PRODUCTION OF QUATERNARY AMMONIUM
COMPOUNDS ADDED ANTIMICROBIAL
POLYURETHANE FOAMS

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Master of Science Thesis

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Assoc. Prof. Hasan Basri KOCER
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PRODUCTION OF QUATERNARY AMMONIUM COMPOUNDS ADDED ANTIMICROBIAL POLYURETHANE FOAMS

A THESIS FOR THE DEGREE OF MASTER OF SCIENCE

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İNTİHAL BEYANI

Bu tezde görsel, işitsel ve yazılı biçimde sunulan tüm bilgi ve sonuçların akademik ve etik kurallara uyularak tarafımdan elde edildiğini, tez içinde yer alan ancak bu çalışmaya özgü olmayan tüm sonuç ve bilgileri tezde kaynak göstererek belgelediğimi, aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul ettiğimi beyan ederim.

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İmzası:

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LIST OF SYMBOLS AND ABBREVIATIONS

ATR	Attenuated Total Reflectance
CEFIC	European Chemical Industry Council
CFU	Colony-Forming Unit
CHC	Clorhexidine
CPPs	Copolymer Polyols
DMA	Dynamic Mechanical Analysis
DMF	N,N-dimethylformamide
EDXRF	Energy Dispersive X-Ray Fluorescence
FPUs	Flexible Polyurethane Foams
FTIR	Fourier-transform Infrared Spectroscopy
MDI	4,4'-diphenylmethane Diisocyanate
MRD	Maximum Recovery Diluent
PHMB	Poly(hexamethylenebiguanide)
QACs	Quaternary Ammonium Compounds
QA-PEI	Quaternary Ammonium Polyethyleneimine
QAP	Quaternary Ammonium Polymer
QASs	Quaternary Ammonium Salts
SEM	Scanning Electron Microscopy
TDI	Toluene Diisocyanate
T_g	Glass transitionTemperature
TGA	Thermo-Gravimetric Analyzer

ABSTRACT

PRODUCTION OF QUATERNARY AMMONIUM COMPOUNDS ADDED ANTIMICROBIAL POLYURETHANE FOAMS

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Bursa Technical University

Graduate School of Natural and Applied Sciences

Department of Fiber and Polymer Engineering Program

Master of Science Thesis

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With the growing awareness of pathogenic microorganisms, there is an increasing need for antimicrobial materials. Flexible polyurethane foams (FPUs) used in various application areas such as mattresses, beds, pillows, filter elements, kitchen cleaners, body sponges, and etc. are good reservoirs for microorganisms and often required to have an antimicrobial property. In this regards, to impart antimicrobial functionality to polyurethane foams, a quaternary ammonium polymer (QAP) having a polyol main chain was incorporated into a foam structure by covalent bonds which is dramatically important to prevent migration of agents from the porous structure. QAP was added to a commercial formulation in various amounts between 1 to 5 wt%. The structures of the produced foams and their QAP content was characterized by FTIR and EDXRF analyses. A linear polymer of QAP was also synthesized to support our investigations. The morphological changes such as the cell size and the cell structure of the produced foams were observed with SEM. TGA and DMA analyse were applied to examine the thermal properties of the produced foams. 1 wt% QAP added foams showed structural and thermomechanical properties very similar to the unmodified foams. In addition, while the unmodified foam did not show any antimicrobial activity, the QAP-added foams provided significant inactivations against *Staphylococcus aureus*, yeast and mould at concentrations of about 10^2 and 10^3 colony-forming unit (CFU) within 5h of contact time. Antimicrobial test results showed that addition of minute amount of QAP can

significantly improve the biocidal performance of the produced foams without deteriorating the commercial formulation.

ÖZET

KUATERNER AMONYUM BİLEŞİKLERİ KATKILI ANTİMİKROBİYEL POLİÜRETAN KÖPÜKLERİN ÜRETİMİ

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Ağustos 2014, 52 sayfa

Mikroorganizmaların patojenik etkilerine karşı artan sağlık bilinci ile birlikte, antimikrobiyel materyallere olan ihtiyaç artmaktadır. Şilte, yatak süngeri, yastık, filtre elemanları, mutfak temizleyiciler, vücut süngerleri gibi esnek poliüretan köpükten yapılan ürünler mikroorganizmalar için iyi rezervuarlardır ve genellikle antimikrobiyel özellik gerektirmektedirler. Bu açıdan, antimikrobiyel köpükler elde etmek amacıyla poliol yan zincirine sahip bir kuaterner amonyum polimer (QAP), gözenekli sünger yapıya sıvılarla migrasyona uğramaması amacıyla kovalent bağlarla bağlanmıştır. Ticari bir köpük formülasyonuna ağırlıkça %1 ila %5 oranında QAP katkısı yapılmıştır. Üretilen köpüklerin yapıları ve QAP içerikleri FTIR ve EDXRF analizleri ile karakterize edilmiştir. Bu araştırmalarımızı desteklemek amacıyla QAP'den lineer bir poliüretan polimer sentezlenmiştir. Elde edilen köpüklerin hücre boyutu ve hücre yapısındaki morfolojik değişimler SEM mikroskobu ile gözlenmiştir. TGA ve DMA analizleri ile üretilen köpüklerin termal özellikleri incelenmiştir. Sonuç olarak, ağırlıkça %1 QAP eklenmiş köpükler, modifiye edilmemiş köpüklere çok benzer yapısal ve termomekaniksel özellikler göstermiştir. Ayrıca, modifiye edilmemiş köpükler antimikrobiyel özellik göstermezken, QAP eklenmiş köpükler 10^2 ve 10^3 koloni oluşturucu *Staphylococcus aureus*, küf ve maya birimine karşı 5 saatlik kontaminasyon sonucunda önemli ölçüde inaktivasyon sağlamıştır. Antimikrobiyel test sonuçları, az miktardaki QAP

ilavesi ile ticari köpük formülasyonu bozulmadan üretilen köpüklerin biyosidal performansının önemli ölçüde geliştirilebileceğini göstermiştir.

Anahtar kelimeler: Antimikrobiyel, Esnek köpükler, Kuaterner amonyum bileşikleri, Poliüretan

1. INTRODUCTION

The earth is approximately 4.54 billion years old, the known primitive bacteria appeared on Earth a billion years later and microbes have coexisted with us ever since [1]. In 1530, the Italian physician Girolamo Fracastoro theorized the origin of syphilis, he express that the disease was spread by "seeds" which cannot be seen by naked eye. In 1683, with the improvements in microscopy, Antonie van Leeuwenhoek visualized animalcules (microorganisms) gathered from his own teeth. That laid the groundwork for germ theory. The theory anticipated by Fracastoro was consolidated by Louis Pasteur and Robert Koch in the late 1870s and the golden period of microbiology began [2, 3].

While the study of infectious disesase growing expeditiously, some epidemics and pandemics such as smallpox, cholera, scarlet fever, tuberculosis, typhoid and etc., was spreading. After World War II, with the developments in antibiotics, antimicrobial agents, vaccines and better sanitation, infectious diseases were eradicated [2, 4]. Unfortunately, the rise of the antibiotics did not take long, the rising resistance of pathogens ended the 'golden era' of antibiotic discovery in 1970s [5].

In 1981, with the outbreak of AIDS, the optimism around the world started after World War II was shattered, with the effect of the globalization, pandemic has been spreading one continent to another. Especially, the increase of international travelling has triggered the spread of HIV/AIDS [2]. Increased global travel, increased trade in goods, food-borne illnesses, urbanization, climate change, other environmental concerns, microbial drug resistance, breakdowns in public health systems are the most important seven ways that infectious diseases are affected by globalization. The tropical disease dengue, mad cow disease, malaria, tuberculosis, Crimean-congo hemorrhagic fever, hepatitis B and C, SARS, Bird flu and Swine flu are some of the epidemics and pandemics spreading over a larger area with the effect of globalization and cause millions of human die every year [6].

Nowadays, healthcare-associated infections (nosocomial infections) has the largest mortality ratio in infectious diseases. Each year, with nosocomial infections about

100,000 people die in the USA alone with extra costs in excess of 35 billion dollars [5, 7]. It is compulsory to identifiy and eliminate all sources of the nosocomial infections. Instead of curing infectious disease afterwards, preventing them is easier, healtier and cheaper.

The majority of nosocomial infections result from cross-contamination and hospital beds are objects which are most commonly and directly touched [8, 9]. Flexible polyurethane foams are good reservoirs for microorganisms and applied cleaning or disinfection measures do not eliminate contamination with *Staphylococcus*, *Bacillus*, *Micrococcus,* and gram-negative rods from hospital beds [10]. Because only surface of the foam can be cleaned by applied cleaning or disinfection measures, the inner wet side of the foam may harbour bacteria which can leak out with the effect of physical pressure [11]. So, there is a need for antimicrobial foams which inhibit bacteria all through the foam, im order to decrease the mortal nosocomial infections.

1.1. Cell Structure of Bacteria

Bacteria have two fundamentally different cell formats named as Gram-positive and Gram-negative. They have similar structures when the outer membrane is not taken into account, and Gram-positive bacteria have relatively simpler structures (Figure 1.1).
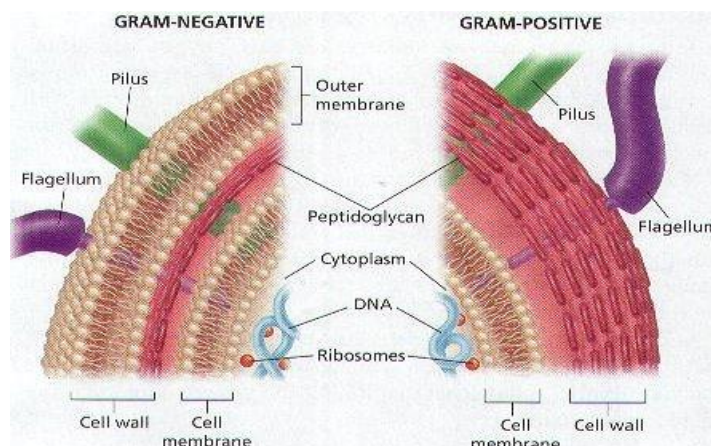
Figure 1.1 Cell structures of Gram-positive and Gram-negative bacteria [12]

Gram-positive bacteria have thicker cell wall, which include peptidoglycan and teichoic acids. On the other hand, Gram-negative bacteria have outer membranes containing lipopolysaccharides, situated above a thin peptidolycan layer. Because of the outer membrane, Gram-negative bacteria are generally more resistant to antimicrobial agents than Gram-positive bacteria. The outer membrane acts as a barrier and can limit the intake of the agents [13, 14].

1.2. Action Mechanisms of Antimicrobial Agents

Antimicrobial agents have various application areas, such as textile, food, cosmetic, military, water treatment, medical implants, agriculture, and etc. To meet requirements in such areas, there are numbers of biocides, for example, the European Chemical Industry Council (CEFIC) has registered several thousands of biocides. Antimicrobial agents inactivate microorganisms by different mechanisms.
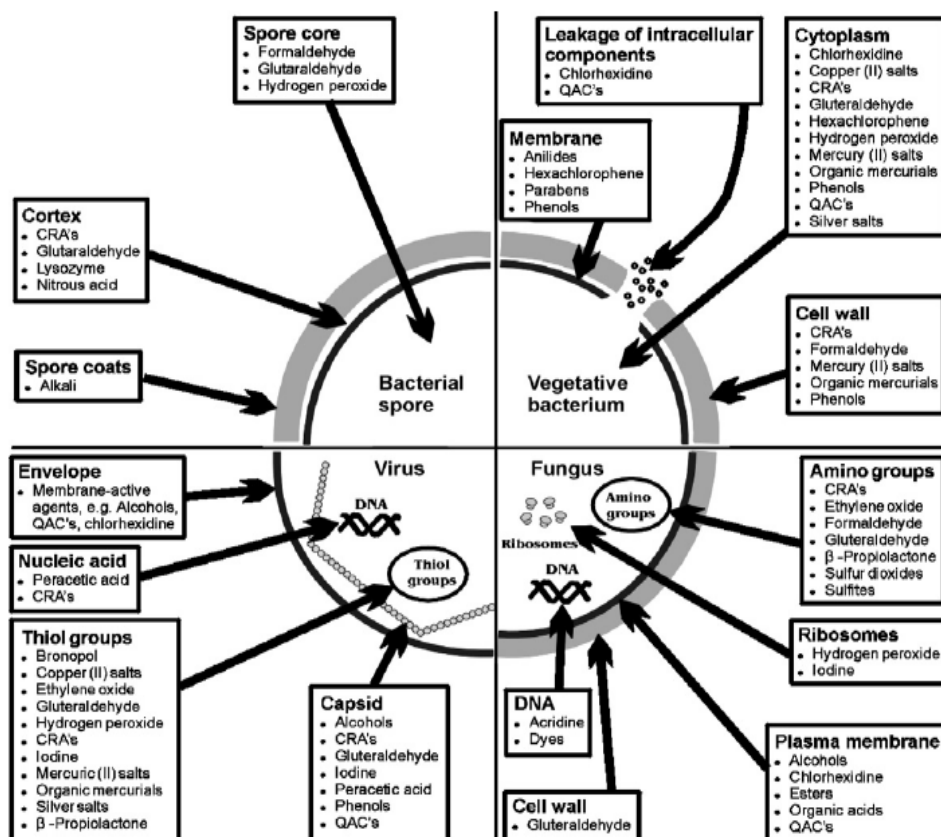
Figure 1.2 Mechanisms of microorganism inactivation by biocides [16]

For lethal action, antimicrobial substances damage the cell wall or alter cell membrane permeability, inhibit enzyme activity or lipid synthesis, denature proteins [15]. And to make one of these action, they can target number of cellular loci, such as cytoplasmic membrane, enzymes, genetic material and etc., as seen in Figure 1.2. For Gram-negative bacteria, it is necessary to traverse the outer membrane to reach the target site(s) [16]. As seen in the figure, antimicrobial agents have multiple targets in the celular structure [17].

