1- Introduction

There is substantial demand in medical and industrial sectors for coatings, films and fibers that prevent bacterial adhesion and growth. Pathogenic bacteria form biofilms that affect human health, producing considerable economic loss and human morbidity/mortality. These films are especially troublesome in the health care field (hospital-acquired infections and infections from indwelling medical devices), the military (infections from protective apparel), drinking water supplies (obstruction of pipes and contamination of water distribution systems), and food industries. 

Waterborne polyurethanes (WBPs) have been gaining importance because of their excellent mechanical properties and new environmental regulations. Therefore, there has been a strong preference for waterborne resins [1]. Quaternary ammonium compounds (QACs) are well-studied antibacterial agents and have been used in many applications especially in polymeric coatings. In 1935, G. Domagk reported the biocidal activity of these compounds. They are active against microorganisms by interaction with the cellular membrane and aimed to kill microorganisms [2].

This work leads to the synthesis of QACs based polyurethanes. The water dispersibility, film formation, and the antibacterial behavior of films were performed.

2- Materials and Methods

Syntheses of Quaternary Ammonium Salt and waterborne polyurethenes (WBPU)

Three type of QACS: i) 1-hydroxy-N- (2 hydroxyethyl) - N, N-dimethyl-3 phenoxypropan -2-aminium, ii) N-(2-hydroxyethyl)-N,N,2 trimethyloctan-1-aminium, and iii) N-(2-hydroxyethyl) - N,N,2-trimethylhexadecan-1-aminium chloride were synthesized by reacting a tertiary amine and alkylene oxide by ring opening reaction in the presence of a strong acid.

The polyurethane was synthesized by reacting toluene di-isocyanate (TDI) (Acros, USA) with poly (tetramethyl glycol) (PTMG) (Aldrich, UK). The reaction proceeded with continuous stirring until the reaction was complete, producing NCO-terminated prepolymer. The NCO groups were detected sampling the reaction mixture at various time intervals and performing
FTIR analysis. Polar functional groups (quaternary ammonium monomer were incorporated into the structure of PU) in order to confer the polymer water solubility or water dispersibility.

3- Results and Discussion

3-1 Reaction Characterization

FTIR spectra were recorded on NICOLET 6700 FTIR spectrometer. During the reaction, NCO group formation was followed by FTIR instrument analysis. The isocyanate peak, observed at 2270 cm\(^{-1}\). While the reaction proceeded: N=C=O peak decreased and disappeared totally. As a result it can be concluded that polyurethane reaction took place. In addition the IR spectrum of QAS monomer was analyzed. The epoxide ring, which was observed in the spectra of the glycidyl phenyl ether, disappeared in IR spectra of the QAS.

\(^{13}\)C NMR and \(^1\)H NMR spectra of the obtained polymers were taken with the use of the spectrometer Bruker AV-400 spectrometer, operating at 400 MHz Analysis was carried out in D\(_2\)O. Chemical structure of both synthesized quaternary ammonium salts were verified on the basis of \(^{13}\)C-NMR and \(^1\)H NMR spectra.

3-2 Thermal Characterization

Properties of both Pus were studied. The melting and crystallization transitions of the soft segment formed by the long diol were reported as 20.70 °C, -2.59 °C.

3-3 Particle Size Analysis

Particle size distribution of the waterborne polyurethane (WBPU) dispersion was measured by dynamic-light scattering using a NICOMP \(^\text{TM}\) 380 ZLS particle sizing system. The experiment was carried out at room temperature (25 °C), and the mean particle size and the size distribution were determined. The sample was first diluted with de-ionized water and the dispersion was
homogenized before testing. The effect of water content, mixing time and mixing speed on particle size was investigated. Moreover, the effect of water content on viscosity was examined.

3-4 Antibacterial Testing - Zone inhibition test

Antibacterial behaviors of the PU polymers grafted with QACs were evaluated with zone inhibition experiment against Gram-negative bacterium Escherichia coli in order to determine the viability of groups attached to the polymer (Figure 1). Nutrient agar plates, coated with the challenge bacteria, were incubated at 37 °C for 24 hours, and the zone of inhibition was measured. The clear zone around #1, #2 and #3 in Figure 2(a) showed prevention to bacteria growth. #4 and #5 are the control samples that do exhibit any biocidal activity.

Figure 1. Antibacterial experiment: pictures of inhibition zone for the three types of QACs.

4- Conclusion

QACs based polyurethane polymers were prepared. Material property characterization and biocidal activity evaluation were performed on a series of cationic polyurethanes containing different type of biocidal groups (QACs) in their structure. The final chemical structure of the polymers and biocidal groups were characterized by NMR and FTIR spectras. Due to smaller particle size distribution (mean particle size 173 nm), the waterborne polyurethane system showed long time stability. Quaternized monomers showed good antibacterial properties. However, it is observed that the diameter of the clear zone was limited with the penetration and dispersion characteristic of the samples. The resulting features of the polymers were a relatively high stability and good antimicrobial properties.

5- References