrogen lauryl sulfate, which, is further neutralized by adding sodium carbonate. Because of this synthesis technique, SLS is not considered as a pure dodecyl sulfate, but a mixture of alkyl sulfate with dodecyl sulfate as its main component. Like other surfactants, SLS molecule has a tail consisting of twelve carbon atoms attached to a sulfate group. This

gives SLS molecules amphiphilic properties [84]. Fig. 3.6 shows the chemical structure of a SLS molecule.

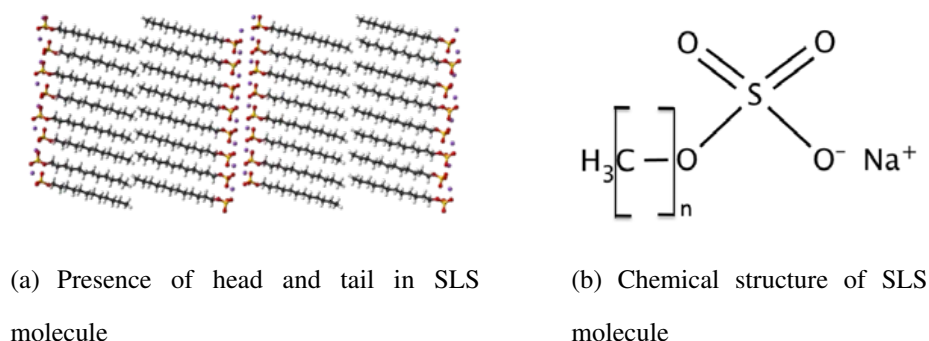


Figure 3.6: Chemical structure of Darvan WAQ, adapted from [84]

Darvan is a basic surfactant with a pH value of 7.5. It is a white colored liquid with high solubility in cold water. The boiling and melting points of Darvan are 100 °C and 10 °C respectively. It is 73% volatile (w/w) and slightly denser than water, having a specific gravity of 1.04. Darvan is not carcinogenic and a very stable chemical to work with. But, it is not compatible with strong oxidizing agents like potassium permanganate and hydrogen peroxide [85].

The second surfactant used in this study was a heat reactive, carboxylated vinylidene chloride copolymer latex (Vycar 660 ×14 emulsion, Lubrizol Inc., Cleveland, OH), a popular synthetic anionic surfactant. Unlike Darvan, it is acidic, having a pH factor of 5.7. It has a surface tension of 30 Dynes/cm and denser than water with specific gravity 1.19. It has a glass transition temperature of +7 °C and is not carcinogenic [86].

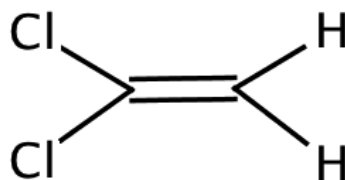


Figure 3.7: Monomer of Vycar 660 ×14, adapted from [87].

Vycar is an excellent flame-retardant. It is durable to washing and takes part in low temperature heat curing without the aid of a catalyst. It is well known for its characteristics

of substrate adhesion, pigment binding, and colloidal stability with a high degree of re-dispersibility. Vycar has the capability of generating good physical properties at very low drying temperature. Generally the polymers of vinylidene chloride are prone to damage to heat and light discoloration. Vycar does not have this drawback. It is compatible with water-soluble flame retardant salts and has good toughness and abrasion resistance [86].

It is to be noted that the selection of a surfactant in polyurethane foam system needs careful attention of the compatibility of the system and the purpose. Generally, popular surfactants for rigid polyurethane foam systems are quite different than that of flexible polyurethane foam system. This is because the rigid foam surfactants are used to produce very fine cells and high closed cell contents. On the contrary, surfactants in flexible foams are used to stabilize the reaction mass. At the same time, they enhance the open cell content inside the structure so that it does not shrink. In this study, these two surfactants were chosen on the basis of the qualitative elemental composition analysis of as received rubber collected by XRF, as discussed later in the next chapter.

Sample Preparation

Different weights of crumb rubber particles were used to reinforce the polyurethane matrix while the amount of polyurethane was kept constant. Four different quantity of rubber particles were used as a reinforcing agent (25, 50, 75, and 100 g, which were 9, 18, 24 and 30 weight % of rubber particles, respectively). The effect of surfactants on the rubber-polyurethane blend was tested using two different approaches. In one set of samples, the amount of surfactant was kept constant for all the samples (at 10 g). The other set of samples was prepared using a surfactant weight equal to 0.1% of rubber weight, i.e. the weight ratio of surfactant to rubber was kept constant (0.025, 0.05, 0.075 and 0.1 g of surfactant). Samples were prepared in $250 \times 250 \times 25$ mm ($10 \times 10 \times 1$ inch) molds, as shown in Fig. 3.8.

To prepare the composite samples, a measured weight of crumb rubber was placed in a

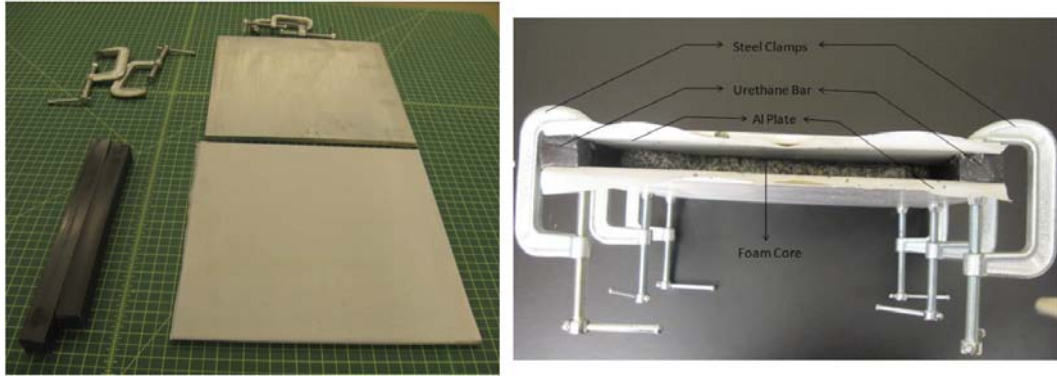


Figure 3.8: Mold for preparing rubber-foam composites used in the present study

mixing bowl, mixed properly with the surfactants using a mechanical stirrer at 2 to 4 rpm for 10 minutes and then dried at room temperature for four hours. After mixing the surfactant, a visible color change was observed throughout the entire mass of the rubber particles, as illustrated in Fig. 3.9. This confirmed the interaction between anionic surfactants with the ions present in the rubber. This visible change in color was seen for both the surfactants Darvan WAQ and Vycar 660 $\times 14$.

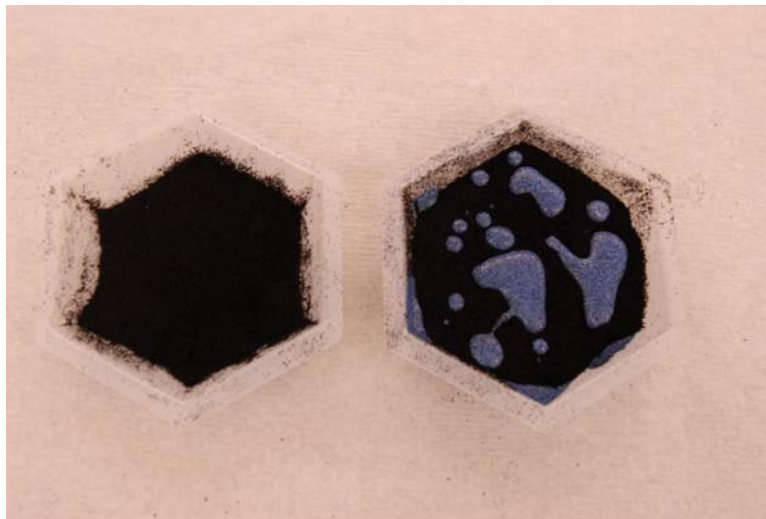


Figure 3.9: Visible color change in rubber by the application of surfactant

The surfactant treated rubber particles were then mixed with Part B of the polyurethane foam using the help of a mechanical stirrer at 2 to 3 rpm for 5 minutes. Finally, Part A was added and the mixture was hand stirred for a very short duration before being poured into

a pre-prepared mold. Due to rapid reaction and foam expansion the slurry was put inside the mold within 45 seconds after mixing Part A. The entire mold was then placed inside a fume hood for 24 hours with the two aluminum plates placed in a vertical orientation. This process resulted in polyurethane foam plates with a nominal dimension of $250 \times 250 \times 25$ mm with the incorporation of crumb rubber particles. Fig. 3.10 shows the picture of one such plate.



Figure 3.10: Rubber–polyurethane foam composites generated in this present study

X-Ray Fluorescence Analyses and Selection of Surfactants

As already discussed, the non-uniform dispersion of rubber particles inside polyurethane foam is a problem. Hence, proper dispersing aids were required in accordance with the chemistry of the rubber particles. To select appropriate surfactants, XRF was performed on the crumb rubber particles to determine elemental composition using the Tracer TurboSD XRF analyzer (Bruker Inc. ,Madison, WI).

During processing, crumb rubber is treated with different chemicals. For example, chlorine is used to remove the pungent odor (characteristic of the sulfur presence), and specific solutions are used to increase fire retardancy. In addition, metal wires that were

incorporated during the manufacturing of tires may also be present in the crumb rubber if not completely removed by magnetic separation. As a result, traces of these treatment chemicals or residual metals are found in crumb rubber particles, and can affect the surface treatment. A knowledge of the elemental composition aids the selection of surfactant as one can plan for a possible bonding between the ions present in the specimen with the polar or non-polar groups present in the respective surfactant.

FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) was used to examine the effect of surfactants on virgin rubber particles. This helped identify the nature of chemical interaction between the two types of surfactants and crumb rubber. Spectra were collected using AVATAR 60 (Waltham, MA) and the spectra without any manipulations or corrections were processed using Omnic 5.1 and overlaid with the reference sample.

Determination of Physical Properties

The fabricated foam materials were characterized to determine the density, porosity, and void volume fractions in accordance with European standard EN 993-1 [89]. Polyurethane foam is a porous material, so porosity is a very important element defining the microstructure. The shape, density, orientation, quantity, type, size, and size distributions of pores significantly affects the properties of foams. There are a significant number of terms affecting the physical properties of rubber–polyurethane foam composites, namely bulk density, skeleton density, solid density, apparent or total porosity (which is the void volume fraction of air), open porosity and closed porosity [89]. In this study, the porosity of the composites was quantified in terms of both open and closed porosity. Fig. 3.11 represents a typical optical micrograph of rubber–polyurethane blend composites showing pores inside the samples.

Measurements were carried out to quantify the spatial distribution of properties. For

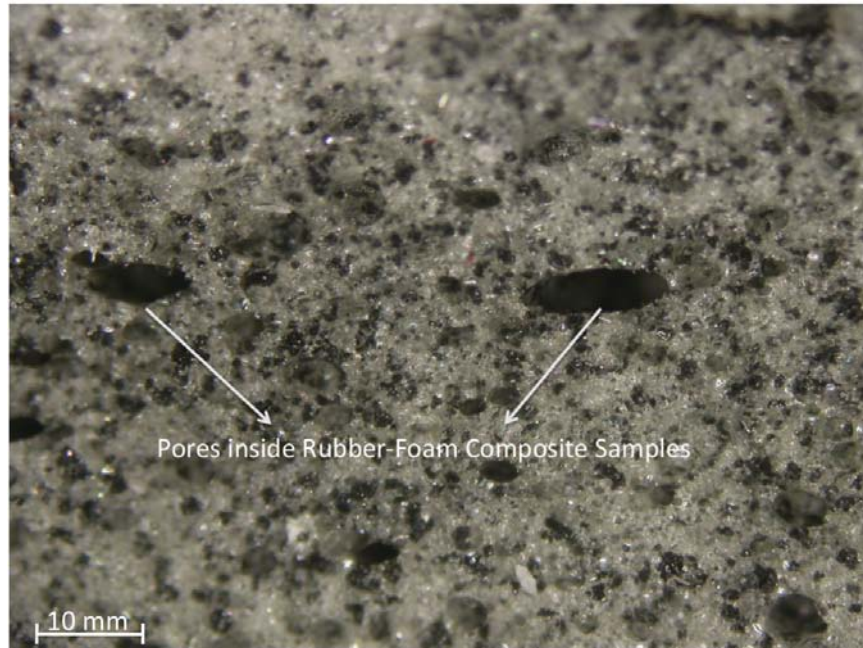


Figure 3.11: Microscope picture of rubber-polyurethane foam composite showing pores inside structure

density and porosity measurement, small cylindrical samples were cut along the height of the composite samples, as shown in Fig. 3.12.

Open porosity is defined as the ratio of the volume of the open pores to the total volume of the porous body. Similarly, closed porosity is the ratio of the volume of closed pores to the total volume of the porous body. Apparent or total porosity is the ratio of the volume of all pores to the total volume of the porous body. This is also the total void volume fraction of the material and the sum of open and closed porosity. Bulk density is the quotient of the mass and total volume of the body. This can be considered as an average of the density of solid and gas present in the pores taking care of the presence of both open and closed pores. The skeleton density is obtained dividing the mass of the samples by the skeleton volume of the sample. In other words, skeleton density accounts the effects of only open pores present in the sample. Solid density is determined dividing the mass of the sample by its solid volume [89]. To determine the solid density, samples were crushed to make powders so that there is no presence of voids inside it anymore and the solid volume was

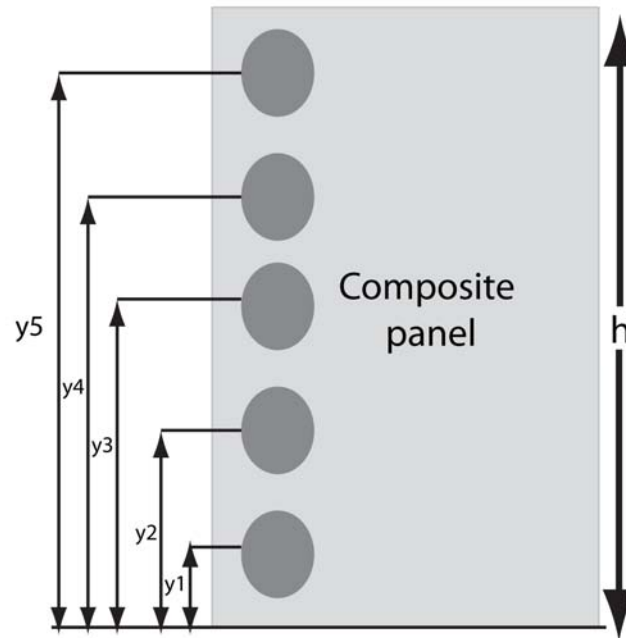
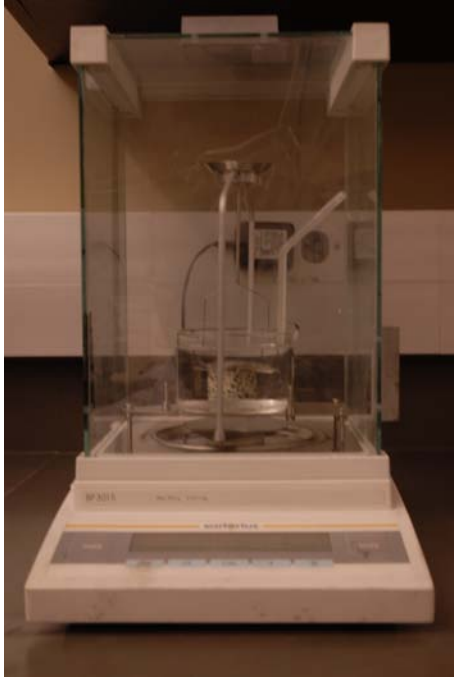


Figure 3.12: Cylindrical samples along the height of rubber–foam composites for characterization obtained.

The principle of buoyancy was used for the measurement of densities and porosities with the help of a density measurement kit (Sartorius Inc., Bohemia, NY). First, the dry samples were weighed in air and this was recorded as m_1 . Then the samples were immersed in water for twenty-four hours in a vacuum infiltration chamber. This process evacuates all the air from open pores and fills them with the saturation liquid (water). The saturated samples were then weighed while immersed to determine the apparent mass m_2 using the density measurement set up. Finally, saturated samples were wiped to remove surface water and weighed in air to determine the saturation mass, m_3 . This was done quickly to minimize any loss of mass due to evaporation of the saturation liquid (water). The density of the saturation liquid, ρ_{fl} , was recorded at the particular temperature. Figures 3.13 and 3.14 show the density determination kit and the vacuum infiltration chamber used in this present study. After all these measurements, the bulk density ρ_b , the skeleton density, ρ_{sk} ,



(a) Determination of sample mass in water



(b) Determination of wet sample mass

Figure 3.13: Determination of physical properties by density determination set up

and the open porosity, π_a , were determined using the following equations, respectively [89],

$$\rho_b = \frac{m_1}{m_3 - m_2} \times \rho_{fl} \quad (3.1)$$

$$\rho_{sk} = \frac{m_1}{m_1 - m_2} \times \rho_{fl} \quad (3.2)$$

$$\pi_a = \frac{m_3 - m_1}{m_3 - m_2} \times 100 \quad (3.3)$$

where, ρ_b is the bulk density (g/cm^3), ρ_{sk} is the skeleton density (g/cm^3), ρ_{fl} is the density of fluid (g/cm^3), and π_a is the open Porosity (in %).