In general, there are three main steps for a biocide and bacteria interaction; partition/passage of biocide to target(s), concentration of biocide at target(s), damage to target(s). The first step is sorption of biocides into the cell with aqueous phase and the cell surface association [18]. Not only the nature and composition of the surface but also the participating environment is important for cell surface and biocide association [17]. After antimicrobial agents reach the target sites, there are two main ways for final attack as seen in Figure 1.3.
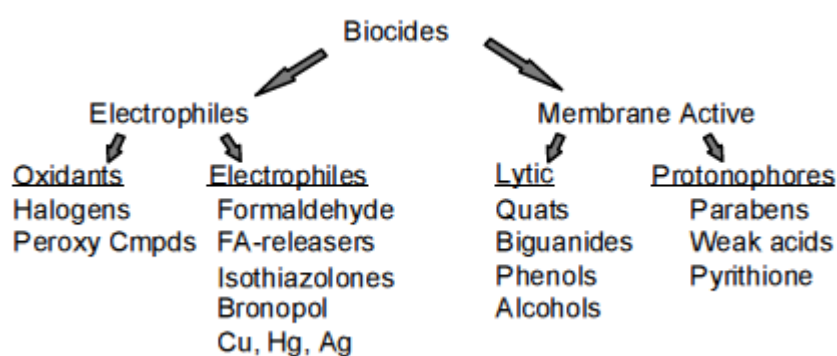
Figure 1.3 Mechanism of action of biocides [19]

Electrophiles perform a chemical interaction with the cell. In this group, oxidants (halogens, peroxides) have a fast-acting mechanism. They oxidize organic material directly via radical-mediated reactions. The other members of this group are inorganic ions such as silver, copper and etc., and organic biocides such as formaldehyde and isothiazolones. These inorganic ions and organic biocides react with cellular nucleophiles. They constitute intracellular free radicals to help their lethal action [19].

Membrane-active agents perform physical interactions with the cell. Quats and biguanides damage the cytoplasmic membrane integrity, while phenols and alcohols damage external membrane integrity. Protonophores, change the membrane pH, causing acidification in cell and disruption of metabolism [17-19].

1.3. Common Biocides

"Biocide" is a general term describing inorganic or organic molecules with antiseptic, disinfectant or preservative activity. For a more specific definition, antimicrobial agents can be considered as "-static" or "-cidal". "-Static" term is used for agents which inhibit the growth of microorganisms, and "-cidal" term is used for agents which kill the microorganisms [17, 20]. In this study, "antimicrobial agent" term refers to disinfectants. Disinfectants are agents used to destroy microorganisms that are living on the inanimate objects. Temperature, contact time, type, and concentration of the active agent, the presence of organic matter, the amount and type of microbial load are the important parameters for efficacy of disinfectants [21].

An ideal disinfectant should have the following properties:
- A wide spectrum of activity
- To destroy microbes within practical period of time
- Being active in the presence of organic matter
- Make effective contact and be wettable
- Being stable
- Being non-toxic, non-allergenic, non-irritative or non-corrosive
- Not having bad odor
- Being effective on reasonable dilution
- Should not be expensive and must be widely available

Halogens, biguanides, heavy metals, peroxides, alcohols, and quaternary ammonium compounds are the most common biocides since they can provide ideal disinfection properties.

1.3.1. Halogens

Chlorine and bromine gas, bleach, iodine and iodophores are examples of halogen based agents. Among those chlorine and iodine based agents are the most commonly used microbicidal halogens. They form chloric and iodic acids in water solutions and then release atomic oxygen or haloids. These ions oxidize proteins of germs and interfere with vital metabolic reactions [22, 23].

Halogens are effective against broad spectrum of microorganisms, and possess bacteriocidal, sporicidal, and virucidal activity [17, 24]. Chlorine is used as a disinfectant for drinking water, in swimming pools and for inanimate objects such as bottles, pipelines, utensils, and etc. Iodine is used as a skin disinfectant, a nonirritant antiseptic on wounds and abrassions [22, 23].

1.3.2. Biguanides

Biguanides are organic compounds which can easily form cationic amines. Chlorhexidine (CHX) is the most commonly used biguanide (Figure 1.4), and poly(hexamethylenebiguanide) (PHMB) is the most important polymeric biguanide. PHMB's antimicrobial activity is much greater than monomeric or dimeric biguanides. They have excellent biocidal activity, chemical stability, low toxicity and reasonable cost [17, 25, 26].

$$Cl-\text{\large⬡}-N(HCN)_2H(CH_2)_6N(HCN)_2H-\text{\large⬡}-Cl$$
$$\overset{\parallel}{NH} \qquad \overset{\parallel}{NH}$$
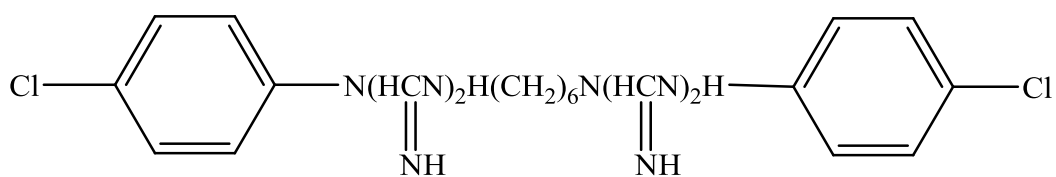
Figure 1.4 Chemical structure of chlorhexidine

Biguanides are effective againts vegetative bacteria, fungi and lipophilic viruses but do not have efficiency againts spores [27]. PHMB reacts with acidic membrane lipids and destroys the cell membrane which increases the membrane fluidity and permeability causing cell death. It has been used in a variety of products including

contact lens cleaning solutions, skin disinfectant solutions, wound dressing, swimming pool sanitizers, cosmetics, leather preservatives, cleanser in agriculture, and etc. [26, 28].

1.3.3. Heavy metals

Several metal ions have been used as antimicrobial agents such as silver, copper, zinc, cobalt, and etc. Their antimicrobial activity is often attribute to their affinity for proteins. They inhibit respiration, electron transfer system's principal metabolism, and the transport of substrate in cell membrane by binding intracellular proteins to inactivate microorganisms [15, 29, 30].

In general, heavy metals are very toxic to human beings but silver is relatively safe among them, since silver in metallic state can be hardly absorbed into human body [29]. But, nanosilver form is different from its macro forms. For nanosilver form, it is easy to be released and go places in the body to enter cells. However, effects of nanosilver to the human body and the environment is still unknown [31].

1.3.4. Peroxides

Peroxides are also powerful antimicrobial agents. Hydrogen peroxide and peracetic (peroxyacetic) acid are the most commonly used agents. They are active against a wide range of microorganisms including viruses, bacteria, and bacterial spores. Peracetic acid is more powerful biocide than hydrogen peroxide. Peracetic acid is characterized by a very rapid action at low concentrations.

Peroxides work as an oxidant by disrupting sulfhydryl (-SH) and sulfur (S-S) bonds. Peroxides denature proteins and enzymes, and increase the cell wall permeability. They are used as wound cleaners, sterilants for medical devices, environmental surfaces, and etc. [17, 32, 33].

1.3.5. Alcohols

Alcohols are generally used as antiseptics. But especially ethyl alcohol (ethanol), isopropyl alcohol (isopropanol, propan-2-ol) and n-propanol are used as disenfectants. Alcohols are effective againts especially vegetative bacteria, viruses and fungi. However, they do not destroy bacterial spores. Alcohols cause membrane damage and denaturation of proteins [17, 21]. Aqueous solutions of alcohols (60-90 wt%) are more active than absolute alcohols. Because absolute alcohols denature only the external membrane proteins while water is needed to increase the diffusion rate through the cell membrane [21, 27].

Alcohols are used for disinfecting instruments such as thermometers and stethoscopes. And because of their rapid evaporation characteristics, they are useful for horizontal surfaces. Their flammability and skin irritation characteristics are their main disadvantages [21, 27].

1.4. Quaternary Ammonium Compounds

Quaternary ammonium compounds (QACs) are cationic and membrane active agents (i.e., with a target site predominantly at the cytoplasmic (inner) membrane in the bacteria or the plasma membrane in yeasts). The molecular structure of QACs consist of two main regions, one is a water-repellent (hydrophobic) hydrocarbon group and the other one is a water-attracting (hydrophilic) group [17].

As seen in Figure 1.5, QACs generally have four same or different organic substituents linked to a positively charged nitrogen atom. The organic substituents can be alkyl, aryl, or heterocylic groups. To provide a hyrophobic segment, at least one of the organic substituents should be a long alkly chain [34]. The lenght of the alkly chain is very important for antimicrobial activity of QACs. For an effective antimicrobial treatment, alkly chains having 12-18 carbon atoms have been recommended [15, 35]. While the short chains do not perform as a powerful bacteriocidal, very long alkyl chains also stick to each other due to hydrophobic interactions and result in declining bacteriocidal property [36]. The number of

cationic ammonium groups and the presence of perfluorinated groups in the structures are other two important properties for antimicrobial activity [25].

$$R - \overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_2}{|}}{N^+}} - R_3 \quad Cl^-$$
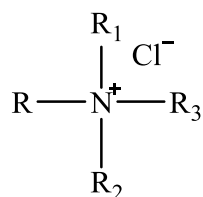
Figure 1.5 General structure of quaternary ammonium compounds

The antimicrobial function of QACs arise from ionic and hydrophobic interactions. The positively charged quaternary nitrogen atom makes an attractive interaction with the negatively charged cell membrane. Hydrophobic interactions occur between the hydrophobic tail group of the QACs and hydrophobic membrane core of the cell [37]. These interactions cause membrane rearrangement, subsequent release of K^+ ions, and intracellular leakage of constituents [38, 39].

QACs have a broad spectrum activity against Gram-positive and Gram-negative bacteria, yeast, fungi and certain type of viruses [25]. In Gram-positive bacteria inactivations, QACs destroy the membrane by bounding to the wall proteins [40]. In Gram-negative species, they damage the outer membrane and cause the leakage of K^+ while cause the leakage of pentose material from yeasts. Protoplast lysis caused by the interaction with crude cell sap is the other effect of QACs on yeasts [17]. They inhibit phospholipase enzyme, which destroy or deranges host cell membranes constituents in fungi [41, 42]. They also have an effect on the lipid of enveloped viruses but they are not effective against nonenveloped viruses [17].

There are various studies with quaternary ammonium compounds to impose antimicrobial properties on various substances. Dizman et al. synthesized monomers and polymers containing pendant quaternary ammonium moieties (based on 1,4-diazabicyclo [2.2.2] octane (DABCO)). While the polymers showed antimicrobial activities against *Staphyloccoccus aureus* and *Escherichia coli*, the small molecules did not show any antimicrobial activity [34]. Son et al. synthesized various quaternary ammonium salts and treated cotton fabrics. The modified cotton fabrics

were effective against *Staphyloccoccus aureus* [43]. Yudovin et al. prepared quaternary ammonium polyethyleneimine (QA-PEI) based nanoparticles which were embedded in restorative composite resin at 1% (w/w) and cured by light polymerization. Octyl-alkylated QA-PEI embedded resins totally inhibited *Streptococcus mutans* growth in 3-month-aged samples [36]. Wong et al. obtained bactericidal and virucidal ultrathin layer by layer films by using polycationic quaternary ammonium compounds (N-alkylated polyethylenimines) and polianions. The layer by layer films were effective against *Escherichia coli*, *Staphylococcus aureus* and *A/WSN (H1N1) virus* [44]. Wang et al. produced a fireproofing, corrosion-resistant, anti-bacterial, anti-static fabric. Antibacterial properties were obtained with an orgonasilicone quaternary ammonium salt. The warp and weft yarns were dipped into the solutions of antimicrobial agents. The fabrics were effective against *Esherichia coli*, *Neisseria gonorrhoeae*, *Chlamydia trachomatis* and other dozens of pathogenic microorganisms [45].

1.5. Polyurethanes

Addition polymerization of isocyanate and polyol components to produce polyurethanes was discovered in 1937 by Otto Bayer. At the begining polyurethanes were used in millitary and aerospace applications. Later on, because of its versatility, polyurethanes have found applications in a wide variety of areas including both nonfoam and foam forms. Coatings, adhesives, sealants, and elastomers are the examples of nonfoam applications. There are also numerous application areas for foam forms. Rigid foams are especially used for insulation while semirigid foams are used for various automotive interior applications, and flexible foams are being used for furniture, mattresses, automobiles, clothing, and etc. Among all those applications, flexible foams have the highest production volume. Figure 1.6 illustrates the major applications of flexible polyurethane foams [46-48].
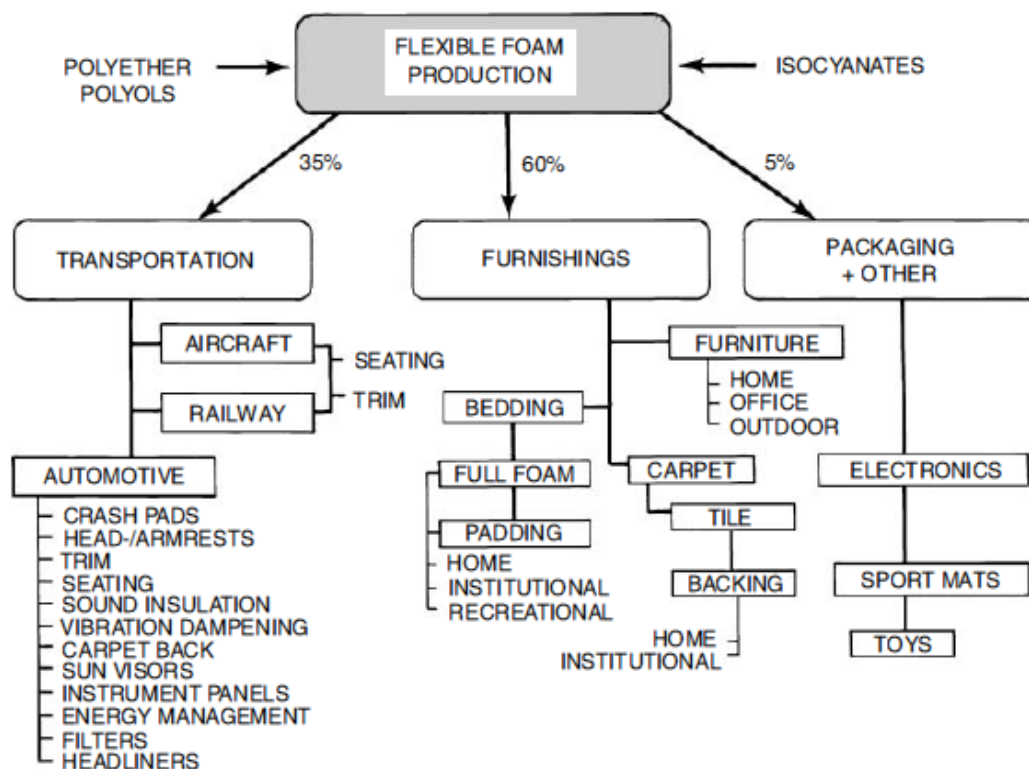
Figure 1.6 Applications of flexible polyurethane foams [47]