The solid density and corresponding closed cell porosity of all the specimens were determined using a helium pycnometer (Ultracycrometer 1000, Quantachrome Inc, Boynton Beach, FL), shown in Fig. 3.15. Samples were crushed using liquid nitrogen inside a grinder to make powders. This would ensure the removal of all pores from the samples.

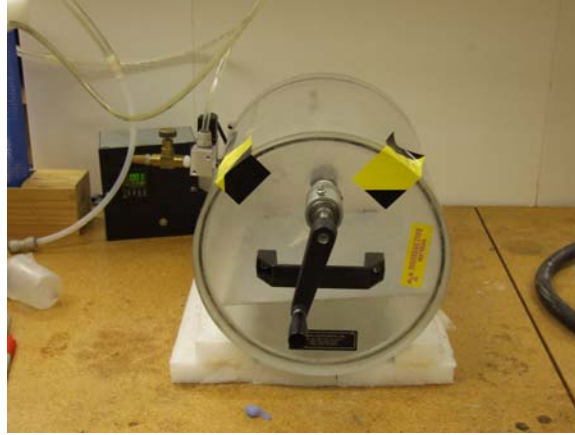


Figure 3.14: Vacuum infiltration chamber set up used in the present study

The powders were then placed inside helium gas chamber of the pycnometer with an input of dry weight of the samples. Five runs were taken for each individual samples using the pulse mode of gas flow. The pycnometer provided the solid volume and solid density of the samples as outputs. From the solid density, closed cell contents of the samples were determined as,

$$\pi_t = \frac{\rho_t - \rho_b}{\rho_t} \times 100 \quad (3.4)$$

$$\pi_f = \pi_t - \pi_a \quad (3.5)$$

where, ρ_t is the solid density (g/cm^3), π_t is the apparent or total porosity (in %), and π_f is the closed porosity (in %).

Compressive Properties

Compressive properties of the foam-rubber composites were determined using cylindrical samples as per ASTM C-365/C-365M [90]. Uniaxial compression tests were performed using a 30 KN cell in a screw-driven test frame (Instron Model no. 5567, Norwood, MA) at a cross-head displacement rate of 0.5 mm/min, as shown in Fig. 3.16. The ultimate

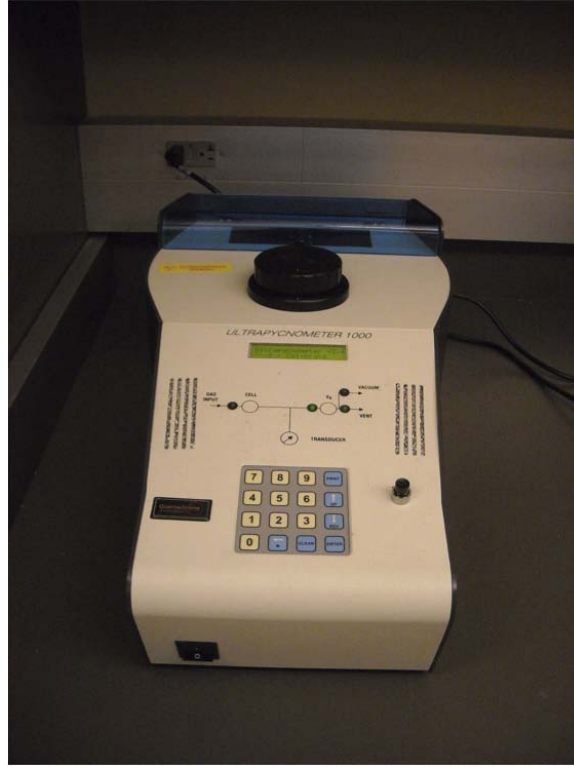


Figure 3.15: Helium ultrapycnometer 1000 used in the present study

flatwise compressive strength was determined using,

$$F_z^{fcu} = P_{max}/A \quad (3.6)$$

where, F_z^{fcu} is the ultimate flatwise compressive strength, P_{max} is the ultimate force prior to failure, and A is the cross sectional area [90].

Flatwise compressive chord modulus was also determined following the same ASTM standard as,

$$E_z^{fc} = \frac{P_{0.003} - P_{0.001}}{\delta_{0.003} - \delta_{0.001}} \times \frac{t}{A} \quad (3.7)$$

where, E_z^{fc} is the flatwise compressive modulus, $P_{0.003}$ is the applied force corresponding to $\delta_{0.003}$, $P_{0.001}$ is the applied force corresponding to $\delta_{0.001}$, $\delta_{0.003}$ is the recorded deflection value such that δ/t is closest to 0.003, and $\delta_{0.001}$ is the recorded deflection value such that δ/t is closest to 0.001 [90]. This formula for determining the compressive modulus is set up such that it accounts for the compliance correction part of the experiment. This is because



Figure 3.16: Foam–rubber specimens subjected to compression test following ASTM C365/C365M

all typical force versus displacement curves consist of a toe region, which is not a property of the material but is caused by a take-up of slack and alignment of seating of the specimen. Hence, a proper positioning of zero point on the displacement axis is always difficult. To get correct compressive modulus values, this artifact has to be compensated so that it gives the corrected zero point on the displacement axis [90].

Fig. 3.17 shows typical force versus displacement curve of a material having Hookean (linear) region (region CD), for example as for polyurethane foam. For actual measurement of modulus values, this linear region should be extended through the zero-force axis. The intersection point thus obtained (B), is the actual or corrected zero displacement point ($\delta = 0.000$) from which the displacements should be measured. For a valid test, it is required that point B fall below $\delta_{0.001}$ [90].

Flexural Properties

Flexural properties were determined according to ASTM D790 [91] with a load rate of 6 mm/min using three point bending. When composites are tested in flexure, as a simply supported beam loaded in middle point, the maximum stress at the outer surface of the test

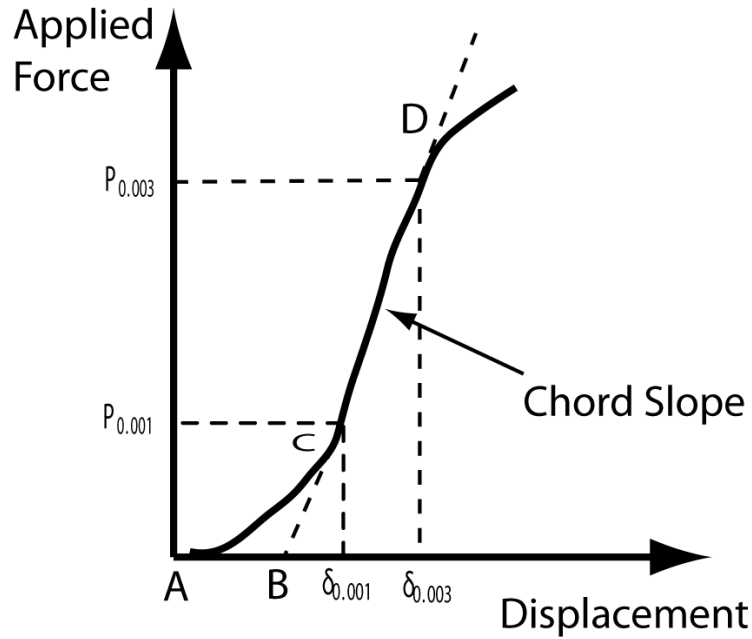


Figure 3.17: Force versus displacement curve of a material with Hookean region, adapted from ASTM standard C365 [90]

specimen acts at the mid point. This stress is calculated for any point on the load deflection curve using

$$\sigma = \frac{3PL}{2wt^2} \quad (3.8)$$

where, σ is the stress in the outer fibers at mid-point and considered as the flexural strength, P is the load at a given point on the load-deflection curve, L is the Support span, w is the width of specimen tested, and t is the depth of specimen tested [91, 92].

The tangent modulus of elasticity, or the modulus of elasticity, is the ratio of stress to corresponding strain within elastic limit. It was measured by drawing a tangent to the steepest initial straight-line portion of the load-deflection curve [91], and calculated as,

$$\tau = \frac{L^3m}{4wt^3} \quad (3.9)$$

where, m is the stiffness of the load deflection curve in the linear elastic region calculated by dividing the maximum load achieved to the corresponding deflection. All rubber-polyurethane foam composite specimens had a specimen length, l of 200 mm, width, w of

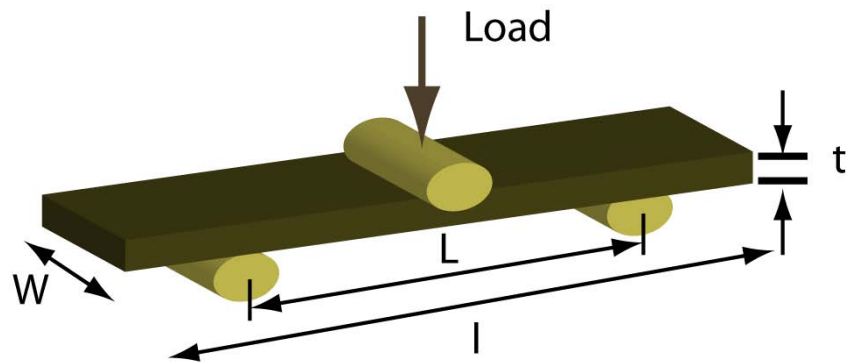


Figure 3.18: The notations for specimen dimensions and 3-point bending test configuration [92].

62.5 mm, span length, L of 150 mm, and average sample thickness, t of 25 mm.

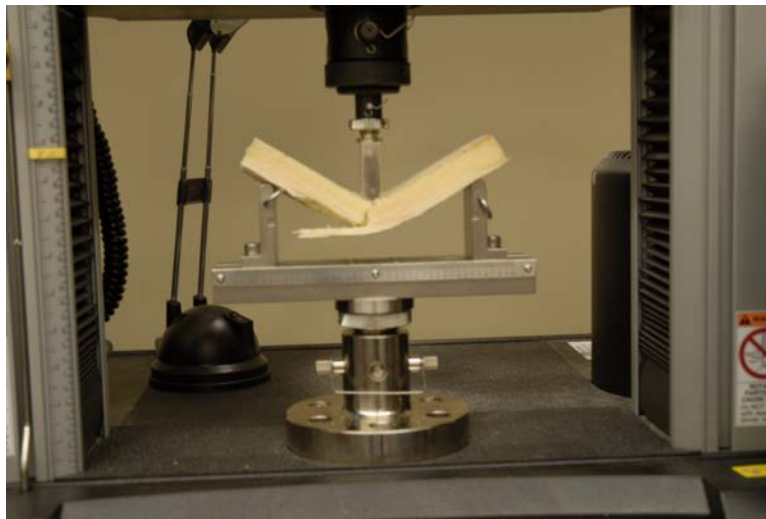


Figure 3.19: Failure of composite specimens subjected to 3 point bending test

Like the load-deflection curve, a typical stress-strain curve consists of a toe region, which is not a property of the material. This was corrected as before [91].

Scanning electron microscopy (SEM)

Scanning electron microscopy studies were performed on selected samples to characterize the cell size, failure of rubber particles, fractured surface topology, and interfacial characteristics between rubber particles and polyurethane matrix. Fractured surfaces of the

bending specimens were managed using a Hitachi Scanning Electron microscope (Hitachi, Model No: S-4800, Dallas, Texas). Before the observation, all the surfaces were gold coated having a depth of 70 nanometer.

CHAPTER 4

RESULTS AND DISCUSSION

X-Ray Fluorescence Data

Fig. 4.1 shows the X-ray fluorescence data collected on crumb rubber. From the radiation spectra, a rich content of Zn^{2+} and Br^- ions was seen in the virgin crumb rubber sample, as shown in Fig. 4.1. This was utilized in selecting the two surfactants. The presence of strong electropositive sodium ions in Darvan has initiated the use of this particular surfactant as sodium ions can form strong bonds with highly electronegative bromine ions present in the as-received rubber particles. Similarly, the presence of highly electronegative chlorine ions has initiated the use of surfactant Vycar as these ions are supposed to form strong bonds with strong electropositive zinc ions present in the rubber particles.

Density and Porosity as Functions of Crumb Rubber and Surfactant Content

The first step was to determine the role of surfactant on the foaming process. Fig. 4.2 shows the variation of bulk density of polyurethane foam as a function of Darvan and Vycar content. These samples were prepared without the incorporation of crumb rubber. The total amount of polyurethane was kept constant at 200 ml (100 ml of Part A and 100 ml of Part B). Four different amounts of both kinds of surfactants, namely 0.025 g, 0.05 g, 0.075 g and 0.1 g (0.1% by weight of rubber particles utilized in other samples) were used. The variation of bulk density was measured as a function of surfactant volume fraction, which was obtained dividing the volume of these surfactants by the solid volume of polyurethane and surfactant.

With an increase in surfactant content, a reduction in bulk density was observed for

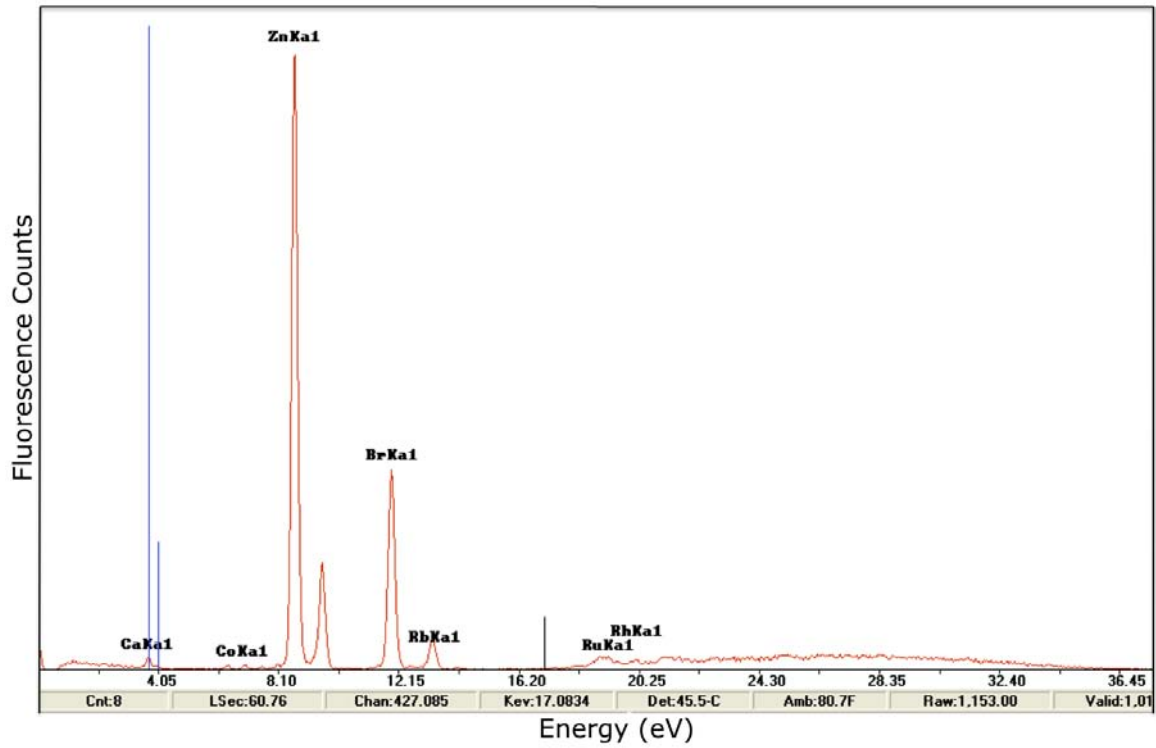


Figure 4.1: XRF analysis for the virgin crumb rubber samples

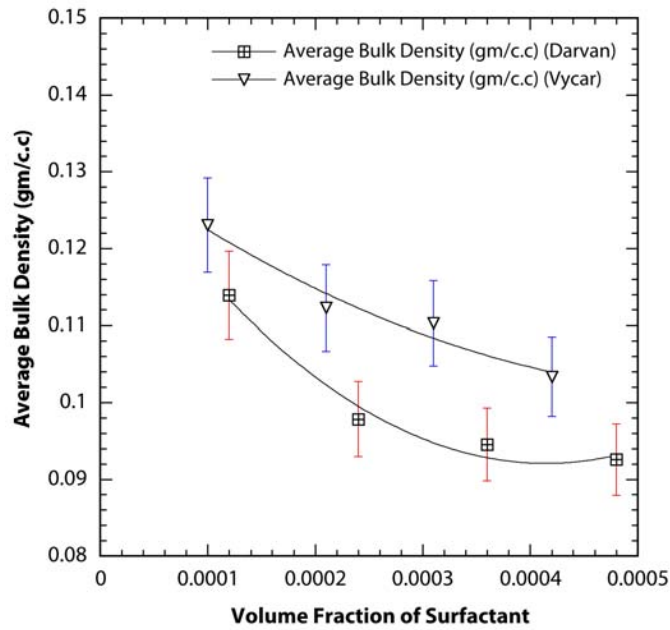


Figure 4.2: Effect of surfactants on the bulk density of polyurethane matrix system without rubber

both Darvan and Vycar, as expected. The addition of surfactant enhances foaming process by reducing the surface tension between individual cells. Surfactants promote improved blowing efficiency by helping the foam ability to create nuclei and also participate in stabilizing the foam. Similar results have been published by Krupers *et al.* [17] who reported an increase of average foam height by the addition of a fluorosurfactant. Lim *et al.* [64] also reported similar results where foam density decreased asymptotically with the addition of silicon surfactant B8404 in rigid polyurethane foam system.