A flexible polyurethane foam is generally manufactured by mixing a polyol, an isocyanate, a foaming agent, a foam stabilizer, and various catalysts [49]. Flexible polyurethane foam production process involves simultaneous reactions: "gelling reaction" and "blowing reaction". As seen in Figure 1.7, the "gelling reaction" is the reaction which generates polyurethane linkages through the interaction of isocyanate component with polyol. As seen in Figure 1.8, the "blowing reaction" is the reaction which produce carbon dioxide gas through the interaction of isocyanate component with water [50].
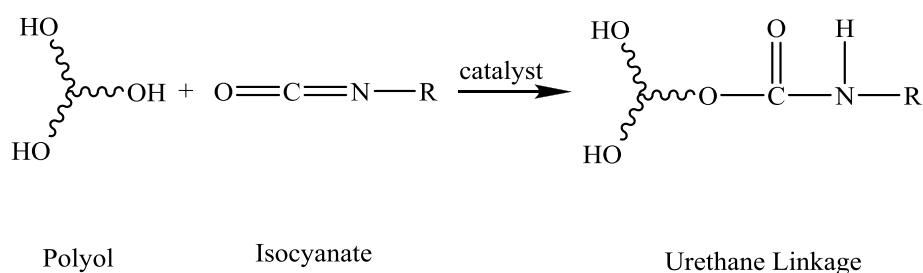
Figure 1.7 Gelling reaction

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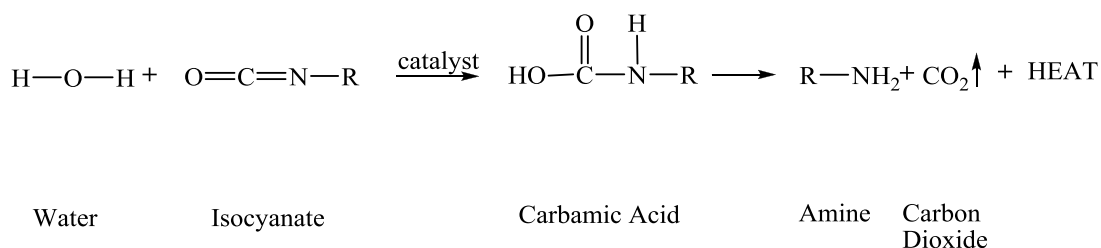
Figure 1.8 Blowing reaction

1.5.1. Isocyanates

Isocyanates are polyfunctional reactants and their -NCO groups can react with functional groups of a polyol and water in the formulation. The mostly used isocyanates are toluene diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI). For flexible foam production mostly used isocyanate is TDI. The most two important isomers of TDI, 2,4-TDI and 2,6-TDI, are shown in Figure 1.9 [51, 52].
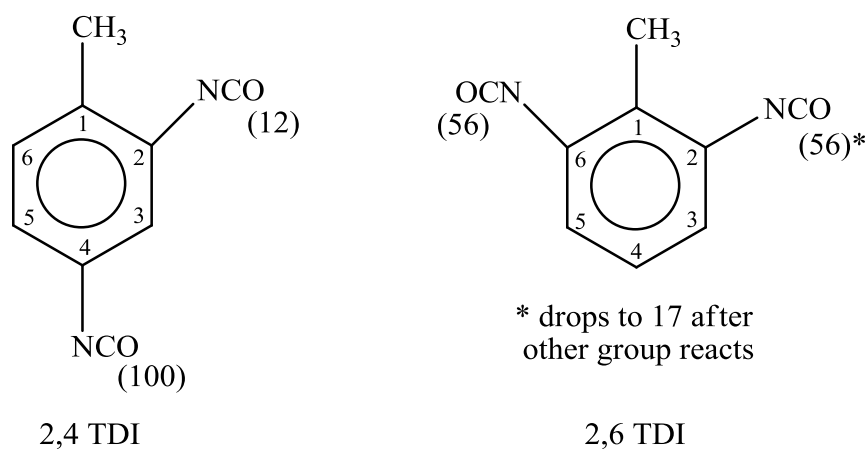
Figure 1.9 Isomers of Toluene Diisocyanate

As seen in Figure 1.9, the reactivity of the isocyanate groups on each molecule is different. The ortho position's reactivity in the 2,4 isomer is approximately 12% of the reactivity of the para position because of the steric hindrance caused by the methyl group. On the other hand, the reactivity of the –NCO groups on 2,6 TDI are same due to the similar steric effects. The second difference between the two isomers

is symmetry. The 2,6 TDI is more symmetric than the 2,4 TDI, so that 2,6 isomer can form hard segments with better packing characteristics [53].

The isomers blend ratio has a dramatic effect on the produced foam properties. The 80/20 isomer ratio of 2,4-TDI and 2,6-TDI is the most used commercial blend ratio. Higher-load-bearing foams can be obtained by 65/35 blend ratio, while low density foams can be produced by 80-85/20-15 blend ratio [47, 52].

There is an another parameter called "isocyanate index" which is the ratio of isocyanate groups to hydroxyl groups, ([NCO/OH]*100) also has an important effect on the foam properties. The covalent crosslinking density increases when the isocyanate index is increased due to the excess isocyanate groups presence. For a flexible foam, the isocyanate index changes between 105 to 115, where foam hardness can be controlled easily and safely. A larger excess of –NCO group usually increase the strength of the produced material, but on the other hand, produces more rigid and brittle foams. Because excess –NCO groups form allophanate, disubstituted urea, biuret, and isocyanurate linkages which increase the crosslinking in the foam structure (see section 1.5.3).

As seen in Figure 1.10, the reaction between the excess isocyanate and urethane bonds forms allophanate linkages. The allophanate reaction requires high temperatures greater than 110°C, while catalysts in the foam formulations generally inhibit this reaction by promoting urethane formation at relatively lower temperature. Therefore, allophanate groups do not have a significant part in a typical flexible polyurethane foam structure [47, 52, 54].
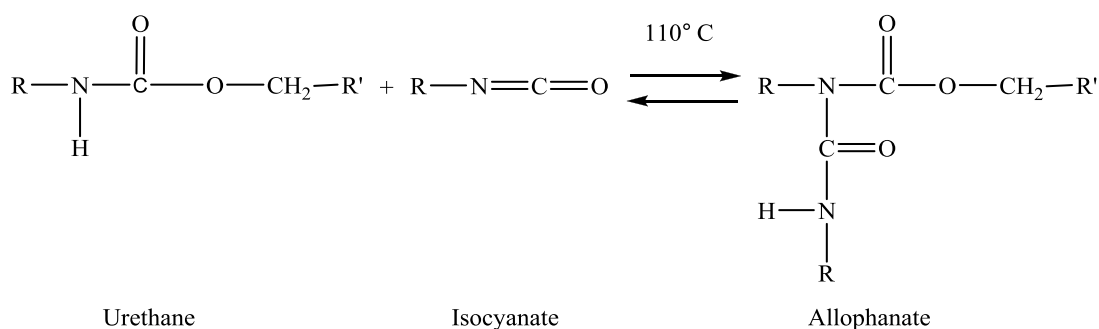
Figure 1.10 Allophanate linkage formation

Figure 1.11 illustrates the isocyanurate structure which also causes crosslinking in the foam structure. Isocyanurates are created by cyclic trimerization of isocyanates, which is related with their electronic structure. Catalyzing by Lewis bases (e.g. tertiary amines) and Lewis acids (e.g. organic metal compounds) increases the positive charge of the isocyanate's carbon atom which promotes the urethane reaction. Substituent in the structure of the isocyanate also effect the electronegativity of the carbon atom. Electron-donating groups adjacent to the NCO-group, enhances the trimerization reaction by decreasing positive charge of the carbon atom [55, 56].
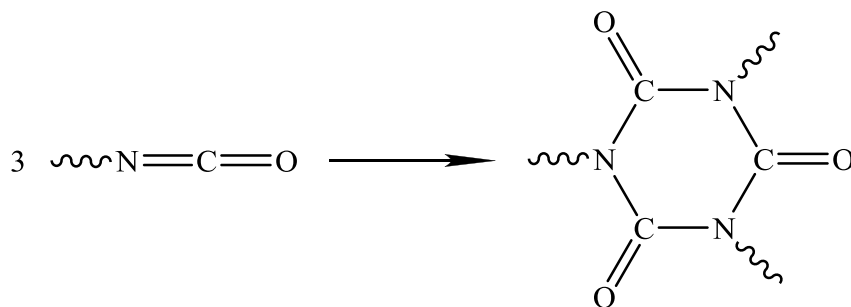
Figure 1.11 Trimerization reaction of isocyanates

1.5.2. Polyol

Polyols are hydroxyl-bearing compounds. They react with isocyanates to form urethane linkages. Polyether and polyester-type polyols are the mostly used compounds. Polyether-type polyols are used more in flexible foam production

(~90%), because they are cheap, easy to handle, and more resistant to hydrolysis compared to the polyester-types. Most of the remaining flexible foams (~10%) are made from polyester-type polyols. They are still being used in some foam applications because the improvement in the mechanical properties of final products [47, 51].

The type of a polyol has a significant impact on foam properties and processing requirements. Therefore, polyols have a wide range of varieties based on their chemical structure, molecular weight, and functionality [57, 58]. The most common used polyol type, polyether polyol, also has varieties. The polyether-type polyols can be broadly grouped into the following categories;

- Polyoxypropylene diols.
- Polyoxypropylene triols.
- Polyoxypropylene tetrols and higher analogs.
- Ethylene oxide caped diols, triols, tetrols, and higher analogs.
- Random and block copolymers of the above in which the polyol is made with both ethylene oxides and propylene oxides. When the oxides are fed as a mixed feed, the products are termed heteropolyols.
- Graft or "copolymer" polyols (CPPs) which contain stable dispersions of a solid particulate polymeric phase in the liquid polyol phase.
- Crosslinkers, which are typically short-chain polyfuctional molecules added to increase load bearing and/ or initial foam stability [47].

Among them the most widely used polyether polyols are copolymers of proplene oxide and ethylene oxide. Ethylene oxide polymers have poor hydrolytic stability whereas propylene oxide polymers have better resistance to hydrolysis, because of their hydrophobicity. In foam formulations, many of the other components are water soluble, so for a good mixing, pure propylene oxide-based polymers are not suitable. Therefore copolymers of propylene oxide and ethylene oxide is preferred to balance hydrolytic stability and water solubility [51].

The stiffness of the resulting polyurethane foams are strongly influenced by the functionality (the number of hydroxyl group/mol) of the polyol [59]. Functionality of

a polyol is generally controlled by the choice of initiator in polyol production. Water and ethylene glycol both lead to diol chains, whereas glycerine leads to triol chains [51]. High molecular weight polyols with low functionality (two-three OH groups/mol) produce flexible foams (with low crosslink density), whereas low molecular weight polyols with high functionality (three-eight OH groups/mol) produce rigid polyurethane foams (with high crosslink density) [59].

Figure 1.12 demonstrates polyether polyol made from ethylene oxide and propylene oxide, respectively. One clear difference between them is ethylene oxide-based polyol has only primary hydroxyl groups whereas propylene oxide-based polyol has secondary hydroxyl groups [59]. Primary hydroxyl groups are roughly three times more reactive than secondary hydroxyl groups, so primary hydroxyl groups speed up gelling reaction without increasing the catalyst loading and thus decrease the manufacturing time. Generally, high content of primary hydroxyl groups are suitable for molded foam production. For slabstock foaming, a series of polyols with different reactivity can be used according to application requirements and processing conditions [51, 57].
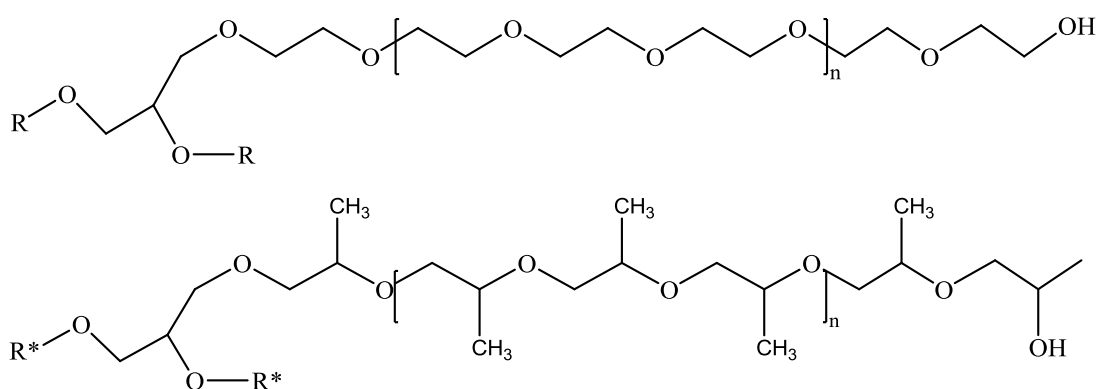
Figure 1.12 Polyether polyols made from ethylene oxide (top) and propylene oxide (bottom)

Like functionality, chain length is also an important parameter on stiffness of the produced foam. The short chain length polymers leads to higher concentrations of urethane and urea bonds. The high cohesive interactions between these bonds cause a rigid structure. Contrarily, the long chain length polymers leads to lower concentration of urethane and urea bonds which result in a significant decrease on

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the cohesive interactions. In addition to the low cohesive effect, the high mobility and elasticity, and low glass transition temperature (T_g) in the main chain of the polyol leads to generate more flexible foam structures [58, 59].

As mentioned above, molecular weight of a polyol is also an important parameter on the final foam properties. A high molecular weight polyol (3000-6500 g/mol) is necessary to create a flexible foam showing mechanical integrity (with low crosslink density). Figure 1.13 shows a hypothetical crosslinked structure of a flexible polyurethane foam obtained by the reaction of an oligo-triol of molecular weight of about 3000-6500 g/mol with a diisocyanate. The rigid polyurethane foam structures are obtained by using low molecular weight polyols (150-1000 g/mol). Figure 1.13 illustrates a hypothetical highly crosslinked structure of a rigid polyurethane foam [59].