Figure 4.3 shows the variation of open porosity of polyurethane foam as a function of Darvan and Vycar content. With an increase in surfactant content, a reduction in open porosity was observed for both the surfactants. The addition of surfactant reduced the surface tension between individual cell, promoted enhanced foaming of the system, and helped in stabilizing the foam matrix system to prevent possible collapsing and surface defects. The increased stability resulted in a reduced amount of open pores in the polyurethane foam system.

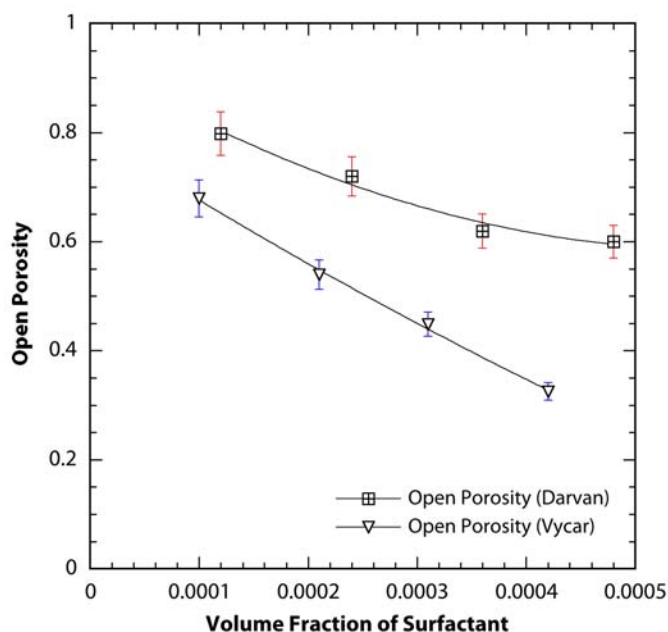


Figure 4.3: Effect of surfactants on the open porosity of polyurethane matrix system without rubber

Figure 4.4 shows the variation of closed porosity of polyurethane foam as a function of surfactant content. An increasing trend of closed porosity was seen with an increasing content of surfactant. As discussed earlier, surfactants reduce the surface tension among the particles and promote foaming process. In other words, they increase the blowing efficiency of the foam. In addition, they increase foam stability. Both these factors contributed to increased closed porosity.

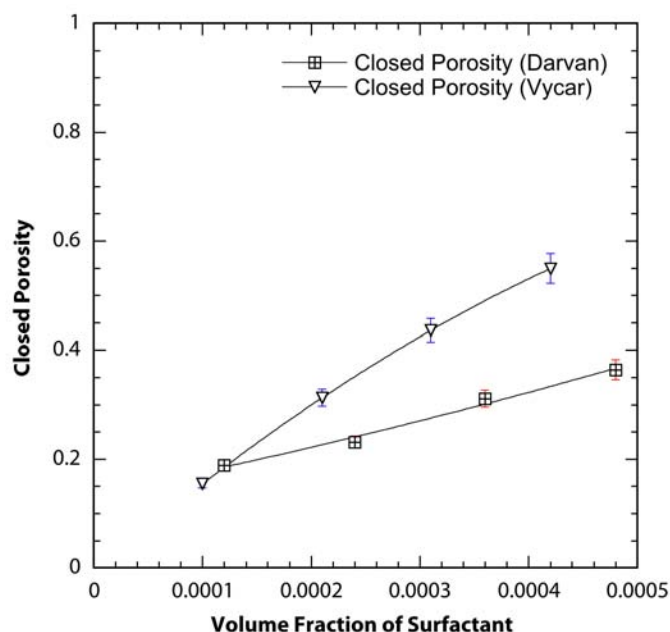


Figure 4.4: Effect of surfactants on the closed porosity of polyurethane matrix system without rubber

Figure 4.5 shows the effect of two surfactants, Darvan and Vycar, on the skeleton density of polyurethane foam. Skeleton density accounts for the presence of open pores, but not the closed pores. With an increase in surfactant content, a reduction in skeleton density values occurred for both kinds of surfactants. The decrease of open porosity along with a simultaneous increase in closed porosity with an increasing surfactant content led to a lower skeleton density.

The presence of particles is also known to affect the foaming process. Figure 4.6 shows the effect of crumb rubber particles on the bulk density of polyurethane foam system with-

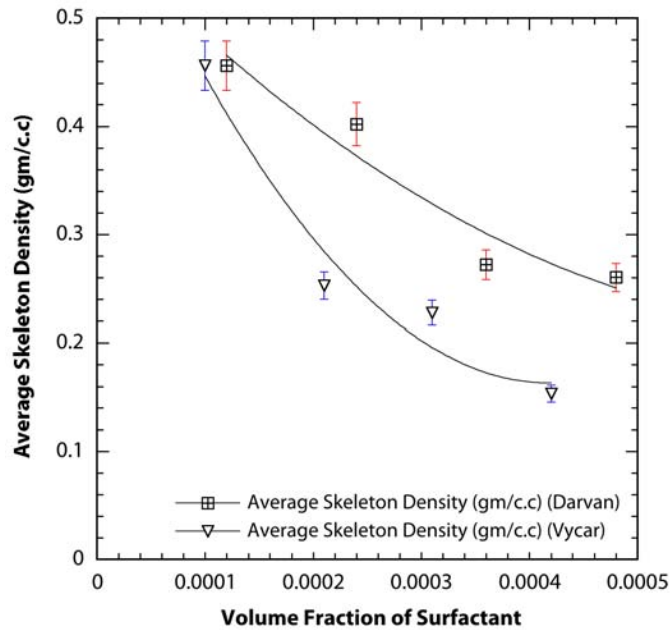


Figure 4.5: Effect of surfactants on the skeleton density of the polyurethane matrix system without rubber

out the presence of surfactants. The most general observation was the increase in bulk density with an increasing rubber content. This was due to the increase of the overall mass of the composite samples along with high content of rubber. The bulk density was not very uniform, as a function of normalized elevation, at the bottom portion of the samples. Nonetheless a uniform trend of bulk density was seen for all the samples, irrespective of the quantity of rubber, at a y/h value more than 0.5, i.e. the bulk density is much more uniform at the top portion of the samples.

In general, for all specimens, the bulk density got increased with height. This means that foam pushed the rubber particles up and there was not much gravitational effect present due to the weight of rubber particles.

Figure 4.7 shows the effect of crumb rubber on the skeleton density of polyurethane foam system without the presence of surfactants. In general, an increasing trend in skeleton density was seen with higher content of rubber. Again, a more uniform and increasing trend of skeleton density could be seen for all the samples, irrespective of the quantity of rubber,

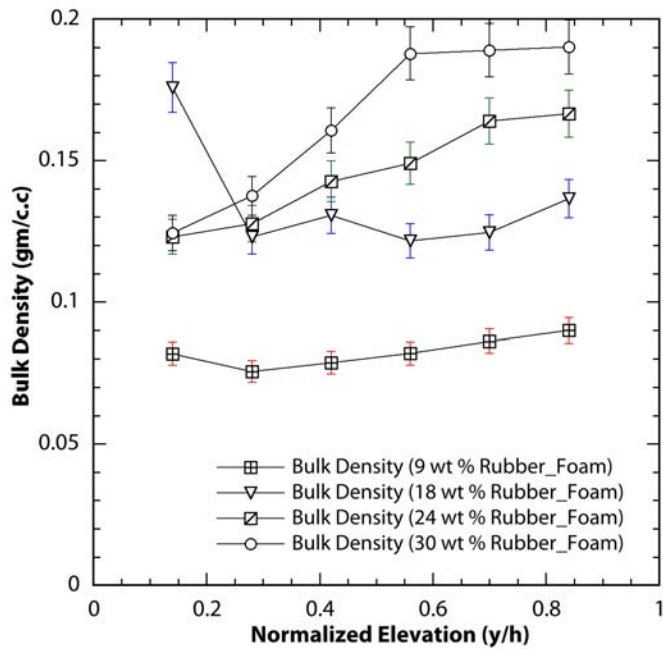


Figure 4.6: Effect of crumb rubber particles on bulk density of polyurethane foam system at a y/h value more than 0.5. This indicated the presence of significant and uniform amount of open pores towards the foaming direction (i.e. towards the top of the sample). This is understandable as open pores increases with decreasing depth [93]. The equation relating the open porosity and depth was formulated by Athy in 1930 and given as, $\phi(z) = \phi_o e^{-kz}$, where, ϕ_o is the surface open porosity, k is the compaction coefficient and z is depth.

Figure 4.8 shows the variation of closed porosity inside the rubber-polyurethane foam composite system, without the presence of surfactant, as a function of normalized elevation. An increasing trend of closed porosity was observed for samples having rubber particles starting from 9 weight % up to 24 weight %. But closed porosity got reduced for samples having 100 g rubber. Probably, the addition of 30 weight % of rubber particles was excessive for this particular polyurethane matrix blend system. Consequently, the polyurethane could not wet the entire amount of rubber particles and some parts remained in agglomerated form. Thus, these particles did not participate in reinforcing the system. Rather, they promoted cell rupture, and decreased closed porosity.

Figure 4.9 shows the effect of rubber particles on the open porosity distribution of

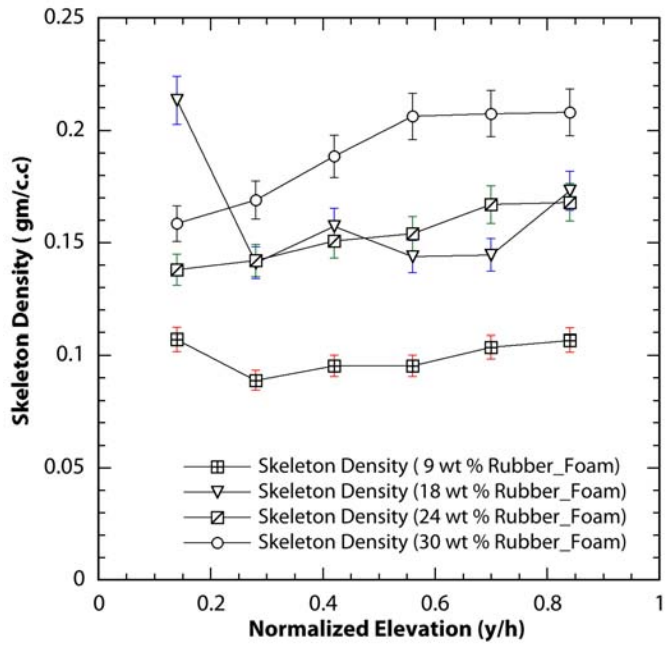


Figure 4.7: Effect of crumb rubber particles on skeleton density of polyurethane foam system

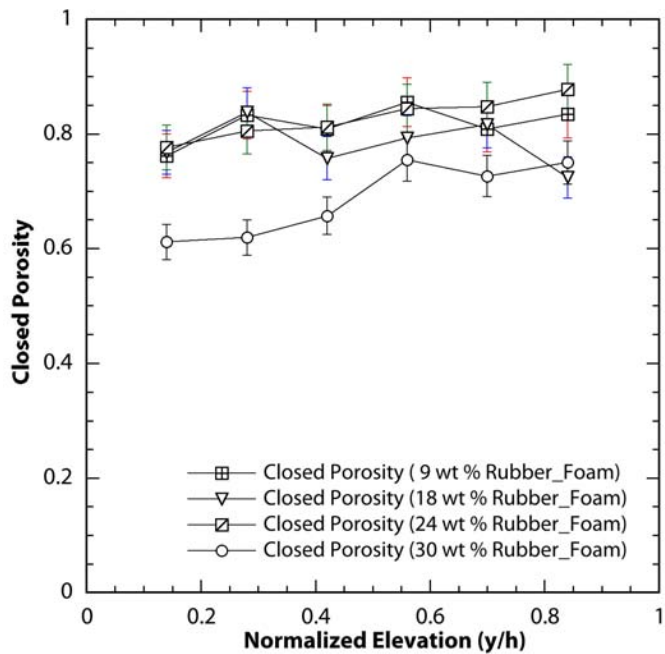


Figure 4.8: Effect of rubber particles on the closed porosity of polyurethane foam system

polyurethane foam matrix without using surfactant. Open porosity appeared to decrease with increasing rubber content, except for the case of 30 weight %. This indicated that rubber helped in stabilizing the foam system. Again, the 100g addition of rubber did not follow the trend, due to possible lack of wetting and agglomeration of rubber particles.

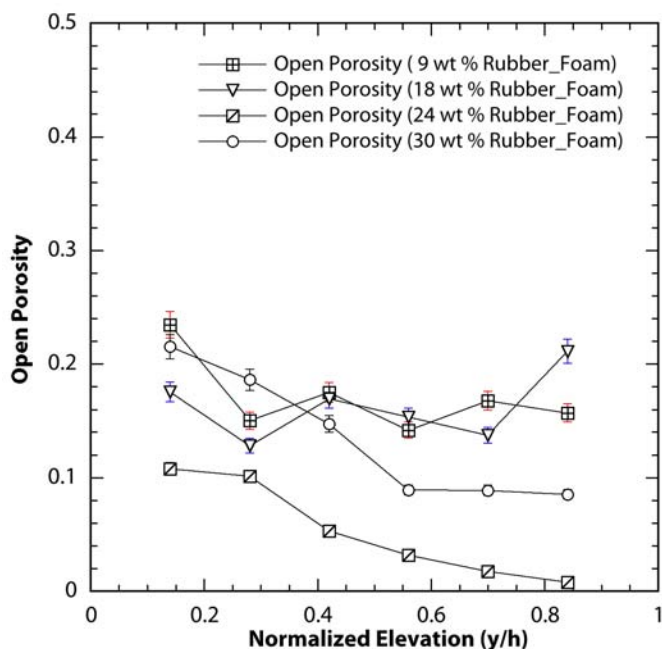
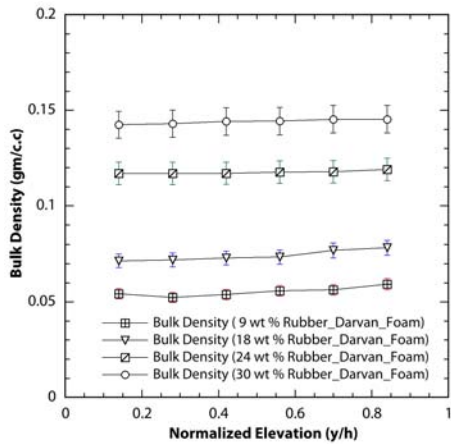


Figure 4.9: Effect of rubber particles on the open porosity of polyurethane foam system

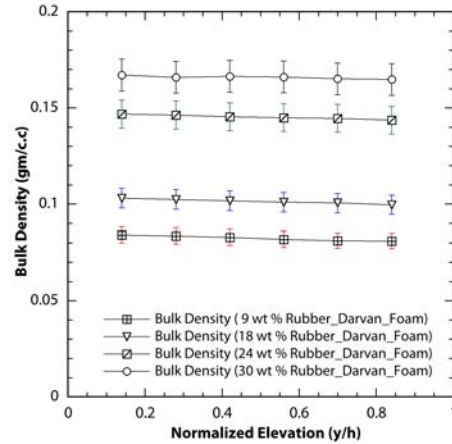
So far, we have investigated the individual effects of surfactants and rubber particles on the physical properties of polyurethane foam matrix. Surfactants tend to increase the closed porosity over open porosity bringing stability to the foam system. Meanwhile, rubber particles also do the same.

Figure 4.10 shows the effect of surfactant Darvan on the bulk density of rubber–polyurethane foam composites. The effects of surfactant were observed in two different manners. One set of samples was prepared by incorporating fixed amount of surfactant (10 g). For another set of samples, a fixed weight ratio of surfactant and rubber was used (0.1%), i.e. for this second set of samples, four different quantities of surfactants, which is 0.1% of weight of the rubber quantities (25 g, 50 g, 75 g, 100 g) were used.

The addition of Darvan, led to very uniform properties as a function of normalized



(a) Samples having fixed quantity (10 g) of surfactant Darvan



(b) Samples having fixed weight ratio (0.1%) of surfactant to rubber

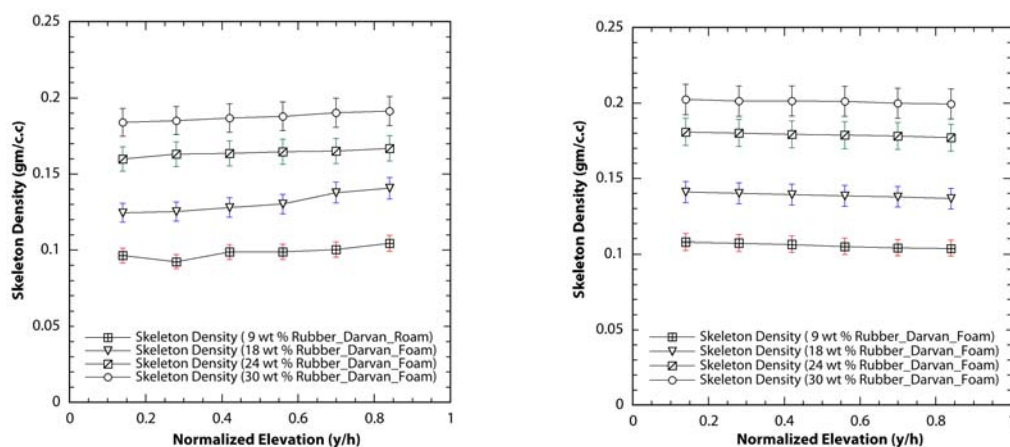
Figure 4.10: Effect of Darvan on the bulk density of rubber and polyurethane foam composites

height, y/h . This implies that the surfactant dispersed the rubber particles uniformly along the foaming direction. Hence, a much more uniform distribution of bulk density was achieved. Another observation was the reduction in overall bulk density by the incorporation of surfactant in comparison to samples prepared without any surfactant. This result is very much expected, as the addition of surfactants helps in enhancing the blowing efficiency and increased overall foaming. Introduction of different quantities of surfactant Darvan reduced the bulk density. The samples with fixed quantity of Darvan showed lesser bulk density than that of samples with fixed weight ratio of surfactant to rubber. This is also in accordance to the same observation. Samples with fixed quantity of Darvan have more weight of surfactant (10 g) in comparison to the other set of samples (Darvan quantity varies from 0.025 to 0.1 g). Hence, they showed lesser values of bulk density.

Rubber and surfactant contents have completely opposite effects on the bulk density of polyurethane foam. Rubber particles tend to increase the bulk density, meanwhile, surfactants try to reduce it. But, when they are working together in a system, surfactants had a greater effect on reducing the bulk density of the foam matrix system in spite of the pres-

ence of rubber. Also, it can be concluded that Darvan served the basic purpose of surfactant as it had uniformly dispersed the rubber particles inside polyurethane network. In addition, it helped in overall foaming process of polyurethane system in spite of the presence of rubber. So, the selection of Darvan was appropriate for our rubber-polyurethane foam blend composite system.

Figure 4.11 shows the effect of Darvan on the skeleton density of rubber–polyurethane foam composites. Again, the use of surfactant Darvan led uniform distribution of skeleton density as a function of normalized height, y/h . Once we increase the quantity of Darvan, the skeleton density values got reduced, which was in agreement with the results showing that more surfactant leads to greater closed porosity.



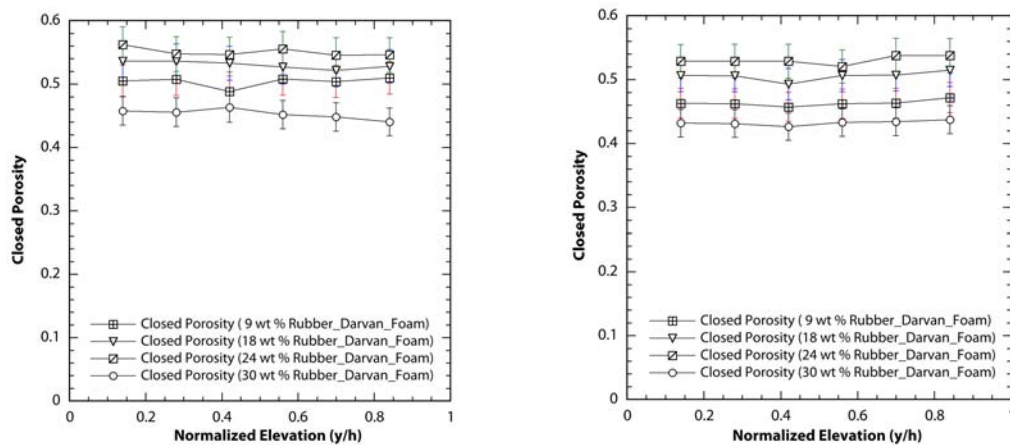
(a) Samples having fixed quantity (10 g) of surfactant Darvan

(b) Samples having fixed weight ratio (0.1%) of surfactant to rubber

Figure 4.11: Effect of Darvan on the skeleton density of rubber and polyurethane foam composites

Figure 4.12 shows the effect of Darvan on the closed porosity of rubber-foam composites. Both kinds of samples with fixed quantity of Darvan as well as fixed ratio of Rubber to Darvan showed an increase in closed porosity values starting from samples having 9 weight % rubber up to 24 weight % of rubber. However, a reduction in closed porosity was seen in samples having 30 weight % of rubber particles, probably due to agglomeration issues.

It was found that both rubber particles and surfactants promote closed porosity. These plots show that rubber particles alone promoted the closed porosity to a greater extent when used with Darvan, as larger number of closed pores were seen in samples with no surfactant. The reasons for this are not clear.



(a) Samples having fixed quantity (10 g) of surfactant Darvan

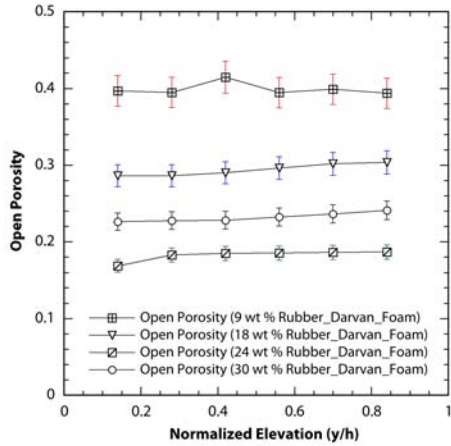
(b) Samples having fixed weight ratio (0.1%) of surfactant to rubber

Figure 4.12: Effect of Darvan on the closed porosity of rubber and polyurethane foam composites

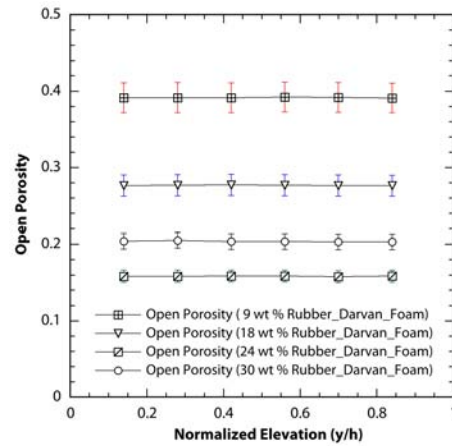
The effect of the surfactant Darvan on the open porosity of rubber-polyurethane foam blend composite was also investigated. It was seen that for the surfactant Darvan, open porosity increased in comparison to samples without surfactant, irrespective of the surfactant quantity, as seen in Fig. 4.13.

Note that neither rubber particles nor surfactants promoted the number of open pores while working individually inside the polyurethane foam system. On the other hand, their combined effect promoted open porosity. Again, the reasons for this are not clear.

Similar plots were drawn to investigate the effect of rubber particles and surfactant Vycar on the physical properties of polyurethane foam matrix system. The results were followed the same trend as for Darvan, and could be explained by the same reasoning. As they showed minimal variation as a function of normalized elevation, individual plots as



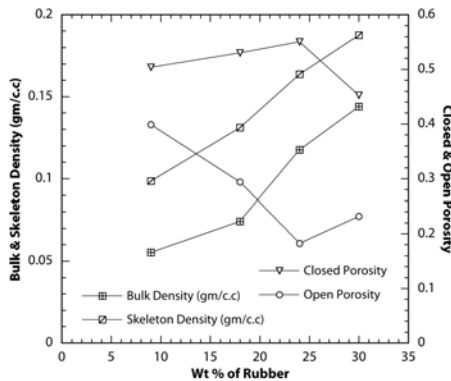
(a) Samples having fixed quantity (10 g) of surfactant Darvan



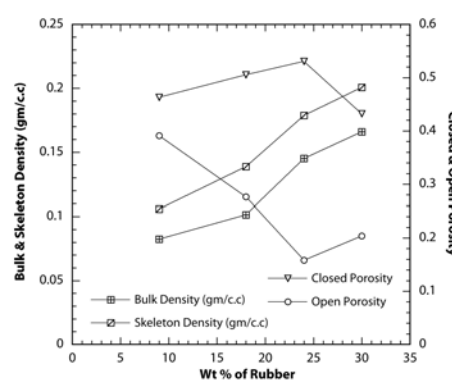
(b) Samples having fixed weight ratio (0.1%) of surfactant to rubber

Figure 4.13: Effect of Darvan on the open porosity of rubber and polyurethane foam composites

function of y/h are not shown here. Rather, the effects of rubber quantity on the physical properties of polyurethane foam matrix are explained as follows.



(a) Samples having fixed quantity (10 g) of surfactant Darvan



(b) Samples having fixed weight Ratio (0.1%) of surfactant to rubber

Figure 4.14: Effect of rubber on the physical properties of polyurethane foam composites

Figure 4.14 shows the effect of different quantities of rubber particles on the various physical properties of polyurethane foam matrix in the presence of surfactant Darvan. The effects of rubber particles were observed on two different set of samples varied by surfactant concentrations. It was seen that rubber particles affected the physical properties of

foam samples in the same manner, irrespective of surfactant concentrations. Both bulk and skeleton densities increased with an increasing content of rubber. This was because of the increase in sample masses by the incorporation of rubber particles as seen earlier. Closed porosity values increased up to sample with 24 weight % of crumb rubber, but, decreased for samples with 30 weight % of rubber. Similar anomaly in open porosity values were also seen for 100 g rubber samples. This is due to possible lack of wetting of rubber particles and agglomeration. Open porosity values decreased with increasing rubber content up to 24 weight % of rubber samples, and then increased for 30 wt % of rubber.

These observations lead to several conclusions. First, the rubber particles promote the stability of the polyurethane foam matrix as their presence always enhance the number of closed pores which is essential for the stability of rigid cell foams. The presence of rubber particles had diminishing effect on the open porosity of the foam system, which further supports foam stability. But, these trends were not seen for samples with 30 weight % of rubber content. This is possibly due to insufficient wetting and possible agglomeration, where high quantity rubber particles disrupted the foam in stead of acting as reinforcing agent. Fig. 4.15 shows an optical micrograph picture showing the agglomeration of rubber particles.

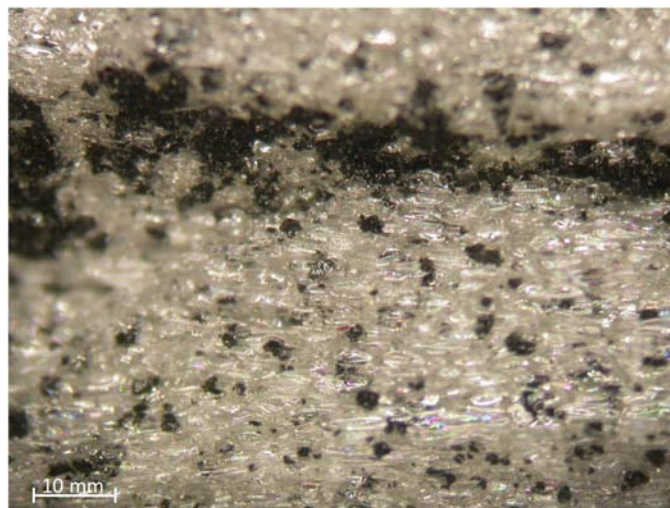
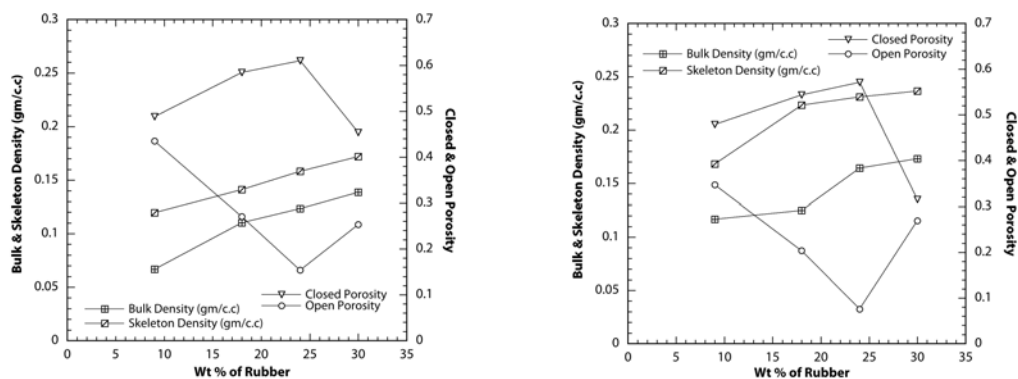


Figure 4.15: Agglomeration of rubber particles inside polyurethane foam

The effect of different rubber quantities on the physical properties of polyurethane foam matrix were found to follow the same trend in the presence of surfactant Vycar. It was seen that rubber particles helped in stabilizing the foam system and their behavior is independent of the surfactant concentrations. The same anomaly was found in the porosity data for 30 weight % of rubber. Figure 4.16 shows the effect of rubber particles on polyurethane foam system in the presence of the Vycar surfactant.



(a) Samples having fixed quantity (10 g) of surfactant Vycar

(b) Samples having fixed weight ratio (0.1%) of surfactant to rubber

Figure 4.16: Effect of rubber on the physical properties of polyurethane foam composites

The incorporation of both the surfactants Darvan and Vycar significantly affected the microstructure of rubber-polyurethane foam composites, especially the porosity. Both closed and open porosity were significantly changed by the introduction of surfactants into the system. Fig. 4.17 shows the variation of the ratio of closed to open porosity as a function of normalized elevation for the rubber-foam composites made without the presence of surfactant.

For samples having low rubber content (9 and 18 weight % of rubber), the variation of open porosity was overall uniform. For samples having 30 weight % of rubber content, both closed and porosity were varied in the same extent at the top portion of samples, i.e. at an y/h value greater than 0.5. Out of all, samples having 24 weight % of rubber particles showed an increasing trend of porosity ratio starting from the bottom up to the top. This indicates that samples having 24 weight % rubber content have promoted the closed pores

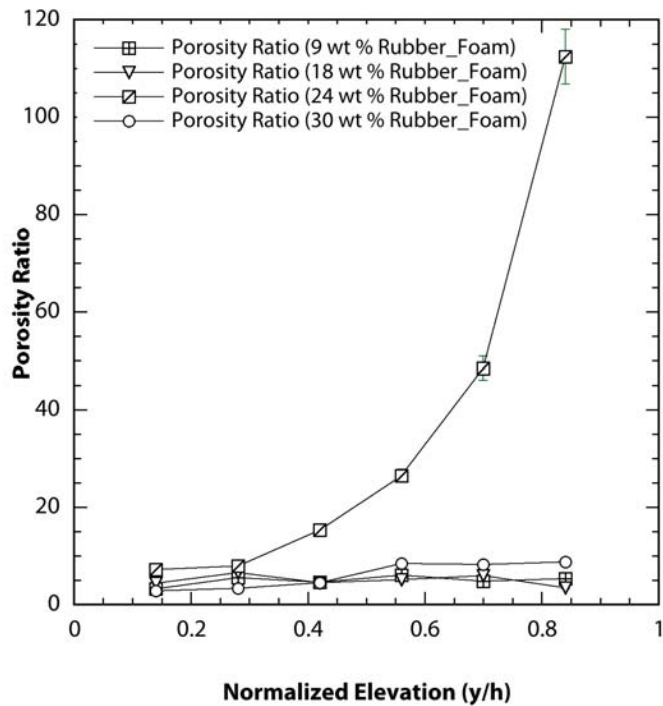


Figure 4.17: Effect of rubber particles on the porosity ratio of polyurethane foam system than open pores to a greater extent. It could be possible that 30 weight % of rubber would have promoted this even further if agglomeration did not take place.

Figure 4.18 shows the effect of rubber particle content and surfactants on the porosity ratio of crumb rubber-polyurethane foam composites. Here the porosity data is average across the normalized height, y/h , because there was no variation along this direction. Samples with fixed quantity of Darvan, i.e. higher quantity of surfactant, showed lower porosity ratio than that with fixed ratio of surfactant. This also concluded that Darvan promoted open porosity more than that of closed porosity. The relative variation of pores had been most significant in samples with 24 weight % of rubber particles as reinforcing agent. In other samples, the porosity ratio was affected by the rubber and surfactant content. Recall that both of these tended to increase closed porosity while decreasing open porosity. The porosity ratio increase all the way upto a rubber content of 24 weight %. It might have increased further for 30 weight % rubber if not for agglomerated issues.

However, the effects of Vycar on the porosity ratio of crumb rubber-polyurethane foam

samples were not the same as for Darvan. The similarity lies in the fact that samples made with Vycar showed reduced porosity ratio in comparison to samples without surfactant. This again indicates that, Vycar promoted open porosity more than closed porosity irrespective of its amount in the blend system. It was further observed that samples made with fixed quantity (10 g) of Vycar showed lower value of porosity ratio in comparison to samples having fixed ratio of surfactant to rubber quantity (0.025 to 0.1 g) except 30 weight % rubber samples. In other words, an increasing content of Vycar promoted open porosity to a greater extent than closed porosity.