☐ -OCONH-R-NHCOO-R'OCONNHCOO- or -OCO NH-R-NH-CO-NH-R-NHCOO

〰〰 -oligo-polyol chains (polyether or polyester chains)
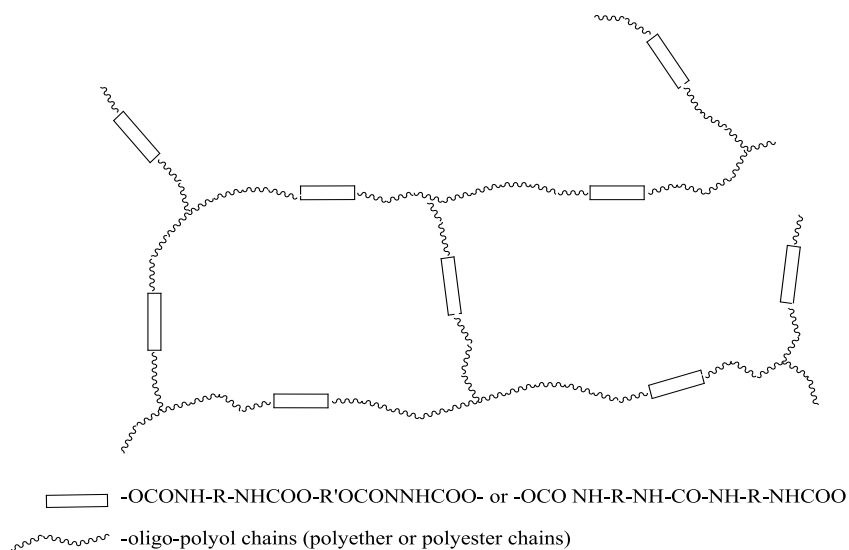
A) Hypothetical crosslinked structure of a flexible polyurethane foam
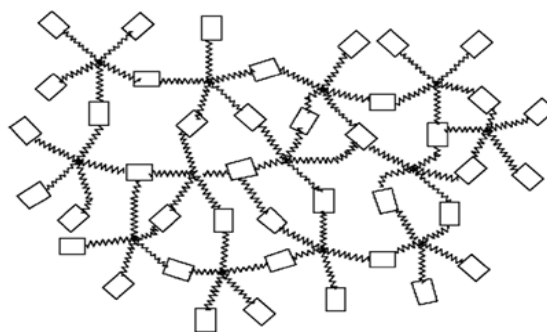
B) Hypothetical crosslinked structure of a rigid polyurethane foam

Figure 1.13 Effect of polyol molecular weight on the foam structure

1.5.3. Water

Water is added to foam formulations as a blowing agent. Water reacts with isocyanate groups to provide polyurea molecules, carbon dioxide gas, and heat. As seen in Figure 1.14, in the first step of the blowing reaction, water reacts with isocyanate to generate thermally unstable carbamic acid, which then spontaneously decomposes to carbon dioxide and an amine with heat generation. The generated heat is important for gas expandation in the liquid reaction medium. The carbon dioxide gas fills the cells and also helps the foam expansion [47, 51].
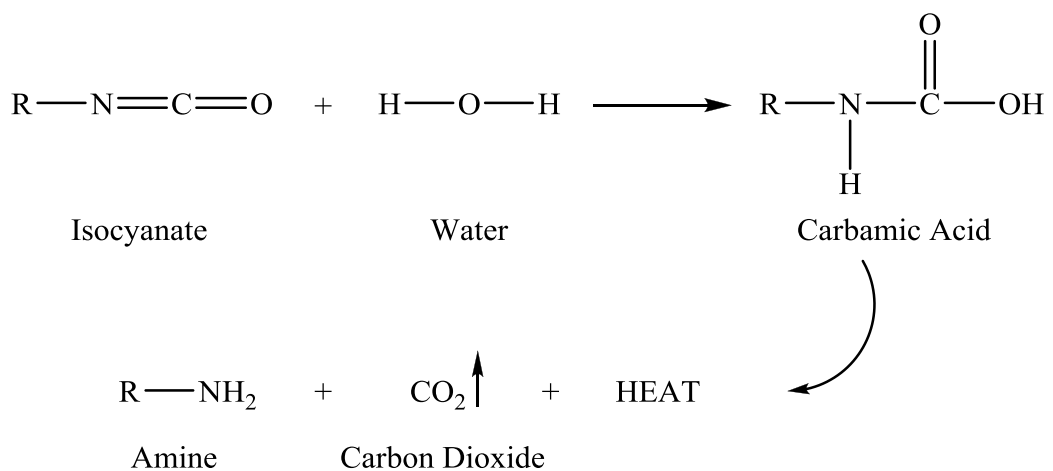
Figure 1.14 First step of the blowing reaction

Figure 1.15 illustrates the second step of the blowing reaction, in this exothermic step, generated amine group reacts with another isocyanate group to form a disubstituted urea linkage. The total heat generated from these two steps is approximately 47 kcal/mole of water reacted. This second step of the reaction can cause covalent cross-linking if the isocyanate has more than two functional groups or polyfunctional amines had been added to the formulation [51, 53].

R—N=C=O   +   R'—NH₂ $\xrightarrow{-\Delta}$ R—N—C—N—R'

$$R\!-\!N\!=\!C\!=\!O \quad + \quad R'\!-\!NH_2 \quad \xrightarrow{-\Delta} \quad R\!-\!\underset{\underset{H}{|}}{N}\!-\!\underset{\overset{\|}{O}}{C}\!-\!\underset{\underset{H}{|}}{N}\!-\!R'$$

Isocyanate   Amine   Disubstituted Urea
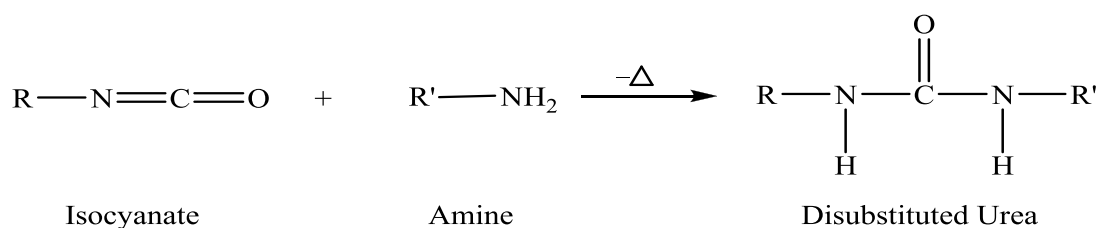
Figure 1.15 Second step of the blowing reaction

There will be an additional reaction between isocyanate and disubstituted urea which can also cause covalent cross-linking. As seen in Figure 1.16, a reaction between isocyanate and disubstituted urea generates biuret linkages. However, this reaction is reversible and generally occurs above 100 °C, therefore biuret groups do not have a significant part in a typical polyurethane foam structure produced by catalysts [51, 53].

$$R\!-\!N\!=\!C\!=\!O \quad + \quad R\!-\!\underset{\underset{H}{|}}{N}\!-\!\underset{\overset{\|}{O}}{C}\!-\!\underset{\underset{H}{|}}{N}\!-\!R' \quad \rightleftharpoons^{\Delta}$$

R—N—C—NH—R'
     | ‖
     | O
     C=O
     |
H—N
     |
     R
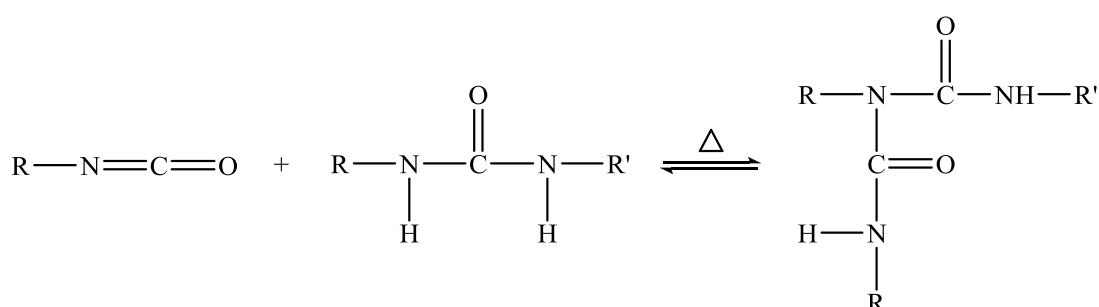
Figure 1.16 Biuret linkage formation

The water amount in the formulation is important for morphology, density, and stiffness of the flexible polyurethane foams. If the amount of water is increased while the other reactants are constant, the foam stiffness increases due to the increasing volume fraction of the polyurea-rich hard segments, and this also causes a decrease on foam density because of the large amount of carbon dioxide gas generation [47].

1.5.4. Surfactants

Surfactants are added to flexible polyurethane foam formulations to realize a variety of functions. Polysiloxane-polyoxyalkylene block copolymers are the most

commonly used surfactants for polyether based foams [52]. The silicone surfactants lower the surface tension, emulsify the incompatible formulation ingredients, promote generation of bubbles during mixing, stabilize cell windows of the rising foam, reduce the foam defoaming effect of any solid added (such as filllers) or formed (such as precipitated polyurea structures) during the foaming reaction [47]. Air permeability (porosity) and cell size of the foam, which have effects on many physical properties of flexible polyurethane foam are affected by the structure and level of the surfactant [60, 61].

Among those functions above, the stabilization of cell walls is the most important. Surfactants are efficiently adsorbed at the air-liquid interface. This adsorption stabilize the interface by changing its mechanical behaviours, in particular, surface tension and vicoelasticity. During the foaming, initial mechanical mixing generates bubbles. When the volume fraction of gas bubbles exceed 74%, the spherical shape of bubbles deform to multisided polyhedrals and cell windows are formed with plateau borders as seen in Figure 1.17. In this structure, the pressure of cell windows is higher than the pressure inside the plateau borders (struts) which can cause liquid drain into the struts. With silicone surfactants, control of this pressure difference is easier because of the surfactant orientation at the interface which result in a very low Si-O bond rotation energy of the siloxane backbone. On the other hand, in the absence of a surfactant, the rate of window film thinning causing from drainage of liquid into the struts will be very fast. And this rapid film thinning causes catastrophic coalescence of cells which will eventually lead to total foam collapse [47, 53, 60].
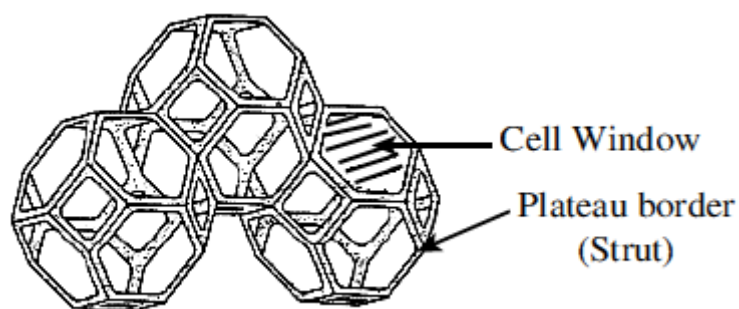

Figure 1.17 Foam cell structure [47]

1.5.5. Catalysts

Isocyanates slowly react with alcohols (gelling) and water (blowing) at room temperature. Proper balance of gelling and blowing reactions in flexible polyurethane foam production is required to make foams with good open-cell structures and desired physical properties, so catalysts are added to accelerate, to control and to balance both of these reactions [62].

The correct balance is required to entrap the gas in the gelling polymer structure and to develop sufficient strength in cell walls to maintain the flexible foam structure without collapsing or shrinkage. If the blowing reaction is faster than the gelling reaction the foam will collapse because of its low viscosity. On the other hand, if the gelling reaction is relatively faster compared to the blowing reaction, the foam will shrink due to more closed cell structure production [47, 63].

Water-blown flexible polyurethane foams are generally catalyzed by a mixture of one or more tertiary amines and organometallic (organo-tin) catalysts. Activity and selectivity of these catalysts towards the gelling and blowing reactions are different so the desired balance between the two reactions can be obtained by adjusting the level and ratio of catalysts. Generally, tertiary amines are regarded as blowing catalysts and metal catalysts are regarded as gelling catalysts [47].

Tertiary amines are compounds containing a nitrogen atom with three substituent groups and a free pair of electrons [64]. The catalytic activity of the amine is due to the presence of the free electron pair. Catalytic activity of amines depends on steric hindrance around the nitrogen atom caused by the substituent groups and the electron withdrawing or releasing nature of the substituent groups [47]. The basicity of the catalyst is also important on the catalyzing activity. Generally, the catalytic activity increases with increasing basicity of an amine catalyst [65]. Though amine catalysts are generally known as blowing agents, they can also slightly accelerate the gelling reaction according to their structure [47]. Generally a tertiary amine catalyst having ether bond and a lower carbon number shows higher blowing activity due to steric effects (Figure 1.18) [66].

Strong blowing catalysts   Strong gelling catalysts
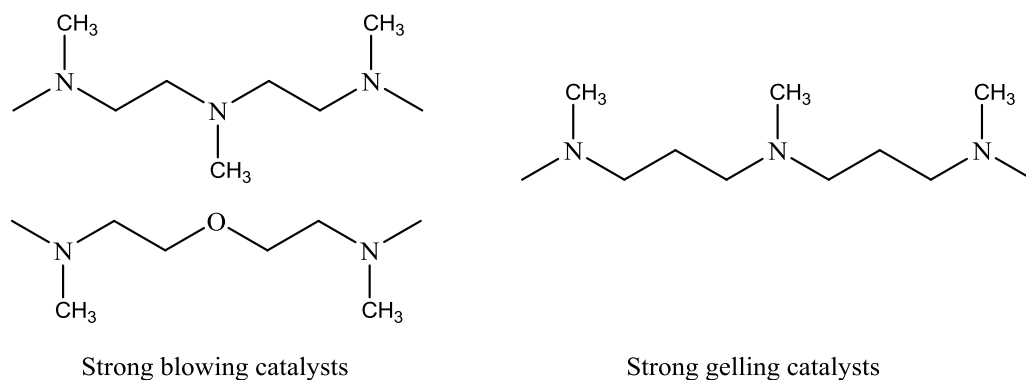
Figure 1.18 Structure of common amine catalysts

Figure 1.19 demostrates the activation mechanism of amine catalyst on the blowing reaction [66]. The amine catalyst first interact with the water molecule through hydrogen bonding. The polarized water molecule then interact with strongly polar –NCO group.

$$R-NH-\underset{\underset{O}{\|}}{C}-NH-R \ + \ CO_2$$
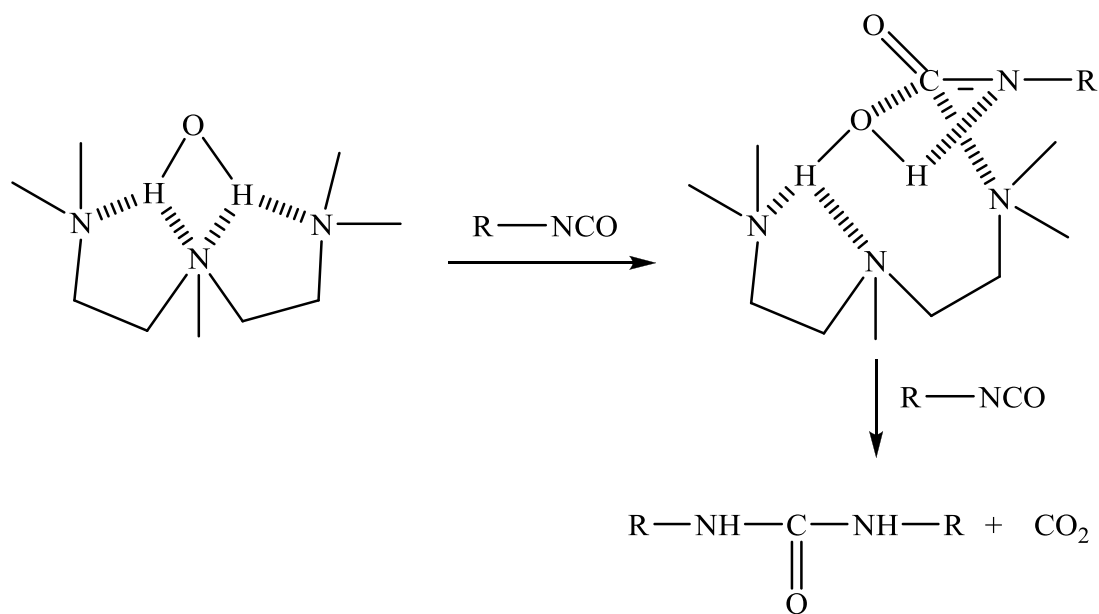
Figure 1.19 Activation mechanism of an amine catalyst on the blowing reaction

As seen in Figure 1.20, a tertiary nitrogen can catalyse the electron-deficient carbon atom of an isocyanate group (mechanism 1) or the hydrogen of an hydroxyl group (mechanism 2) and creates a resonating intermediate to accelarate the gelling reaction [47, 65].