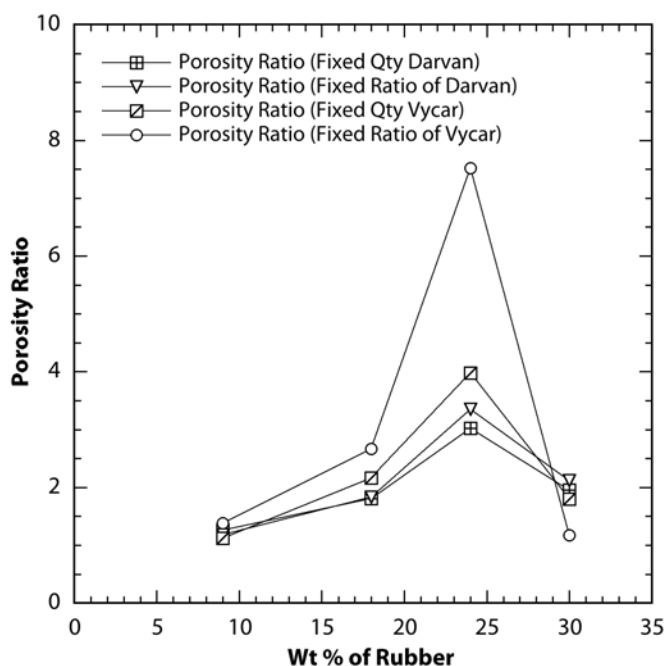
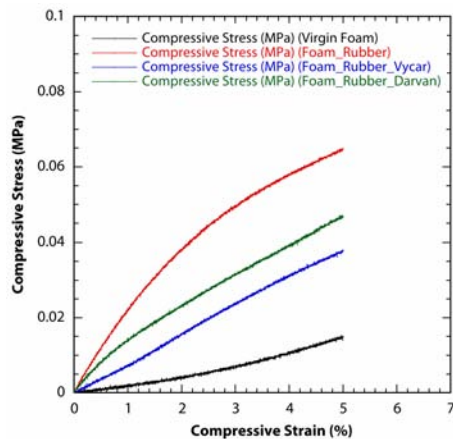


Figure 4.18: Effect of rubber particles and surfactants on the porosity ratio of polyurethane foam System

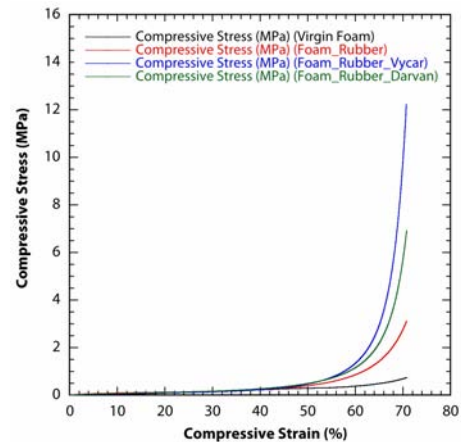
After carefully analyzing all the physical properties, a few things can be concluded. First of all, both the surfactants worked well for the dispersion of rubber particles. Also, both of the surfactants promoted closed porosity over open porosity. Nonetheless, Vycar was more effective than Darvan in promoting the closed porosity, which implies that the former is a better surfactant.

Compressive Properties

Figure 4.19 shows the generalized compressive stress-strain curve of virgin foam samples without the presence of rubber and composite samples with and without the presence of surfactants. The stress-strain diagram of crumb rubber-foam composites indicated that the stress-strain behavior was affected, but the qualitative nature remained the same, which implies that the macroscopic deformation mechanism was unchanged. The foams showed linear elasticity at low strains, followed by a long collapse plateau, and finally a regime of densification where the stress rose steeply. The linear elastic region is controlled by cell wall bending and face stretching of the individual cells; the plateau is governed by the collapse of cells. When all the cells have collapsed, the opposing cell walls touch each other and the solid is further compressed by the strains thus generated resulting in final region of rapidly increasing stress. This enhances the stresses very quickly with a crushing of the next adjacent layer [94, 95].



(a) Linear elasticity showed by composite samples at low strain



(b) General stress-strain curve of composite samples showing all the regions

Figure 4.19: Compressive stress-strain curve of rubber-polyurethane composites at different strain level

Figure 4.20 shows the effect of crumb rubber quantity and surfactants on the compressive modulus of polyurethane foam. Like compressive strength, an enhancement in com-

pressive modulus was seen with increasing content of crumb rubber. This was expected because of the introduction of the stiffer rubber content into much softer polyurethane matrix. The presence of higher closed porosity was another reason behind the increase of compressive modulus. Closed pores entrap gases in polyurethane foams. Samples with more closed pores have greater quantity of entrapped gases, which produce higher resistance towards cell wall buckling. This contributes to increased compressive modulus.

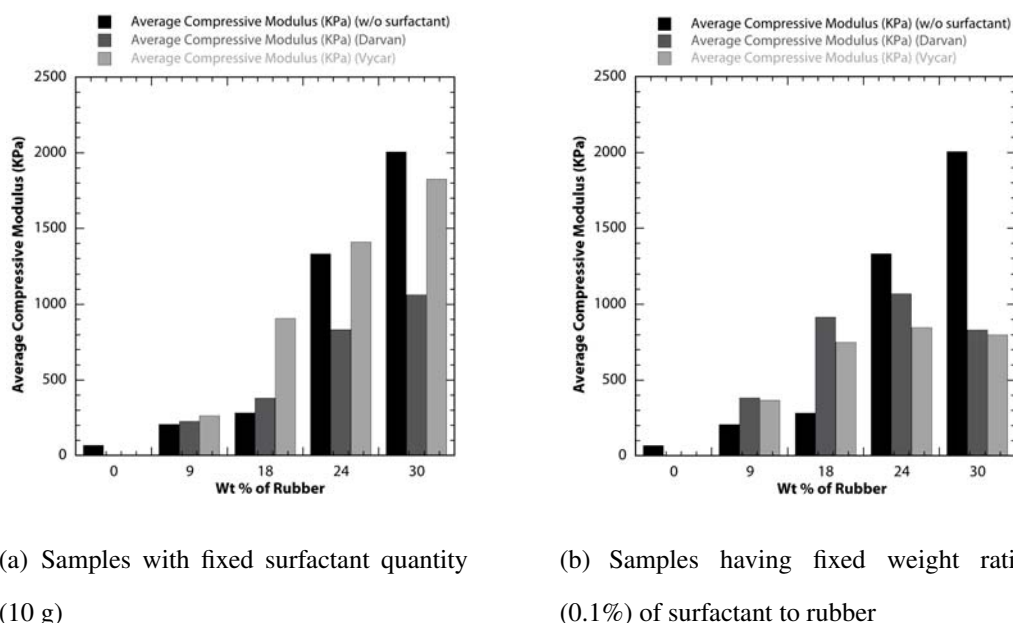
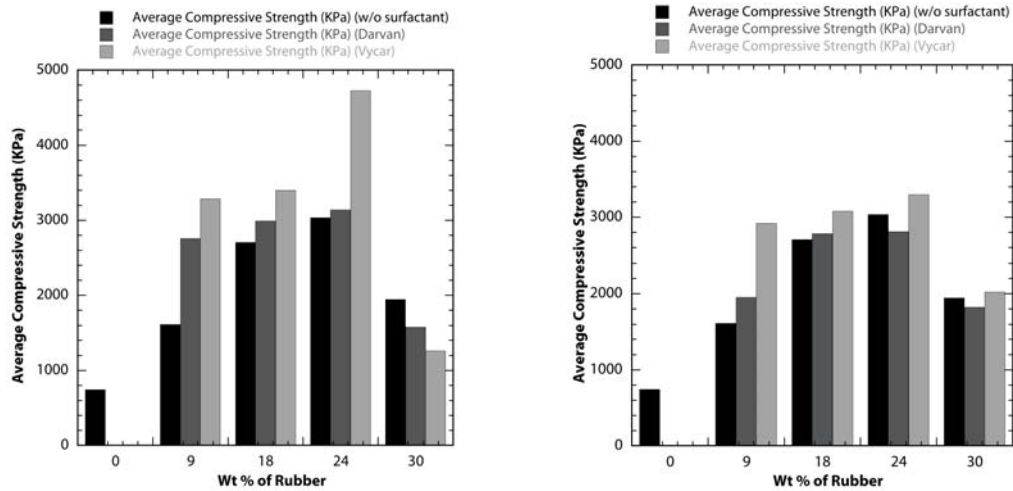


Figure 4.20: Compressive modulus of rubber-foam composites

In general compressive modulus was higher with the addition of only rubber without surfactants. This cannot be explained in a simple manner, as it was shown earlier that surfactants stabilize the foam and should lead to greater compressive modulus. The highest compressive modulus was found for a fixed surfactant quantity of Vycar. This fixed quantity of surfactant is more close to its CMC values. On the other hand, for samples with fixed surfactant ratio (0.1%), Darvan acted in a better way as 0.1% is the CMC value for Darvan.

Figure 4.21 shows the variation of solid compressive strength of rubber-foam composites as a function of rubber and surfactant content.

The addition of rubber increased the compressive strength for all values except for



(a) Samples with fixed surfactant quantity

(b) Samples having fixed weight ratio

(10 g)

(0.1%) of surfactant to rubber

Figure 4.21: Compressive strength of rubber-foam composites

samples having 30 weight % of rubber. The latter had agglomeration and poor wetting of rubber particles. The increase in strength, for 9–24 weight % case was probably due to an increase in closed porosity and due to rubber acting as a reinforcing agent. In this case, both surfactants, especially fixed quantity of Vycar lead to further increase in strength, perhaps by promoting closed porosity over open porosity.

Flexure Properties

This section discusses the effects of rubber quantity and different concentrations of surfactants on the flexural properties of polyurethane foam.

Figure 4.22 shows the load-deflection curve of rubber-foam specimens subjected to three point bending. The stress-strain response was qualitatively same for all the cases.

Figure 4.23 shows the flexural modulus of different crumb rubber–polyurethane foam blend composites, where an increasing trend in flexural modulus was seen with increasing rubber content. For the samples made with fixed surfactant ratio with rubber, an increasing trend was observed from samples up to 24 weight % of rubber and not for 30 weight % of rubber. This is probably because of the variation of closed porosity. We observed an

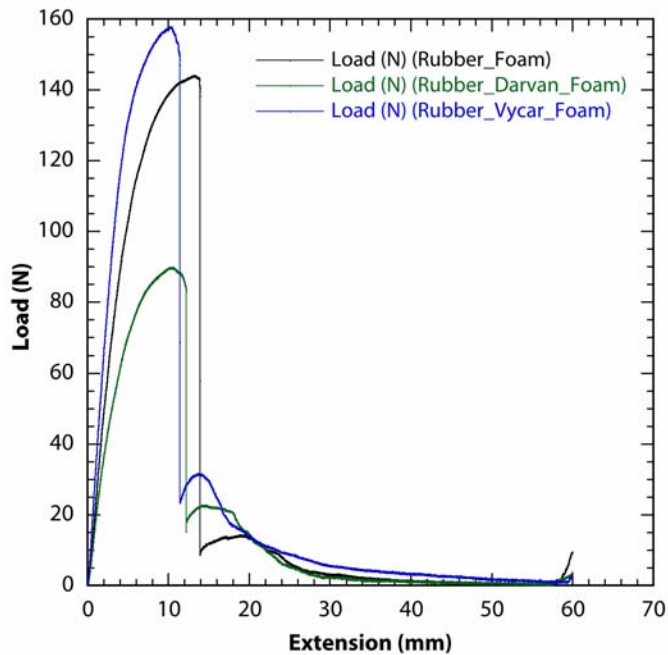
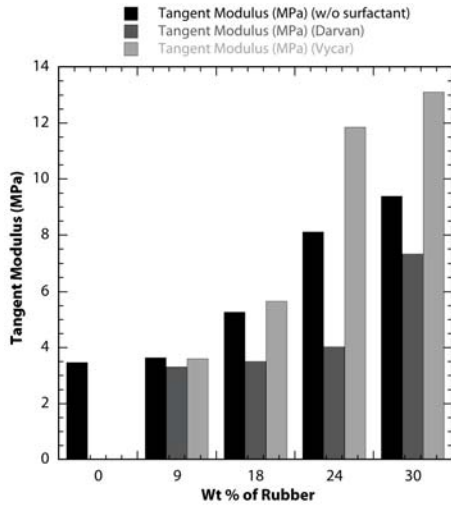


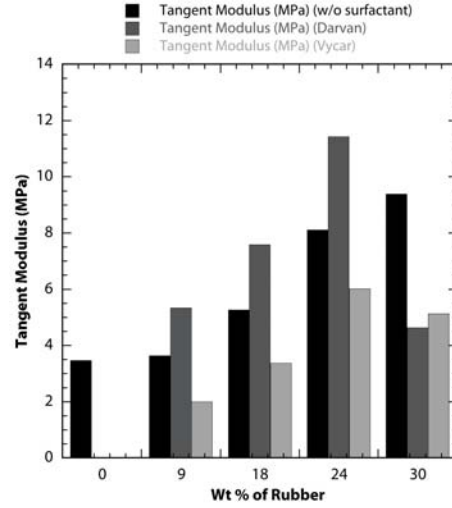
Figure 4.22: Load-deflection curve of rubber-foam composites

increasing trend in closed porosity from 9 up to 24 weight % of rubber and then a reduction for samples having 30 weight % of rubber because of agglomeration issues. Darvan acted better in this case as it is working in its CMC. For samples having fixed surfactant quantity, flexural modulus increased with increasing rubber content.

Figure 4.24 shows the effect of different quantity of rubber particles and surfactants on the flexural strength of polyurethane foam matrix system. Neither the presence of rubber nor the surfactants seemed to have played an important role in enhancing the flexural strength of the foam-rubber composites samples as virgin foam samples showed pretty high flexural strength in comparison to other samples having rubber crumb. Flexural strength depends mostly on the proper bonding between reinforcing agent and the matrix in a heterogeneous composite system. It is very evident that, though surfactants helped in uniform dispersion of rubber particles all over the polyurethane matrix, it did not promote the strong bonding between rubber particles and polyurethane matrix. Or, strong bonding did occur and the stiffer rubber particles acted as stress concentration points. Because, rubber particles are much stiffer than polyurethane.

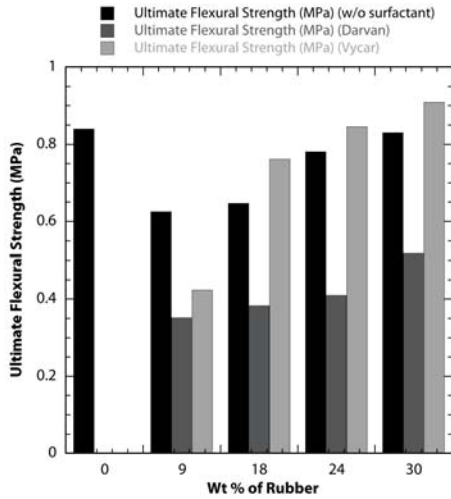


(a) Samples with fixed surfactant quantity
(10 g)

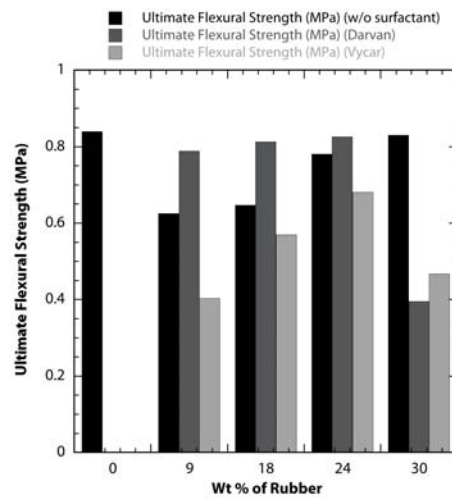


(b) Samples having fixed weight ratio
(0.1%) of surfactant to rubber

Figure 4.23: Flexural modulus of rubber-foam composites



(a) Samples with fixed surfactant quantity
(10 g)



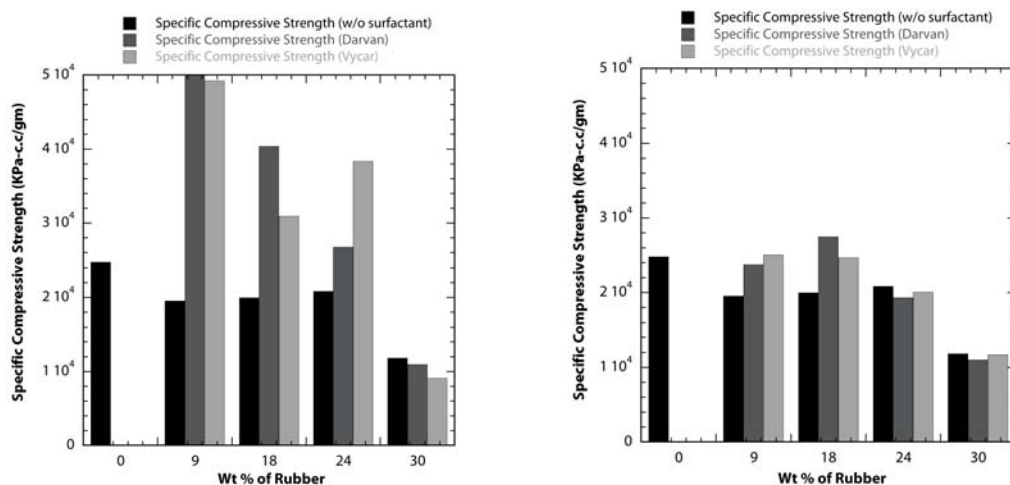
(b) Samples having fixed weight ratio
(0.1%) of surfactant to rubber

Figure 4.24: Flexural strength of rubber-foam composites

The failure modes of rubber particles inside polyurethane matrix is an important factor in analyzing the bending strength and moduli of rubber-polyurethane composites. Failures initiated on the tension side of all the specimens and rubber particles were found to be torn out from the polyurethane network. This cohesion would lead to a decrease in flexural strength (but not compressive strength). Scanning electron microscopy images will be furnished to show the tearing of particles.

Specific Properties

Specific strength and modulus values were calculated in order to assess the net effect of adding crumb rubber to polyurethane foam.



(a) Samples with fixed surfactant quantity

(b) Samples having fixed weight ratio

(10 g)

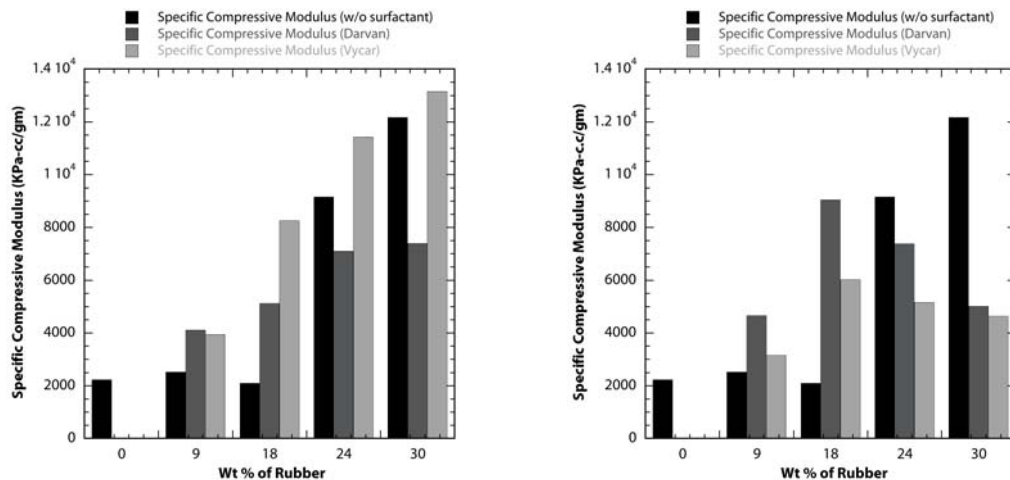
(0.1%) of surfactant to rubber

Figure 4.25: Specific compressive strength of rubber-foam composites as a function of rubber content

Figure 4.25 and 4.26 shows the effect of rubber particles and surfactant concentrations on the specific compressive strength and modulus of the blend composite system, respectively. In the absence of surfactants, increasing rubber content led to decreased compressive strength. However, by the use of fixed surfactant quantity, this was offset, except for the 30 weight % case resulting in a decrease in specific strength. The use of surfactants at fixed

weight ratio did not result similar.

In samples having maximum rubber content, the variation in bulk density has been much more promoted than that of compressive strength, which makes sense as we have investigated the reduction in strength along with highest bulk density for samples with 100 g rubber content as a reinforcing agent. It is quite obvious that, an increasing surfactant quantity would promote the compressive strength much more than the bulk density so as to get higher values of specific compressive strength. This also makes sense as we know that with an increasing content of surfactant, two things occur simultaneously. Firstly, surface tension between individual cells reduces significantly which promotes more foaming and a reduction in bulk density. At the same time, surfactant promotes closed porosity in the cell structure. As discussed earlier, materials having more closed pores contain larger amount of entrapped air, which offers an opposite force towards cell wall buckling and an enhancement of compressive strength, i.e. increasing surfactant increases the numerator factor and makes the denominator factor lesser in the parameter specific compressive strength. Consequently, specific compressive strength increases.



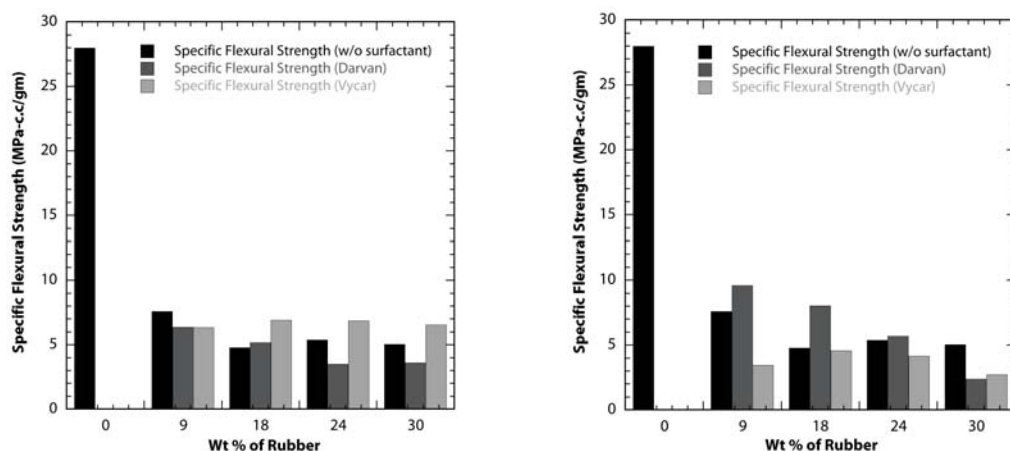
(a) Samples with fixed surfactant quantity
(10 g)

(b) Samples having fixed weight ratio
(0.1%) of surfactant to rubber

Figure 4.26: Specific compressive modulus of rubber-foam composites as a function of rubber content

The specific compressive moduli values of blend composites were found to follow an increasing trend. Again Vycar, when used in fixed quantity, improved modulus even further. Darvan was effective in only specific cases, and only for fixed weight ratio of surfactants. This results indicate that surfactant effectiveness was controlled by concentration being closer to the CMC value. Both the surfactants performed better at a concentration closer to their respective CMC. Sample with fixed surfactant quantity showed this increasing trend up to 30 weight % of rubber content, while the other set of samples showed a rising trend up to samples having 18 weight % of rubber, which might be due to improper wetting of rubber in polyurethane as well as non uniform dispersion of rubber particles inside polyurethane foam by the application of respective surfactants concentration for higher rubber contents. Hence, we can conclude that though, surfactants have helped in overall dispersion of rubber particles, it did not promote strong bonding in between rubber and polyurethane. It could be seen that introduction of rubber particles had promoted the increase in moduli to a greater extent than that of bulk density. Increasing the content of rubber signifies the introduction of more and more stiffness inside the composite system and accordingly modulus increases significantly. To say a few words about the effect of surfactants, we can conclude that both the surfactants worked better in comparison to other at a concentration closer to their respective critical micelle concentration as expected. A higher quantity of surfactants always had promoted the increase in compressive moduli to a greater extent than the bulk density as seen from the samples with fixed quantity of surfactants as, they showed an increasing trend with an increasing content of rubber, irrespective of the type of surfactants. Same inference could not be drawn for samples made with a fixed ratio of rubber to surfactant as they showed optimum performance for samples with 50 g rubber content. This again signifies that an optimum performance can be achieved by the proper combination of rubber quantity and surfactant concentration as both have different effects on physical and mechanical property in a system where more than one parameter changes simultaneously. For both surfactant concentrations, we can see that up to 50 g of rubber, surfactants worked

in a better way in comparison to samples with no surfactant, but the trend got changed for higher quantity of rubber. This might be because of the fact that at low volume fraction of rubber, the amount of surfactant used in the system had been able to orient the reinforcing rubber particles in a plane vertical to stress direction so that rubbers could exert their reinforcing ability. This orientation introduced strong interfacial strength and consequently samples with surfactants showed better results. The overall effect of surfactants had been good on the compressive moduli of composite system as it dispersed the rubber particles uniformly and increased the effective surface area in between reinforcing agent and matrix. This would enable improved adhesion between the two components of this heterogeneous system and increasing moduli values could be seen.



(a) Samples with fixed surfactant quantity
(10 g)

(b) Samples having fixed weight ratio
(0.1%) of surfactant to rubber

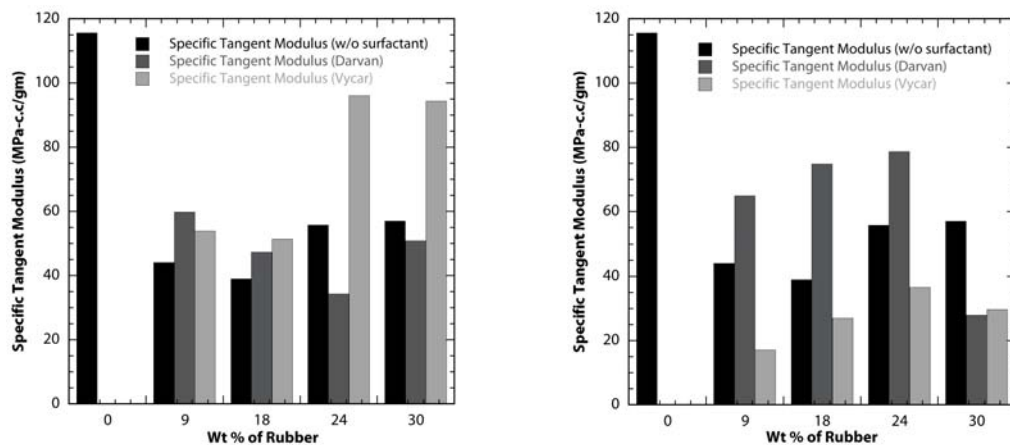
Figure 4.27: Specific flexural strength of rubber-foam composites as a function of rubber content

Figure 4.27 and 4.28 shows the effect of rubber particles and surfactant concentrations on the specific flexural strength and modulus of blend composites, respectively. Both specific modulus and strength values were found to follow a diminishing trend in comparison to virgin foam samples. While, a moderate decrease in specific modulus occurred, significant decrease in specific strength was observed. This happened possibly due to rubber

particle decohesion. It is very evident that, though surfactants helped in uniform dispersion of rubber particles all over the polyurethane matrix, they did not promote strong bonding between rubber particles and polyurethane matrix. Or, strong bonding might have occurred and the stiffer rubber particles acted as stress concentration points resulting in a reduction of specific flexural properties.

Because, rubber particles are much stiffer than polyurethane. We could see much more reduced values of flexural strength in comparison to virgin foam samples without the presence of rubber as well as surfactants. Any specimen in flexure is subjected to two directly opposite kind of loading phenomenon simultaneously. One part of it is subjected to tension, while the other part is subjected to compression. Flexural strength depends mostly on the proper bonding between reinforcing agent and the matrix in a heterogeneous composite system. From the figure, it could be concluded that, even though surfactants helped in uniform dispersion of rubber particles all over the polyurethane matrix, it did not promote the bonding between rubber particles and polyurethane matrix. At the same time, rubber particles are much stiffer than polyurethane. Effectively, we got a system where higher stiffness particles were loosely bonded in a softer matrix material, especially in that part of the specimen subjected to tension. This had adverse effects on the micromechanics of the blend composites as, rubber particles had acted as a mean of creating defective sites inside the composite materials because of decohesion in between rubber and polyurethane system in stead of acting as a reinforcing agent. This is the reason behind a decreasing trend in specific flexural strength irrespective of the concentrations of surfactants as bulk density had been promoted to a much greater extent than that of flexural strength. Both the surfactants worked better closer to their critical micelle concentration while comparing their performances relative to each other. The similar trend was obtained for the specific flexural moduli values, which can be explained in the same way like strength. One important observation was the relative difference in specific flexural moduli value for samples with rubber and surfactants in comparison to virgin foam samples. In comparison to specific flexural

strength properties, the difference in flexural moduli had been much less for these different set of samples. This is because of the fact the effects of decohesion and debonding are much more prominent on flexural strength rather than that of flexural modulus. That is the reason why the difference had not been so much for the case of moduli values.



(a) Samples with fixed surfactant quantity

(b) Samples having fixed weight ratio

(10 g)

(0.1%) of surfactant to rubber

Figure 4.28: Specific flexural modulus of rubber-foam composites as a function of rubber content

Comparison of Experimental Results With Other Models

The experimental observation of mechanical properties were compared to current existing models for foams. Figure 4.29 shows the cubic cell model of a closed cell foam. When foams are constructed from a liquid, surface tension draws the material into the cell edges keeping across the faces of the cell and ruptures easily. The dimensions of the unit cell and the thickness of the cell walls have significance impacts on the mechanical properties of polymeric foams [94]. Though, the foam cells are initially closed, stiffness is calculated from that of edges and moduli are similar to those of open cell foams. In some of the polymeric closed cell foams, a fraction of solid is always in the cell faces, which contributes to the cell faces. Some cellulosic materials have closed cells with thick cell faces. In that case, moduli depend on density in slightly different manner [94].

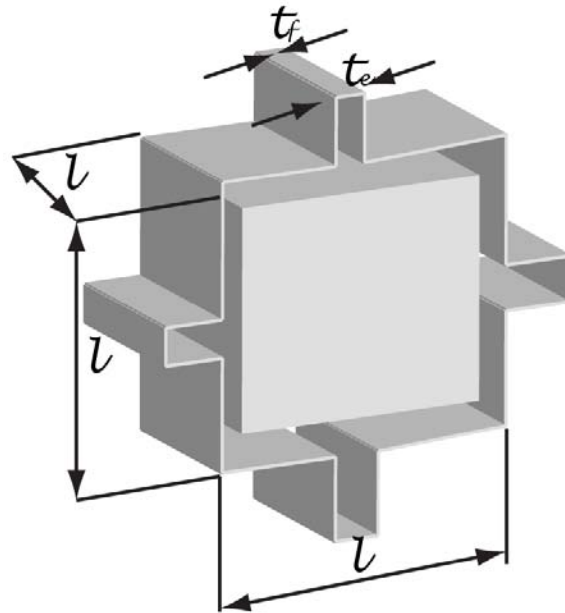


Figure 4.29: Cubic cell model of a closed cell foam [94]

Mechanical properties of closed cell foams (basically any type of polyurethane foams) depend heavily on the density of the materials. Therefore, several researchers have modeled the relative elastic (compressive) modulus of closed cell foams as a function of relative density. Relative elastic modulus is the ratio of elastic modulus of final foam or foam-particles composites to the elastic modulus of virgin foam. Similarly, relative density is the ratio of the density of the final foam or foam-particles composites to the density of the virgin foam material. This kind of study has been very helpful as it always helps in design foam composites with controllable mechanical properties. One very popular model is the Square Relationship Model, where the relative elastic modulus is considered as the square of the relative density [55].

$$\frac{E^*}{E_s} = \left(\frac{\rho^*}{\rho_s}\right)^2 \quad (4.1)$$

Another popular model has been the Simple Bend Model. This model considers gas cells as fillers of zero modulus and predicts that relative elastic modulus follows a linear

relationship with relative density having slope of 1.

$$\frac{E^*}{E_s} = \frac{\rho^*}{\rho_s} \quad (4.2)$$

Ashby *et al* [94] predicted the relative elastic modulus of closed cell foams using a generalized method considering stretching of the cells, cell membrane tension, and pressure of the gases inside closed pores. According to them, the relationship between the relative elastic modulus and relative density is as follows,

$$\frac{E^*}{E_s} = (\phi)^2 \left(\frac{\rho^*}{\rho_s}\right)^2 + (1 - \phi) \left(\frac{\rho^*}{\rho_s}\right) + \frac{p(1 - 2\nu)}{E_s(1 - \frac{\rho^*}{\rho_s})} \quad (4.3)$$

where, ϕ is a variable fraction having a value 0.8 for rigid polyurethane closed cell foams, ν is the Poisson ratio of closed cell foams having a value of 0.33, E_s is the Compressive Modulus of virgin polyurethane foam obtained from US Composites manual, and p is the atmospheric pressure of 0.1 MPa.

Figure 4.30 compares the experimental value of relative elastic modulus versus relative density of all the samples made with different compositions of crumb rubber content and surfactant ratio along with these three above mentioned model. It is very much evident that irrespective of the composition of foam, amount of rubber and type of surfactant, experimental results match closely with the general Ashby-Gibson model. This clearly shows that composition did not change the basic foaming process and the basic nature of closed cell foam.

The reason why experimental values did not match with either the Simple Bend Model or Square Model is because of the non-homogeneous reinforcement of rubber reinforcement in our present study. The non homogeneous distribution of rubber provides might enforce the foam-rubber composites to follow different mechanism based on density and deformation ratio altogether.

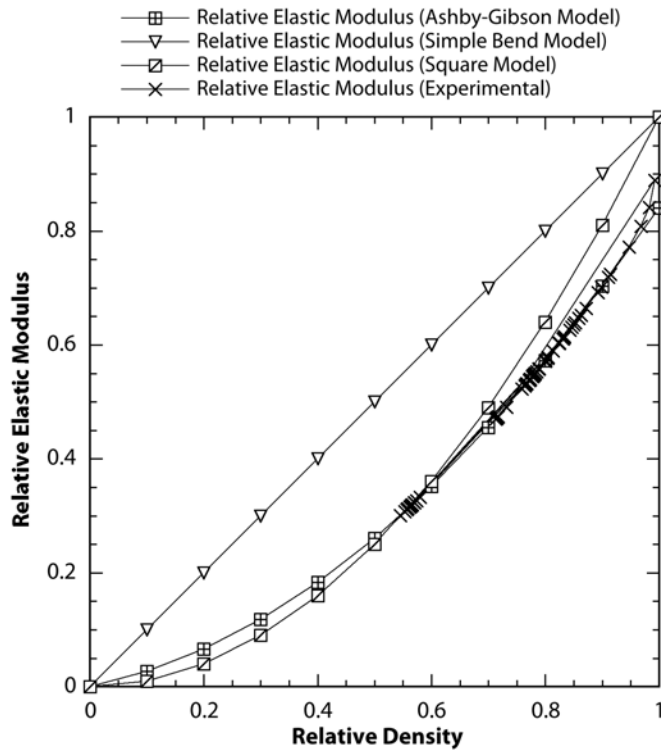


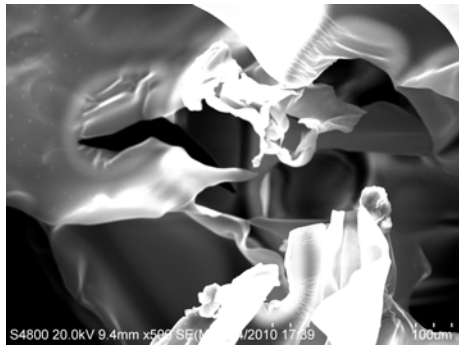
Figure 4.30: Comparison of experimental relative elastic modulus with different models

SEM Images

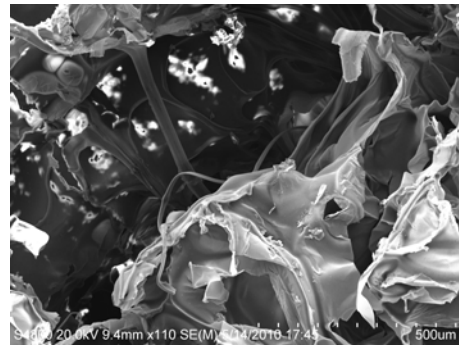
Possible tearing of rubber particles inside the rubber-polyurethane foam composite samples could be a deciding factor in determining the flexural strength and moduli. Figures 4.31 and 4.32 show the SEM images of the fractured surfaces from flexural experiments. They showed the presence of rubber particles tearing inside the samples.