22
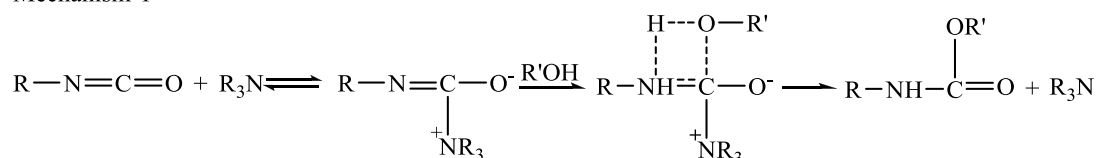
Mechanism-1
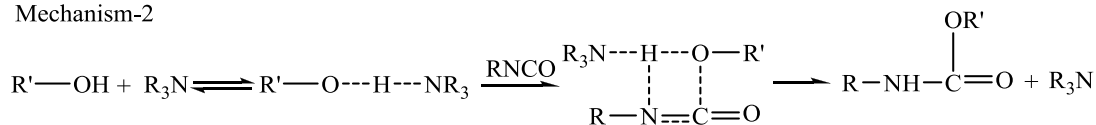
Mechanism-2

Figure 1.20 Activation mechanism of an amine catalyst on the gelling reaction

In general, the gelling reaction is promoted by organometallic catalysts, of which the tin compounds such as stannous octoate are the most widely used. The catalytic activity of metal catalysts is explained by several hypotheses. These compounds act as Lewis acids and are generally assumed to catalyse the gelling reaction by interacting with the basic sites in isocyanate and polyol compounds. Figure 1.21 illustrates the organometallic catalyst activation mechanisms which primarily coordinate the oxygen atom of the NCO group or OH group and activate the electrophilic nature of the carbon atom to generate urethane linkage [47, 65].

Mechanism-1
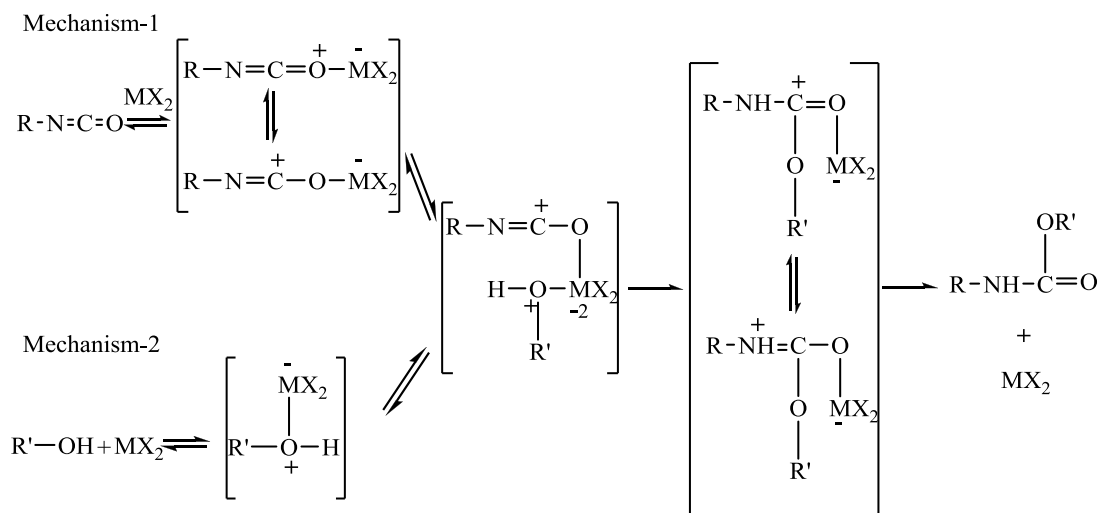
Mechanism-2

Figure 1.21 Activation mechanism of an organometallic catalyst on the gelling reaction

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1.6. Use of Quaternary Ammonium Compounds in Polyurethane Foams

First Decker et al. (1966) used quaternary ammonium compounds (QACs) as an antimicrobial agent in PU foams. They impregnated solutions of QACs with an amphoteric detergent or with a surface-active agent to flexible closed-cell polyurethane foams. They targeted only single use antimicrobial pads, where the antimicrobial property is only needed at the exterior surface. Therefore, they chose a closed cell polyurethane foam to block the solution penetration into the foam structure. The impregnated or coated pads were effective against *Escherichia coli* and *Staphylococcus aureus* [67].

Fujii et al. (1976) used QACs as an antistatic agent. They used QACs either as an additive in the foam formulation or in a solution which impregnated to produced foams. They obtained antistatic foams by those two methods, however; did not investigate their antimicrobial properties. They also found that when QACs are used as an additive, they promote the gelling reaction which allows to reduce the amount of tin catalyst [68].

Cianciolo et al. (1984) used QACs as an antimicrobial additive in a flexible polyurethane foam formulation. They applied zone inhibition tests to produced foams and reported an antimicrobial activity against *Staphylococcus aureus* and *Klebsiella pneumonia* [69]. Nekmard et al. (2012) also used QACs as an antimicrobial agent in a polyurethane foam formulation. Even the QACs were not covalently bound to the foam structure, the produced foams exhibited gradually reducing antimicrobial effect even after 50 or more rinse/squeeze cycles. This long term antimicrobial property was achieved by the affinity between the polyurethane foam and QACs. The QACs were entrapped by the cell walls of the polyurethane foams. The produced foams exhibited a good "contact kill" property against, Gram-negative (e.g., *Salmonella choleraesuis*) and/or Gram-positive bacteria (e.g. *Staphylococcus aureus*) and some preferred embodiments foams demonstrated efficacy against, *Enterobacter aerogenes* species [70].

In the above studies, QACs were not covalently bonded to foam structures. Therefore, the produced antimicrobial materials can lose their efficiency over time

due to migration of non-bonded agents with the flowing liquids. Therefore, for specific foam applications, incorporation of the agents into the materials by covalent bonds is dramatically important.

In this regards, Toreki et al. (2009) improved water-insoluble and either alcohol-soluble or glycol-soluble antimicrobial polymers by QACs. Quaternary ammonium moieties were covalently bonded to backbone of a polymer, or attached to side of a polymer by covalent bonds. Those produced polymers were then added to foam formulations to provide antimicrobial property. The produced foams were effective against *Candida albicans*, *Staphylococcus aureus*, and *Psedomonas auerginosa*. The produced foams were designed for wound dressing applications and therefore the study was limited to specific type of QACs. However, for our study, we do not have such a limitation. [71].

2. EXPERIMENTAL DESIGN

2.1. Materials

The polyol used in the study was Caradol SC 48-08 (Shell Chemicals), which is a polyether type polyol having three functional end groups, a hydroxyl group number of 48.08 mgKOH/g, and a molecular weight of 3500 g/mol. The used toluene diisocyanate (TDI) was a mixture of 2,4 and 2,6 (80:20) isomers (Shell Chemicals). A silicone-based surfactant Tegostab BF 2470 (Evonik Industries) was used to stabilize the foam cellular structure. The gelling and blowing catalysts used in the study were Tegoamin 33, Tegoamin BDE, and Kosmos 29 (Evonik Industries). The chemical composition of the catalysts and their specific performance in polyurethane foam production are given in Table 2.1.

Table 2.1 Properties of the catalysts

Product Name	Chemical Composition	Specific Performance
TEGOAMIN 33	33% Triethylenediamine 67% Dipropyleneglycol	Preferred as a co- catalyst, catalyzes both the gelling and the blowing reaction
TEGOAMIN BDE	70% Bis(2-dimethylaminoethyl)ether 30% Dipropyleneglycol	Preferred as a very active co-catalyst, catalyzes particularly the blowing reaction
KOSMOS 29	Stannous octoate	Preferably used to accelerates the gelling reaction

The quaternary ammonium salt polymers used in the study were Ethoquad 18/25 [Octadecylmethyl[polyoxyethylene (15)] ammonium chloride) (QAP) and Ethoquad O/12 PG (Oleylmethylbis (2-hydroxyethyl) ammonium chloride) (AkzoNobel) having molecular weights of 496 g/mol and 406 g/mol, respectively. Chemical structures of the quaternary ammonium salt polymers are shown in Figure 2.1.

$$HO-[CH_2-CH_2-O]_n-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\underset{(CH_2)_{17}}{N^+}}}-CH_2-CH_2-[O-CH_2-CH_2]_n-OH \quad Cl^-$$

(A) QAP

$$H_3C-\overset{\overset{\displaystyle CH_2-OH}{|}}{\underset{\underset{\displaystyle CH_2}{|}{\underset{\displaystyle HO}{}}}{\underset{\displaystyle H_2C}{\overset{\displaystyle H_2C}{N^+}}}}-(CH_2)_8-CH=CH-(CH_2)_7-CH_3 \quad Cl^-$$
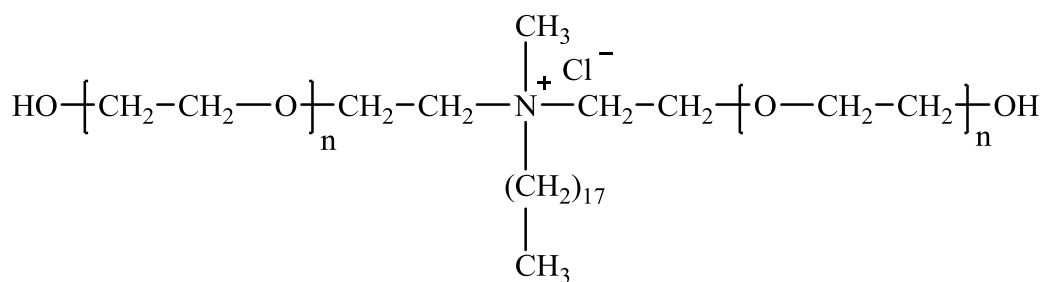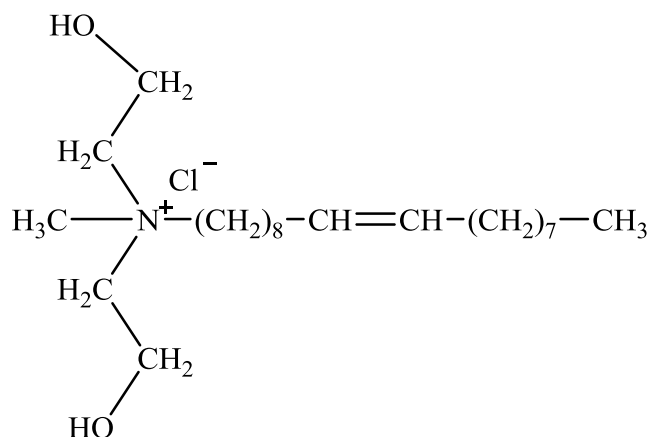
(B)

Figure 2.1 Chemical structure of Ethoquad 18/25 - QAP (A) and Ethoquad O/12 PG (B)

The produced unmodified, 1 wt% Ethoquad 18/25 added, and 1 wt% Ethoquad O/12 PG added foams are shown in Figure 2.2. As seen in the figure, even a very low amount addition of Ethoquad O/12 PG results in a dramatic shrinkage in the foam structure, therefore the study was continued with Ethoquad 18/25 (QAP).
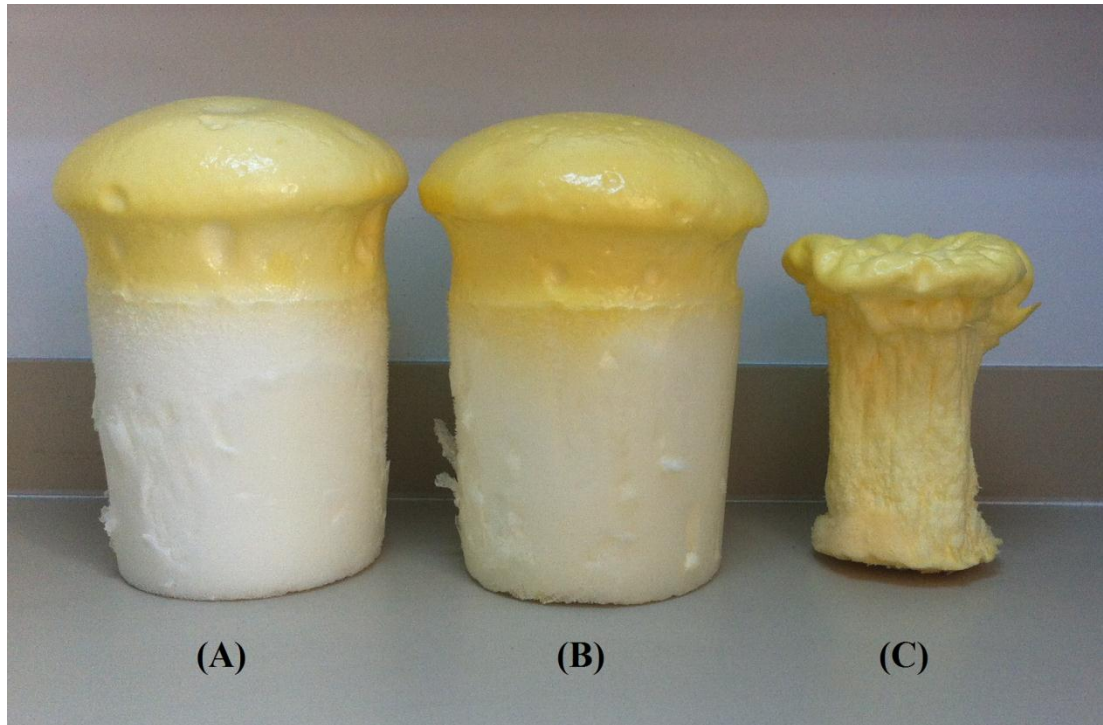
Figure 2. 2 The produced foams; unmodified (A), 1 wt% Ethoquad 18/25 added (B),
1 wt% Ethoquad O/12 PG added (C)

2.2. Method

2.2.1. Foam production

A commercial polyurethane foam formulation was used in the study which is summarized in Table 2.2. All ingredients except TDI were put into a 114 x 130mm (d x h) plastic cup in the order of Caradol SC 48-08, water, Tegostab BF 2470, Tegoamin 33, Tegoamin BDE, Kosmos 29, and then mixed vigorously with a kitchen-type mixer about for one minute. TDI was added to the above mixture and mixing was continued until the mixture begins to swell. Total height of the unmodified foams reached approximately 180mm from the bottom of plastic cup and addition of 1 wt% QAP did not cause a big change on the total height of the foams. The expanded foams were kept in the room temperature for one week until the reaction is completed, and then removed from the plastic cups.

Table 2.2 The unmodified foam formulation

Ingredients	Parts by Weight (g)
CARADOL SC 48-08	80.000
Water	2.560
TEGOAMIN 33	0.024
TEGOAMIN BDE	0.048
KOSMOS 29	0.144
TEGOSTAB BF 2470	0.640
TDI	35.312

To produce antimicrobial polyurethane foams, the commercial foam formulation was modified by addition of a QAP into the polyol part. Various amounts of QAP (1 wt%, 2 wt% and 5 wt%) were added to formulations as summarized in Table 2.3. In all produced foams, the total amount of the polyol and QAP was kept constant at 80g. (Table 2.3). All other ingredients used in the formulations were same as described in Table 2.2.

Table 2.3 Polyol content of the produced foams

	Polyol (g)	QAP (g)	QAP (%)
PU	80.00	0	0
PU1	78.80	1.20	1
PU2	77.60	2.40	2
PU5	74.08	5.92	5

To understand the chemical structure of the produced foams, a linear polymer of QAP and TDI was synthesized as a preliminary study (Figure 2.3). A solution was prepared by dissolving 5g. of QAP (10.08 mmol) in N,N-dimethylformamide (DMF). To that solution, 2ml. of TDI (14.08 mmol) was gradually added within 30min. by controlling the temperature and viscosity. After the addition of TDI, the solution was stirred at 55 °C for 10min. A rapid viscosity increase was observed at that point. The polymer was obtained by dropwise addition of the reaction solution

into acetone, and the precipitated polymer was dried at room temperature for one day.
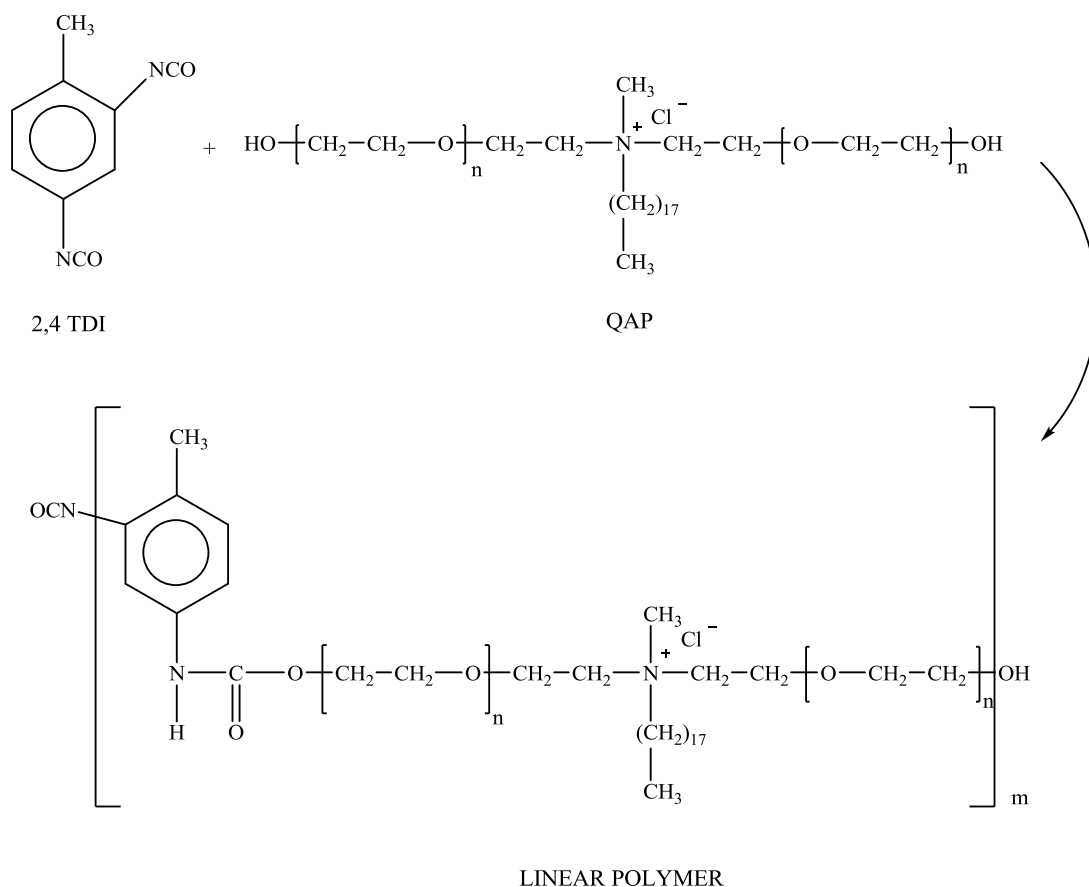
Figure 2. 3 Reaction mechanism of the linear polymer

FTIR spectrum of the synthesized polymer is shown in Figure 2.4. The disappearance of the -NCO band at $2233cm^{-1}$ and the appearance of -NH vibration band at $3543cm^{-1}$, urethane -C=O vibration band at $1704cm^{-1}$, and urethane -C-O vibration band at $1223cm^{-1}$ confirms the completion of reaction and formation of urethane linkages. The bands at $1596\ cm^{-1}$ and $1539cm^{-1}$ can be assigned to aromatic C=C vibration of the reacted TDI, and the band at $1085cm^{-1}$ can be assigned to C-O-C vibration of the reacted polyol. The polymer obtained by the reaction between TDI and QAP gave typical polyurethane peaks at 3543, 3270, 1704, 1596, 1539, 1223 and $1085cm^{-1}$ indicating that QAP can succesfully react with TDI to form urethane linkages. This supports that QAP can permanently be introduced (covalently bonded)

into the foam structure and will not migrate with liquid vehicles during end use applications.
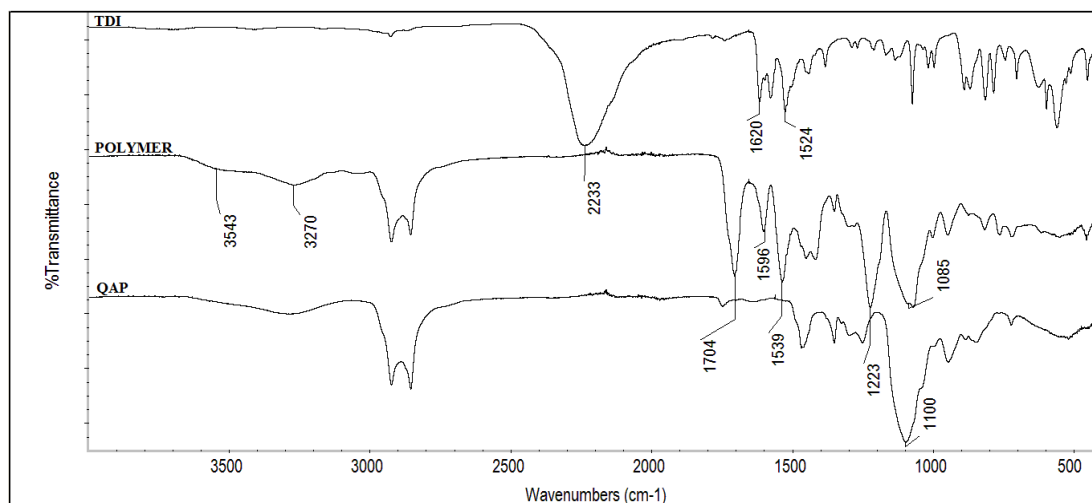
Figure 2. 4 FTIR spectra of the polymer obtained by the reaction between TDI and QAP

2.2.2. Characterization

A Fourier-transform infrared (FTIR) spectroscopy (Thermo Nicolet, iS50) with an attenuated total reflectance (ATR) accessory was used to collect spectra of the produced polyurethane foams and polymers. FTIR spectra were recorded with 32 scans at 2 cm^{-1} resolution in 400 to 4000 cm^{-1} wavenumber range.

Energy dispersive X-ray fluorescence (EDXRF) measurements of the produced foams (washed in DMF solution), were carried out at the Bursa Test and Analysis Laboratuary (BUTAL), using a EDXRF spectrometer (SPECTRO, X-LAB 2000). The spectrometer is composed of a palladium end window X-ray tube with maximum 300W power and 50kV voltage. The fluorescence X-rays are detected by a liquid nitrogen cooled Si(Li) detector with an energy resolution of approximately 139eV at 1,5keV and an entrance beryllium window. HOPG, Al$_2$O$_3$ polarization targets and Molybdenum secondary targets were used. Measurement and evaluation was made with a multichannel analyzer, TURBOQUANT. Measurements were made

with powder samples. The samples were grinded by a mixer mill (Retsch, mm 400) after treated 2,5min. with liquid nitrogen.

Thermo-gravimetric analyzer (TGA) (Perkin Elmer, STA 600) was performed to assess the effect of addition of QAP on the thermal stability of the produced foams. Experiments were carried out under nitrogen gas atmosphere. Samples of 4-5 mg. were heated to 500 °C from 50 °C at a heating rate of 10 °C /min.

Viscoelastic behavior of the produced foams were evaluated by a dynamic mechanical analyzer (TA Instrument, Q800). Compression/DMA Multi-Frequency-Strain and Compression/DMA Strain Rate modes were used to obtain tan α – temperature and stress – strain data, respectively. Square samples in the dimension of 8.2 x 19.3mm (w x t) were prepared. For Multi-Frequency-Strain test, samples were equilibrated at 30 °C and holded for 5 min, followed by a cooling to -80 °C at 10 °C /min and holded for 5 min before heating up to 30 °C at 5 °C/min. For Strain-Rate test, samples were isothermal at 40 °C during test and compressed until strain reach 50% at 5%/min. For each sample, three specimens were tested.

Tensile behavior of the produced foams were evaluated by using a universal tester (Shimadzu Autograph AGS-X) with 0.5kN load cell at a crosshead speed of 20mm/min. Rectangular specimens, notched from middle of the gauge length, in the dimension of 6.7 x 9.3 x 50mm (t x w x l) with a gauge length of 20mm were prepared. For each sample, ten specimens were tested. Length of the specimen were placed in the grips along the growing direction of the foams.

The differences in the cellular structure of the foams were evaluated and compared using scanning electron microscopy (SEM-QUANTA 400F Field Emission). Images were obtained operating at 30kV and at a magnification of 100x and 150x. The scanning electron micrographs were performed by Middle East Technical University Central Laboratory.

The biocidal efficacy tests were performed with *Staphylococcus aureus,* Yeast and Mould (AATCC 100-1999) suspensions of microorganism in a pH 7 Maximum Recovery Diluent (MRD-Peptone Saline Diluent). 1ml. of microorganism

suspensions (2-3 log concentration) were injected to 30 x 30 x 40mm samples in a sterile pouch. The contact time for the microorganism with the sample were 5min. and 5h., afterwards the foam surface was scanned with a swap. The swap was put in a tube which contains 9ml MRD and homogenized with a vortex stirrer. For *S. aureus* 0.5ml. and for Yeast and Mould 0.1ml. solution taken from the tube was plated on an agar plate. Baird-Parker agar was used for *S. aureus* and Dichloran Rose Bengal agar was used for Yeast and Mould tests. Agar plates were incubated for 24h at 37 °C for *S. aureus*, 5d. at 25°C for Yeast and Mould. The number of the microorganisms counted after 5min. of contact time was stated as "Initial concentration of microorganisms", and the number of the microorganisms counted after 5h of contact time was stated as "Remaining concentration of microorganisms". The biocidal efficacy of the foams were evaluated according to percent reduction of the microorganisms between their initial and remaining concentrations. The biocidal efficacy tests were performed by the Bursa Central Research Institute of Food and Feed Control.

3. RESULTS AND DISCUSSION

The produced polyurethane foams PU, PU1, PU2, and PU5 are shown in Figure 3.1. Addition of 1 wt% QAP (PU1) did not alter the physical appearance of the produced foams, while higher amount additions (PU2 and PU5) cause dramatic shrinkage in the foam structure. This effect might be due to the cationic charges in the QAP parts which causes a gelling instability during the foam formation. Because of its poor physical properties, PU5 was not investigated except antimicrobial efficacy testing. The shrinkage of the expanded foams can be reduced by changing the foam formulations or by applying heat setting. However, since one of our target is providing permanent antimicrobial property on a commercial product, those enhancement methods were not applied.
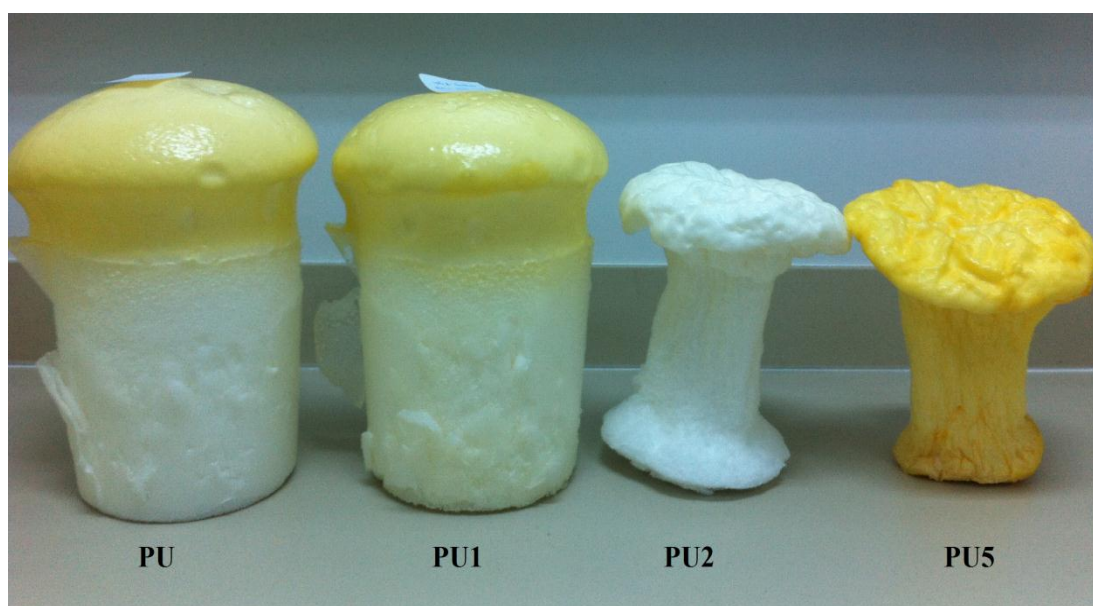
Figure 3.1 The produced polyurethane foams; PU, PU1, PU2, and PU5