Figure 4.33 shows the SEM images of fractured surfaces of composite samples used for flexural testing. Though, high quantity of rubber particles had created a possibility of the presence of great amount of rubber particles used in any fracture plane for the purpose of crack bridging, as seen in the figure, materials were not free from defects as particle decohesion was observed in microscopy images.

These defects might have come into the specimens because of two possible mechanisms acting differently or simultaneously. Firstly, the presence of excess rubber particles inside the foam samples might have allowed them to come closer to each other. The particles in-

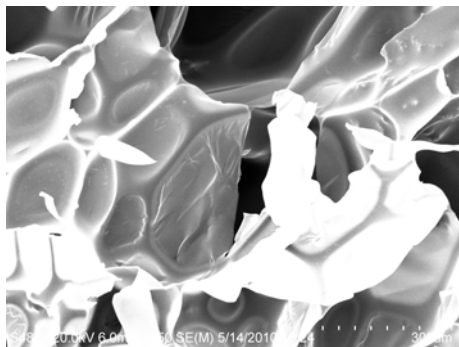


(a) Teared rubber particles inside blend composites

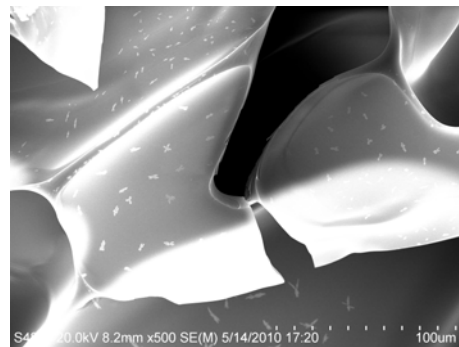


(b) Debonding of rubber particles by tearing failure

Figure 4.31: SEM images showing tearing of rubber particles in the tension side of test specimens

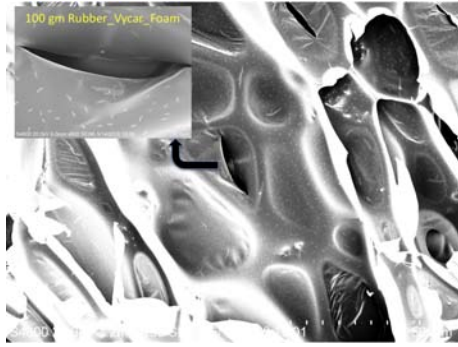


(a) Rubber particles creating defects inside composite specimens

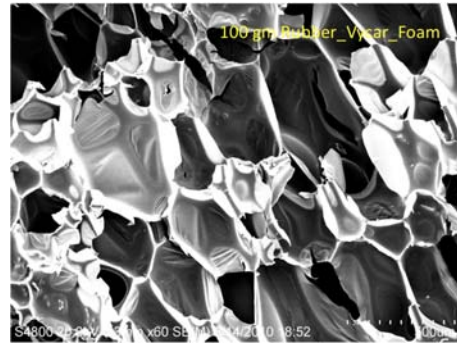


(b) Microcracks generated inside composite samples by the poor bonding between rubber and foam

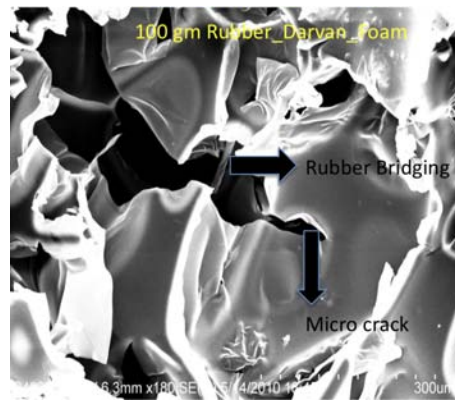
Figure 4.32: SEM images showing defects inside blend composites with highest rubber content



(a) Crack in surfaces made with Vycar



(b) Other defects in samples made with Vycar



(c) Crack in surfaces made with Darvan

Figure 4.33: SEM images of fractured surfaces of composite samples with 30 weight % of rubber

teracted and got ruptured introducing flaws inside the specimens. Another reasoning might be the poor bonding between high stiffness rubber particles and soft polyurethane foam matrix. The loosely bonded rubber particles, especially in the tensile side of the specimens than compressive side had made the specimens defective in terms of crack propagation rather than acting as a reinforcing agent because of decohesion in between two heterogeneous component system. The SEM pictures showing the teared rubber particles inside polyurethane foam supported this fact further.

FTIR Spectra

Preliminary FTIR was conducted to investigate chemical reactions due to the introduction of surfactants in the rubber-polyurethane foam system. Figure 4.34 shows the FTIR spectra of the surfactant Darvan along with the blend composites made with Darvan. The large peak at a wave number in between 3000 cm^{-1} and 4000 cm^{-1} , for the surfactant is due to the presence of hydroxyl groups in form of water in Darvan. Urethane linkages consist of bonding of N-H or C=O groups. These groups are neither isolated nor free in the condensed state but stay in a large combination of polar and non polar groups. A rule of thumb indicates the position of intermolecular chains of hydrogen bonds to be normal to the polymer chains. At a shoulder near wave number of 1725 cm^{-1} , some carbonyl stretching was seen. This might be the result of strong hydrogen bond formation in between the carbonyl group present in Part A of the polyurethane foam system along with the hydrogen atom of surfactant Darvan. Similar peaks were identified by Coleman *et al.* [96] to be a result of carbonyl group stretching due to hydrogen bond formation in between polyurethane and ether interaction. This hydrogen bonding indicates that the surfactants had a good interaction with the polyurethane system. The formation of intermolecular hydrogen bonding can make a material stronger. FTIR spectra of Vycar treated samples also showed similar possibility.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

On the basis of experimental results obtained, a few conclusions can be drawn. It is very clear that addition of rubber particles significantly affected the microstructure as well as the mechanical properties of the blend composite system. The addition of rubber particles did not affect the basic foaming process of polyurethane matrix system though, it led to greater bulk density than that for virgin foam. Compressive properties were greatly enhanced by the incorporation of rubber particles, as seen from the experimental results. At the same time, reduction in flexural properties occurred. This was due to lack of bonding between high stiffness rubber particles and soft polyurethane matrix.

Application of surfactants was another major aspect of this present work. Consequently, the effect of surfactants on the microstructure and mechanical properties of the blend composites was also investigated. On the basis of experimental results, it can be concluded that both the surfactants used in this study were effective. They helped in dispersing the rubber particles uniformly inside the polyurethane matrix system in a much better way as compared to samples made without surfactants. In addition, both the surfactants helped reducing the total porosity of the system and promoted the generation of closed pores. Both surfactants showed better performance at concentrations closer to their critical micelle concentration. In spite of all these advantages, the surfactant did not help much in the bonding between rubber particles and polyurethane matrix. Though, the compressive properties were not affected much, as they were dependent on some other parameters, the flexure properties were significantly affected by this lack of bonding. Surface treated rubber-foam

samples showed better compressive strength in comparison to untreated rubber-foam sample. Surfactants seemed to have reacted well with polymeric rubber particles and strengthen the cells, which, eventually delayed the collapse of the cells and raised the densification strain resulting in an enhancement in the compressive strength. Last but not the list, was the reduction of average cell size distribution by the application of surfactants which resulted in the promotion of more open pores inside the system and not favorable for an ideal closed cell foam. This made us believe that, though the blend composite system has been benefited by the use of surfactants, both Darvan and Vycar can not be depicted as perfect surfactant for our combination of crumb rubber and polyurethane foam, as they might tend to change the nature of our foam matrix. This also concludes that knowledge of an optimum combination of rubber and polyurethane foam quantity is very important for the maximum performance of the particulate composite in this present study.

It has been clearly understood that microstructure of the present blend composite system had a considerable impact on the mechanical properties. The basic nature of the particle reinforced foam was carefully investigated in terms of mechanical properties and it was seen to be the same as that for virgin closed cell foam irrespective of material composition. In general, both strength and modulus were seen to follow a linear relationship with closed porosity content of composite samples except for very high percentage of rubber. Materials having more closed pores possessed more gas pressure inside the pores, which offered resistance to cell wall buckling, resulting an increase in both strength and modulus values. Excess rubber particles inside the system introduced defects inside the composite structure due to combined effect of stress concentration due to rigid rubber particles and agglomeration.

There are a few things which can be addressed to further understand the micromechanics of this rubber particle reinforced polyurethane foam system.

- The presence of both rubber particles and surfactant had a significant effect on the properties of blend composite system, and there was a relationship between the microstructure and property. While the incorporation of rubber particles directly changed the physical as well as mechanical properties, the effects of surfactants were more prominent on the interaction of particles in the heterogeneous material system and change of morphology. Hence, the introduction of both rubber and surfactant changed several parameters simultaneously inside the present material system and it became complex to analyze any particular property as a function of single change in parameter. For that, a detailed study is needed to understand the deformation mechanism of closed cell polyurethane foam. The multi scale nature of foam deformation could be examined from individual struts to foam deformation to resolve this issue. This needs a detailed understanding between the localization of individual struts and deformation bands at the macro-scale. Digital Image Correlation (DIC) technique can be very helpful in this connection, as it would provide continuous mapping of strain fields along any cross section of foam sample.
- In this study, crumb rubber particles were of one particular size. The effect of different rubber particle sizes on the microstructure and mechanical properties of blend composites could be a good study. It will also be interesting work to check the effect of hydroxyl concentrations of polyol on the mechanical properties of rubber polyurethane blend system.
- Since, this two part foam system consists of a blowing agent, it was not possible to wash the surface of the rubber particles with a high volatile organic solvent in order to coat the same to make an effective component. There were always the creation of negative pressure gradient along the surfaces as carbon dioxide gas diffused through the cell walls creating a much more brittle end product. A possible approach could be to use some strong dispersing agent like xanthum gum.

- It would be good to focus on the thermal properties of composite system as well.
- FTIR is always an effective tool to characterize fiber-matrix surface chemistry to study the changes. Although, significant changes were found in the FTIR spectra between composite samples with surfactant and only surfactant, further analysis is needed to understand the chemical interactions.

BIBLIOGRAPHY

- [1] B. Adhikari, D. De, and S. Maiti, "Reclamation and recycling of waste rubber," *Progress In Polymer Science*, vol. 25, pp. 909–948, SEP 2000.
- [2] R. Siddique and T. Naik, "Properties of concrete containing scrap-tire rubber - an overview," *Waste Management*, vol. 24, no. 6, pp. 563–569, 2004.
- [3] P. Sukontasukkul and C. Chaikaew, "Properties of concrete pedestrian block mixed with crumb rubber," *Construction and Building Materials*, vol. 20, pp. 450–457, SEP 2006.
- [4] S. G. C. From the Office of Mosquito Abatement Coordination, "Mosquitoes Disease and Scrap Tires," <http://www.p2pays.org/ref/11/10504/html/biblio/htmls2/prh8.html>.
- [5] T. Amari, N. Themelis, and I. Wernick, "Resource recovery from used rubber tires," *Resources Policy*, vol. 25, pp. 179–188, SEP 1999.
- [6] E. Ganjian, M. Khorami, and A. A. Maghsoudi, "Scrap-tyre-rubber replacement for aggregate and filler in concrete," *Construction and Building Materials*, vol. 23, pp. 1828–1836, MAY 2009.
- [7] A. R. Khaloo, M. Dehestani, and P. Rahmatabadi, "Mechanical properties of concrete containing a high volume of tire-rubber particles," *Waste Management*, vol. 28, pp. 2472–2482, DEC 2008.
- [8] K. Fukumori, M. Matsushita, H. Okamoto, N. Sato, Y. Suzuki, and K. Takeuchi, "Recycling technology of tire rubber," *JSAE Review*, vol. 23, pp. 259–264, APR 2002.

- [9] N. Sunthonpagasit and M. Duffey, "Scrap tires to crumb rubber: feasibility analysis for processing facilities," *Resources Conservation and Recycling*, vol. 40, pp. 281–299, MAR 2004.
- [10] F. Smith, E. Daniels, and A. Teotia, "Testing and Evaluating Commercial Applications of New Surface-Treated Rubber Technology Utilizing Waste Tires," *Resources Conservation and Recycling*, vol. 15, pp. 133–144, NOV 1995.
- [11] A. Yilmaz and N. Degirmenci, "Possibility of using waste tire rubber and fly ash with Portland cement as construction materials," *Waste Management*, vol. 29, pp. 1541–1546, MAY 2009.
- [12] "The Many Uses of Crumb Rubber," *Waste Tire Recycling Program, Texas Natural Resource Conservation Commission*, 1999.
- [13] "From the Official Website of Green Energy Industries," <http://gecorpusa.com>.
- [14] L. Schramm and D. Marangoni, "Surfactants: Fundamental and Application in PET Industry," *Cambridge Unix Press*, pp. 3–22, 2000.
- [15] "From the Official Website of Vaibhav Rubbers Pvt Ltd," <http://product-image.tradeindia.com>.
- [16] "From the Official Website of Google Inc," <http://en.wikipedia.org/wiki/polyurethane>.
- [17] M. Krupers, C. Bartelink, H. Grunhauer, and M. Moller, "Formation of rigid polyurethane foams with semi-fluorinated diblock copolymeric surfactants," *Polymer*, vol. 39, pp. 2049–2053, MAY 1998.
- [18] K. M. Zia, H. N. Bhatti, and I. A. Bhatti, "Methods for polyurethane and polyurethane composites, recycling and recovery: A review," *Reactive & Functional Polymers*, vol. 67, pp. 675–692, AUG 2007.

- [19] D. Allport, D. Gilbert, and S. Outterside, "MDI and TDI: Safety, Health and the Environment: A Source Book and Practice Guide," *John Willey and Sons Ltd*, 2003.
- [20] T. N. Hunter, R. J. Pugh, G. V. Franks, and G. J. Jameson, "The role of particles in stabilising foams and emulsions," *Advances in Colloid and Interface Science*, vol. 137, pp. 57–81, MAR 18 2008.
- [21] R. Romine and M. Romine, "Rubbercycle: a bioprocess for surface modification of waste tyre rubber," *Polymer Degradation and Stability*, vol. 59, no. 1-3, Sp. Iss. SI, pp. 353–358, 1998.
- [22] M. K. Batayneh, I. Marie, and I. Asi, "Promoting the use of crumb rubber concrete in developing countries," *Waste Management*, vol. 28, pp. 2171–2176, NOV 2008.
- [23] M. Bignozzi and F. Sandrolini, "Tyre rubber waste recycling in self-compacting concrete," *Cement and Concrete Research*, vol. 36, pp. 735–739, APR 2006.
- [24] H. Toutanji, "The use of rubber tire particles in concrete to replace mineral aggregates," *Cement & Concrete Composites*, vol. 18, no. 2, pp. 135–139, 1996.
- [25] T.-C. Ling, H. M. Nor, and M. R. Hainin, "Properties of Crumb Rubber Concrete Paving Blocks with SBR Latex," *Road Materials and Pavement Design*, vol. 10, pp. 213–222, JAN-MAR 2009.
- [26] C. K. Akisetty, S.-J. Lee, and S. N. Amirhanian, "High temperature properties of rubberized binders containing warm asphalt additives," *Construction and Building Materials*, vol. 23, pp. 565–573, JAN 2009.
- [27] S. H. Baek, H. H. Kim, Y. S. Doh, and K. W. Kim, "Estimation of high-temperature properties of rubberized asphalt using chromatograph," *KSCE Journal Of Civil Engineering*, vol. 13, pp. 161–167, MAY 2009.