3.1. FTIR Characterization of the Foams

The FTIR spectrum of the produced unmodified foam (PU) is shown in Figure 3.2. The spectrum is suggestive of urethane bond formation. The band at 3296 cm^{-1} is assigned to the N-H stretching vibrations. The bands at 2974 cm^{-1} and 2867 cm^{-1} are caused by the asymmetric and symmetric stretching vibrations of CH$_2$ groups,

respectively. The band at 2273 cm^{-1} is assigned to the N=C=O group of the unreacted isocyanate groups. The region between 1800 - 1550 cm^{-1} is carbonyl region. The region > 1700 cm^{-1} is free species region, comprising both free urethane and free urea groups, and the region < 1700 cm^{-1} is H-bonded species region. The bond at 1536 cm^{-1} corresponds to aromatic C=C vibration of reacted TDI, while the bond at 1089 cm^{-1} correspond to the C-O-C stretching vibrations.
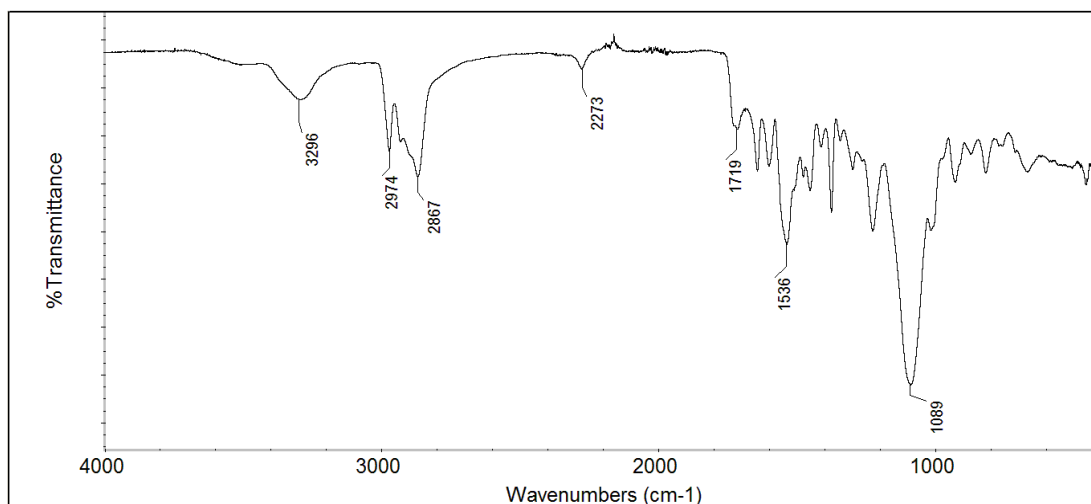
Figure 3.2 FTIR spectrum of PU

FTIR spectra of both PU and modified foams are shown in Figure 3.3. As one can observe, the relative position of the distinctive bands for PU are identical with that of the modified foams (PU1, PU2, and PU5). Because, the characteristic quaternary ammonium salt vibrational bands were overlapped by the amide (~3300cm^{-1} and ~700cm^{-1}), ethylene (~2900cm^{-1}), and ether (~1100cm^{-1}) bond stretching bands of the polyurethane foam.
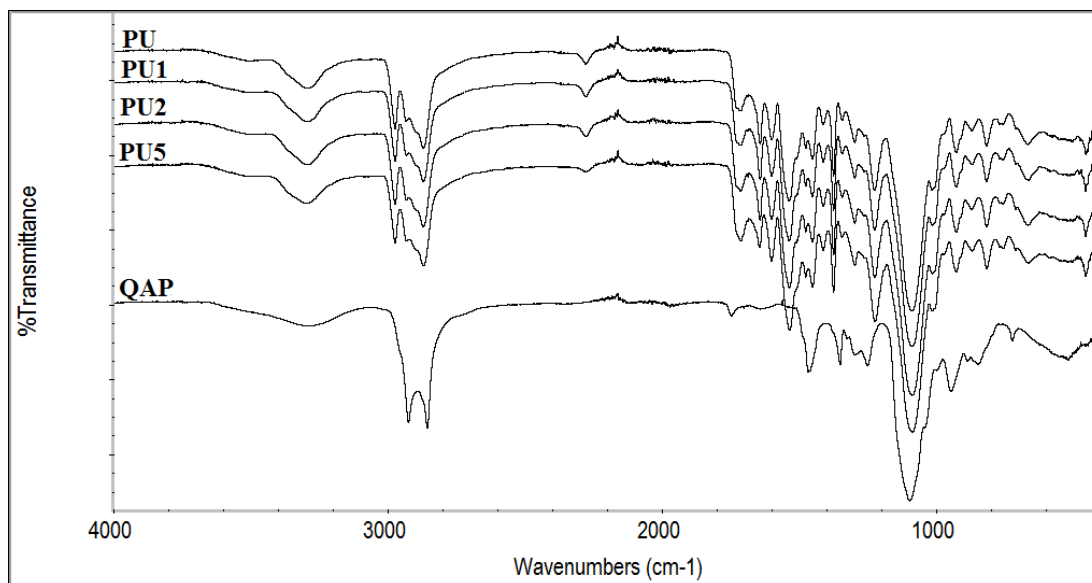
Figure 3.3 FTIR spectra of the produced foams

3.2. EDXRF Characterization of the Foams

EDXRF tests were performed on the DMF-rinsed foam samples, and the results were shown in Figure 3.4. The peak at 2.61 E/keV is assigned to the chlorine atom energy. The unmodified foam (PU) showed a small band at that point, probably due to the chlorine content in the catalysts and surfactant. Moreover, QAP-added foams exhibited relatively larger bands indicating an increase in the chlorine content due to the quaternary ammonium structure.
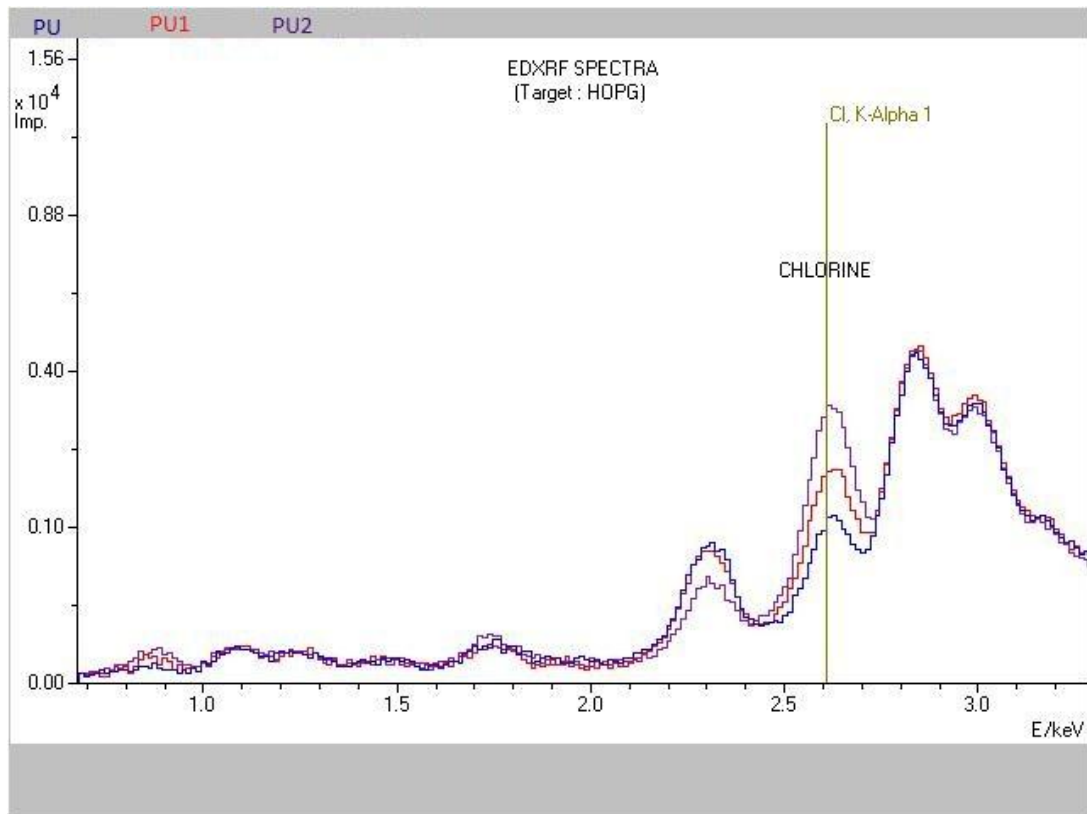
Figure 3. 4 EDXRF spectra of the produced foams

3.3. Thermal and Mechanical Properties of the Produced Foams

TGA thermograms of the produced foams in the form of percent weight loss as a function of temperature are shown in Figure 3.5. The decomposition behaviour of all produced foams occurs in a two step-degradation process. The thermal stability of the modified foams (PU1 and PU2) is higher than PU, especially in the second step of the degradation. The residual contents, after the degradation process, of the modified foams were higher compared to PU, due to increasing inorganic content by QAP.
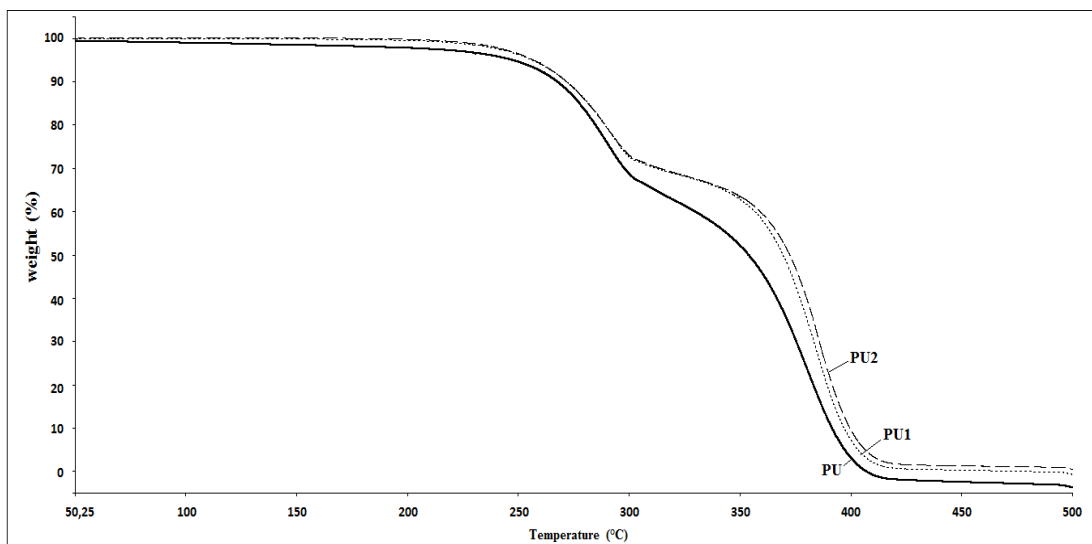
Figure 3.5 TGA thermograms of the produced foams

DMA is an useful technique to reveal some properties of polymer materials such as the glass transition temperature (T_g) and the rigidity. The measurement of the tan α maximum point allows the determination of T_g which represents soft segment's melting point. Figure 3.6 presents the curves of the tan α of the produced foams. While the melting point of polyol is -65°C, polymerization caused an increase in the melting point of the soft segments to -32°C. On the other hand, T_g of all produced foams are at about same value, which indicates the introduction of QAP into the structure does not alter the bond composition. Because, changing cross-linking density would be expect to effect the T_g of the produced foams.

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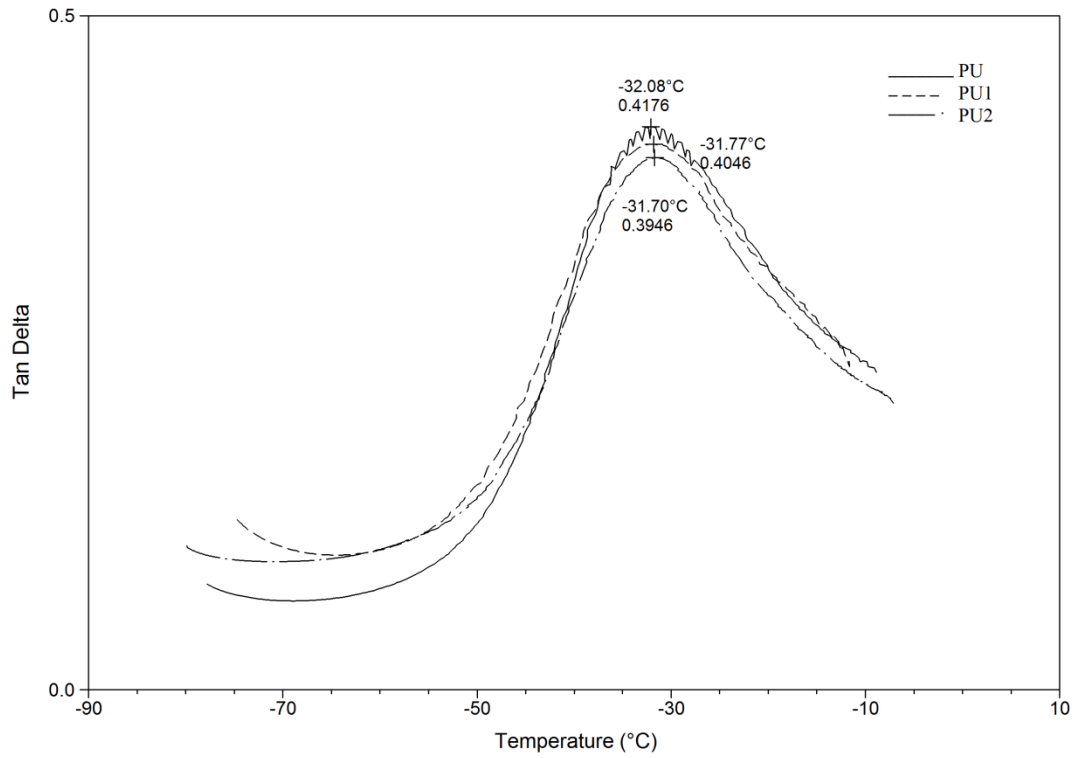
Figure 3.6 Influence of the QAP content on T_g