- [28] J. E. Crespo, F. Parres, and A. Nadal, "Mechanical behavior analysis of sintered products of natural rubber crumb rubber (NRCCR) using adhesives," *Material Wissenschaft Und Werkstofftechnik*, vol. 40, pp. 211–217, MAR 2009.
- [29] S. G. Jahromi and A. Khodaii, "Empirical Model for Determining Rutting Parameter in Rubber Modified Bitumen," *International Journal of Civil Engineering*, vol. 6, pp. 246–254, DEC 2008.
- [30] S.-J. Lee, S. N. Amirghanian, and B. J. Putman, "Characterization of Recycled Aged RAP Binders Containing Crumb Rubber Modifier Using Gel Permeation Chromatography," *Journal of Materials in Civil Engineering*, vol. 21, pp. 382–391, AUG 2009.
- [31] S.-J. Lee, S. N. Amirghanian, and S.-Z. Kwon, "The effects of compaction temperature on CRM mixtures made with the SGC and the Marshall compactor," *Construction and Building Materials*, vol. 22, pp. 1122–1128, JUN 2008.
- [32] H. Li, H. Zhao, and K. Liao, "Study on the Technological Conditions of Crumb Tire Rubber-Modified Bitumens," *Petroleum Science and Technology*, vol. 27, no. 14, pp. 1521–1533, 2009.
- [33] S. Liu, W. Cao, J. Fang, and S. Shang, "Variance analysis and performance evaluation of different crumb rubber modified (CRM) asphalt," *Construction and Building Materials*, vol. 23, pp. 2701–2708, JUL 2009.
- [34] A. A. Mohamed, H. Omar, M. O. Hamzah, and H. Ismail, "Rheological Properties of Crumb Rubber-Modified Bitumen Containing Antioxidant," *Arabian Journal for Science and Engineering*, vol. 34, pp. 3–12, APR 2009.
- [35] K. M. Shatanawi, C. C. Thodesen, and S. N. Amirghanian, "Effects of crumb rubber variability on failure temperature of Crumb Rubber Modified binders," *Road Materials and Pavement Design*, vol. 9, pp. 291–309, APR-JUN 2008.

- [36] J. Shen, S. Amirkhanian, F. Xiao, and B. Tang, "Influence of surface area and size of crumb rubber on high temperature properties of crumb rubber modified binders," *Construction and Building Materials*, vol. 23, pp. 304–310, JAN 2009.
- [37] F. Xiao, S. N. Amirkhanian, J. Shen, and B. Putman, "Influences of crumb rubber size and type on reclaimed asphalt pavement (RAP) mixtures," *Construction and Building Materials*, vol. 23, pp. 1028–1034, FEB 2009.
- [38] Z. Tang, M. A. Butkus, and Y. F. Xie, "Enhanced performance of crumb rubber filtration for ballast water treatment," *Chemosphere*, vol. 74, pp. 1396–1399, MAR 2009.
- [39] J. Kim and S. Lee, "New Technology of Crumb Rubber Compounding for Recycling of Waste Tires," *Journal of Applied Polymer Science*, vol. 78, pp. 1573–1577, May 2 2000.
- [40] N. Fattuhi and L. Clark, "Cement-based materials containing shredded scrap truck tyre rubber," *Construction and Building Materials*, vol. 10, pp. 229–236, JUN 1996.
- [41] R. Fenner and K. Clarke, "Environmental and structural implications for the re-use of tyres in fluvial and marine-construction projects," *Journal of the Chartered Institution of Water and Environmental Management*, vol. 17, pp. 99–105, MAY 2003.
- [42] G. Li and M. John, "A crumb rubber modified syntactic foam," *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, vol. 474, pp. 390–399, FEB 15 2008.
- [43] J. Cawse and J. Stanford, "Rubber-Toughened Polyurethane Network and Composite-Materials," *Polymer*, vol. 28, pp. 356–367, MAR 1987.
- [44] J. Datta and A. Iwanowska, "Use of rubber wastes for filling the cast urethane elastomers," *Przemysl Chemiczny*, vol. 86, pp. 872–874, SEP 2007.

- [45] N. Manoj, P. Sivaraman, S. Praveen, R. Raut, L. Chandrasekhar, and B. Chakraborty, "Miscibility and fracture toughness of thermoplastic polyurethane/poly(vinyl chloride)/nitrile rubber ternary blends with special reference to the blend composition," *Journal of Applied Polymer Science*, vol. 97, pp. 1763–1770, SEP 5 2005.
- [46] M. PastorBlas, R. TorregrosaMacia, J. MartinMartinez, and J. Dillard, "Failure analysis of surface-treated unvulcanized SBS rubber/polyurethane adhesive joints," *International Journal of Adhesion and Adhesives*, vol. 17, no. 2, pp. 133–141, 1997.
- [47] J. Tan, Y. M. Ding, X. T. He, Y. Liu, Y. An, and W. M. Yang, "Abrasion resistance of thermoplastic polyurethane materials blended with ethylene-propylene-diene monomer rubber," *Journal of Applied Polymer Science*, vol. 110, pp. 1851–1857, NOV 5 2008.
- [48] A. Danch, S. Ilisch, W. Sulkowski, M. Moczynski, A. Radon, and H. Radusch, "DMTA study of the urethane network in rubber waste-urethane composites," *Journal of Thermal Analysis and Calorimetry*, vol. 79, pp. 623–630, FEB 2005.
- [49] R. Dhamodharan, P. Maiti, and G. Radhakrishnan, "Study on blends of ethylene propylene diene rubber and thermoplastic polyurethanes," *Polymer-Plastics Technology and Engineering*, vol. 46, pp. 163–168, FEB 2007.
- [50] A. B. Ortiz-Magan and M. M. Pastor-Blas, "Improved adhesion of RF plasma treated rubbers by isocyanate incorporation to polyurethane adhesive," *Plasma Processes and Polymers*, vol. 5, pp. 681–694, SEP 15 2008.
- [51] P. Pachpinyo, P. Lertprasertpong, S. Chuayjuljit, R. Sirisook, and V. Pimpan, "Preliminary study on preparation of unsaturated polyester resin/natural rubber latex blends in the presence of dispersion aids," *Journal of Applied Polymer Science*, vol. 101, pp. 4238–4241, SEP 15 2006.

- [52] W. Sulkowski, A. Danch, M. Moczynski, A. Radon, A. Sulkowska, and J. Borek, "Thermogravimetric study of rubber waste-polyurethane composites," *Journal of Thermal Analysis and Calorimetry*, vol. 78, no. 3, pp. 905–921, 2004.
- [53] G. Li and N. Jones, "Development of rubberized syntactic foam," *Composites Part A-Applied Science and Manufacturing*, vol. 38, no. 6, pp. 1483–1492, 2007.
- [54] A. El Lawindy, K. Abd El-Kade, W. Mahmoud, and H. Hassan, "Physical studies of foamed reinforced rubber composites - Part 1. Mechanical properties of foamed ethylene-propylene-diene terpolymer and nitrile-butadiene rubber composites," *Polymer International*, vol. 51, pp. 601–606, JUL 2002.
- [55] G. Lin, X. Zhang, L. Liu, J. Zhang, Q. Chen, and L. Zhang, "Study on microstructure and mechanical properties relationship of short fibers/rubber foam composites," *European Polymer Journal*, vol. 40, pp. 1733–1742, AUG 2004.
- [56] D. De Mello, S. H. Pezzin, and S. C. Amico, "The effect of post-consumer PET particles on the performance of flexible polyurethane foams," *Polymer Testing*, vol. 28, pp. 702–708, OCT 2009.
- [57] M. Hawkins, B. O'Toole, and D. Jackovich, "Cell morphology and mechanical properties of rigid polyurethane foam," *Journal of Cellular Plastics*, vol. 41, pp. 267–285, MAY 2005.
- [58] K. Morimoto, T. Suzuki, and R. Yosomlya, "Flexural Properties of Glass-Fiber Reinforced Rigid Polyurethane Foam," *Industrial & Engineering Chemistry Product Research and Development*, vol. 23, no. 1, pp. 81–85, 1984.
- [59] W. Seo, J. Park, Y. Sung, D. Hwang, W. Kim, and H. Lee, "Properties of water-blown rigid polyurethane foams with reactivity of raw materials," *Journal of Applied Polymer Science*, vol. 93, pp. 2334–2342, SEP 5 2004.

- [60] W. Seo, H. Jung, J. Hyun, W. Kim, Y. Lee, K. Choe, and S. Kim, "Mechanical, morphological, and thermal properties of rigid polyurethane foams blown by distilled water," *Journal of Applied Polymer Science*, vol. 90, pp. 12–21, OCT 3 2003.
- [61] F. Saint-Michel, L. Chazeau, and J.-Y. Cavaille, "Mechanical properties of high density polyurethane foams: II Effect of the filler size," *Composites Science and Technology*, vol. 66, pp. 2709–2718, DEC 2006.
- [62] H. Singh, T. P. Sharma, and A. K. Jain, "Reactivity of the raw materials and their effects on the structure and properties of rigid polyurethane foams," *Journal of Applied Polymer Science*, vol. 106, pp. 1014–1023, OCT 15 2007.
- [63] S. Goods, C. Neuschwanger, L. Whinnery, and W. Nix, "Mechanical properties of a particle-strengthened polyurethane foam," *Journal of Applied Polymer Science*, vol. 74, pp. 2724–2736, DEC 9 1999.
- [64] H. Lim, S. H. Kim, and B. K. Kim, "Effects of silicon surfactant in rigid polyurethane foams," *Express Polymer Letters*, vol. 2, pp. 194–200, MAR 2008.
- [65] Z. Yang, B. Zhao, S. Qin, Z. Hu, Z. Jin, and J. Wang, "Study on the mechanical properties of hybrid reinforced rigid polyurethane composite foam," *Journal of Applied Polymer Science*, vol. 92, pp. 1493–1500, MAY 5 2004.
- [66] J. Yuan and S. Q. Shi, "Effect of the Addition of Wood Flours on the Properties of Rigid Polyurethane Foam," *Journal of Applied Polymer Science*, vol. 113, pp. 2902–2909, SEP 5 2009.
- [67] W. Zatorski, Z. K. Brzozowski, and A. Kolbrecki, "New developments in chemical modification of fire-safe rigid polyurethane foams," *Polymer Degradation and Stability*, vol. 93, pp. 2071–2076, NOV 2008.

- [68] N. Mumford, D. Chatfield, and I. Einhorn, "Component Analysis of Rigid Polyurethane Foams," *Fire Research*, vol. 1, no. 2, pp. 107–117, 1977.
- [69] V. Izakson, E. Aprosimova, and S. Shkulev, "Mechanical and thermophysical properties of polyurethane foam thermal insulation coatings intended for controlling the stability of deep quarry banks," *Journal of Mining Science*, vol. 34, pp. 317–319, JUL-AUG 1998.
- [70] M. Johlitz, H. Steeb, S. Diebels, A. Chatzouridou, J. Batal, and W. Possart, "Experimental and theoretical investigation of nonlinear viscoelastic polyurethane systems," *Journal of Materials Science*, vol. 42, pp. 9894–9904, DEC 2007.
- [71] D. Niyogi, R. Kumar, and K. Gandhi, "Water blown free rise polyurethane foams," *Polymer Engineering and Science*, vol. 39, pp. 199–209, JAN 1999.
- [72] M. Sonnenschein, B. L. Wendt, A. K. Schrock, J.-M. Sonney, and A. J. Ryan, "The relationship between polyurethane foam microstructure and foam aging," *Polymer*, vol. 49, pp. 934–942, FEB 18 2008.
- [73] S. Subramani, Y. Park, Y. Lee, and J. Kim, "New development of polyurethane dispersion derived from blocked aromatic diisocyanate," *Progress in Organic Coatings*, vol. 48, pp. 71–79, NOV 2003.
- [74] Z. Tu, V. Shim, and C. Lim, "Plastic deformation modes in rigid polyurethane foam under static loading," *International Journal of Solids and Structures*, vol. 38, pp. 9267–9279, DEC 2001.
- [75] K. Haibach, A. Menner, R. Powell, and A. Bismarck, "Tailoring mechanical properties of highly porous polymer foams: Silica particle reinforced polymer foams via emulsion templating," *Polymer*, vol. 47, pp. 4513–4519, JUN 14 2006.

- [76] H. Mahfuz, V. Rangari, M. Islam, and S. Jeelani, "Fabrication, synthesis and mechanical characterization of nanoparticles infused polyurethane foams," *Composites Part A-Applied Science and Manufacturing*, vol. 35, no. 4, pp. 453–460, 2004.
- [77] H. Rozman, Y. Yeo, G. Tay, and A. Abubakar, "The mechanical and physical properties of polyurethane composites based on rice husk and polyethylene glycol," *Polymer Testing*, vol. 22, pp. 617–623, SEP 2003.
- [78] R. Yosomiya and K. Morimoto, "Compressive Properties of Glass-Fiber Reinforced Rigid Polyurethane Foam," *Industrial & Engineering Chemistry Product Research and Development*, vol. 23, no. 4, pp. 605–608, 1984.
- [79] J. Kim, "Experimental and theoretical studies on crumb rubber polyurethane blend system," *Korea Polymer Journal*, vol. 5, pp. 241–247, DEC 31 1997.
- [80] "Sieve Analysis Results for Crumb Rubber Particles (Batch ID ABR409909210901)," *Entech Inc*, 2009.
- [81] "From the Official Website of US Composites Inc," <http://www.uscomposites.com/foam.html>.
- [82] "From the Official Website of Inchem Organization," <http://www.inchem.org/documents/cicads/cicads/V27C102.gif>.
- [83] "From the Official Website of Chemyq," <http://www.chemyq.com/xz/img/img4/460-73-1.gif>.
- [84] "From the Official Website of Google Inc," http://en.wikipedia.org/wiki/sodium_lauryl_sulfate.
- [85] "Material Safety Data Sheet from the Official Website of R. T. Vanderbilt Company Inc," <http://www.vanderbilt.com/documents/MSDS/US/13899.pdf>.

- [86] “Material Safety Data Sheet from the Official Website of Lubrizol Inc,”
<http://www.lubrizol.com/coatings/Vycar/default.html>.
- [87] “From the Official Website of Lookchem Inc,”
<http://www.lookchem.com/keyimages//2009-10/8bb9df5b-1887-4f89-94fe-9e994fee94a3.jpg>.
- [88] B. Kaiser, “Fundamental XRF Technology Overview,” *From the Official Website of Bruker AXS*.
- [89] “Manual of Weighing Applications,” *Sartorius Inc*.
- [90] “Standard test Method for Flat wise Compressive Properties of Sandwich Cores,”
ASTM International, 2005.
- [91] “Standard test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials,” *ASTM International*, 2007.
- [92] R. Maharsia, N. Gupta, and H. Jerro, “Investigation of flexural strength properties of rubber and nanoclay reinforced hybrid syntactic foams,” *Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing*, vol. 417, pp. 249–258, FEB 15 2006.
- [93] “From the Official Website of Google Inc,” *<http://en.wikipedia.org/wiki/porosity>.*
- [94] L. Gibson and M. Ashby, “Cellular Solids-Structure and Properties,” *Cambridge Solid State Science Series*, 2001.
- [95] V. Koissin and A. Shipsha, “Deformation of foam cores in uniaxial compression-tension cycle,” *Journal of Sandwich Structures & Materials*, vol. 8, pp. 395–406, SEP 2006.

- [96] M. Coleman, D. Skrovanek, J. Hu, and P. Painter, "Hydrogen-Bonding in Polymer Blends .1. FTIR Studies of Urethane Ether Blends," *Macromolecules*, vol. 21, pp. 59–65, JAN 1988.

VITA

Abhisek Bhadra

Candidate for the Degree of
Master of Science

Thesis: AN EXPERIMENTAL STUDY OF THE MICROSTRUCTURE–MECHANICAL
PROPERTY RELATIONSHIP OF CRUMB RUBBER–POLYURETHANE
FOAM COMPOSITES

Major Field: Mechanical Engineering

Biographical:

Personal Data: Born in Kolkata, India on November 5th, 1983.

Education:

Received the B.E. degree from Jadavpur University, Kolkata, India, 2006, in
Mechanical Engineering

Completed the requirements for the degree of Master of Science with a major
in Mechanical Engineering Oklahoma State University in July, 2010.

Experience:

Worked as a Graduate Research Assistant at the Mechanics of Advanced Mate-
rials Laboratory headed by Dr. Raman P. Singh in the area of particle reinforced
composites

Name: Abhisek Bhadra

Date of Degree: July, 2010

Institution: Oklahoma State University

Location: Stillwater, Oklahoma

Title of Study: AN EXPERIMENTAL STUDY OF THE MICROSTRUCTURE-
MECHANICAL PROPERTY RELATIONSHIP OF CRUMB RUBBER-
POLYURETHANE FOAM COMPOSITES

Pages in Study: 94

Candidate for the Degree of Master of Science

Major Field: Mechanical Engineering

With the enormous growth of automobile industry initiating the needs of tire production all over the world, the disposal of scrap tires has become a significant environmental burden. Several research groups have investigated the development of novel products using waste tires. Nonetheless, the presence of non-degradable ingredients in tires makes the process of decomposition extremely difficult. Another issue is the need for proper surface treatment of waste rubber to enhance its interaction with polymeric compounds. This current work is aimed to remedy the difficulties related to the recycling of polymeric rubber tires. This project is developing technology to fabricate composite panels in which recycled rubber from tires is an inherent constituent. These resulting composite panels can also be used as core materials inside Sandwich Composites and can definitely be seen as a means of utilizing post-consumer waste tires. The inherent higher resilience of rubber particles is utilized to make best core materials in resisting impact damage. Not only that, this study involves an effective surface treatment methodology of as-received rubber particles using various organic functional groups. FTIR analysis will be utilized to understand the efficacy of various surface treatments. The compressive modulus and strength of crumb rubber reinforced foam are determined using ASTM standards as a function of crumb rubber content and surface treatment. Initial studies show that materials can be easily fabricated using various volume fractions of crumb rubber. The modulus and compressive strength increase with greater rubber contents.

ADVISOR'S APPROVAL: _____