The measurement of the stress according to increasing strain values gives information about the rigidity of the prepared foams. Figure 3.7 demonstrates the stress – strain curves of the produced foams under compression. The rigidity of PU1 foam was very similar to the PU, indicating a similar cellular structure. The rigidity of PU2 was significantly high compared to other foams, which is due to the dramatic shrinkage increasing the number of cells per unit area.
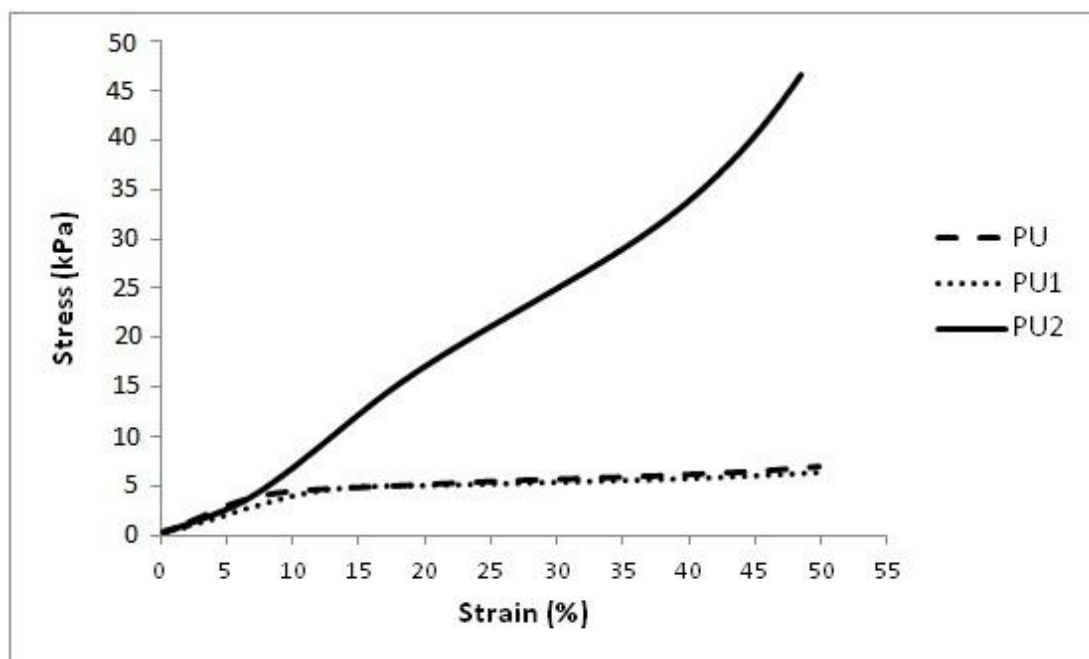
Figure 3.7 Influence of the QAP content on the stress-strain behaviour

Tensile tests were performed to examine the influence of QAP on the tensile properties of produced foams. Tensile test results are shown in Table 3.1. PU1 showed a mechanical performance similar to PU, while PU2 showed a very high elongation and a very low tenacity. This is due to the shrinkage which deteriotes the the polymerization stability.

Table 3.1 Summary of the tensile test results

Sample	Tenacity (N/mm^2)*		Elongation at break (%)*	
	Average	S.D.	Average	S.D.
PU	0.113	±0.034	119.648	±13.201
PU1	0.104	±0.025	123.307	±6.311
PU2	0.035	±0.021	192.193	±31.160

* Data taken is the average of ten samples and the standard deviation (S.D) is reflective of the largest deviation from the average.

3.4. Morphology of the Foams

SEM micrographs of PU, PU1 and PU2 are shown in Figure 3.8 and Figure 3.9 with magnifications of 100x and 150x. The cellular structure of the foams were relatively unaffected by the 1 wt% addition of QAP. First, the cell size and distribution in PU1 was not changed compared to PU. Secondly, open cell structure was also very similar to PU. The amount of open cells are very important in antimicrobial applications due to the increasing surface area interacting with microorganisms. Increasing amount of QAP (PU2) deteriorate the cellular structure of the produced foams due to the dramatic shrinkage after foam expansion.
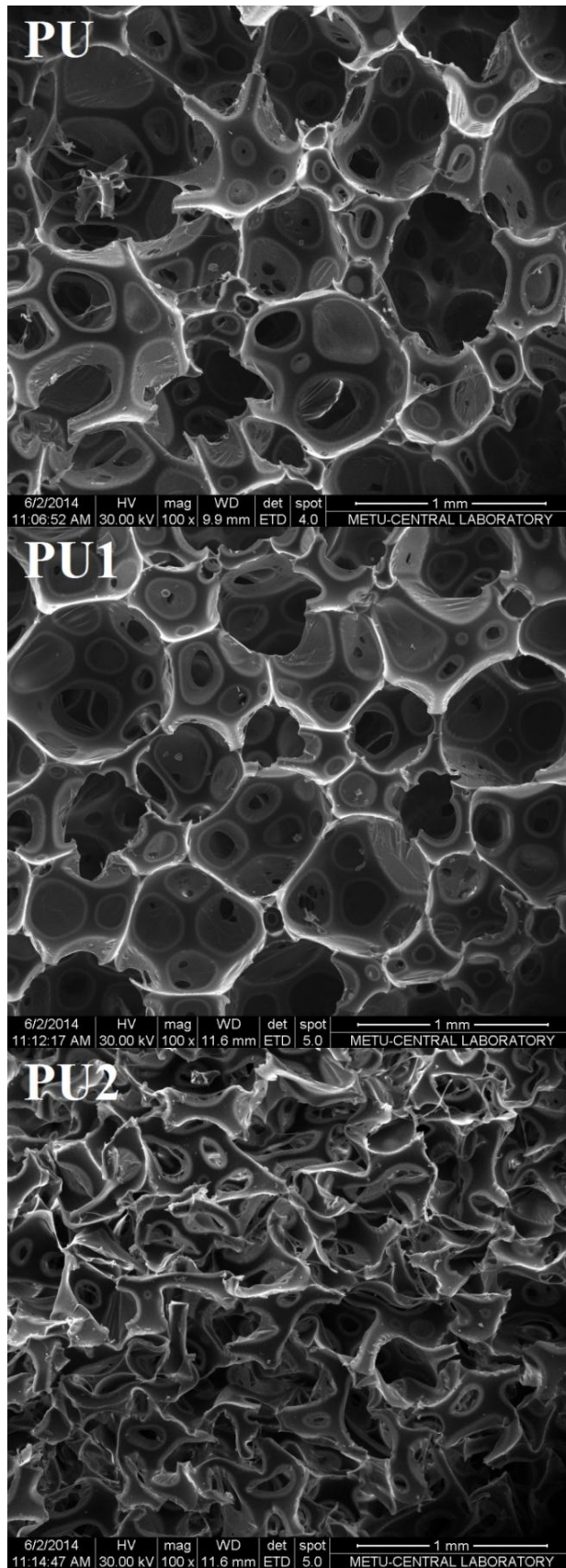
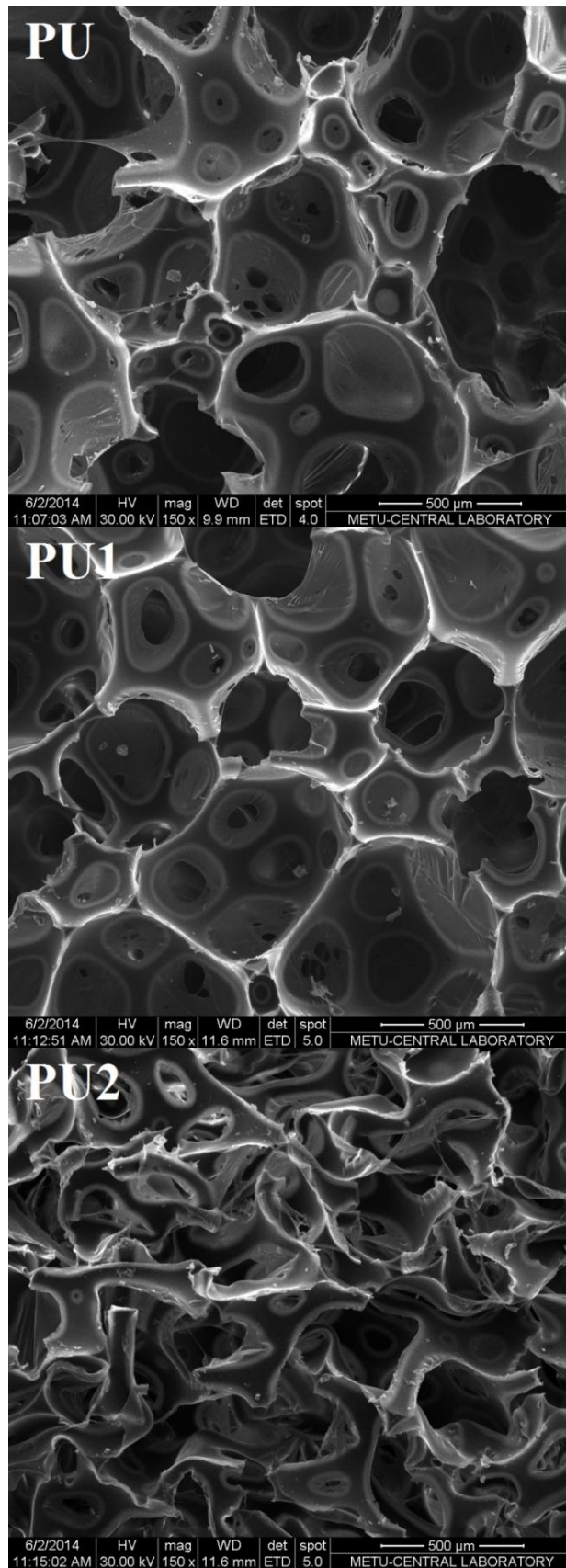**Figure 3.8** SEM micrographs of PU, PU1, and PU2 at 100x magnification

Figure 3.9 SEM micrographs of the PU, PU1, and PU2 at 150x magnification

3.5. Biocidal performance of the Foams

Biocidal performance of the produced foams were evaluated by a Gram-positive bacteria, yeast, and mould. The produced foams were evaluated by two tests. First, with a low concentration of microorganisms and then with a higher concentration of microorganisms to investigate their behavior at different conditions.

In the antimicrobial tests, unmodified (PU) and QAP added (PU1, PU2, and PU5) foam swatches were challenged with *S. aureus* at concentrations of around 10^2 (Test I) and 10^3 (Test II) CFU, and the results are summarized in Table 3.2. The unmodified control foam (PU) did not exhibit any significant biocidal efficacy in both Test I and Test II. PU1 provided an inactivation of 90% within 5h., and provided an inactivation of 76.5% when challenged with higher concentration of bacteria. PU2 and PU5 showed a better performance by providing about 97% and 99% reductions throughout the tests.

Table 3.2 Antimicrobial tests with *S. aureus*

| | | *S. aureus* | | | | |
| | | Test I | | | Test II | |
	Initial conc. of microorg.	Remaining conc. of microorg. *	% reduction	Initial conc. of microorg.	Remaining conc. of microorg.*	% reduction
PU	6.0×10^2	6.3×10^2	0.30	4.8×10^3	4.7×10^3	2.08
PU1	6.0×10^2	4.0×10^1	90.00	2.9×10^3	6.8×10^2	76.50
PU2	6.0×10^2	2.0×10^1	96.70	7.2×10^3	2.2×10^2	96.90
PU5	6.0×10^2	<10	99.20	5.3×10^3	1.2×10^1	99.80

* Remaining concentration of microorganisms counted after 5 h.

In the yeast and mould tests, unmodified (PU) and QAP added (PU1, PU2, and PU5) foam swatches were challenged with yeast and mould at concentration of around 10^2 (Test I) and 10^3 (Test II) CFU, and the resuts are summarized in Table 3.3. The unmodified control foam (PU) did not exhibit any significant biocidal efficacy in both Test I and Test II, like the antimicrobial tests. Yeats and mould inactivation of produced foams were up to 95% within 5h. in both Test I and Test II even with 1

%wt addition of QAP (PU1). The increasing amount of QAP (PU2 and PU5) almost completely inactivated the yeast and mould (~99%) within 5h. of contact time.

Table 3.3 Antimicrobial tests with yeast and mould

| | Yeast and Mould | | | | | |
| | Test I | | | Test II | | |
	Initial conc. of microorg.	Remaining conc. of microorg. *	% reduction	Initial conc. of microorg.	Remaining conc. of microorg.*	% reduction
PU	6.0×10^2	5.4×10^2	10.00	9.7×10^3	8.8×10^3	9.30
PU1	6.0×10^2	2.0×10^2	96.70	7.2×10^3	3.0×10^2	95.80
PU2	6.0×10^2	<10	98.30	8.0×10^3	4.0×10^1	99.50
PU5	6.0×10^2	<10	99.20	8.7×10^3	<10	99.90

∗ Remaining concentration of microorganisms counted after 5 h.

All QAP added foams showed sufficient inactivation against bacteria, yeast, and mould (Table 3.2, Table 3.3). Increasing amount of added QAP improves the biocidal performance of the produced foams.

4. CONCLUSIONS

In this study, flexible open-cell polyurethane foams were produced with the addition of a quaternary ammonium salt polymer (QAP) into the foam structure to provide antimicrobial property. QAP was a diol and introduced to a commercial foam formulation by forming urethane linkages. QAP was added to formulation in various amounts between 1 and 5 wt%. Increasing QAP content (2-5 wt%) caused shrinkage due to its cationic charges which destabilizes the gelling reaction.

The proof of QAP content in the foams was difficult with FTIR characterization due to band overlapping. However, the synthesis of a linear polymer of QAP and TDI and the increasing content of chlorine in EDXRF spectra support that QAP can permanently be introduced into the foam structure which will not migrate with liquid vehicles during end use applications.

Thermal analysis, TGA and DMA, showed that the addition of QAP increased thermal stability of the produced foams while did not alter the T_g, indicating that the chemical composition, such as the number of free urethane linkages and cross-linking density, was also not altered.

Mechanical tests and SEM micrographs indicated that 1 wt% addition of QAP (PU1) nearly unaffected the cellular structure of the produced foams. Therefore, the rigidity and tensile properties of PU1 were very similar to unmodified foam (PU). On the other hand, destabilization of the cellular structure with 2 wt% addition of QAP (PU2) caused a significant increase on the rigidity and elongation while decreasing the tenacity of the produced foam.

Addition of QAP significantly improved the biocidal performance of the produced foams. PU2 and PU5 showed perfect inhibition towards bacteria, yeast, and mould but unfortunately were not suitable for use due to their shrinkage problem. PU1 also showed sufficient inactivations against *S.aureus*, yeast, and mould which is suitable for applications such as hospital mattresses, beds, and kitchen cleaners. In addition, further studies are needed to overcome the shrinkage problem to improve further the antimicrobial properties of the foams.

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